Bioelectrochemical methane (CH₄) production in anaerobic digestion at different supplemental voltages

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ABSTRACT

Microbial electrolysis cells (MECs) at various cell voltages (0.5, 0.7 1.0 and 1.5 V) were operated in anaerobic fermentation. During the start-up period, the cathode potential decreased from −0.63 to −1.01 V, and CH₄ generation increased from 168 to 199 ml. At an applied voltage of 1.0 V, the highest methane yields of 408.3 ml CH₄/g COD glucose was obtained, which was 30.3% higher than in the control tests (313.4 ml CH₄/g COD glucose). The average current of 5.1 mA was generated at 1.0 V at which the maximum methane yield was obtained. The other average currents were 1.42, 3.02, 0.53 mA at 0.5, 0.7, and 1.5 V, respectively. Cyclic voltammetry and EIS analysis revealed that enhanced reduction currents were present at all cell voltages with biocatalyzed cathode electrodes (no reduction without biofilm), and the highest value was obtained with 1 V external voltage.

1. Introduction

Many researchers have attempted to develop and optimize alternative renewable energy technologies as a combat to climate change (Kondaveeti & Min, 2015; Moon et al., 2015). In this aspect, Microbial fuel cell (MFC) has proven to be advantageous due to their ability in biotransformation of anthropogenic waste to energy (Ahn & Logan, 2012). MFCs employ an electrogenic active biocatalyst at anaerobic anode for energy generation. However, due to limited voltage yields from MFCs, researchers had opted for other bioelectrochemical technologies such as microbial electrolysis cell (MEC) where valuable products or contaminant removal could be achieved with supplementation of additional energy (Call et al., 2009). The MEC systems with microbial biocathodes have been explored due to their tremendous applications such as mineralization/oxidation of pollutants (He & Angenent, 2006), conversion of NO₃⁻ to N₂ (Lee et al., 2013), VFAs (acetate) from CO₂ (Mohanakrishna et al., 2015), and generation of CH₄ (Guo et al., 2013).

The methane generation from conventional anaerobic digestion (AD) process are often limited with longer hydraulic retention time (HRT), low organic removals, and low methane yields (Chen et al., 2016; Liu et al., 2016). Several methods for overcoming these limitations have been suggested and attempted, but they required a hefty amount of energy and chemicals, which would result in high operational cost and possible secondary pollution (Appels et al., 2008; Dang et al., 2016). Bioelectrochemical methane production in MEC by supplementation of additional energy (flow of electrons from electrode) was noticed, and hydrogenotrophic methanogenesis or homoacetogenic pathway was proposed as the main metabolic route (Feng et al., 2015; Wang et al., 2009). This might be due to the generation of H₂ and O₂ at cathode and anode, respectively. Therefore, the indirect increase in methane yields can be expected by applying additional electrical field. Also from previous studies, it was proven that direct methanogenesis can occur on electrode surface, in which methanogenic archaea are able to convert the CO₂, electrons, and protons into methane (Clauwaert et al., 2008). Simultaneously, the micro aerobic O₂ generation at anode can elevate the hydrolysis rate towards high methane yield generation (Chen et al., 2016; Zamalloa et al., 2013).

The practical applications of MEC with microbes have been reported for sewage treatment, ground water purification and soil remediation (Elmidaoui et al., 2001; Li et al., 2010). However, studies on MEC application to AD process for methane production are limited and other optimizations such as applied voltage in MEC operations combined with AD process is needed for their practical applications. In other previous studies of MEC with variation in external voltage are restricted in using of AD sludge effluents as an inoculum and substrate. These studies are limited in mimicking the AD conditions. Moreover, the variation of the external cell voltage can indirectly effect the solution pH and alkalinity due to abiotic reactions on electrode surface of MEC, and also could influence the environment for increase in performance of biocatalyst (Guo et al., 2013). Therefore in MEC, the optimization of external energy (current or voltage) plays a key role in product formation (CH₄).
In this study, we integrated microbial electrolysis cell system directly into AD process using fermentable substrate for accelerating methane production during fermentation processes. The startup period for initial and stable methane generation by MEC was determined, and during this period, changes in current generation, COD removal, and methane production were investigated. The AD combined with the MEC system was performed at different applied voltages and their performance was compared to obtain the optimum external power supply for maximum methane production and COD removal. Soluble COD (SCOD) and volatile fatty acids, gas generation, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) were analyzed to interpret the MEC performance under various applied voltages.

