Journal of Power Sources 356 (2017) 348–355

Contents lists available at ScienceDirect

Journal of Power Sources

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

Combined carbon mesh and small graphite fiber brush anodes to enhance and stabilize power generation in microbial fuel cells treating domestic wastewater

Shijia Wu [a], Weihua He [b], Wulin Yang [c], Yaoli Ye [c], Xia Huang [a, **], Bruce E. Logan [c, *]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, PR China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 73 Huanghe Road, Nangang District, Harbin 150090, PR China
[c] Department of Civil and Environmental Engineering, 212 Sackett Building, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- A novel composite anode was developed that combined brushes and carbon mesh.
- The composite anode had higher power output and CEs than either of the other anodes.
- Power overshoot was mitigated with the composite anode MFCs at higher CODs.
- MFCs with the composite anode had less cathode biomass growth.
- The carbon mesh with biofilms in the composite anode also functioned as a separator.

ARTICLE INFO

Article history:
Received 6 November 2016
Received in revised form
19 December 2016
Accepted 9 January 2017
Available online 16 January 2017

Keywords:
Microbial fuel cells
Power generation
Oxygen contamination
Power overshoot
Anode configurations

ABSTRACT

Microbial fuel cells (MFCs) need to have a compact architecture, but power generation using low strength domestic wastewater is unstable for closely-spaced electrode designs using thin anodes (flat mesh or small diameter graphite fiber brushes) due to oxygen crossover from the cathode. A composite anode configuration was developed to improve performance, by joining the mesh and brushes together, with the mesh used to block oxygen crossover to the brushes, and the brushes used to stabilize mesh potentials. In small, fed-batch MFCs (28 mL), the composite anode produced 20% higher power densities than MFCs using only brushes, and 150% power densities compared to carbon mesh anodes. In continuous flow tests at short hydraulic retention times (HRTs, 2 or 4 h) using larger MFCs (100 mL), composite anodes had stable performance, while brush anode MFCs exhibited power overshoot in polarization tests. Both configurations exhibited power overshoot at a longer HRT of 8 h due to lower effluent CODs. The use of composite anodes reduced biomass growth on the cathode (1.9 ± 0.2 mg) compared to only brushes (3.1 ± 0.3 mg), and increased coulombic efficiencies, demonstrating that they successfully reduced oxygen contamination of the anode and the bio-fouling of cathode.

1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices that are being investigated for accomplishing wastewater treatment and energy production due to their ability to generate electricity from the degradation of organic matter in the wastewater [1,2]. Air-cathode MFCs are the most promising design for practical applications since they use passive transfer oxygen to the cathode, avoiding energy needed for water aeration [3]. Scaling up MFCs to treat real wastewaters, such as domestic wastewater which has a low conductivity (~1 mS cm^{-1}), requires a compact design with closely spaced electrodes to minimize solution and electron transfer resistances [4]. To avoid direct electrode contact when the anode and cathode placed next to each other, a cloth or battery separator is placed between the electrodes, creating a configuration

* Corresponding author.
** Corresponding author.
E-mail addresses: xhuang@tsinghua.edu.cn (X. Huang), blogan@psu.edu (B.E. Logan).

http://dx.doi.org/10.1016/j.jpowsour.2017.01.041
0378-7753/

known as a separator electrode assembly (SEA) design [5]. Although the SEA designs should generate higher power densities than MFCs with greater spacing between the electrodes due to the reduction in ohmic resistance [6], close electrode spacing can result in decreased power generation due to oxygen crossover through the cathode, which reduces the activity of exoelectrogens on the anode [7]. Power generation using a flat carbon cloth anode decreased when it was moved from 2 cm to 1 cm near a cathode in the absence of a separator [7], and power generation could not be maintained using wastewater with a carbon mesh anode placed directly against the separator in an SEA configuration [8].

MFCs with graphite fiber brush (GFB) anodes have been shown to produce higher power densities than flat carbon cloth or carbon mesh anodes due to their high specific surface area, high porosity, and low electrical resistance, and they are relatively inexpensive and easy to fabricate [9,10]. Brushes (typically 25 mm in diameter) can be placed close to the cathode in an SEA configuration without impaired power production [8], suggesting that the thick and porous structure helps to maintain the anoxic conditions needed within the anode for electricity generation even with oxygen transfer through the cathode and separator. However, larger brush anodes do not necessarily produce more power than smaller brushes, and thus the size of the brush, its distance from the cathode, and the concentration of organic matter in the solution can all impact performance. Brushes 25 mm in diameter produce stable power in small (28 mL) and larger (ranging from 170 mL to 6.1 L) MFCs when placed near to the cathode using acetate (~1000 mg L^{-1}, equal to ~780 mg L^{-1} of chemical oxygen demand, COD) in a phosphate buffer or domestic wastewater [11–14]. Smaller diameter brushes (8 mm) produced much higher power (1020 mW m^{-2}) than three larger brushes (25 mm, 560 mW m^{-2}) in continuous flow MFC tests using acetate (1000 mg L^{-1}) due to the closer spacing between the center of brushes and the cathode, despite the fact that the larger brushes had more surface area for biofilm growth [11]. When these smaller brushes were used in the same MFCs with lower-strength domestic wastewater (~300 mg-COD L^{-1}), the reactor produced at the start of the fed batch cycle a lower power (~320 mW m^{-2}) as expected due to the lower COD of the wastewater compared to tests with acetate [15]. However, power generation was unstable in continuous flow mode, with two identical reactors producing much lower and much different power densities (150 and 250 mW m^{-2}). Not only was power production erratic, polarization data showed that the anodes could not sustain power at lower resistances, as shown by power overshoot (where the power density curve doubles back to lower current densities as the external resistance was decreased) [15]. It was concluded in that study with low-strength wastewater that power was reduced with small brushes due to the impact of oxygen crossover from the cathode. It is well known that when a thin anode (carbon cloth or carbon mesh) is placed close to the cathode that power decreases due to oxygen crossover, despite the improved reduction in ohmic resistance [7,8,16]. Thicker carbon felt electrodes can increase power with acetate when distant from the cathode and thus not influenced by oxygen crossover, but there is very little impact of anode thickness when they are placed close to the cathode [17]. It has also been shown in several studies that placing any porous material between the electrodes, such as non-conductive separators (cloth, nylon mesh and glass fiber) or an ion exchange membrane, reduces oxygen crossover [18,19]. However, the use of separators or membranes that hinder hydroxide ion from the cathode increases ohmic resistance and thus can decrease power generation [20].

