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A new design of activated carbon membrane air-cathode for wastewater treatment and energy recovery

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Peng Zhang,[a] Youpeng Qu,[b] Jia Liu,[a]* Yujie Feng[a]*

A novel design of membrane air-cathode (MAC) with double activated carbon layer was developed and served as filtration cathode in single chambered microbial fuel cell. This new kind of air-cathode, with simple fabrication process, greatly reduced the energy consumption, cost and complexity of air-cathode fabrication. The double layer MAC (DMC) obtained a power output of 1030 ± 31 mW m^{-2}, which was similar to traditional activated carbon air-cathode (TAC). Moreover, the DMC design significantly reduced the effluent concentrations of microorganisms in wastewater from 38.5±4.2 mg L^{-1} to 8.8±1.2 mg L^{-1} compared with TAC, and chemical oxygen demand (COD) removal was higher than that of TAC. These results indicated that the new design of DMC provided a promising and energy-saving way to prepare air-cathode and simultaneously achieved electricity generation and higher-quality effluent.

Introduction

Microbial fuel cell (MFC) is a biological electrochemical technology that utilizes bacteria to degrade organic wastewater and produce electricity[1-3]. The single chambered MFC with air-cathodes, which used the most cost-effective oxygen as exhaustless electron acceptor has attracted considerable attention due to the simple construction and low operation cost[4, 5]. Advances have been made to improve the power output by developing new electrode materials and fabrication processes[6-8]. The utilization of inexpensive material, activated carbon[9-11], significantly reduced the cost of cathodes, which could enhance the construction of MFC systems for practical application. The activated carbon rolling-press air-cathode is considered as a promising technology for large scale construction and application of MFCs[11]. However, the fabrication process is relatively complicated and the energy consumption is high for the sinter procedure at 340 °C for 25 min. So the fabrication of activated carbon air-cathode with simple and energy-effective process needs to be further improved. On the other hand, with regarding to the wastewater treatment performance of MFC technology, this technology alone could not produce the effluent with high quality, which fulfills the water reuse purpose.

Membrane bioreactors (MBRs) have gained increasing attention for wastewater treatment[12] and combined biological reactions for organic removal with membranes for solid and liquid separation to produce higher-quality effluent. The integrating MBRs with MFC for high efficient wastewater treatment and simultaneous electricity generation. were considered in previous studies[13-25]. In a recent study, a conductive ultrafiltration (UF) membrane[21] that functioned as both biocathode and filtration membrane was utilized in single-chamber MFC reactors, achieving higher-quality effluent and lower energy consumption. However, the preparation process of this kind of conductive UF membrane was complex and costly. Although the low cost carbon powder has been used as the filtration membrane material of air cathode MFC, its preparation process was still complicated and energy-costly[25]. Therefore, there is need for further investigation of low-cost and simple fabrication processes.

The activated carbon layer prepared by simple rolling-press method, with thickness of about 0.2 mm[11] and pore size of micrometer level[10, 26], could act both as a filtration membrane and air-cathode in MFC-MBR integrating system. This kind of structure may be cheap and excellent alternative to achieve the goal of simultaneous efficient wastewater treatment and energy recover. In this study, membrane air-cathode with activated carbon layers rolled on both sides of the stainless steel mesh, was prepared and used as both an air-cathode for electricity generation and membrane for wastewater filtration in MFC. This design will not only simplify the fabrication process of activated carbon air-cathodes and conductive filtration membrane but will also significantly reduce the cost and energy consumption of cathode fabrication. The following two aspects were investigated: (1) the electrochemical performance and power output of these novel design air-

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, China.
[b] School of Life Science and Technology, Harbin Institute of Technology. No. 2 Yikuang Street, Nangang District, Harbin 150080, China.
Email: yujief@hit.edu.cn; jia14921@163.com.
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cathodes in MFC reactors, (2) effects of membrane air-cathode on the wastewater treatment performance.

