Journal of Power Sources 187 (2009) 471–479

Contents lists available at ScienceDirect

Journal of Power Sources

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

Improved performance of air-cathode single-chamber microbial fuel cell for wastewater treatment using microfiltration membranes and multiple sludge inoculation

Jian Sun [1], Yongyou Hu *, Zhe Bi [2], Yunqing Cao [3]

Department of Environmental Science and Engineering, South China University of Technology, Guangzhou 510006, China

ARTICLE INFO

Article history:
Received 16 September 2008
Received in revised form 1 November 2008
Accepted 5 November 2008
Available online 17 November 2008

Keywords:
Microbial fuel cell
Microfiltration membrane
Multiple sludge
Performance improvement

ABSTRACT

Substantial optimization and cost reduction are required before microbial fuel cells (MFCs) can be practically applied. We show here the performance improvement of an air-cathode single-chamber MFC by using a microfiltration membrane (MFM) on the water-facing side of the cathode and using multiple aerobic sludge (AES), anaerobic sludge (ANS), and wetland sediment (WLS) as anodic inoculums. Batch test results show that the MFC with an MFM resulted in an approximately two-fold increase in maximum power density compared to the MFC with a proton exchange membrane (PEM). The Coulombic efficiency increased from 4.17% to 5.16% in comparison with the membrane-less MFC, without a significant negative effect on power generation and internal resistance. Overall performance of the MFC was also improved by using multiple sludge inoculums in the anode. The MFC inoculated with ANS + WLS produced the greatest maximal power density of 373 mW m^{-2} with a substantially low internal resistance of 38 Ω. Higher power density with a decreased internal resistance was also achieved in MFC inoculated with ANS + AES and ANS + AES + WLS in comparison with those inoculated with only one sludge. The MFCs inoculated with AES + ANS achieved the highest Coulombic efficiency. Over 92% COD was removed from confectionery wastewater in all tested MFCs, regardless of the membrane or inoculum used.

1. Introduction

Microbial fuel cells (MFCs) are a promising and novel approach to wastewater treatment that can be used to capture energy in the form of electricity or hydrogen gas.

In an MFC, organic matter is oxidized by anaerobic microorganisms to produce electrons, which are transferred to the anode and then flow across a conductive material containing a resistor and are ultimately released to a terminal electron acceptor, such as oxygen [1–8] or other chemicals [9–12]. The acceptors are reduced in the cathode, and protons are simultaneously transported in solution from the anode into the cathode.

MFCs are not yet commercialized due to their low power output due primarily to high internal resistance. A recently developed single-chamber MFC substantially reduced the internal resistance and produced additional energy by replacing the aerated cathode used in two-chamber MFCs with a direct air cathode, as used in hydrogen fuel cells [13]. This MFC appears to be scalable for practical application. Liu et al. [14] demonstrated that the power output can be maintained or even increased during reactor scale-up by comparing the performance of a relatively large membrane-less single-chamber microbial fuel cell (total volume of 520 ml) with a smaller MFC (total volume of 28 ml).

Membranes are an optional component that also affects the overall performance of MFCs. The adverse effect of the membrane on performance is usually a result of increased internal resistance that reduces the power production [7]. Kim et al. [15] measured the internal resistance of various membranes and found that the internal resistance attributable to the membrane depended on the system architecture used and on how the membrane is incorporated. Although further reductions in cost, configuration simplification, and increase in power density can be achieved in air-cathode membrane-less single-chamber MFCs, the Coulombic efficiency is much lower than for MFCs containing a membrane because of substrate consumption by oxygen diffusion though the cathode. Moreover, omitting a membrane can lead to deactivation of the Pt-catalyst in the cathode from the contaminated environment of the anode.

Any permeable material can function as a solution barrier in an MFC if it allows charge transfer. Yan et al. [16,17] found that

* Corresponding author. Tel.: +86 20 39380506/13602746125; fax: +86 20 39380508.
E-mail addresses: sunjian472@163.com (J. Sun), ppyyhu@scut.edu.cn (Y. Hu), bidagelasi@tom.com (Z. Bi), cyq_jenny@163.com (Y. Cao).
[1] Tel.: +86 20 39383779/13570387379.
[2] Tel.: +86 13580487282.
[3] Tel.: +86 13560154968.

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.11.022

using only a layer of cloth on the water-facing side of an air cathode significantly improved the performance of single-chamber MFCs and enabled a variety of MFC designs. Many membranes or filters applied in wastewater treatment have also been tested and are suited for MFC use, as reported in literature [15,18]. Microfiltration membranes (MFM, ≥0.01 μm in pore size) are increasingly used to separate microorganisms, colloids, suspended solids, and macromolecule compounds from water, and they could be used in place of the proton exchange membrane (PEM) in MFCs.

Improvements in the system architecture and materials will soon result in power generation that is dependent on the capabilities of the microorganisms. Currently, electricity can be generated from seemingly any biodegradable material, ranging from pure compounds [6,7,11,19,20] to complex mixtures of organic matter present in wastewater [4,21–23]. MFCs operated using mixed cultures can utilize far more complicated carbon sources and achieve substantially greater power densities than those using pure cultures. Ren et al. [24] reported that cellulose was successfully biodegraded and transformed into electricity under co-culture in a two-chamber MFC while no electricity was produced in pure culture alone. A strain of *Pseudomonas aeruginosa* was able to utilize glucose and produce an electron shuttle in a mixed culture system, but it was inefficient in converting glucose to electricity when it was isolated from the system in part because it incompletely oxidized glucose to fatty acids [25]. Isolates obtained in one study were electrochemically active, yet their power densities when they were grown in pure culture were 2–3 orders of magnitude less than those of the mixture from which they were derived [26]. Some bacteria are known to transfer electrons to the electrode via convenient self-excreted soluble electron shuttles. These shuttles, however, can be also used by other bacterial species to achieve an enhanced electron transfer in a mixed culture system [25,26]. Interspecies electron transfer via nanowires is another approach to achieve higher electricity generation in a mixed culture system [27].

Various types of sludge, aquatic sediments, and wastewaters are usually used as anode inoculums to provide such microbial diversity [1,3,11,22,28–31]. These diverse anode communities probably possess a wealth of undiscovered electrochemical capabilities that can be exploited in different MFC applications.

In this study, laboratory experiments were conducted to simultaneously optimize the anode and cathode in order to improve MFC performance during wastewater treatment. A series of air-cathode single-chamber MFCs (total volume of 1 l) was used to examine whether using an MFM improves cathode performance as compared to using a PEM or a membrane-less cathode. Single and multiple sludge and sediments were used as anodic inoculums in the same MFC architecture to investigate how the various inoculations affect the performance of MFCs.