Compact MFC configurations are needed to maximize power production per volume of reactor and make the process more economical. Therefore, while larger brushes (2.5 cm diameter) have stable power generation and more surface area for biofilm growth than small brushes (0.8 cm diameter), they require more anode space and thus constrain the design of more compact reactors. To reduce the impact of oxygen crossover on anode performance, we devised a composite anode configuration where a carbon mesh was placed on the separator and several smaller brushes were pressed against the outer side of the carbon mesh. The air cathode was positioned directly on the other side of the separator, in an SEA configuration. Previous work has shown that using only the mesh, or using only the small brushes, resulted in unstable power production [4,15]. It was hypothesized that the brush and mesh combination could help to sustain current generation by an anaerobic biofilm similar to the situation with larger brushes, but that this combination would occupy less anode space than larger brush anodes. The use of the mesh also was hypothesized to serve as a type of “separator” because placing any porous material on top of the separator would necessarily reduce oxygen transfer to the brush electrodes. In addition, since the mesh and brush are electrically connected and have small ohmic resistance (as discussed below), they would have the same potential. Thus, the brush could act to stabilize the mesh electrode electrical potential, and enable the carbon mesh to function as an additional anode surface area while using very little volume compared to a reactor with larger brushes.

In order to test this composite anode design, we examined power generation and COD removal with the composite anodes using domestic wastewater in two different reactors: small, fed batch MFCs, and larger reactors under continuous flow conditions for three different hydraulic retention times (HRTs). Performance was compared to reactors with mesh or brush anode in the smaller MFCs, but only compared to brushes anode in the larger reactors due to the erratic performance reactors with only flat anodes with domestic wastewater and an SEA configuration. Anode and cathode total biomass were also investigated after long-term operation of MFC with or without the additional carbon mesh to evaluate the growth of biofilm on the electrodes due to the presence of the carbon mesh.

2. Materials and methods

2.1. MFC construction

The composite electrodes were examined in two different MFCs reactors in order to evaluate anode performance under fed-batch and continuous flow conditions. For fed-batch tests, MFCs were smaller cubic-shaped reactors that have previously been examined in many MFC studies [4,8]. The MFCs had a 3 cm diameter anode chamber that was 4 cm in length (28 mL empty bed volume). Three different anodes were used: a single mesh anode; a single brush anode; and a composite anode, with the brush pressed against the carbon mesh. All the anode materials in the experiment were presoaked in acetone overnight and then heated at 450 °C for 30 min prior to use [21]. The carbon mesh (Gaojieshi Graphite Products Co., Ltd., Fujian, China) anode was 3 cm in diameter, and it was placed right on the separator surface and connected to the circuit using a titanium wire (M-MFC) (Fig. 1A). The graphite fiber brush (Mill-Rose, Mentor, OH) was made with two titanium core wires (25 mm diameter) (B-MFC) and compressed against the separator forming a half cylinder (Fig. 1B). For the composite anode, the brush was pressed against the carbon mesh that was placed on the separator (BM-MFC) (Fig. 1C). Cathodes (7 cm^2 projected surface area) were fabricated by a phase inversion technique using a polyvinylidene fluoride binder and a mixture of activated carbon (8.8 mg cm^{-2}) and carbon black (Vulcan XC-72, Calbot Corporation, USA) as previously described [22]. Two layers of textile (46% cellulose, 54%

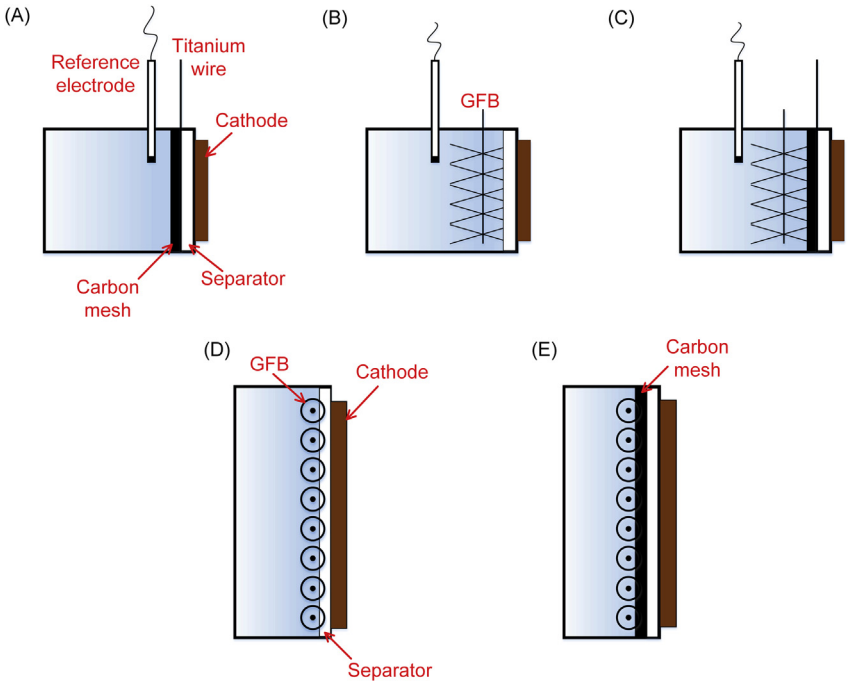

Fig. 1. Schematic showing the components of three small cubic MFCs: (A) BM-MFC, (B) B-MFC and (C) M-MFC in fed-batch operation mode; and the components of two larger volume MFCs in continuous flow mode: (D) B-LMFC containing 8 GFB anode (GFB = graphite fiber brush), a separator and air cathode; (E) components of the BM-LMFC which further contains a carbon mesh anode.

polyester; 0.3 mm thick; Amplitude Prozorb, Contec Inc.) were used as separators on the cathode surface of all MFC reactors. An Ag/AgCl reference electrode (+197 mV versus SHE; RE-5B; BASi) was inserted into each reactor (about 1 cm away from the anode, outside the electric field) to measure the anode potentials [23]. All the potentials reported here were versus Ag/AgCl reference electrode.