Experimental

The fabrication of membrane air-cathode

The membrane air-cathodes (MAC) were prepared by the rolling-press method. The single layer MAC (SMC), which was made of activated carbon powder (Carbosino Material Co., Ltd, Shanghai, China) and PTFE (60 wt %, Hesen, Electrical Co., Ltd, Shanghai, China) with the mass ratio of 6:1, was rolled on the water facing side of stainless steel mesh. The double layers MAC (DMC) were prepared by rolling-press method on the both water facing and air facing sides of SSM. The traditional activated carbon rolling air-cathode (TAC) was made as positive control in the previous study[11].

MFC construction and operation

Single chamber cubic shaped MFCs were constructed with a chamber volume of 28 mL (4 cm length and 3 cm diameter) as previously described[4]. The graphite fiber brush anodes of each reactor were heated at 450 °C for 30 min before use. The distance between the edge of brush anode and air-cathode was 0.5 cm. Titanium wire was used to connect the air-cathode to the resistor. The external resistance was fixed at 1000 Ω (except as noted), which was connected to anode and cathode by titanium wires. Each reactor was constructed in duplicate. All experiments were conducted at 30 °C in a constant temperature room.

All reactors were acclimated with the effluent collected from other MFC reactors before fed-batch operations. The operation diagram of SMC and DMC reactor is as showed in Fig. 1. The influent was pumped in the open tank at a height of 1.6 m over the reactors and flowed into the reactors through a plastic pipe. A switch was placed on the pipe near reactor to control the water flow. During the batch cycle, the switch was closed and water could not permeate through the membrane air-cathode due to the atmospheric pressure on the air facing side of cathode. At the end of each fed-batch cycle, when the voltage decreased to < 50 mV, the switch was turned to the open state and the solution in the reactors was pressed through SMC and DMC electrodes by hydraulic pressure. A fed-batch cycle started when the switch turned off after the effluent volume reached 5 mL. Since the distance between water inlet and membrane air cathode was just 4 cm, larger volume effluent may lead to the pollution by the influent. For the traditional activated carbon air-cathode reactors, after each fed-batch cycle, 5 mL of the treated water was replaced by the same volume influent. The medium which was utilized as the influent, contained sodium acetate (2 g L^{-1}) and 50 mM phosphate buffer solution (PBS) (Na_2HPO_4 $12H_2O$, 10.32 g L^{-1}; NaH_2PO_4 $2H_2O$, 3.32 g L^{-1}; NH_4Cl, 0.31 g L^{-1}; KCl, 0.13 g L^{-1}; trace minerals and vitamins).

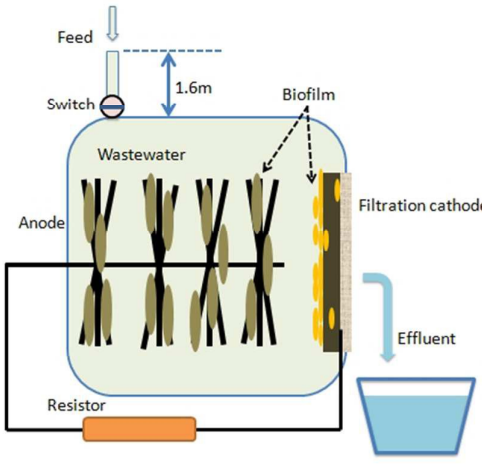

Fig. 1 Schematic representation of single chamber MFC with activated carbon membrane air-cathode.

Measurements and electrochemical analysis

The voltage (U) across an external resistor (1000 Ω) in the MFC circuit was monitored at 30 min intervals using a data acquisition system (PISO-813, ICP DAS Co., Ltd.) connected to a personal computer. The current (I) was calculated by I=U/R where R is the resistance (Ω) and U is the voltage across the resistor. The power output (P, W) was calculated as P=IU and normalized by the cathode area, A = 7 cm^2. Maximum power density was calculated through the polarization tests by varying the external resistance from the 1000 Ω to 50 Ω. The chemical oxygen demand (COD) was measured in duplicate using test kit that uses a spectrophotometer (HACH Company). Protein content in the effluent was measured by bicinchoninic acid (BCA) method[27]. Meanwhile, columbic efficiencies (CE) were calculated as the ratio of total recovered coulombs to the theoretical amount of electrons derived from the oxidation of acetate to carbon dioxide, which was calculated according to the following equation:

$$CE = \frac{3\int Idt}{FV(C_i - C_e)}$$

where F is Faraday constant (96,485 C mol^{-1}), V is the volume of treated wastewater (L), t is operation time (s), C_i and C_e are the COD concentrations of influent and effluent (g L^{-1}), I is produced current (A).

Furthermore, all electrochemical experiments were performed in 50 mM PBS solution at ambient temperature in an abiotic reactor which was a 4 cm cubic shaped reactor [4]. Linear sweep voltammetry (LSV) was performed at 1 mV s^{-1} on the cathodes with a platinum plate as a counter electrode and an Ag/AgCl reference electrode (0.197 V versus standard hydrogen electrode, Spsic-Rex Instrument Factory, China) by Auto Lab PGSTAT128N (Metrohm, Swiss). In addition, electrochemical impedance spectroscopy (EIS) was operated at the polarized potential of −0.1V, which was similar to the operation potentials of cathodes in MFCs, over a frequency range of 10 mHz - 100 kHz with an amplitude of 10 mV. Also, Nyquist plots were simulated by fitting the data into an equivalent circuit using Zsimpwin software and the equivalent circuit model was $R_o(Q(R_dW))(QR_{ct})$[28]. The morphology of new and used air-cathodes was examined by a scanning electron microscope (SEM).

The electrode samples were washed with deionized water and dried in an oven at 100 °C for 24 h. The specific surface area of the membrane cathode was determined using Brunauer-Emmett-Teller (BET) method. The membrane thickness of DMC and SMC was the average thickness measured by using an electronic micrometer (IP65, Qinghai Measuring & Cutting Tools Group Company, China). The flux of the membrane air-cathode was measured by utilizing the nitrogen gas to provide the trans-membrane pressure, which was detected by a pressure sensor, while the specific flux was normalized to the air-cathode projected area.

Results and discussion

Membrane cathode characteristics

The DMC was 1.2 mm thick, while the SMC was 0.7 mm thick. The SEM (Fig. S1) results showed that the activated carbon layer has a pore size of about 2 µm, which was consistent with previous reports[10, 26]. Both DMC and SMC can hold water pressure of over 100 kPa. This is mainly due to the support of stainless steel mesh. The specific surface area of membrane cathode layer was 1578 m^2 g^{-1}, which could be due to the large surface area of activated carbon. On the other hand, specific flux was 5.38 ± 0.3 L/(h m^2 kPa), which was at same level with other carbon membrane air-cathode[25].

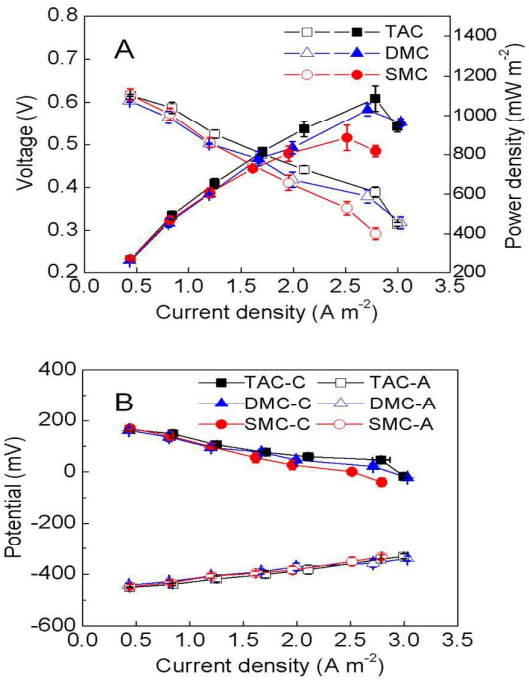

Fig.2 Polarization, power density curves (A) and electrode potentials curves (B) of MFC reactors with DMC, SMC and TAC air-cathodes. Error bars ±SD were based on averages measured in duplicate.