2. Materials and methods

2.1. MEC construction, operation and inoculation

Single chamber bottle type MEC reactors, was constructed and operated with a total and working volumes of 330 and 270 ml, respectively. Carbon fiber brush (2.5 cm × 4.0 cm; BRUSH21, Korea) were prepared by winding the carbon fibers with stainless steel wire and used as an anode and cathode electrode (Kakarla & Min, 2014a). The electrical connections to electrode were established using copper wire. Ag/AgCl (sat’d NaCl) was used as a reference electrode (+196 mV vs. SHE) for measuring cathode potential and during electrochemical analysis. The MEC were operated at 35 ± 2 °C by placing in low-temperature incubator (MIR-553, Sanyo Electric Co., Japan). To avoid mass transfer limitation MEC reactors were continuously stirred at 200rpm by placing on magnetic stirrer (ATL-4200, Anytech Co., Korea) (Kondaveeti et al., 2014b). MEC were operated in batch mode with a supplemental voltage of 0.5, 0.7, 1.0 and 1.5 V. Along with MEC, three additional sets of reactors were operated as a control (Table 1). The first control (C1) reactors were operated at similar conditions with MEC, except for the absence of electrode. The second control reactors were identical as first control reactors, except for the presence of electrodes (C2). The third control reactor was operated with only AD effluent, without substrate and electrode (C3). All the experiments were carried out in repeated cycles to maintain consistency and were calibrated to the volumes of gas from control reactors (C3) (Steinbusch et al., 2009).

The effluent of anaerobic digestion was used as inoculums, which was obtained from Suwon Wastewater Treatment Plant (Suwon-si, South Korea). The general characteristics of AD effluent were as follows: pH: 8.06 ± 0.13, TSS: 18,534 ± 1,603 mg/l, VSS: 13,050 ± 1,344 mg/l, TCODCr: 19,363 ± 1,679 mg/l, SCOD Cr: 585 ± 164 mg/l. Glucose with a concentration of 2 g/l were used as a carbon source in gasification of anaerobic digestion was used as inoculums, which was obtained from Suwon Wastewater Treatment Plant (Suwon-si, South Korea). The general characteristics of AD effluent were as follows: pH: 8.06 ± 0.13, TSS: 18,534 ± 1,603 mg/l, VSS: 13,050 ± 1,344 mg/l, TCODCr: 19,363 ± 1,679 mg/l, SCOD Cr: 585 ± 164 mg/l. Glucose with a concentration of 2 g/l were used as a substrate. The operational solution were prepared by mixing the seed sludge with growth media (GM) at a ratio of 1:1 (based on volume) (Kakarla & Min, 2014b). GM solutions, were prepared as follows: phosphate buffer, 50 mM/l; NH4Cl, 0.53 g/l; CaCl2·2H2O 0.08 g/l; MgCl2·2H2O 0.1 g/l; trace elements solution, 1 ml. The trace elements solution consists of: HCl 5.1 ml/L; FeCl3·4H2O, 1500 mg/l; H3BO3, 60 mg/l; MnCl2·4H2O, 100 mg/l; CoCl2·6H2O, 120 mg/l; ZnCl2, 70 mg/l; NiCl2·6H2O, 25 mg/l; CuCl2·2H2O, 15 mg/l; NaMoO4·2H2O, 25 mg/l (Pfennig et al., 1981). Prior to operation, solutions were sterilized at 121 °C for 5 min and purged with N2 gas to maintain anaerobic conditions. Solutions in the MEC reactors were replaced, when current generations were decreased.