For continuous flow tests, larger volume (100 mL empty bed volume) MFCs (LMFC) were used to compare the performance of the composite anode (BM-LMFC) with that of the brush-only MFCs (B-LMFC), using reactors constructed as previously described [24]. Flat mesh anode MFCs were not examined as their performance would be too unstable [8]. For the B-LMFCs, eight small brushes (8 mm in diameter, 95 mm in length) were pressed against the separator and connected externally in parallel by a single copper wire (Fig. 1D). For the BM-LMFCs, eight brushes of the same size were compressed against a piece of carbon mesh (5 cm × 8 cm) which was positioned on top of the cloth separator (Fig. 1E). Both MFCs had air cathodes (40 cm^2 of projected area) containing a catalyst layer, current collector, and diffusion layer which were fabricated and pressed together as previously described [25]. The catalyst layer was activated carbon powder (AC, Norit SX plus, Norit Americas Inc., USA) with an AC loading of ~30 mg cm^{-2}. The diffusion layer was made of carbon black (CB, Vulcan XC-72) and polytetrafluoroethylene (PTFE) with a CB loading of 25 mg cm^{-2} and PTFE loading of 38 mg cm^{-2}. Stainless steel mesh (50 × 50, type 304, McMaster-Carr, USA) was used as a current collector. Two layers of textile cloth were used as the separator. An Ag/AgCl reference electrode was inserted into each reactor (about 0.5 cm away from the anode) to measure the anode potentials.

2.2. MFC operation

All MFCs were inoculated and operated using domestic wastewater collected from the primary clarifier effluent at the Penn State University wastewater treatment plant. Wastewater samples were collected once a week and stored in a refrigerator (4 °C). MFCs tests were conducted in duplicate, and all reactors were operated at ambient temperature (27 ± 3 °C).

The smaller cubic MFCs were inoculated by refreshing the anolyte daily until the MFCs showed stable and repeatable cycles of maximum voltages at an external resistance of 1000 Ω. MFCs were then operated in fed-batch mode, with the external resistances gradually lowered from 1000 to 100 Ω (3 d or more at each external resistance) to accommodate the anode biofilm to a higher current density to minimize the possibility of power overshoot [26]. Electrochemical tests were then conducted, including polarization tests, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to characterize the electrochemical performance of the three different anode configurations.

For the larger MFCs, the reactors were initially operated in fed-batch mode at an external resistance of 1000 Ω, with the resistances gradually lowering from 1000 to 100 Ω until both MFCs delivered a stable and repeatable maximum voltage at each external resistance. After this start-up procedure, the external resistances of the LMFCs were fixed at 100 Ω, and the reactors were operated with continuous flow using domestic wastewater fed from an external reservoir using peristaltic pumps (model no. 7523-90, Masterflex, Vernon Hills, IL) (Fig. S1). The wastewater in the reservoir was stored on ice, and refreshed daily. During the experiment, three different HRTs (2, 4, and 8 h) were examined for power generation, COD removal, and coulombic efficiency. At each HRT, these tests were conducted after the MFCs demonstrated a stable voltage and effluent COD concentrations. The tests were repeated three times, for ~2 weeks at each HRT. After concluding these tests, cathodes from both types of MFCs were removed to measure the cathodic biomass. The cathodes were then chemically cleaned by soaking them in 0.1 M HCl for 12 h, and then rinsed three times with deionized water before reinstalling them back into the reactors. COD removal and coulombic efficiencies were then re-examined at the same three HRTs to investigate changes in performance due to the removal of the cathode biofilms. At the conclusion of these

tests, the anodes were also examined for biomass growth.

2.3. Analysis and calculations

Voltages (E, mV) across an external resistor were measured every 20 min using a data acquisition system (Model 2700, Keithley Instruments) connected to a computer. Current (I) and power (P) were calculated as previously described [24] and normalized by the projected surface area of the cathode (7 cm^2 for MFCs and 40 cm^2 for LMFCs). Polarization curves were obtained using the single-cycle method by varying the external resistances (from open circuit to 50 Ω) in a single fed-batch cycle. All reactors were operated under open circuit conditions for at least 2 h before polarization tests. Cathode potentials were calculated as the difference between the anode and whole cell potentials. The total internal resistance and the cathodic as well as anodic resistance of MFCs were determined by fitting the linear region of their polarization curves [1].

CV and EIS scans were conducted using a potentiostat (VMP3; BioLogic, Claix, France), with the anode as the working electrode and the cathode as the counter electrode. For the CV tests, anode potential was scanned from −0.6 to +0.1 V at 1 mV s^{-1}. EIS was performed at an anode potential where the maximum power generation occurred, using a scan range of 100 kHz to 100 mHz, with a sinusoidal perturbation of 10 mV of amplitude. Ohmic resistance and charge transfer resistances of the anode were determined from the first point of intersection of the x-axis, and by fitting the semi-circles in Nyquist plots [27]. The analytes of all small cubic reactors were replaced before the electrochemical tests to ensure similar COD concentrations among the MFC reactors during the tests. All of the measurements were repeated three times to ensure repeatable results could be achieved.

The COD concentration was measured according to standard methods (method 5220, HACH Company, Loveland, CO). COD removal efficiency (%) was calculated based on the differences between the influent and effluent CODs for the LMFCs. HRTs were calculated from the set flow rate (Q, mL h^{-1}) and reactor volume (V, mL) as HRT = V/Q. Coulombic efficiency of the LMFCs was calculated from the ratio of the total coulombs produced to the theoretical amount of coulombs available from the substrate, as previously described [24].

Cathodic and anodic biofilm growth in LMFCs were evaluated on the basis of protein concentrations measured using the bicinchoninic acid method [6,28]. The electrode material was placed in a sealed beaker with 40 mL of 0.2 N NaOH, and then shaken for 12 h to dissolve the biofilm into the solution. The electrode was then washed with an additional 10 mL of deionized water and all the above liquids were combined (50 mL total) for protein analysis (all reagents from Sigma Chemical Co., St. Louis, MO).

3. Results and discussion

3.1. Power production of small cubic MFCs using different anode configurations

The performance of the B- and BM-MFCs were similar to each other during startup, with all reactors reaching a maximum voltage of about 460 mV (1000 Ω) after 4 d, with stable cycles of voltage production over subsequent cycles (Fig. S2A). The M-MFCs started up much more slowly, and their maximum voltages were erratic during the same startup period. For example, one of the replicate M-MFCs produced only 300 mV after 7 days of inoculation, while the duplicate M-MFC produced up to 470 mV by day 4, but it then decreased to 210 mV at day 11 (Fig. S2B). The unstable and poor start-up performance of M-MFC was expected based on previous studies where it has been shown that a mesh anode placed near the cathode did not perform well due to oxygen contamination from the cathode [4].