Performance of MFCs using different cathodes

According to the power density curves (Fig. 2A), similar maximum power density of 1030 ± 64 mW m^{-2} and 1086.70 mW m^{-2} were observed using DMC and TAC respectively, which were more than 16% higher than that obtained with SMC reactor (885 ± 55 mW m^{-2}). Potential analysis at different current densities (Fig. 2B) showed that the anode potentials were nearly identical, while all differences in maximum power density oriented from differences of cathodes. These results indicated that DMC design possessed a similar ability to support cathodic reactions with TAC. And the two layer structures, DMC and TAC, facilitated better cathode performance than SAC design, showing the positive function of the carbon layer facing the air side in promoting cathode behavior. The power outputs of DMC were significantly higher than that of the conductive ultrafiltration membrane biocathode (380 mW m^{-2}) [21] and carbon filtration cathode (582 mW m^{-2}) [25], indicating that the novel membrane air-cathode appeared to be the best choice for power output.

The CEs of DMC was 22.53 ± 2.79%, nearly similar to that obtained by TAC reactor (23.36 ± 3.76%) (Fig. 3). These similarity of CEs indicates that the DMC has a comparable energy recovery performance to TAC construction. The SMC had the lowest CE of 19 ± 6%, which may be due to the single layer membrane cathodes, limiting cathode reaction and promoting more oxygen leaking into the reactors[7, 29]. The difference of CEs showed the consistent variation trend with power density, indicating that different air-cathode designs were responsible for the differences in MFC performance [29].

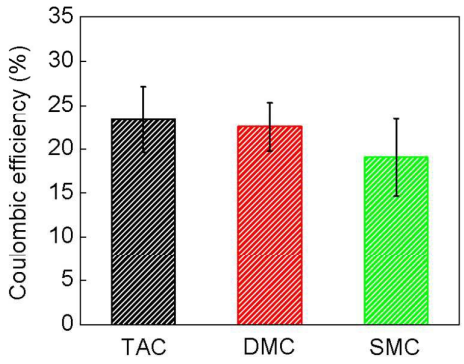

Fig. 3 Columbic efficiencies of MFC reactors with DMC, SMC and TAC air-cathode

Electrochemical analysis of membrane cathode

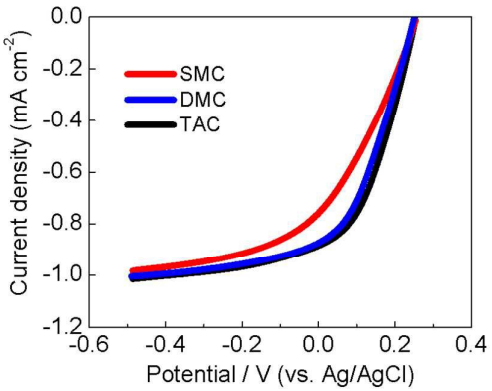

Fig. 4 LSV curves of DMC, SMC and TAC design of air-cathode.

The oxygen reduction reaction (ORR) characteristics of DMC, SMC and TAC were analyzed by LSV (Fig. 4). The cathode with DMC generated current densities of 0.93 ± 0.01 mA cm^{-2} at −0.1 V. This was also observed with TAC, indicating that the design of DMChad similar performance on ORR with TAC. Moreover, the current density of single layer membrane cathode (SMC) was lower than those of double layer membrane cathode (DMC). At the potential of -0.1 V for SMC, the current density of 0.86 ± 0.01 mA cm^{-2} was 6.7 % lower than DMC was observed, demonstrating that the ORR performance of air-cathodes were related with the activated carbon layers where its air facing side also played an important role in ORR, other than the water facing side layer. Also, LSV tests were performed in N_2-saturated and O_2-saturated solutions (Fig.S2), and it was noted that the DMC design had a superior electrocatalystic activity in comparison to SAC for ORR and while it registered similar ORR performance with TAC. In N_2-saturated situation, the double layer current of DMC design was higher than that of SAC design, which was due to the higher surface area with more carbon layer[30].