2.2. Analytical methods

Liquid analysis (VFAs and SCOD) and head space gas (CH4, CO2) analysis were pursued at a regular time intervals (24–48 h) till the end of operational cycle. Liquid samples were collected using a sterile syringe and filtered using acrodisc syringe filter (0.2 µm). VFAs were measured using ion chromatography (Model: 792, Metrohm, Swiss) equipped with organic acid column (Metrosep 250/7.8, Metrohm, Swiss) (Kondaveeti & Min, 2015). The biogas generated from the MEC reactor was collected in gasbag, and its composition was analyzed using the Gas chromatogram (GC) equipped with TCD (Thermal conductivity detector) and carboxen column (Supelco, USA). The oven, detector, and injector were maintained at 150, 150 and 200 °C, respectively (Sharma et al., 2013). Nitrogen was used a carrier gas with a flow rate of 6 ml/ min. The percentage of gas was calculated, based on peak area difference between the sample and standard. Later the percentile of gas was converted to ml of gas by calculating headspace volume and ml of gas present in gas bag. Gas samples were collected from gas bag by using gas tight syringe (Hamilton, USA) and analyzed immediately. For all analytical analysis, systems (GC and IC) were calibrated with standard chemical with in a sample range.

2.3. Electrochemical measurements and calculations

The effect of external supplemental voltage of 0.5, 0.7, 1.0 and 1.5 V were tested on the CH4 generation by using glucose as a substrate. DC power supply (Hwasung electronics Co., Korea) was used to supplement desired external voltage (Ding et al., 2016). The cathode and anode electrodes were connected to the negative and positive lead of the power supply, with an external resistance of 10 Ω (Logan, 2008). The voltage was measured across the external resistance at a regular time interval of 5 min using digital multimeter by connecting to personal computer (National instrument 9205, USA). The current density was calculated by using MEC working volume (270 ml). All the electrochemical analysis (CV and EIS) were carried out using potentiostat (Versastat 3, USA) with a three-electrode system, by connecting cathode, anode and Ag/AgCl to working, counter and reference electrodes, respectively. Cyclic voltammetry (CV) analysis were pursued in a three-electrode system within a potential range of −0.9 V to 0.9 V (vs. Ag/AgCl) with a scan rate of 5 mV/s. The CV analysis for only growth medium and medium with AD inoculum were carried out by using two pristine plain carbon brush electrodes without biofilm as both WE and CE, respectively. Ag/AgCl was placed near to working electrode and used as a reference electrode. EIS analysis was carried from 1000 kHz to 10 mHz, with a sinusoidal voltage of 10 mV. Total coulombs were calculated by integrating current with time (Kondaveeti et al., 2014a).

3. Results and discussion

3.1. MEC performance during lag period (startup)

A methanogenic biofilm on the cathode was developed through the startup period in a single chamber MEC. Following the inoculation initial current generation of 0.32 mA was noticed after a 1.1-day operation with an applied voltage of 0.7 V (Fig. 1A). The increase in current generations was noticed with consecutive cycles of operations, which suggest that more electroactive biofilm was developed over this lag period of operations (Moon et al., 2015). During 2, 3 and 4th cycles of MEC operations, the average current generations were 2.19, 3.04, and 3.03 mA respectively. The similar maximum current generations were noticed after the third cycle of operation. After noticing the stabilized current generation and product formations with repeated cycles, the
variation in external cell voltage were pursued for evaluating the influence of different voltages on MEC performance. During the following four operational cycles, the similar cathode potentials of approximately $-1.04 \, \text{V (vs Ag/AgCl)}$ were noticed. These values of cathode potentials were decreased to $-0.9 \, \text{V (vs Ag/AgCl)}$ with depletion of substrate (Zhao et al., 2015). The variation in cathode potential from $-1.04 \, \text{V}$ to $-0.9 \, \text{V}$, with respective to time, might be due to decrease in glucose concentrations, which might can alter the reductive condition of cathode towards methane generation. Additionally, the reduction process condition (CO2) on the cathode changed due to reduced CO2 availability/diffusion resulting in changes in cathode potentials.

In cyclic voltamogram (CV) analysis, there was no oxidation and reduction peaks of the cathode with only growth medium and medium with AD inoculum on day 0 (Fig. 1A). After the lag phase and observing stable current generations (5th cycle, 34-day operation with substrate), the cathode electrode showed two reduction peaks at $-378.5 \, \text{mV}$ and $-730.0 \, \text{mV}$, suggesting that there was biocatalyst formation having a capability of extracellular transferring electrons to the electrode in the presence of substrate. The maximum oxidation and reduction currents were also increased with biocatalyst development on the electrode. Control reactors with only growth media and inclusion of AD medium without biofilm exhibited reduction current generations of $-2.9$ and $-3.0 \, \text{mA}$, respectively. With biofilm on the cathode, the maximum current was increased to $-5.24 \, \text{mA}$.