2. Materials and methods

2.1. Anode inoculation and growth media

To investigate the effect of sludge diversity on MFC performance, different types of aerobic sludge (AES), anaerobic sludge (ANS), and wetland sediment (WLS) were used as anodic inoculums. Six MFCs were inoculated with ANS + AES, ANS + WLS, ANS + AES + WLS, as well as three controls using the separated AES, ANS and WLS. Each type of sludge was mixed in equal volume along with the single sludge to a final concentration of 2 g VSS l^{-1} in the anodic chamber.

Confectionery wastewater collected from a sugar refinery (initial COD of 22,000 mg l^{-1}) was used as the sole carbon source and added into the anodic chamber (900 ml liquid volume) with an initial concentration of 1000 mg l^{-1} COD with a medium containing (per liter of de-ionized water): $NaH_2PO_4 \cdot 2H_2O$ (2.98 g), $Na_2HPO_4 \cdot 12H_2O$ (9.28 g), NH_4Cl (0.31 g), KCl (0.13 g), a mineral solution (12.5 ml), and a vitamin solution (12.5 ml) as reported by Lovley and Phillips [32]. The final pH of this medium was adjusted to 7.0 using 0.1 M NaOH or HCl.

2.2. MFC construction

The air-cathode single-chamber MFC was constructed using plane Plexiglas, with a total volume of 1 l (10 cm × 10 cm × 10 cm in height with an operating volume of approximately 900 ml plus a 100 ml headspace). The top had five ports for purging, sampling, and introducing electrodes, and the ports were sealed with thick rubber stoppers during operation. Porous carbon papers (without waterproofing or catalyst) with a projected surface area of 6 cm × 6 cm on one side were used as anode electrodes. Prior to use, they were soaked in de-ionized water for a period of 24 h. The air cathode was similar to the anode in size and consisted of a catalyst layer (containing 0.5 mg cm^{-2} of Pt) on the water-facing side and a polytetrafluoroethylene (PTFE) diffusion layer on the air-facing side, as previously described by Liu et al. [33]. The microfiltration membrane (0.22 μm in pore size) was applied directly onto the water-facing side of the cathode. The entire cathode was covered with a thick plexiglass cover with holes to allow oxygen to reach the cathode. Air-cathode MFCs with anaerobic sludge inoculation were also used to compare the performance using MFMs, PEMs, and no membranes. The carbon paper/PEM composite cathode was manufactured as reported by Liu et al. [8]. The membrane-less cathode was a carbon paper containing 0.5 mg cm^{-2} of Pt catalyst in the water-facing side. The anode was set parallel to the cathode at a distance of 5 cm and connected by copper wires. All exposed metal surfaces were sealed with a nonconductive epoxy resin. The schematic details of the MFCs along with photographs are in Fig. 1.

2.3. MFC operation

MFCs were all operated in a batch-fed mode at a fixed load (500 Ω, unless stated otherwise) and mixed using a magnetic stirrer. Nitrogen gas was flushed for 15 min into the anodic chamber before each test to remove dissolved oxygen so as to maintain anoxic conditions. The solution of confectionery wastewater and medium in each MFC was refreshed when the voltage decreased below 0.05 V. Polarization curves were used to obtain the maximum power density by varying the external resistance from 1000 Ω to 50 Ω using a resistor box. At least two batches were run for each resistance to ensure repeatability of the MFC's power output. A Ag/AgCl reference electrode (0.195 V versus normal hydrogen electrode; NHE) in the anode chamber measured individual electrode potentials. All experiments were conducted in at least duplicate, in a constant-temperature room (30 ± 1 °C), and the average value is reported for all data.

2.4. Analysis

The concentration of organic matter in the MFC was measured as COD using standard methods [34]. All samples were filtered through a 0.22 μm-pore-size syringe filter unit prior to COD measurements.

Cyclic voltammetry (V/A Computrace, Metrohm, Switzerland) was used to characterize the oxidation-reduction reactions on the electrode surface by measuring the current response at the electrode surface to a specific range of potentials in an unstirred solution at a scan rate of 20 mV s^{-1} (minimum of 3 scans). The anode was the working electrode, and the counter electrode was the MFC cathode with a Ag/AgCl reference electrode. The potential range was −450 to +450 mV.

The bacterial morphologies on the surface of the carbon paper (anode) were determined using an environmental scanning electron microscope (ESEM) (XL-30, Philips, Holland). Before

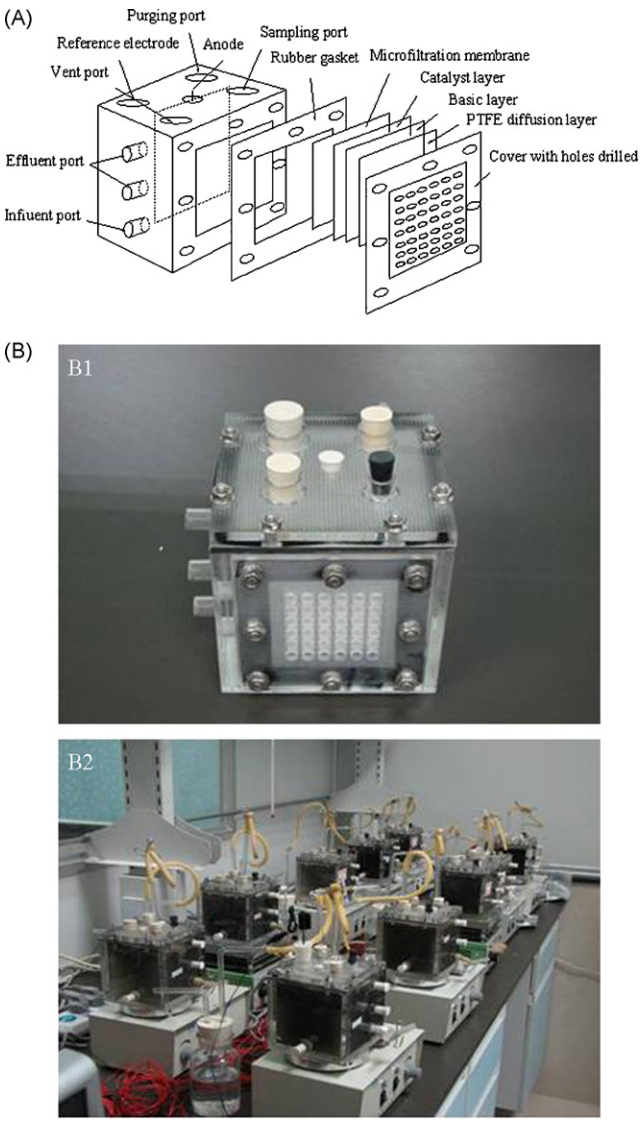

Fig. 1. Schematic (A) and photograph (B) of the air-cathode single-chamber microbial fuel cells used in the experiment, which allows alteration in operation mode (continuous or batch).

observation, a sample of anodic granules was collected and fixed overnight with paraformaldehyde and glutaraldehyde in a buffer solution (0.1 M cacodylate, pH 7.5; 4 °C), followed by washing and dehydration in water/ethanol. Samples were then coated with Au/Pt before ESEM observation.