After this start-up period, and further acclimation to low external resistances, polarization tests were conducted with the MFCs. The composite anode BM-MFCs produced a power density of 524 ± 20 mW m^{-2}, which was 20% higher than the brush-only B-MFCs (436 ± 17 mW m^{-2}) and 150% higher than the mesh-only M-MFCs (206 ± 22 mW m^{-2}) (Fig. 2A). The polarization curves showed that the cathodic resistance of three MFCs were similar (~180 Ω), but the anode resistance of the BM-MFCs (67 Ω) was much less than the other two reactors (103 Ω, B-MFC; 489 Ω, M-MFC) (Fig. 2B). While power overshoot was observed for both the B- and M-MFC in the high current ranges (>0.4 mA, M-MFC; >1.24 mA, B-MFC), no overshoot was observed for the BM-MFC (Fig. 2A and B). Therefore, the combined mesh and brush anode effectively lowered the anode resistance and improved the performance as shown by the elimination of power overshoot.

3.2. Electrochemical performance of different anode configurations

CVs showed that the BM-MFC produced a higher maximum current density (4.3 ± 0.7 A m^{-2} at the anode potential of 0.1 V) than the other two reactor configurations (1.2 ± 0.7 A m^{-2}, M-MFC;

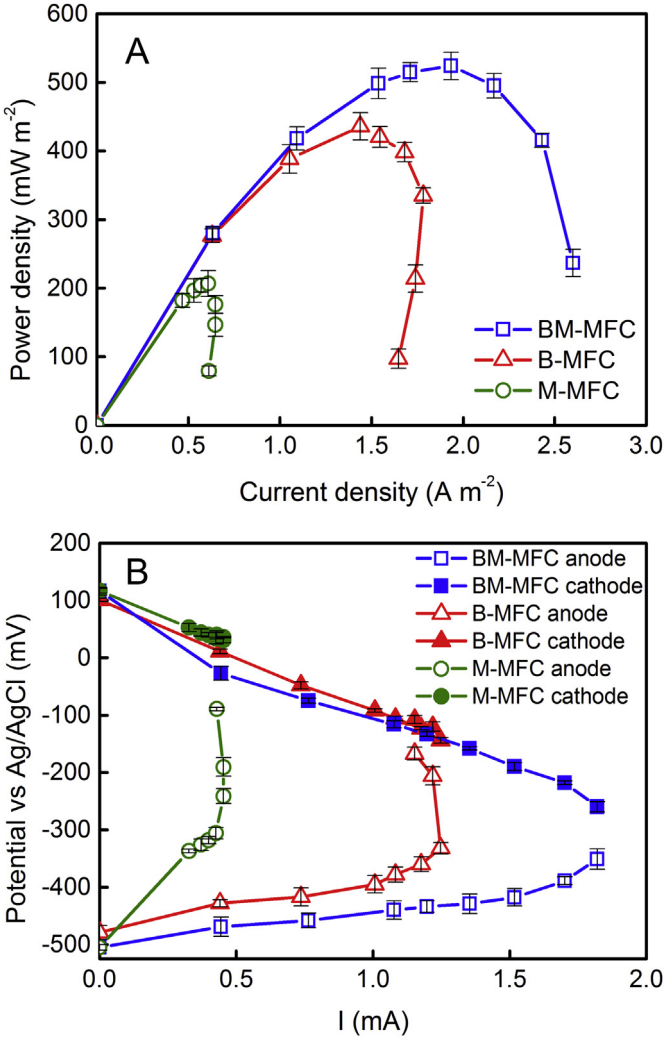

Fig. 2. (A) Power density curves and (B) polarization curves for the anodes and cathodes of small cubic MFCs with different anode configurations: B = brush, M = mesh, and BM = brush and mesh.

3.8 ± 0.3 A m^{-2}, B-MFC) (Fig. 3A). The BM-MFC showed a stable maximum current in the high potential range (−0.2 to 0.1 V), the maximum current density of the B-MFC was erratic, as it initially increased to 3.8 ± 0.3 A m^{-2} at −0.17 V and then gradually declined to 3.5 ± 0.3 A m^{-2} at 0.1 V. These results show that the biofilm on the composite anode had both more stable electrochemical performance at high anode potentials, and that it produced a higher current density.

EIS tests showed that the composite anode had the lowest charge transfer resistance of 85 Ω, which was consistent with its better performance in CV and polarization tests (Fig. 3B). The mesh anode had the largest charge transfer resistance of 581 Ω, indicating the lack of effective electron transfer within the anode biofilm. The ohmic resistance of three anodes were similar (~0.5 Ω), which was expected as they had the same electrolyte conditions and indicated that combing carbon mesh with brush in this way did not increase the anode ohmic resistance. Thus, the use of the composite anode configuration helped to reduce the anode resistance, likely by a combination of reducing oxygen crossover and enabling more stable current generation through the growth of a biofilm that could effectively produce current up to higher power densities than the other anode configurations.