With increase in current generations by consecutive operations, the methane gas percentage in the headspace was increased. The methane gas percentage within 1 day during the first cycle was 48.3%, and this percentage was increased by about 30% to 61.9% by fourth cycle (Fig. 2A). The methane percentage at fourth cycle was always higher through the operations than the value at the first cycle. The final volume of methane generation was also increased from 168 to 204 ml after 6-day operation (data not shown). The increase in current generation and CH4 production might be due to development of electroactive biofilm on cathode electrode (Ding et al., 2016; Zhao et al., 2015). In terms of SCOD removal, with development of biofilm (1st to 4th cycles) the increase in removal percentages was noticed (Fig. 2B). After 24-h operation, the 1st cycle of MEC exhibited a SCOD concentration at 1056.5 mg/l. This was followed by 2nd, 3rd and 4th cycles with SCOD concentrations of 890.0 mg/l, 770.3 mg/l and 731.3 mg/l, respectively. From the fourth cycle, MEC exhibited a 25.4% increase in SCOD removal during 24 h. operation and till the end (6 days). Similarly, the removal percentage was increased from 82.6 (1st cycle) to 86.6% (4th cycle) was noticed. The methane yield was enhanced by biocatalyst formation on the cathode with repeated cycles. The initial methane yield at the first cycle was 310 ml CH4/g COD glucose, and then the yield was increased further to 380 ml CH4/g COD glucose in the third cycle and stood similar for the fourth cycle of operation (375 ml CH4/g COD glucose) during the startup period.
3.2. Current generation in MEC with variation of supplemental voltage

By closing external circuit of reactor, the immediate increase in current generations was noticed suggesting that MEC systems were effective with electroactive biofilms (Lee et al., 2016). The variation in current generations was noticed with change in external cell voltages of MEC at 0.5, 0.7, 1.0 and 1.5 V (Fig. 3). The MEC operations at 0.5, 0.7, and 1.0 V, exhibited current generations of 1.42, 3.02 and 5.06 mA, respectively (Table 2). The current generation at 1.0 V was about 3.6 times higher than the value at 0.5 V externally applied voltage. However, with further increase in external cell voltage to 1.5 V, current generation was decreased to 0.53 mA, which was 9.5 times smaller than the value of MEC operation with 1.0 V. In a closed system with 1.0 V, the total number of coulombs, which was transported from the anode to cathode, was 1,354 C, which was about 8.5 times higher than with 1.5 V (159 C). MEC operation with 0.5 and 0.7 V revealed coulombs generation of 377 and 616 C, respectively. These results suggest that applied voltage values significantly affect the electron transports between the electrodes, which consequently result in difference in oxidation and reductions reaction rates on the electrodes (Ding et al., 2016). Similarly Ding et al. noticed an increase in current generations from 1.05 to 1.45 A with an increase in applied voltage from 0.4 to 2.0 V in two chambered MECs for methane generation (Ding et al., 2016). The lower current generations in their study might be due to variation in operational conditions such as reactor configuration, electroactive microorganisms, and type of substrate. With the variation in external supplemental voltage (0.5, 0.7, 1.0 and 1.5 V), the cathode potential was −1.08, −1.13, −1.14 and −1.03 V, respectively. Cheng et al., evaluated the effect of different poised cathode potentials (−0.6 to −1.2 V) in a single chamber MEC for methane generation using CO2. In their study, the methane generation were only noted when the cathode potentials were higher than −0.9 V (Cheng et al., 2009). These values of cathode potential were much higher in comparison to theoretical redox potential of CO2 to CH4 (−0.24 V vs. SHE) or CO2 to acetate (−0.29 V vs. SHE) conversion (Logan, 2008). This distinction in the cathode redox potentials can be attributed to overpotentials at cathode electrode for the conversion reaction.