2.5. Calculations

The COD removal efficiency (δCOD) during operation was calculated using

Eq. (1):

$$\delta\text{COD} = \frac{\text{COD}_{\text{int}}}{\text{COD}_{\text{out}}} \times 100\% \quad (1)$$

COD_{int} and COD_{out} denote the initial and final concentrations (mg l^{-1}), respectively.

The voltage difference between the anode and cathode (V) was recorded every 2 min using a precision multimeter and a data acquisition system (Model 2700, Keithly Instruments, USA). Power density (mW m^{-2}) was calculated according to

$$P = \frac{IV}{A} \quad (2)$$

where I is the current, V is the voltage, and A is the projected cross-sectional area of the anode.

The Coulombic efficiency was calculated as

$$Ec(\%) = \frac{C_{\text{P}}}{C_{\text{T}}} \times 100\% \quad (3)$$

where C_{P} is the total Coulombics calculated by integrating the current over time and C_{T} is the theoretical amount of Coulombics based on the COD removed by assuming 4 mol of electrons per mol of COD.

The internal resistance (R_{int}) of each MFC was calculated from the slope of plots of V and I using

$$V = E_{\text{cell}} - IR \quad (4)$$

where E_{cell} is the electromotive force of the cell [35].

3. Results

3.1. Effect of MFM on performance of air-cathode single-chamber MFC

3.1.1. Voltage output

The effect of the MFM on the performance of an air-cathode single-chamber MFC was examined in a batch-fed mode and compared to the PEM and non-membrane configurations. The cycles of voltage generation shown in Fig. 2A were all obtained after two acclimation cycles with reproducible levels of power generation. The MFC with an MFM generated a comparable voltage (average 0.59 V) that was comparable to that generated by the membrane-less MFC (average 0.56 V), and that was 29% higher than that generated by the MFC with a PEM (average 0.42 V).

3.1.2. Power density

The overall performance of each MFC was evaluated on the basis of power density normalized to the projected anode surface area or reactor volume. The maximum power density was determined by varying the circuit resistance from 1000 Ω to 50 Ω. At a current density of $0.552\ \text{A m}^{-2}$, the MFC with an MFM had maximum power densities ($214\ \text{mW m}^{-2}$ and $878\ \text{mW m}^{-3}$) that were comparable to those of the membrane-less MFC ($208\ \text{mW m}^{-2}$ and $819\ \text{mW m}^{-3}$), and both had power densities that were much higher than those of the MFC with a PEM ($104\ \text{mW m}^{-2}$ and $419\ \text{mW m}^{-3}$) (Fig. 2B).

3.1.3. Electrode potential

The membrane effect on anode and cathode performance was examined by placing a reference electrode (0.195 V corrected to a normal hydrogen electrode; NHE) into the anode chamber. The MFM with an MFC had a similar change in working electrode potential to the membrane-less MFC: with increasing current density, the anode working potential increased gradually, and the cathode working potential decreased gradually. There were significant differences in the cathode working potential between the MFC with an MFM and the MFC with a PEM. The potential of the former decreased slightly when current density increased from $0.3\ \text{A m}^{-2}$ to $0.85\ \text{A m}^{-2}$, while the potential of the latter rapidly decreased in a narrow range of current density from $0.2\ \text{A m}^{-2}$ to $0.4\ \text{A m}^{-2}$, indicating severe polarization in the cathode.

3.2. Effect of multiple sludge inoculation on MFC performance

3.2.1. Voltage output

The effect of sludge inoculation diversity on voltage output of the MFC with an MFM was examined using AES, ANS and WLS alone

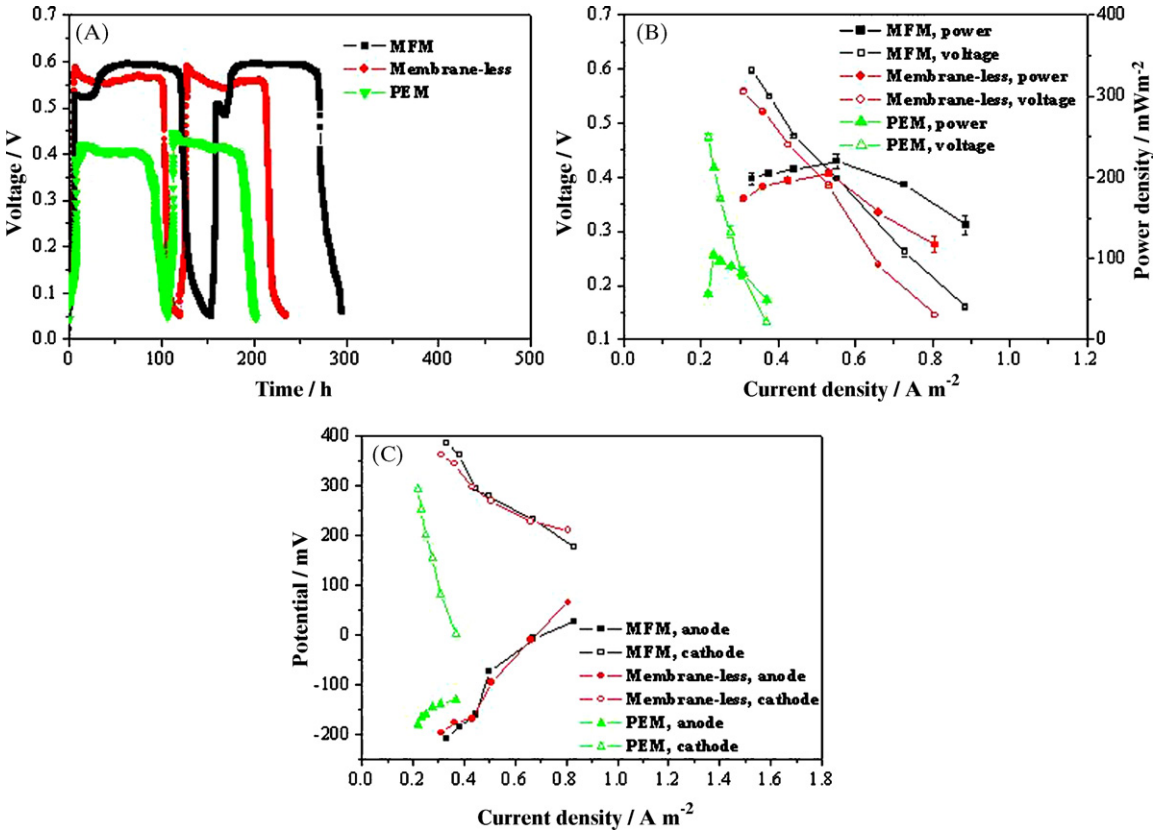

Fig. 2. (A) Time–voltage curves at 500 Ω, (B) power density and polarization curves (mean value ± standard deviation) and (C) electrode potential–current density curves of air-cathode single-chamber MFCs with MFM, PEM and membrane-less cathode (confectionery wastewater, 1000 mgCOD l^{-1} at final).

or in different combinations as anodic inoculums (Fig. 3A). Similar voltage outputs of about 0.6 V were obtained for each of the sludge inoculations after acclimation and once a steady state was reached.