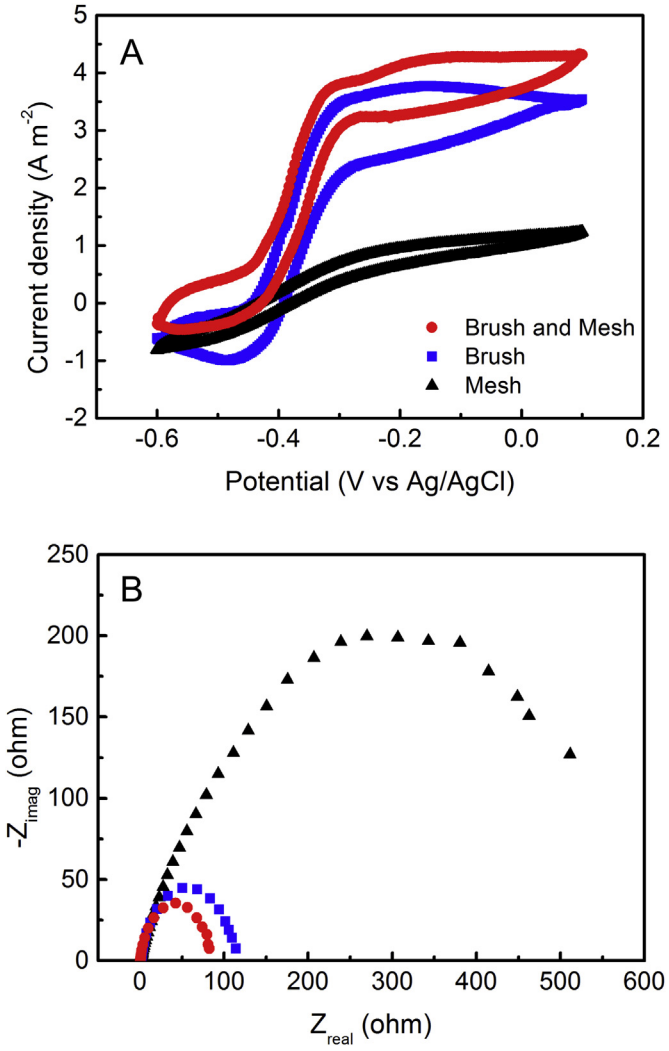

Fig. 3. (A) CVs for the small cubic MFCs with the three different anode configurations and (B) Nyquist plots obtained using EIS at the anode potentials that produce the maximum power densities.

3.3. Power production of the BM- and B-LMFCs with continuous flow

After acclimation of the two LMFCs under continuous flow conditions, the BM-LMFC produced a higher maximum power density with lower anode resistances than the B-LMFC at the two shorter HRTs of 2 and 4 h (Fig. 4A, B, D and E). For example, the BM-LMFC produced 471 ± 13 mW m^{-2} at an HRT = 2 h, which was 14% higher than that of B-LMFC (413 ± 20 mW m^{-2}) (Fig. 4A). This relative improved performance was similar to that observed for the increase in power for the same anode configurations using the small cubic MFCs that were operated in fed-batch mode. However, at the longest HRT of 8 h, the power density of BM-LMFC decreased to 181 ± 9 mW m^{-2}, which was similar to the B-LMFC (173 ± 12 mW m^{-2}) (Fig. 4C). The large reduction in power for both types of MFCs was likely due to the lower average COD concentration in the reactor, as low CODs are known to reduce current production by the anode [29]. This indicated that power could be enhanced by using the composite anode only when there was a higher influent COD loading and thus a higher effluent COD, as discussed further below.

Power overshoot was not observed for the composite anode BM-LMFCs at the 2 and 4 h HRTs (Fig. 4A and B). The B-LMFCs showed power overshoot in all tests, and at the 8 h HRT the BM-MFCs also showed power overshoot (Fig. 4C). Based on the changes in the electrode potentials, most of power overshoot and differences in the performance of the MFCs with the two anode configurations were due to the change in anode potentials at higher current densities. The observation that power overshoot also occurred in BM-LMFC at the 8 h HRT indicated that stable performance could not even be maintained with the BM-LMFC if the COD loading was too low. Additionally, the cathode resistance of the BM-LMFC (35 Ω at 2 h; 58 Ω at 4 h) were lower than those of B-LMFC (43 Ω at 2 h; 70 Ω at 4 h) at HRT = 2 and 4 h (Fig. 4D and E), which might imply a more serious cathode fouling in B-LMFC after long-term running due to the absence of the additional carbon mesh.

The power densities of B- and BM-LMFCs achieved in continuous flow mode were lower than those obtained in fed-batch tests, especially for continuous flow tests at the lowest HRTs. In general, power densities under continuous flow conditions are equal to, or less than, those obtained in fed batch tests due to lower COD concentrations in the reactor under steady conditions compared to the high COD concentrations at the start of a fed-batch cycle. For example, tests with a pilot-scale (72 L) stack of MFCs produced a lower power density under continuous operation (42.1 W m^{-3}) than that obtained during fed-batch operation (50.9 W m^{-3}) due to lower COD concentrations caused by uneven loading among three anode chambers [30]. Recirculation used in another study to equalize the COD concentrations in an MFC produced power densities in continuous flow similar to that obtained in fed batch mode with recirculation [31]. In previous tests using acetate in the same MFC as the one used here, but with 3 larger brushes each 2.5 cm in diameter, 975 mW m^{-2} was produced in fed-batch mode compared to 880 mW m^{-2} with continuous flow at an HRT of 8 h [32]. This power density was further reduced to 659 mW m^{-2} at an HRT of 16 h due to the greatly reduced COD concentration. However, some studies have shown improved performance with continuous flow operation. For example, a microfluidic MFC operated under continuous flow conditions produced nearly 15 times the power obtained under fed-batch conditions [33]. Therefore, the power generation performance of MFCs in continuous operation is highly dependent on the COD loading, reactor architecture, and operating conditions. In this study, the lower COD loading in continuous flow tests at HRTs of 4 and 8 h was likely the reason for the lower power