The differences in performance were reflected in the changes of internal resistance of the DMC, SMC and TAC (Fig. 5). The SMC had the highest total resistance of 30.5 Ω, which was 41.2% higher than that of DMC (21.7 Ω). The lowest total resistance of 18.2 Ω was produced by TAC. The solution resistances (R_s) and diffusion resistances (R_d) were similar for these three kind of cathode, while charge transfer resistance (R_{ct}) led to the most differences in the total internal resistance. The charge transfer resistance primarily reflected the electrode reaction kinetics. The DMC had lower charge transfer resistance than that of SMC, which had decreased by 47.3% from 11.2 Ω to 5.9 Ω. This can be attributed to the addition of activated carbon layer on the air facing side hence promoting the oxygen diffusion and oxygen reduction reaction.

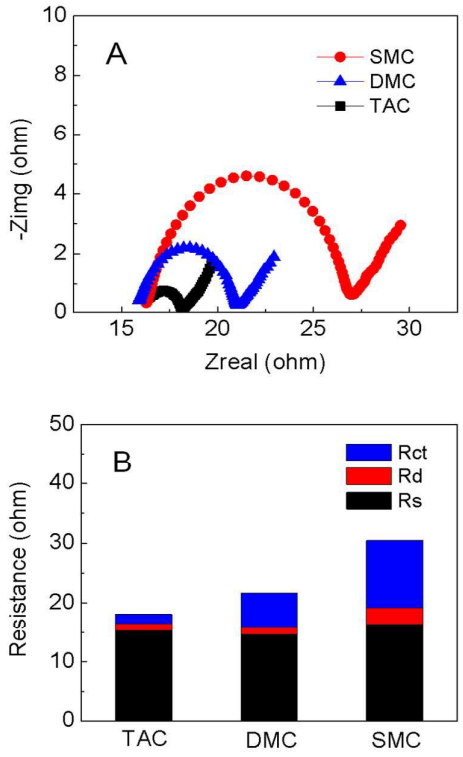

Fig. 5 Nyquist plots (A) and total resistances (B) of DMC, SMC and TAC design of air-cathode.

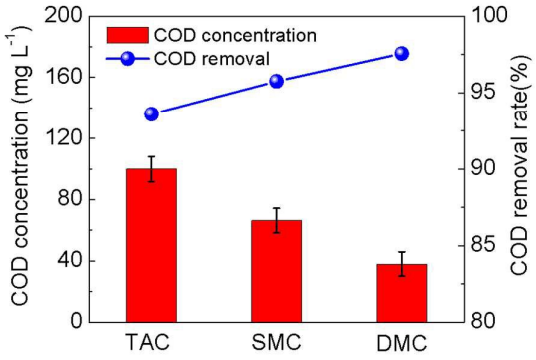

Fig. 6 COD removal efficiency and effluent CODs concentration of reactors with DMC, SMC and TAC air-cathode.

Performance of wastewater treatment

The effect on wastewater treatment was evaluated using COD removal efficiency and effluent CODs concentration in performance with the different cathodes (Fig. 6 and Fig. S3). As the cycle time increased, the COD concentration in the effluent decreased and became stable after 4 cycles (Fig. S3A). The maximum COD removal efficiency of 97.6 ± 0.5% was obtained in DMC reactor, which was higher than those obtained for SMC (95.8 ± 0.4%) and TAC ((93.0 ± 0.5%). When using membrane cathode, the CODs concentration was significantly decreased in the effluent. The minimum effluent COD concentration of 38 ± 8 mg L^{-1} was obtained by using DMC, which was 42.7% lower than that of SMC (66 ± 8 mg L^{-1}) and 62% lower compared to TAC (100 ± 8 mg L^{-1}). The wastewater treatment

performance was tested by varing the organic loading and the results (Fig. S3B) indicated that DMC design cathode showed a continous better performance with even higher organic substrate loading. These results indicated that the DMC achieved high quality treatment levels in terms of effluent COD concentrations.