3.2.2. Power density

There were large differences in the maximum power density measured in MFCs inoculated with multiple sludge compared to those inoculated with a single sludge inoculations (Fig. 3B). Inoc-

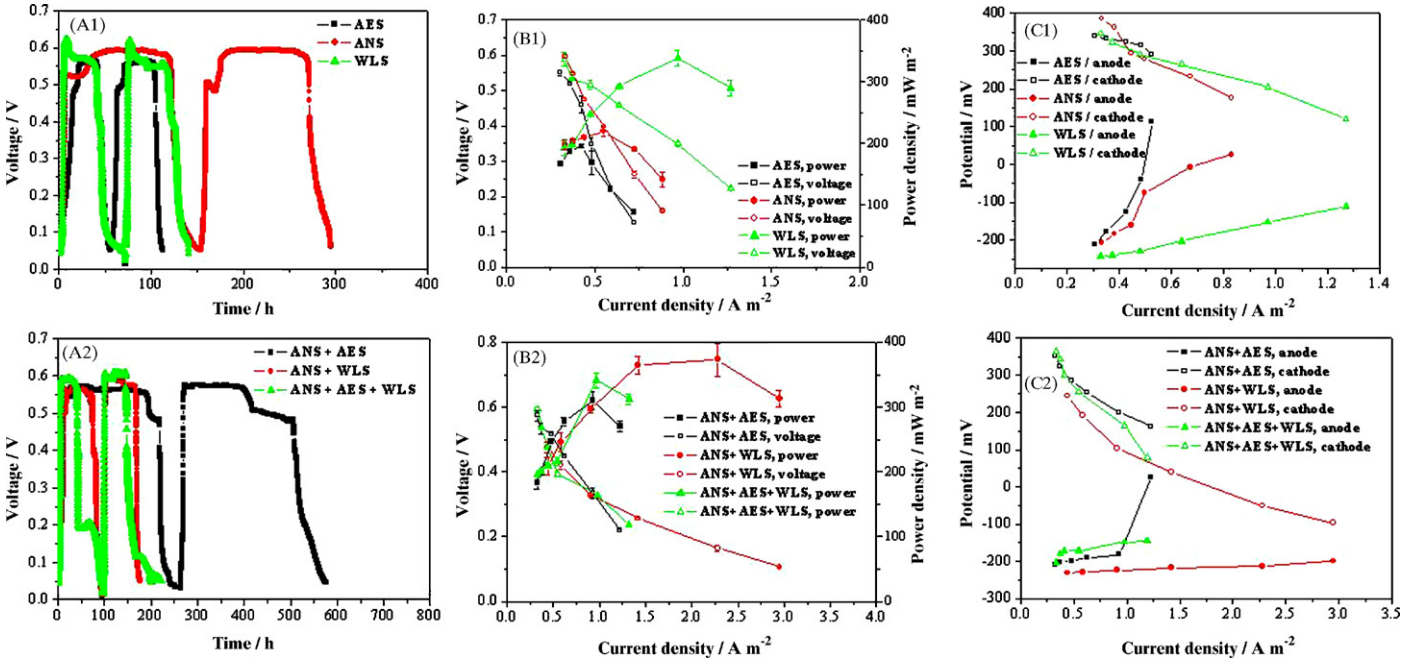

Fig. 3. (A) Time–voltage curves at 500 Ω, (B) power density and polarization curves (mean value ± standard deviation) and (C) electrode potential–current density curves of air-cathode single-chamber MFCs inoculated with single ANS, AES and WLS and multiple ANS + AES, ANS + WLS, ANS + AES + WLS (confectionery wastewater, 1000 mgCOD l^{-1} at final).

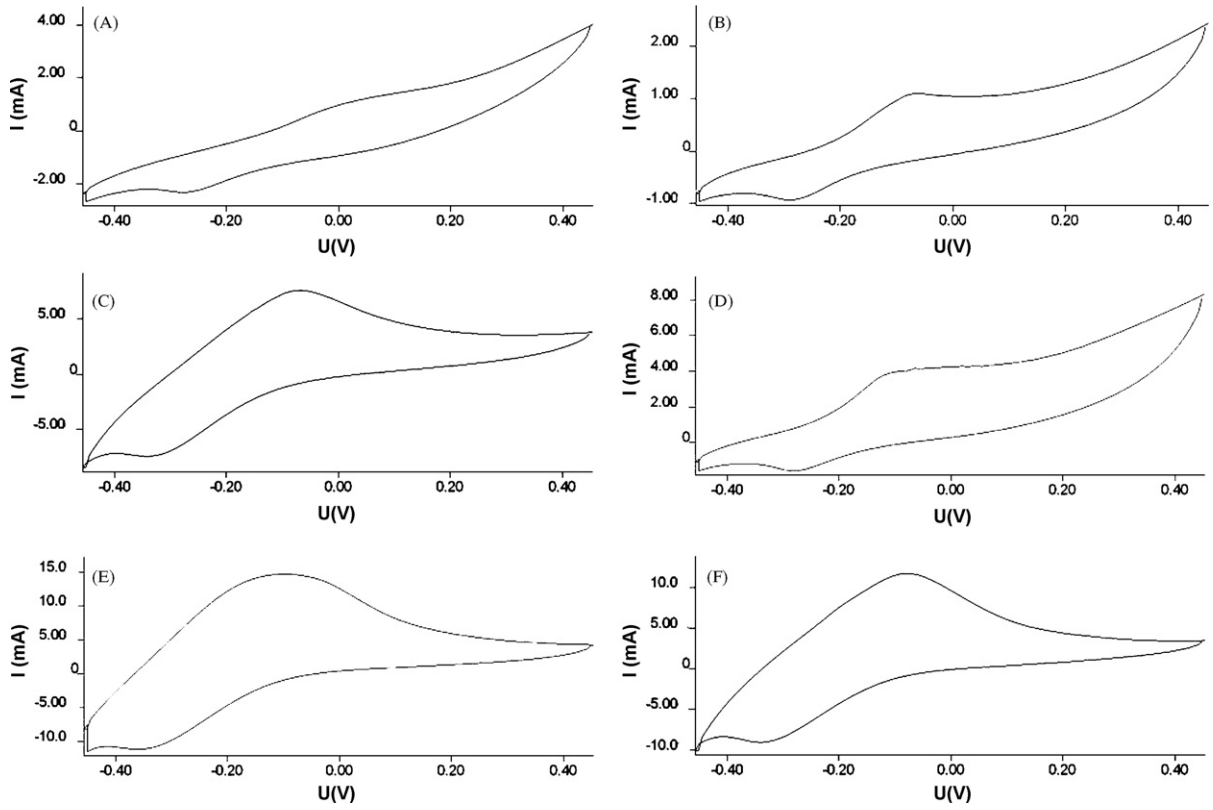

Fig. 4. Cyclic voltammograms of anodes from MFCs inoculated with (A) AES, (B) ANS, (C) WLS, (D) ANS + AES, (E) ANS + WLS and (F) ANS + AES + WLS at the end of a batch test (voltage <50 mV) after more than six months of stable operation with the anode as the working electrode, the cathode as the counter electrode, and a Ag/AgCl reference electrode (+0.195 V against the NHE) at a scan rate of 20 mV s^{-1}.