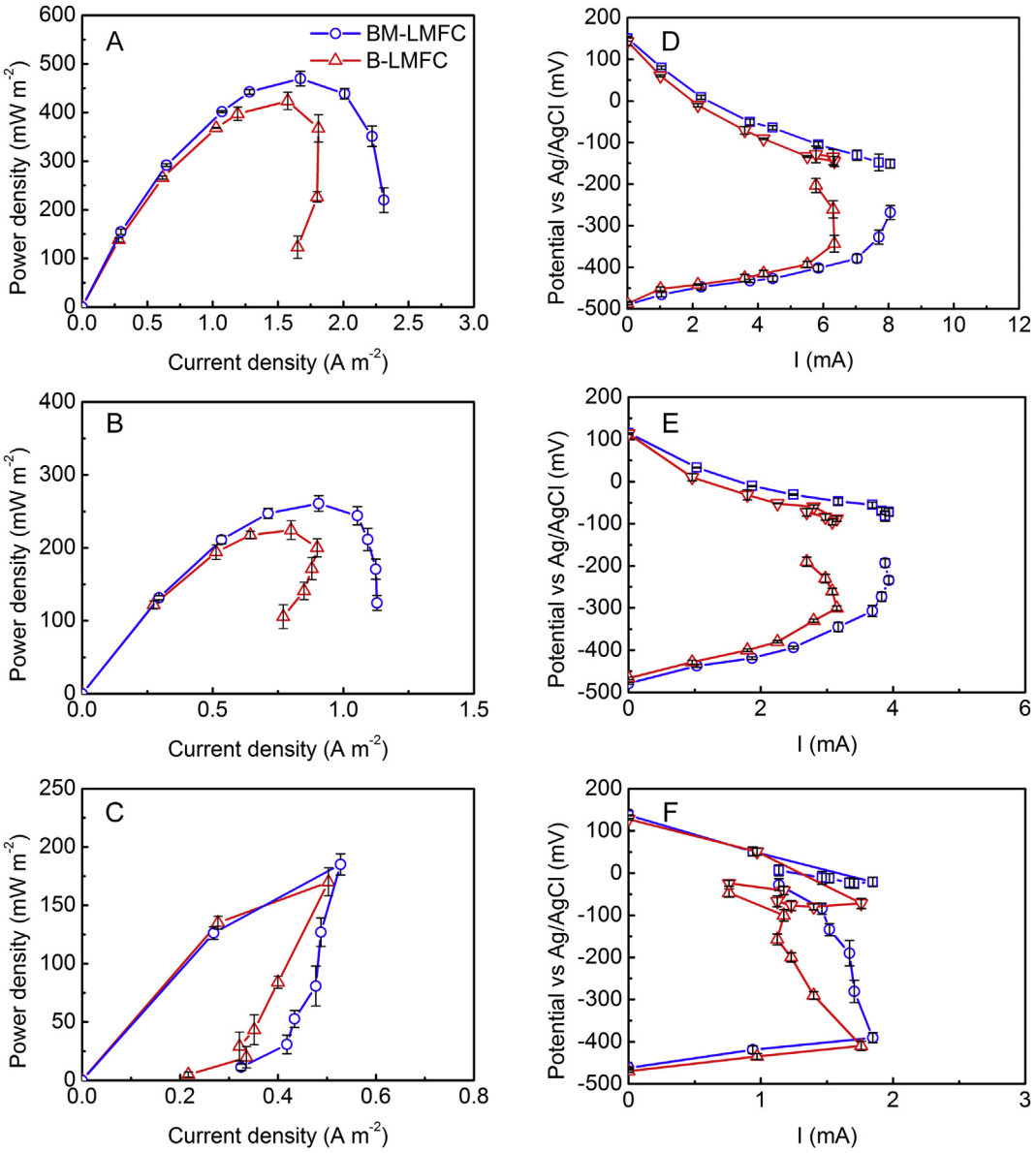

Fig. 4. (A), (B) and (C) Power density curves, and (D), (E) and (F) polarization curves of B-LMFCs and BM-LMFC at HRTs of (A, D)2, (B, E) 4 and (C, F) 8 h.

densities of LMFCs compared to smaller cubic MFCs that were only operated in fed-batch conditions.

3.4. COD removals at different HRTs

COD removals with the composite anode BM-LMFC were significantly lower ($p < 0.05$, Student's t-test; Table S1) than those of the B-LMFCs at all HRTs before cathode refurbishment (Fig. 5A). The result was unexpected since the total protein content (biomass content) of the composite anode was 44% higher (8.2 ± 0.2 mg) than that of the graphite fiber brush anode MFCs (5.7 ± 0.2 mg). In addition, the BM-LMFCs had higher current densities at all HRTs and thus it was expected the BM-LMFCs would have greater COD removals than the B-LMFC [34]. To examine reasons for less COD removal by the BM-LMFCs, cathodes of all the MFCs were removed, examined for biomass based on protein content, and cleaned. Results showed that the total protein content in the cathode biofilm of B-LMFC was 3.1 ± 0.3 mg (78.5 μg cm^{-2}), which was 65% higher than that the cathode of the BM-LMFC (1.9 ± 0.2 mg (47.6 μg cm^{-2})). Therefore, the higher COD removals of B-LMFC was probably due to more extensive heterotrophic bacteria on the cathode that used the oxygen transferred through the cathode to degrade organic matter [34].

After the cathode refurbishment (removal of cathodic biofilms), BM-LMFCs exhibited significantly higher COD removals than B-LMFC at HRTs of 2 and 4 h ($p < 0.05$; Table S2). This demonstrated that the composite anode did have better COD removal performance than the MFC with only a graphite fiber brush due to its higher anode biomass and higher current densities once the cathode biofilms was removed. At an HRT = 8 h, the B-LMFC again showed higher COD removals (Fig. 5B), likely as a result of biofilms re-growing on the cathode after extended operation (more than a month) at the two previous HRTs. The reason for less cathodic biomass (less cathode biofouling) in BM-LMFC after long-term operation was likely due to a lower biomass yield with current generation than that with oxygen and a reduction of oxygen transfer into the anode chamber.

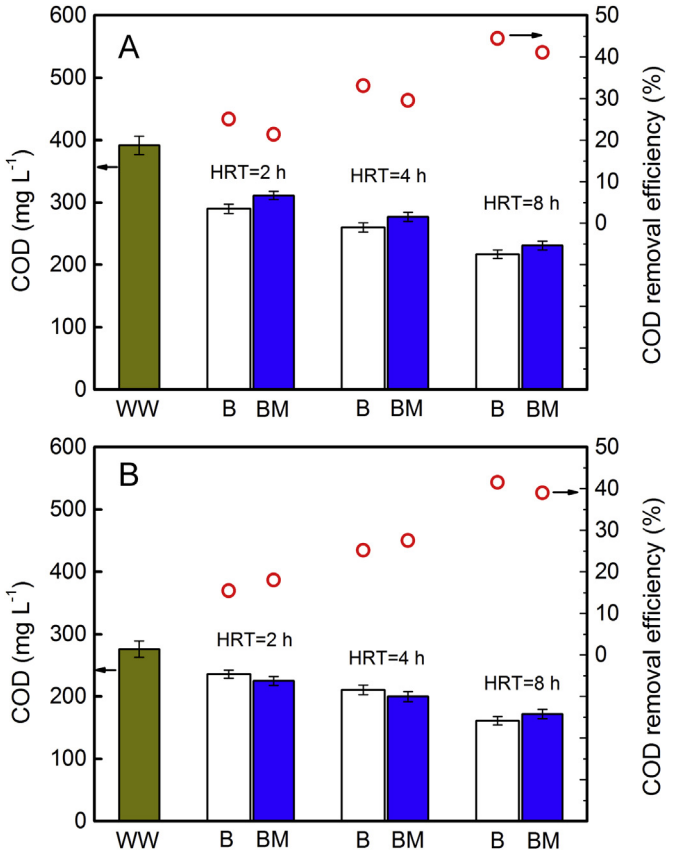

Fig. 5. COD removals of the B-LMFCs ("B" at the bottom of x-axis represented B-LMFC) and BM-LMFCs ("BM" represented BM-LMFC) at HRTs of 2, 4 and 8 h (A) before and (B) after cathode refurbishment.