3.3. Methane generation in MEC with indistinct applied external voltages

The methane generation in AD combined with MEC was affected by the applied voltages, and the amount of methane volume at the end of MEC operation was higher in this voltage order of 1.0 V, 0.7 V, 1.5 V, and 0.5 V. (Fig. 4). In all cases with an external power in MEC, the methane gas production was higher than the value in control tests. The maximum methane volume at an applied voltage of 1.0 V was 218.5 ± 4.1 mL, which was 30.5% higher than the amount (170 mL) in the control operations. Zhao et al. observed the increase in methane production by 30.2% in comparison with control tests at a similar voltage of 0.6 V to this study (Zhao et al., 2016).

The variation in methane yield was noted with change in external cell voltage. The increase in methane yields was noticed from 368.6 to 408.3 ml CH4/g COD glucose with increase in cell voltage from 0.5 to 1.0 V. However, with a further increase to 1.5 V, the methane yield was decreased down to 371.0 ml CH4/g COD glucose. The highest amount of CH4 generation was noted at the applied voltage of 1.0 V rather than at 1.5 V. This might be due to optimal voltage in the present system for the active electrogens. This can be supported by the cyclic voltammetry analysis, at which the maximum reduction peak was noted. The methane yields at all applied voltages were higher than the theoretical methane yield of 350 ml CH4/g COD at standard temperature and pressure (Logan, 2008). The high methane yield for MEC noted, in comparison to control reactors and theoretical methane generation values might be due to conversion of CO2 to CH4 or CO2 to acetate and further conversion to CH4, by electrogenic homoacetogens and by other bacterial culture species that were present in AD sludge. The maximum methane yield at 1.0 V was higher by 16.7% than the theoretical value. The methane yields in control reactors (C1 and C2), which were operated at open circuit voltage (OCV) and without electrode, were 320.7 and 313.4 ml CH4/g COD glucose, respectively. The maximum yield at 1.0 V was 1.28 times higher than the average methane yield from the controls. This might be due to enhanced COD removals.

Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.5 V</th>
<th>0.7 V</th>
<th>1.0 V</th>
<th>1.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>current density (A/m²)</td>
<td>5.84 ± 0.16</td>
<td>12.28 ± 0.94</td>
<td>19.04 ± 0.29</td>
<td>2.36 ± 0.07</td>
</tr>
<tr>
<td>Total coulomb (C)</td>
<td>377.8 ± 12.6</td>
<td>616.8 ± 77.1</td>
<td>1,354.1 ± 145.7</td>
<td>159.1 ± 38.2</td>
</tr>
<tr>
<td>cathode potential (V)</td>
<td>−1.08 ± 0.02</td>
<td>−1.13 ± 0.01</td>
<td>−1.14 ± 0.02</td>
<td>−1.03 ± 0.02</td>
</tr>
</tbody>
</table>
or due to supplementation of external energy to MEC. In general, for the MEC reactors the methane can be theoretically produced by either two pathways. At first, the CH₄ can be generated from sludge, by utilizing the organics such as VFAs. Secondely, the electrons from the electrode or from organics can react with headspace CO₂ and generate methane by cathode reactions as follows:

\[
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E = -0.441\text{V}, \text{vs Ag/AgCl}
\]  

(1)

Among these, the methane generation from MEC reactors was highest at 1.0 V indicating that the electrogenic microbial activity or other electrochemical reduction conditions were improved with the voltage of 1.0 V. Based on current generation, the methane productions other electrochemical reduction conditions were improved with the highest at 1.0 V indicating that the electrogenic microbial activity or other processes except methane electro-fermentation from CO₂ are also involved in more methane production by AD integrated with MEC.

Based on other studies carried out by Ding et al., the increase in methane generation from around 18–63 ml was noticed with increase in cell voltage from 0.4 to 0.8 V (Ding et al., 2016). However, the methane volume was decreased to 42 ml with further increase of cell voltage to 1.0 V. The methane yields were different in comparison to other studies, which might be due to variation in operation conditions, such as type of electrode, electrolyte, and microbial community. Luo et al. studied the effect of applied direct current on cell surface properties of phenol degrading microbes and noticed a damage of its hydrophobicity at higher applied current (20 mA) (Luo et al., 2005). The OD₆₀₀ of bacteria were decreased in 20 mA applied current in comparison to OD₆₀₀ with no current. This study suggests that application of direct current beyond certain value can be inhibitory to bacterial growth at the electrode.