ulating the MFC with AES + ANS produced a rapid increase in power density (309 mW m^{-2}, 1243 mW m^{-3}), while using either AES or ANS alone yielded values of 187 mW m^{-2} (783 mW m^{-3}) or 214 mW m^{-2} (878 mW m^{-3}), respectively. When WLS was added, an even higher power density was obtained (341 mW m^{-2}, 1365 mW m^{-3}), which is also higher than that of WLS inoculation alone (324 mW m^{-2}, 1299 mW m^{-3}). The largest maximum power density (373 mW m^{-2}, 1495 mW m^{-3}) was achieved in an MFC with ANS + WLS inoculation.

3.2.3. Electrode potential

To further examine the effects of anodic inoculation on power generation, the electrode working potentials were measured as a function of current by varying the circuit load from 1000 Ω and 50 Ω. Obvious anode limitation (high overpotential) occurred in the MFC with single AES and ANS inoculation, as verified by the rapid elevation of anodic potential at current density <0.83 A m^{-2}, but that was not observed in the MFC with WLS inoculation. The anodic potential of the MFC inoculated with AES + ANS was not significantly affected until current densities were >1.23 A m^{-2}. Notable cathode limitation, however, was observed for MFCs inoculated with ANS + AES + WLS and with ANS + WLS, with decreases in working potential from 352 mV (0.32 A m^{-2}) to 162.4 mV (1.26 A m^{-2}) and from 244 mV (0.44 A m^{-2}) to −96 mV (2.95 A m^{-2}), respectively.

3.2.4. Cyclic voltammetry

Cyclic voltammetry was used to distinguish the electron transfer mechanism and to evaluate the redox activities of the components at the end of batch tests (Fig. 4) [8,25,26,35]. Only two oxidation peaks were observed in MFCs with different types of sludge as anodic inoculums, and there were no significant changes in the relative position of the peaks. As clearly indicated by the results, it is the membrane-bound electron transfer, other than a mediator presented in solution that is responsible for the observed redox reactions. Significantly more electrochemical activity of the mixed consortium in multiple-inoculation MFCs was observed than for single-inoculation MFCs, as the activity of electricity-producing bacteria can be evaluated according to peak intensity using cyclic voltammetry [26].

3.2.5. Biofilm on anode

Biofilm samples collected from MFCs inoculated with various types of sludge were observed by ESEM. ESEM revealed that bacteria growing on the anodes of MFCs inoculated with AES, AES, and AES + ANS appeared to be somewhat more uniform in morphology (many bacteria grew as globularity and bacilliform) than in MFCs inoculated or modified with WLS, while the former had a sparse biofilm and the latter developed a thick one.

4. Discussion

4.1. Performance improvement of MFCs by application of microfiltration membrane

The internal resistance calculated from the slope of the polarization curves was used to evaluate MFC performance (Table 1). A substantial reduction in internal resistance from 672 Ω to 248 Ω was observed when an MFM was used in place of a PEM, giving a similar value to that of a membrane-less MFC (238 Ω). As a result, the MFC with an MFM produced a comparable average power density (214 mW m^{-2}, 878 mW m^{-3}) to the membrane-less MFC (200 mW m^{-2}, 819 mW m^{-3}) and showed an increasing of almost 100% compared to the MFC with a PEM (103 mW m^{-2}, 415 mW m^{-3}).

Table 1
Comparison of the performance of MFCs with MFM, PEM and membrane-less cathode in terms of maximal power density, internal resistance, COD removal, Coulombic efficiency, and suspended biomass (mean value ± standard deviation).

Membrane	Maximal power density ($mW\,m^{-2}$)	Maximal power density ($mW\,m^{-3}$)	Internal resistance (Ω)	Batch test (500 Ω resistor)		
				COD removal (%)	Coulombic efficiency (%)	Suspended biomass[a] ($g\,VSS\,l^{-1}$)
MFM	214 ± 8	878 ± 53	248	96 ± 2.4	5.37 ± 0.1	3.1 ± 0.4
PEM	103 ± 3	415 ± 14	672	92 ± 1.0	2.53 ± 0.1	2.2 ± 0.2
No membrane	200 ± 4	819 ± 12	238	96 ± 1.7	4.16 ± 0.3	3.7 ± 1.6

[a] Suspended biomass at the end of batch test.

Coulombic efficiency was enhanced in a similar manner to COD removal efficiency by applying the MFM on the water-facing side of the cathode. The Coulombic efficiency of the MFC without a membrane was 4.16%. Application of an MFM on the water-facing side of the cathode increased the Coulombic efficiency by 29–5.37%. This indicates that using an MFM reduces the aerobic loss of substrate by oxygen diffusion from the cathode into the anode. It should be noted that the larger surface area of the cathode (36 cm^2) used in this study may weaken the role of the MFM in reducing this oxygen diffusion compared with the 100% increase in Coulombic efficiency observed by the application of two layers of cloth to a cathode with a relatively smaller surface area [16]. The Coulombic efficiency of the MFC with an MFM was even higher than for the MFC with a PEM (2.53%). The most likely reason may be that the negative effect of internal resistance on recovering electrons from the organic substrate exceeded the positive effect of reduction on the aerobic loss of substrate in the MFC with a PEM, since both effects have opposite contributions to Coulombic efficiency. However, excessive aerobic biomass growth was still observed in the MFC with an MFM compared to that with a PEM (Table 1).

The obvious improvement in performance of air-cathode single-chamber MFCs by using an MFM on the water-facing side of the cathode may be due to the MFM's high permeability (0.22 μm in pore size), which facilitates overall charge transfer better than a PEM. In addition, the reduced oxygen diffusion into the anode chamber compared to membrane-less MFCs yields higher power density, lower internal resistance, and increased Coulombic efficiency. The MFM could also be used to isolate the catalyst from the anodic microorganisms, which would inhibit fouling and catalyst inactivation, especially for long-term operation [18]. In theory, any permeable material can function as a solution barrier in an MFC if charge can be transferred, but the MFM may be not suitable for a two-chamber MFC with an aqueous-phase cathode due to MFM's high permeability. Furthermore, the low costs of MFMs make them attractive for MFCs for a large-scale application (e.g., wastewater treatment).