There is a close correlation between microorganism quantity and protein content in the effluent, so the protein content was utilized to represent microorganism quantity in the effluent. The effluent protein content of DMC was 8.8±1.2 mg L^{-1}, which was significantly lower than that of SMC reactor (18.3 ± 2.7 mg L^{-1}) and TAC reactor (38.5 ± 4.2 mg L^{-1}). It can be argued therefore that the microorganism removal was likely due to the filtration effect of activated carbon membrane, which held back most of the microorganism in the treated wastewater. In fact, lower protein content of DMC demonstrated that the double activated carbon layers showed better filtration performance than SMC with only single layer, indicating that activated carbon membrane played an important role in microorganism filtration, which may have been due to longer filtration path in activated carbon layer for the effluent.

Membrane fouling and fabrication energy consumption

During the experiment, influent height was always about 1.6 m above cathodes, while trans-membrane pressure (TMP) was kept at 15.68 KPa when the switch was open. The reason why TMPs for SMC and DMC reactors were slightly higher than TMPs in former study[21] was to increase effluent water velocity through air-cathodes. The permeate flow velocity was observed to decreased gradually. This can be attributed to membrane fouling and steady TMP.Moreover, the surfaces of TAC，DMC and SMC were covered by a layer of biofilm (Fig. S4). Meanwhile, the biofilm of SMC was observed to be thicker than that of DMC and TAC, which may due to the more convenient cathode structure for oxygen cross than the latter pair. To reduce the membrane electrode pollution and fouling processes may be further resolved by using surface modification and configuration optimization.

It is worth noting that the power required for pumping the feed to the height of 1.6 m in the system was 0.0043 KWh m^{-3}, which was much lower than the energy required for large-scale MBRs (0.5-1 kWh m^{-3})[31]. The avoidance of aeration in typical MBR systems by membrane air-cathodes used in the system led to the decrease of energy consumption. Optimization of the system and air-cathode for energy consideration will improve the performance further. The energy consumption during preparation process decreased greatly due to the improvement in our new design. Taking a piece of TAC for example, the energy required for GDL sinter procedure was about 1.04 kWh (Power of muffle furnace, 2.5 kW), which drastically reduced in our new design. As shown in Table 1 and in comparison to the conductive UF membrane[21] reported before, utilization of activated carbon in this design avoided the use of expensive carbon nanotube and reduced the cost of membrane fabrication from almost 500 to 61 (DMC) USD m^{-2}. Even though the cost is still higher than that reported by Zuo[25] (7.1 USD m^{-2}), energy consumption during the fabrication process is greatly reduced from 4.5 KWh to 0.24 KWh. In addition, DMC design of membrane air-cathode achieved the highest maximum power density among all the membrane air-cathode design in single chamber MFC. These results show that the novel membrane air-cathode with simple, energy-saving and cost-effective fabrication process is very promising for future application.

Table 1 Comparison of the power output, COD removal rate and fabrication main energy consumption of membrane air-cathode in single chamber MFC reported previously.

	Material	Power output (mWm^{-2})	COD removal rate	FMEC (KWh)	Ref
DMC	AC	1029.77	98.1%	0.24	
SMC	AC	885.03	96.7%	0.12	
TAC	AC	1086	95.0%	1.04	11
FAC	Carbon powder	581.5	93.7%	4.5	21
UFM	MCNT	820	96.9%	0.04	25

FMEC: Fabrication main energy consumption, AC: activated carbon, FAC: Filtration air cathode UFM: ultrafiltration membrane, MCNT: multi-wall carbon nanotube

Conclusions

This new utilization way of double layer membrane air-cathodes (DMC) reached a maximum power density of 1030 ± 64 mW m^{-2}, which was comparative to that of common TAC (1086 ± 31 mW m^{-2}). Compared with the TAC reactors, higher COD and microorganism removal efficiencies were obtained in DMC reactors. In addition to the higher effluent quality and similar power output, the fabrication process of air-cathode was greatly simplified. Though there is still a lot of optimization to be done, this kind of simple-preparing and cost-effective activated carbon membrane air-cathode would actually promote the application of the MFC-MBR system in treating wastewater and recovering electricity.