3.5. Coulombic efficiencies at different HRTs

The Coulombic efficiencies (CEs) increased with the HRT for all LMFCs (Fig. 6). CEs of BM-LMFC ranged from 42.5% to 53.8%, and exceeded those of B-LMFC (35.3%–46.7%) at all HRTs before cathode refurbishment. The higher CEs of BM-LMFC were expected since this reactor had higher current densities and lower COD removals.

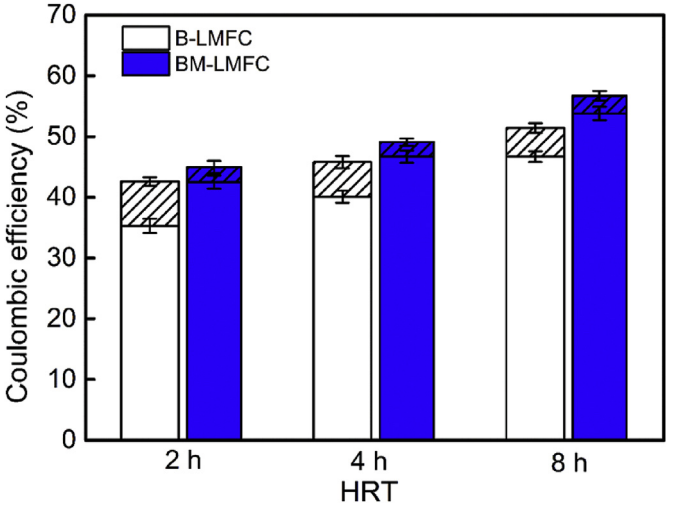

Fig. 6. CEs of B-LMFCs and BM-LMFCs at three different HRTs (2.4 and 8 h) before and after cathode refurbishment. The patterned areas in the columns indicate the increment of CEs after cathode refurbishment.

Although oxygen crossover was not measured directly for these reactor configurations, the higher CEs of the combined brush and mesh reactors compared to the brush reactors alone shows that less COD was lost to oxygen crossover. After cathode refurbishment, the CEs of both types of MFCs increased due to the removal of cathodic biofilms which were rapidly consuming substrate using oxygen. The BM-LMFC still had higher CEs at all HRTs than B-LMFC once the cathode biofilm was removed, further indicating that the additional carbon mesh could serve as a "separator" to reduce oxygen intrusion based on the higher CEs of the BM-LMFCs. The relative increase in the CEs was greater for the B-LMFC than the BM-LMFC at all HRTs after cathode refurbishment. For example, at HRT = 2 h, CE of B-LMFC increased by 7.3% (from 35.3 ± 1.7% to 42.6 ± 0.8%) while CE of BM-LMFC increased by only 2.6% (from 42.5 ± 1.3% to 45.1 ± 1.0%). The greater relative increases in the CEs demonstrated that the B-LMFC had greater cathode biofouling than BM-LMFC before refurbishment, and thus it showed more improvement after removal of the cathodic biofilms.

4. Conclusions

Small cubic MFCs with composite anodes had higher power densities than other anode configurations tested here, with a maximum power density of 524 ± 20 mW m^{-2} for the BM-MFCs treating domestic wastewater in fed batch mode. This power density was 20% higher than MFCs with only graphite fiber brush anodes (436 ± 17 mW m^{-2}) and 150% larger than MFCs with carbon mesh anodes (206 ± 22 mW m^{-2}). The use of a composite anode resulted in a lower charge transfer resistance, and therefore a higher power density and more stable current densities at high anode potentials in the electrochemical tests. When larger-scale MFCs were operated in continuous flow mode, the composite anode BM-LMFCs also showed enhanced power generation (471 ± 13 mW m^{-2}) compared to those with only brush anodes (413 ± 20 mW m^{-2}) at short HRTs (2 h). The use of the composite anode helped to mitigate power overshoot, higher CEs were also obtained in continuous flow tests at HRTs ranging from 2 to 8 h. This improved and more stable performance of the composite anode MFCs was due to carbon mesh placed close to the cathode, which increased the total anode biomass near the cathode and helped to reduce oxygen intrusion from the cathode without adding ohmic resistance to the system. The BM-LMFCs had a lower cathode internal resistances and less cathode biofouling than B-LMFCs after long-term operation. Therefore, the composite anode configuration proposed in this study may provide a feasible strategy to effectively enhance and stabilize power generation performance of SEA MFCs when treating domestic wastewaters that have much lower CODs and buffering capacities than acetate-based solutions typically used in laboratory studies.

Acknowledgments

This research was financially supported by the Key Program of the National Natural Science Foundation of China (No.51238004), and the Strategic Environmental Research and Development Program (**ER-2216**).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.01.041.