The MFM used here was hydrophilic and was 0.22 μm in pore size. Considering of the diversity of type of the MFM, how the pore size and hydrophilicity affect the performance of MFC will be further investigated.

4.2. Improved performance of MFCs using multiple sludge inoculation

MFC performance also depends on the type of inoculums [28]. It is notable that multiple sludge inoculation has a direct relationship with microbial diversity in the anode chamber and that it further improved the performance of MFCs in this study. A substantial increase in power density concomitant with an obvious reduction in internal resistance (Table 2) was observed in multiple sludge inoculations. High internal resistances of 312 Ω and 248 Ω for MFCs were observed with single AES and ANS inoculations, respectively, while the use of multiple inoculations of ANS + AES, ANS + WLS and ANS + AES + WLS resulted in substantial reductions in internal resistance of 106 Ω, 38 Ω, and 91 Ω, respectively. The highest maximal power density of 373 $mW\,m^{-2}$ (1495 $mW\,m^{-3}$) along with the lowest internal resistance of 38 Ω was achieved in the MFC with ANS + WLS inoculation. Addition of WLS to the MFC with AES + ANS inoculation further increased power density and decreased internal resistance. This result suggests that WLS plays an important role in increasing power density, which is supported by the higher power density and lower internal resistance observed for WLS inoculated alone than single AES or ANS inoculations. This is not surprising, since sediments are relatively enriched in iron-reducing bacteria as part of an abundant microbial species population [28].

Power density is limited by internal resistance as a result of various factors. The multiple sludge inoculations have a direct effect on the working potential of the anode and were responsible for a substantial increase in power output and reduction in internal resistance as compared to the single sludge inoculations (Fig. 3C).

More than 92% of COD was removed for MFCs inoculated with various types sludge at the end of the batch test (voltage was lower than 50 mV) (Table 2). However, the Coulombic efficiency that was calculated based on the total substrate concentration was only in the range of 2.21–10.01% at 500 Ω, indicating that a substantial number of electrons were lost. Except for the effect of diffusion of oxygen from the cathode, species of electricity-producing bacteria in the anode chamber also affect the overall Coulombic efficiencies, since the ability to recover electrons from the substrate of these bacteria differs with species. The Coulombic efficiency is significantly

Table 2
Comparison of the performance of MFCs using AES, ANS, WLS and multiple ANS + AES, ANS + WLS, and ANS + AES + WLS as anode inoculums respectively in terms of maximal power density, internal resistance, COD removal, Coulombic efficiency and suspended biomass (mean value ± standard deviation).

Inoculums	Maximal power density ($mW\,m^{-2}$)	Maximal power density ($mW\,m^{-3}$)	Internal resistance (Ω)	Batch test (500 Ω resistor)		
				COD removal (%)	Coulombic efficiency (%)	Suspended biomass[a] ($g\,VSS\,l^{-1}$)
AES	187 ± 3	783 ± 74	312	92 ± 2.9	2.21 ± 0.4	3.4 ± 0.2
ANS	214 ± 8	878 ± 53	248	96 ± 2.4	5.37 ± 0.1	3.1 ± 0.4
WLS	324 ± 2	1299 ± 75	102	94 ± 1.5	2.31 ± 0.3	3.8 ± 0.6
ANS + AES	309 ± 13	1243 ± 82	106	93 ± 1.9	10.01 ± 1.0	2.9 ± 0.4
ANS + WLS	373 ± 25	1495 ± 102	38	96 ± 1.0	3.1 ± 0.1	3.9 ± 1.0
AES + ANS + WLS	341 ± 12	1365 ± 61	88	94 ± 1.1	2.6 ± 0.4	3.9 ± 0.6

[a] Suspended biomass at the end of batch.

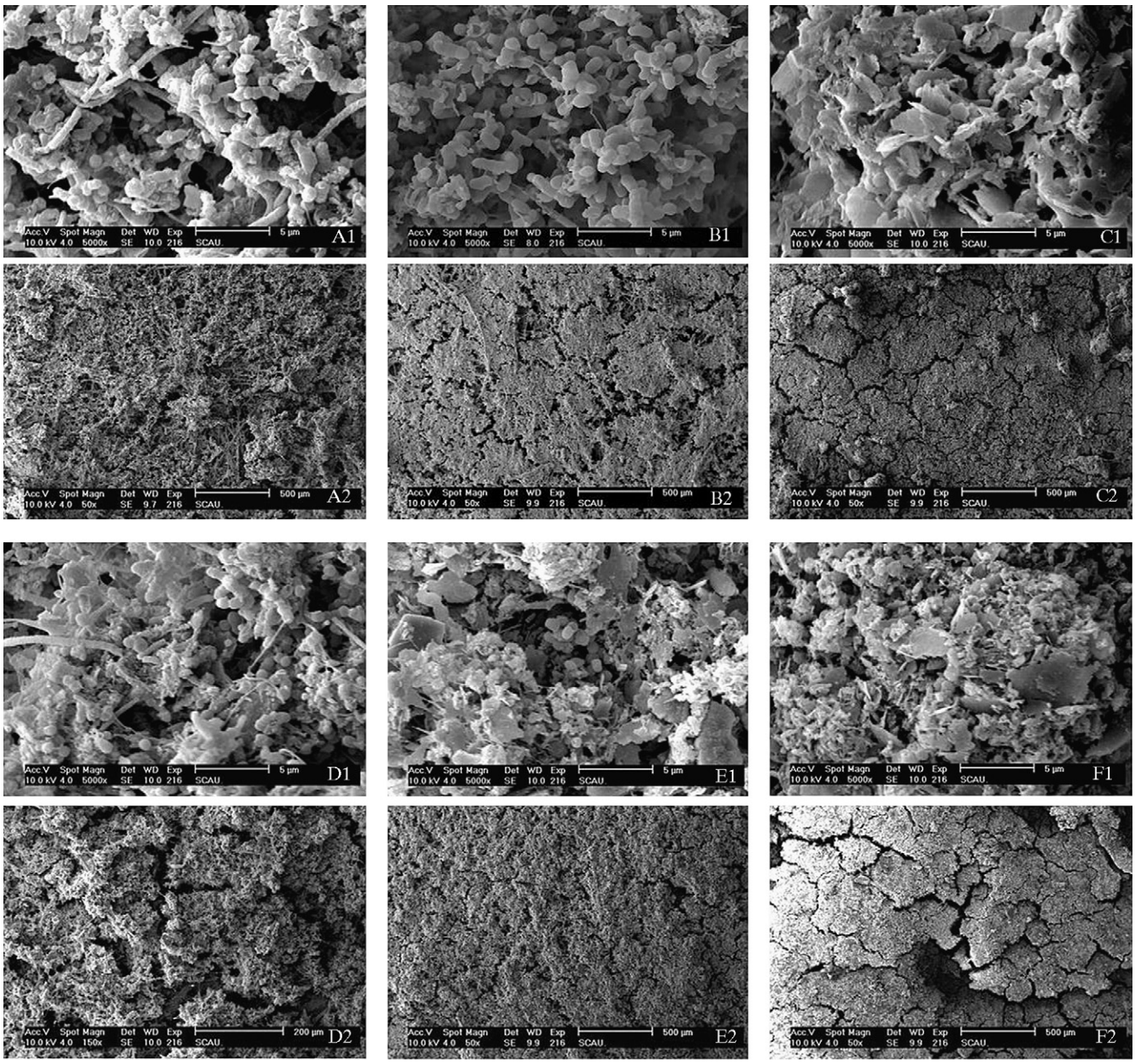

Fig. 5. ESEM images of the anode surface of MFCs inoculated with (A) AES, (B) ANS, (C) WLS, (D) ANS + AES, (E) ANS + WLS and (F) ANS + AES + WLS after more than six months of batch operation.