Acknowledgements

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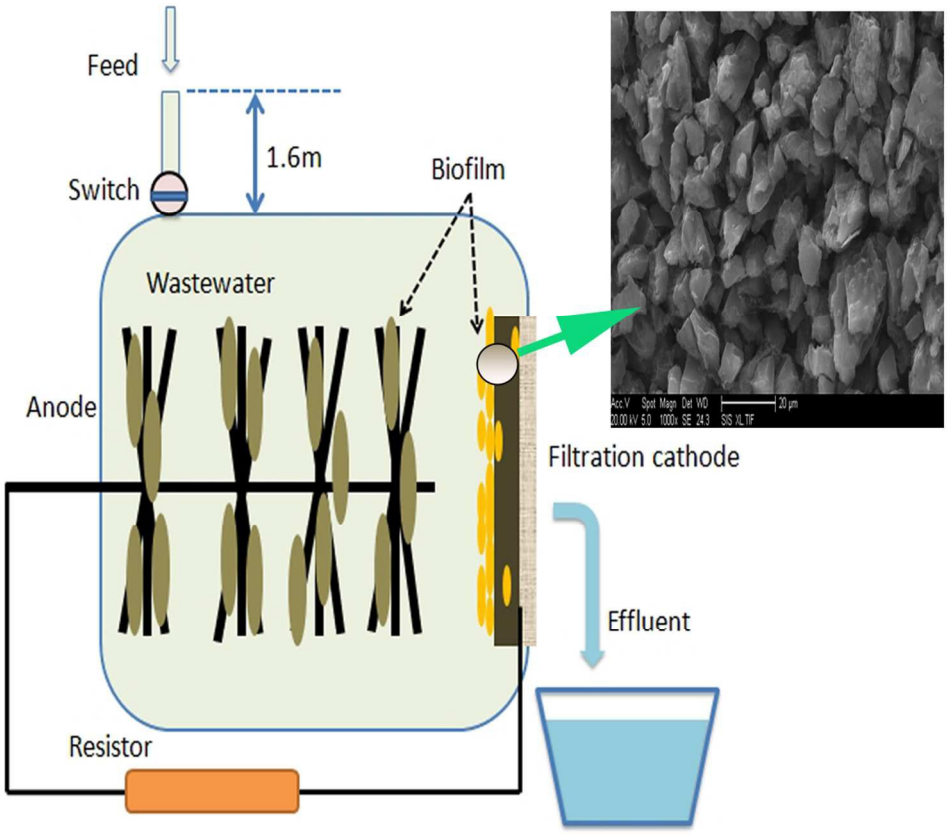
Notes and references