References

[1] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia,

P. Aelterman, W. Verstraete, K. Rabaey, Microbial fuel cells: methodology and technology, Environ. Sci. Technol. 40 (2006) 5181–5192.
[2] K. Rabaey, W. Verstraete, Bacterial potential for electricity generation, Trends Biotechnol. 23 (2005) 291–298.
[3] Y. Ahn, M.C. Hatzell, F. Zhang, B.E. Logan, Different electrode configurations to optimize performance of multi-electrode microbial fuel cells for generating power or treating domestic wastewater, J. Power Sources 249 (2014) 440–445.
[4] F. Zhang, X. Xia, Y. Luo, D. Sun, D.F. Call, B.E. Logan, Improving startup performance with carbon mesh anodes in separator electrode assembly microbial fuel cells, Bioresour. Technol. 133 (2013) 74–81.
[5] X. Zhang, S. Cheng, P. Liang, X. Huang, B.E. Logan, Scalable air cathode microbial fuel cells using glass fiber separators, plastic mesh supporters, and graphite fiber brush anodes, Bioresour. Technol. 102 (2011) 372–375.
[6] X. Zhang, S. Cheng, X. Wang, X. Huang, B.E. Logan, Separator characteristics for increasing performance of microbial fuel cells, Environ. Sci. Technol. 43 (2009) 8456–8461.
[7] S. Cheng, H. Liu, B.E. Logan, Increased Power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing, Environ. Sci. Technol. 40 (2006) 2426–2432.
[8] S. Hays, F. Zhang, B.E. Logan, Performance of two different types of anodes in membrane electrode assembly microbial fuel cells for power generation from domestic wastewater, J. Power Sources 196 (2011) 8293–8300.
[9] C. Liu, J. Li, X. Zhu, L. Zhang, D. Ye, R.K. Brown, Q. Liao, Effects of brush lengths and fiber loadings on the performance of microbial fuel cells using graphite fiber brush anodes, Int. J. Hydrogen Energy 38 (2013) 15646–15652.
[10] B. Logan, S. Cheng, V. Watson, G. Estadt, Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells, Environ. Sci. Technol. 41 (2007) 3341–3346.
[11] V. Lanas, Y. Ahn, B.E. Logan, Effects of carbon brush anode size and loading on microbial fuel cell performance in batch and continuous mode, J. Power Sources 247 (2014) 228–234.
[12] W. He, X. Zhang, J. Liu, X. Zhu, Y. Feng, B.E. Logan, Microbial fuel cells with an integrated spacer and separate anode and cathode modules, Environ. Sci. Water Res. Technol. 2 (2016) 186–195.
[13] W. He, M.J. Wallack, K.Y. Kim, X. Zhang, W. Yang, X. Zhu, Y. Feng, B.E. Logan, The effect of flow modes and electrode combinations on the performance of a multiple module microbial fuel cell installed at wastewater treatment plant, Water Res. 105 (2016) 351–360.
[14] V. Lanas, B.E. Logan, Evaluation of multi-brush anode systems in microbial fuel cells, Bioresour. Technol. 148 (2013) 379–385.
[15] J.L. Stager, Impact of Anode-separator Configurations and Cathode Materials on Microbial Fuel Cell Performance, The Pennsylvania State University, 2015 (Master's Thesis).
[16] C.S. Butler, R. Nerenberg, Performance and microbial ecology of air-cathode microbial fuel cells with layered electrode assemblies, Appl. Microbiol. Biotechnol. 86 (2010) 1399–1408.
[17] Y. Ahn, B.E. Logan, Altering anode thickness to improve power production in microbial fuel cells with different electrode distances, Energy Fuels 27 (2013) 271–276.
[18] X. Zhang, S. Cheng, X. Huang, B.E. Logan, The use of nylon and glass fiber filter separators with different pore sizes in air-cathode single-chamber microbial fuel cells, Energy Environ. Sci. 3 (2010) 659–664.
[19] V. Yousefi, D. Mohebbi-Kalhori, A. Samimi, M. Salari, Effect of separator electrode assembly (SEA) design and mode of operation on the performance of continuous tubular microbial fuel cells (MFCs), Int. J. Hydrogen Energy 41 (2016) 597–606.
[20] S.C. Popat, D. Ki, B.E. Rittmann, C.I. Torres, Importance of OH − transport from cathodes in microbial fuel cells, ChemSusChem 5 (2012) 1071–1079.
[21] X. Wang, S.A. Cheng, Y.J. Feng, M.D. Merrill, T. Saito, B.E. Logan, The use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells, Environ. Sci. Technol. 43 (2009) 6870–6874.
[22] W. Yang, W. He, F. Zhang, M.A. Hickner, B.E. Logan, Single-step fabrication using a phase inversion method of poly(vinylidene fluoride) (PVDF) activated carbon air cathodes for microbial fuel cells, Environ. Sci. Technol. Lett. 1 (2014) 416–420.
[23] F. Zhang, J. Liu, I. Ivanov, M.C. Hatzell, W. Yang, Y. Ahn, B.E. Logan, Reference and counter electrode positions affect electrochemical characterization of bioanodes in microbial electrochemical systems, Biotechnol. Bioeng. 111 (2014) 1931–1939.
[24] K.Y. Kim, W. Yang, B.E. Logan, Impact of electrode configurations on retention time and domestic wastewater treatment efficiency using microbial fuel cells, Water Res. 80 (2015) 41–46.
[25] X. Zhang, W. He, W. Yang, J. Liu, Q. Wang, P. Liang, X. Huang, B.E. Logan, Diffusion layer characteristics for increasing performance of activated carbon air-cathodes in microbial fuel cells, Environ. Sci. Water Res. Technol. 2 (2016) 266–273.
[26] Y. Hong, D.F. Call, C.M. Werner, B.E. Logan, Adaptation to high current using low external resistances eliminates power overshoot in microbial fuel cells, Biosens. Bioelectron. 28 (2011) 71–76.
[27] Z. He, F. Mansfeld, Exploring the use of electrochemical impedance spectroscopy (EIS) in microbial fuel cell studies, Energy Environ. Sci. 2 (2009) 215–219.
[28] D.R. Bond, D.R. Lovley, Electricity production by Geobacter sulfurreducens attached to electrodes, Appl. Environ. Microbiol. 69 (2003) 1548–1555.
[29] H. Liu, B.E. Logan, 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 (2004) 4040–4046.
[30] S. Wu, H. Li, X. Zhou, P. Liang, X. Zhang, Y. Jiang, X. Huang, A novel pilot-scale stacked microbial fuel cell for efficient electricity generation and wastewater treatment, Water Res. 98 (2016) 396–403.
[31] C.-H. Lay, M.E. Kokko, J.A. Puhakka, Power generation in fed-batch and continuous up-flow microbial fuel cell from synthetic wastewater, Energy 91 (2015) 235–241.
[32] Y. Ahn, B.E. Logan, A multi-electrode continuous flow microbial fuel cell with separator electrode assembly design, Appl. Microbiol. Biotechnol. 93 (2012) 2241–2248.
[33] D. Vigolo, T.T. Al-Housseiny, Y. Shen, F.O. Akinlawon, S.T. Al-Housseiny, R.K. Hobson, A. Sahu, K.I. Bedkowski, T.J. DiChristina, H.A. Stone, Flow dependent performance of microfluidic microbial fuel cells, Phys. Chem. Chem. Phys. 16 (2014) 12535–12543.
[34] X. Zhang, W. He, L. Ren, J. Stager, P.J. Evans, B.E. Logan, COD removal characteristics of air-cathode microbial fuel cells, Biores. Technol. 176 (2015) 23–31.