increased in the MFC inoculated with ANS + AES compared to MFCs inoculated with only AES or ANS. The reason may be that the aerobic bacteria contained in AES scavenge oxygen diffused from the cathode with a reduced aerobic loss of substrate [7]. In contrast with the improvement on power output in the WLS-modified MFC, the Coulombic efficiency decreased when WLS was added to ANS and ANS + AES. The most likely reason is that the thick biofilm that forms on the surface of the anode of WLS-modified MFCs maintains many active bacteria that participate in power generation, thus resulting in substantially increased power densities and a decrease of the overpotential of the anode compared to the sparse biofilm formed in MFCs without WLS (Fig. 5). This increase in power can partially offset the increased oxygen flux, as a higher power density will reduce the overall time needed to fully degrade the substrate. The ratio of facultative aerobes in WLS may also account in part for the decrease in Coulombic efficiency since WLS contains numerous facultative aerobes that consume substrate under the anoxic environment. This was demonstrated by the excessive growth of suspended biomass in the anode chamber since the cell yield for aerobic bacteria is generally high compared to anaerobic bacteria [36].

Higher power density is achieved in MFCs when self-produced or endogenous chemical mediators are present in anode biofilm or solution [25,26]. In this study, however, these redox chemical mediators were not detected by cyclic voltammetry. This could result from the frequent replacement of the fluid, which is a poor stratagem for the accumulation of a high concentration of mediators in MFCs [25].

Performance improvement of air-cathode single-chamber MFCs via sludge diversity is encouraging evidence that MFC technology may prove useful for remediating a wide array of xenobiotics. It is also important to note that, in a mixed-culture MFC, it is not necessarily the case that all microbes utilize the electrode as an electron acceptor in a direct or indirect method. Rather, a mixed cul-

ture allows for potentially beneficial interactions among microbes to further enhance biodegradation [24–27].

4.3. Implications for real wastewater treatment and further optimization

Scale-up is an important issue for the application of MFCs, especially in the field of wastewater treatment. The air-cathode single-chamber MFC used here had a total volume of 1 l (900 ml liquid volume), which is much larger than that used by most researchers, although an air-cathode MFC of 1.5 l has been developed [12]. Maximizing power output while minimizing cost should be the first consideration in scaling up MFCs for practical application. As an optional component, membranes affect both the performance and cost of MFCs. The disadvantages of membranes in MFCs are their high cost and diminishment of system performance. For example, the price of a PEM is \$ 1400 m^{-2}, and the power density is substantially decreased when used in MFCs [7]. The MFM used in this study, however, does not adversely affect and even improves MFC performance while also being cheaper than the PEM. Additionally, the MFM may prevent the catalyst from anodic biofilm contamination, especially in long-term operation, since MFMs are widely used for the filtration of microorganisms. Despite the relatively low Coulombic efficiencies of using an MFM, it may still have a role in wastewater treatment since the organic substrate in wastewater is free; thus, its loss to the aerobic processes is not intrinsically a problem as such a loss accomplishes wastewater treatment [4].

Utilization of substrate diversity was limited by using pure species of electricity-generating bacteria in MFCs in previous studies [5,7,26,37]. A mixed bacterial culture is therefore superior to a pure culture in terms of electricity generation since complicated carbon sources are present in real wastewater. High COD removal efficiency from confectionery wastewater in this study also accounted for the predominance of mixed bacterial cultures in biodegrading complicated organic substrates.

The preliminary research was conducted to investigate the effect of microfiltration membranes and multiple sludge inoculation on MFC performance. The systems described here are not yet optimized with respect to the many other factors that might also contribute to overall performance, such as relative space between the anode and cathode [30,36], the surface area of the electrodes [14,38], the ion intensity of the solution [21,38], etc. Additional work will be needed to better understand how these factors affect the performance of the microfiltration membrane air-cathode single-chamber MFC. Combining both engineering and biological approaches, a successful design of MFCs with increased performance could be utilized in wastewater treatment with minimal cost.

5. Conclusions

Microfiltration membranes can be successfully substituted for PEMs in air-cathode single-chamber MFCs for wastewater treatment, resulting in a substantial increase in Coulombic efficiency (5.37% versus 2.53%) and power output (214 mW m^{-2} versus 103 mW m^{-2}) and a decrease in internal resistance (248 Ω versus 672 Ω). The Coulombic efficiency of membrane-less single-chamber MFCs can also be enhanced (5.37% versus 4.16%) by applying an MFM on the water-facing side of the cathode without negatively affecting power generation or internal resistance.

The overall performance of air-cathode single-chamber MFCs in wastewater treatment was improved by using multiple sludge and sediments as anodic inoculums, rather than a single sludge inoculation, giving an increase in power density and decrease in internal resistance. The MFCs inoculated with ANS + WLS produced the greatest maximal power density of 373 mW m^{-2} (1495 mW m^{-3}, 38 Ω). WLS was a good source of inoculums for air-cathode single-chamber MFCs due to its role in increasing maximal power density and decreasing internal resistance when compared to AES and ANS. The MFCs inoculated with AES + ANS achieved the highest Coulombic efficiency of 10.01%, which is substantially higher than that by MFCs inoculated with other sludge. Over 92% of COD was removed from confectionery wastewater in all tested MFCs and the COD removal was not significantly affected by membrane and inoculums. Many other factors should be considered for further optimization.

Acknowledgement

We thank Professor Liu Hong at Oregon State University for her comments on the manuscript.