1. B. E. Logan and J. M. Regan, *Trends in Microbiology*, 2006, **14**, 512-518.
2. H. Liu, S. Cheng and B. E. Logan, *Environmental science & technology*, 2005, **39**, 658-662.
3. R. A. Rozendal, H. V. Hamelers, K. Rabaey, J. Keller and C. J. Buisman, *Trends in biotechnology*, 2008, **26**, 450-459.
4. H. Liu and B. E. Logan, *Environmental science & technology*, 2004, **38**, 4040-4046.
5. X. Xia, F. Zhang, X. Zhang, P. Liang, X. Huang and B. E. Logan, *ACS applied materials & interfaces*, 2013, **5**, 7862-7866.
6. Y. Fan, H. Hu and H. Liu, *Journal of Power Sources*, 2007, **171**, 348-354.
7. X. Zhang, H. Sun, P. Liang, X. Huang, X. Chen and B. E. Logan, *Biosensors & bioelectronics*, 2011, **30**, 267-271.
8. F. Zhang, Y. Ahn and B. E. Logan, *Bioresource technology*, 2014, **152**, 46-52.
9. F. Zhang, S. Cheng, D. Pant, G. V. Bogaert and B. E. Logan, *Electrochemistry Communications*, 2009, **11**, 2177-2179.
10. H. Dong, H. Yu and X. Wang, *Environmental science & technology*, 2012, **46**, 13009-13015.
11. H. Dong, H. Yu, X. Wang, Q. Zhou and J. Feng, *Water research*, 2012.
12. S. Judd, *Trends Biotechnol*, 2008, **26**, 109-116.
13. J. Sun, Y. Hu, Z. Bi and Y. Cao, *Journal of Power Sources*, 2009, **187**, 471-479.
14. Y. K. Wang, G. P. Sheng, W. W. Li, Y. X. Huang, Y. Y. Yu, R. J. Zeng and H. Q. Yu, *Environmental science & technology*, 2011, **45**, 9256-9261.
15. F. Zhang, K. S. Brastad and Z. He, *Environmental science & technology*, 2011, **45**, 6690-6696.
16. Z. Ge and Z. He, *Bioresource technology*, 2012, **109**, 70-76.
17. Y.-P. Wang, X.-W. Liu, W.-W. Li, F. Li, Y.-K. Wang, G.-P. Sheng, R. J. Zeng and H.-Q. Yu, *Applied Energy*, 2012, **98**, 230-235.
18. Z. Ge, Q. Ping and Z. He, *Journal of Chemical Technology & Biotechnology*, 2013, **88**, 1584-1590.
19. K.-Y. Kim, K.-J. Chae, M.-J. Choi, E.-T. Yang, M. H. Hwang and I. S. Kim, *Chemical Engineering Journal*, 2013, **218**, 19-23.
20. J. Liu, L. Liu, B. Gao and F. Yang, *Journal of Membrane Science*, 2013, **430**, 196-202.
21. L. Malaeb, K. P. Katuri, B. E. Logan, H. Maab, S. P. Nunes and P. E. Saikaly, *Environmental science & technology*, 2013, **47**, 11821-11828.
22. K. P. Katuri, C. M. Werner, R. J. Jimenez-Sandoval, W. Chen, S. Jeon, B. E. Logan, Z. Lai, G. L. Amy and P. E. Saikaly, *Environmental science & technology*, 2014, **48**, 12833-12841.
23. J. Ma, Z. Wang, D. He, Y. Li and Z. Wu, *Water research*, 2015, **78**, 98-110.
24. Y. Tian, H. Li, L. Li, X. Su, Y. Lu, W. Zuo and J. Zhang, *Biosensors and Bioelectronics*, 2015, **64**, 189-195.
25. K. Zuo, S. Liang, P. Liang, X. Zhou, D. Sun, X. Zhang and X. Huang, *Bioresource technology*, 2015, **185**, 426-430.
26. X. Li, X. Wang, Y. Zhang, N. Ding and Q. Zhou, *Applied Energy*, 2014, **123**, 13-18.
27. F. Liu, A.-E. Rotaru, P. M. Shrestha, N. S. Malvankar, K. P. Nevin and D. R. Lovley, *Energy & Environmental Science*, 2012, **5**, 8982.
28. X. Wang, N. Gao, Q. Zhou, H. Dong, H. Yu and Y. Feng, *Bioresource technology*, 2013, **144**, 632-636.
29. D. Li, Y. Qu, J. Liu, W. He, H. Wang and Y. Feng, *Journal of Power Sources*, 2014, **272**, 909-914.
30. K. Wan, G.-F. Long, M.-Y. Liu, L. Du, Z.-X. Liang and P. Tsiakaras, *Applied Catalysis B: Environmental*, 2015, **165**, 566-571.
31. A. Drews, *Journal of Membrane Science*, 2010, **363**, 1-28.



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