References

[1] D.R. Bond, D.E. Holmes, L.M. Tender, D.R. Lovley, Science 295 (2002) 483–485.
[2] S.K. Chaudhuri, D.R. Lovley, Nat. Biotechnol. 21 (2003) 1229–1232.
[3] B. Min, B.E. Logan, Environ. Sci. Technol. 38 (2004) 5809–5814.
[4] H. Liu, R. Ramnarayanan, B.E. Logan, Environ. Sci. Technol. 38 (2004) 2281–2285.
[5] D.R. Bond, D.R. Lovley, Appl. Environ. Microbiol. 69 (2003) 1548–1555.
[6] B.E. Logan, C. Murano, K. Scott, N.D. Gray, I.M. Head, Water Res. 39 (2005) 942–952.
[7] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4040–4046.
[8] H. Liu, S. Cheng, B.E. Logan, Environ. Sci. Technol. 39 (2005) 5488–5493.
[9] S.E. Oh, B. Min, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4900–4904.
[10] U. Schröder, J. Nieben, R. Scholz, Angew. Chem. Int. Ed. 42 (2003) 2880–2883.
[11] K. Rabaey, G. Lissens, S.D. Siciliano, W. Verstraete, Biotechnol. Lett. 25 (2003) 1531–1535.
[12] S.J. You, Q.L. Zhao, J.N. Zhang, J.Q. Jiang, S.Q. Zhao, J. Power Sources 162 (2006) 1409–1415.
[13] S. Gottesfeld, T.A. Zawodzinski, Adv. Electrochem. Sci. 5 (1997) 195–301.
[14] H. Liu, S.A. Chen, L.P. Huang, B.E. Logan, J. Power Sources 179 (2008) 274–279.
[15] J.R. Kim, S.A. Cheng, S.E. Oh, B.E. Logan, Environ. Sci. Technol. 41 (2007) 1004–1009.
[16] Y. Fan, H. Hu, H. Liu, J. Power Sources 171 (2007) 348–354.
[17] Y. Fan, H. Hu, H. Liu, Environ. Sci. Technol. 41 (2007) 8154–8158.
[18] J.C. Biffinger, R. Ray, B. Little, B.R. Ringeisen, Environ. Sci. Technol. 41 (2007) 1444–1449.
[19] J.R. Kim, S.H. Jung, J.M. Regan, B.E. Logan, Bioresour. Technol. 98 (2007) 2568–2577.
[20] T. Catal, K.C. Li, H.K. Bermek, H. Liu, J. Power Sources 175 (2008) 196–200.
[21] G.C. Gil, I.S. Chang, B.H. Kim, M. Kim, J.K. Jang, H.S. Park, H.J. Kim, Biosens. Bioelectron. 18 (2003) 327–338.
[22] B. Mina, J.R. Kim, S.E. Oh, J.M. Regan, B.E. Logan, Water Res. 39 (2005) 4961–4968.
[23] S.A. Cheng, B.A. Dempsey, B.E. Logan, Environ. Sci. Technol. 41 (2007) 8149–8153.
[24] Z.Y. Ren, T.E. Ward, J.M. Regan, Environ. Sci. Technol. 41 (2007) 4781–4786.
[25] K. Rabaey, N. Boon, M. Hofte, W. Verstraete, Environ. Sci. Technol. 39 (2005) 3401–3408.
[26] K. Rabaey, N. Boon, S.D. Siciliano, M. Verhaege, W. Verstraete, Appl. Environ. Microbiol. 70 (2004) 5373–5382.
[27] G. Reguera, K.D. Mccarthy, T. Mehta, J.S. Nicoll, M.T. Tuominen, D.R. Lovldy, Nature 435 (2005) 1098–1101.
[28] D.E. Holmes, D.R. Bond, R.A. O'Neill, C.E. Reimers, L.R. Tender, D.R. Lovley, Microb. Ecol. 48 (2004) 178–190.
[29] M. Booki, E.L.B.E. Logan, Environ. Sci. Technol. 38 (2004) 5809–5814.
[30] S.A. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 2426–2432.
[31] B.C. Jong, B.H. Kim, I.S. Chang, P.W.Y. Liew, Y.F. Choo, G.I.S. Kang, Environ. Sci. Technol. 40 (2006) 6449–6452.
[32] D.R. Lovley, E.J.P. Phillips, Appl. Environ. Microbiol. 54 (1988) 1472–1480.
[33] S.A. Cheng, H. Liu, B.E. Logan, Electrochem. Commun. 8 (2006) 489–494.
[34] APHA, AWA, WPCF, American Public Health Association, Washington, DC, 1992.
[35] B.E. Logan, B. Hamelers, R. Rozendal, U. Schroder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Environ. Sci. Technol. 40 (2006) 5181–5192.
[36] K. Rabaey, W. Ossieur, M. Verhaege, W. Verstraete, Water Sci. Technol. 52 (2005) 515.
[37] P.T. Ha, B. Tae, I.S. Chang, Energy and Fuel 22 (2008) 164–168.
[38] H. Liu, S.A. Cheng, B.E. Logan, Environ. Sci. Technol. 39 (2005) 5488–5493.

Glossary

Anaerobe: An organism that does not need free-form oxygen for growth. Manyanaerobes are even sensitive to free oxygen. Obligate (strict) anaerobes grow only in

the absence of oxygen. Facultative anaerobes can grow either in the presence or in the absence of molecular oxygen

Anode: Electrode at which oxidation takes place

Biomass: Material produced by the growth of microorganisms, plants or animals

Batch reactor: In a batch reactor the reactants and the catalyst are placed in the reactor which is then closed to transport of matter and the reaction is allowed to proceed for a given time whereupon the mixture of unreacted material together with the products is withdrawn. Provision for mixing may be required

Cathode: Electrode at which reduction takes place

Current density: The current density jB of a species B in a given point of the solution is obtained by multiplying the flux density of that species at the given point by the Faraday constant F and by the charge number zB of the species: $j\mathrm{B} = z\mathrm{B}F\mathrm{N}\mathrm{B}$, where jB is a vector which indicates the direction in which the charges transported by the species B flow and which gives the number of these charges going through a plane oriented perpendicular to the vector, divided by time and by area, and NB is the flux density of a minor constituent of the solution with respect to a fixed frame of reference

Chemical oxygen demand (COD): A measure of the amount of oxygen, divided by the volume of the system, required to oxidize the organic (and inorganic) matter in wastewater using a chemically oxidizing agent. In practice, it is usually expressed in milligrams O_2 per litre

Electron: Elementary particle not affected by the strong force having a spin quantum number 1/2, a negative elementary charge and a rest mass of 0.000,548,579,903 (13) u

Filtration: The process of segregation of phases; e.g., the separation of suspended solids from a liquid or gas, usually by forcing a carrier gas or liquid through a porous medium

Membrane: Structure, having lateral dimensions much greater than its thickness, through which transfer may occur under a variety of driving forces

Morphology: Shape, optical appearance, or form of phase domains in substances, such as high polymers, polymer blends, composites, and crystals

Oxidation: Gain of oxygen and/or loss of hydrogen of an organic substrate

Polarization (in electrochemistry): The difference of the electrode potential from the corrosion potential

Reduction: The complete transfer of one or more electrons to a *molecular entity* (also called "electronation"), and, more generally, the reverse of the processes described under oxidation

Sediment: The highly concentrated suspension which may be formed by the sedimentation of a dilute suspension