3.4. Effect of applied voltage on variation in liquid chemicals

Complex substrates in anaerobic digestion (AD) process are converted to methane gas through a series of microbial metabolic processes of hydrolysis, acidification and methanogenesis. However, the input substrates are not completely converted to methane and so some of them remained in the liquid in the form of volatile fatty acids (VFAs) (Appels et al., 2008; Barret et al., 2010). The variations in SCOD and acetate concentration in both MEC and control reactors were plotted with respect to time (Fig. 5). After 24 h of operation, all the MEC reactors exhibited a high SCOD removal in comparison to control operations. The maximum SCOD removal was 70.9% with MEC operation at 1.0 V, which was 25.3% higher than the value from control operation. The other removal percentages of SCOD in MEC with 0.5, 0.7, and 1.5 V were 67.3%, 69.3%, and respectively. During the 24-h operational time, the control reactors, C1 and C2, were 56.6% and 60.8%, respectively. However, at the end of operational cycles, similar effluent concentrations in MEC and control reactors were noticed. Acetate is considered as the main intermediates during methanogenesis processes (Venkata Mohan et al., 2014). The variation in acetate concentrations for MEC and control reactors was presented with respect to time (Fig. 5B). After 24-h operation, the highest concentration of acetate was observed in controls of C1 and C2, with concentrations of 6.5 mmol/l and 6.4 mmol/l, respectively. This was followed by 1.5, 1.0, 0.7 and 0.5 V with a concentration of 5.9, 5.5, 5.0 and 3.5 mmol/l, respectively. Later (2d) these were decreased to 0.4 mmol/l for MEC and 1.4 mmol/l for control. For MEC these concentrations of acetate (0.4 mmol/l) were similar till the end of operation (4 d). However the complete reduction of acetate (0.3 mmol/l) in control reactors were noticed at the end of 4 d. Low concentrations of acetate were noticed in MEC in comparison to controls suggesting the faster reactions in MEC over controls (Cheng et al., 2009). As like acetate, the homogenous trend in propionate concentrations were noticed. In all the reactors, the increase in propionate concentrations was observed up to 24 h of operation. MEC reactors in operation with 1 V exhibited a higher concentration of 2.3 mmol/l. These values were decreased by the end of 4d operation.

3.5. Electrochemical analysis with variation of supplemental voltage

Cyclic voltammetry analysis helps in understanding the biological activity on cathode electrode that drives the reductive reactions of glucose to methane (Mohan & Chandrasekhar, 2011). CV revealed that enhanced reduction current was observed with electrochemically active cathode electrode in comparison to without biofilm (Reddy et al., 2011). No oxidation and reduction peaks were observed in MEC control reactors as shown in Fig. 1B. With biofilm-formed cathode electrode, the current generations were \(-4.4, -5.2, -5.8\) and \(-4.0\) mA by varying the supplemental voltage of 0.5, 0.7, 1.0, and 1.5 V, respectively (Fig. 6A). With variation in applied cell voltages, the reduction peaks were noticed at \(-485.2, -378.5, -514.7\) and \(-449.6\) mV (vs Ag/AgCl) with a peak current of \(-3.7, -3.2, -3.7\) and \(-3.0\) mA, respectively. The CV reduction peaks noticed in present study were in similar range to theoretical values of CO₂ to bioenergy generation (CO₂
increased applied cell voltages up to 1.0 V (Srikanth et al., 2010). EIS measurements on the MECs at different angles suggested the presence of 201, and 146 mC, respectively (Raghavulu et al., 2009; Velvizhi & Venkata Mohan, 2015). These results suggest the presence of various conditions. CV data of MEC reactors with variation in applied voltages. All the MEC reactors operated at different external cell voltages. Based on peak current generations (5.06 mA) during the bioelectrochemical methane production processes in the cathode chamber. The higher reductive current and peak current generation in CV analysis pointing the performance of Microbial Electrolysis cell (MEC) under different applied voltages.

Fig. 6. Cyclic voltammetry (A) and Electrochemical Impedance Spectroscopy (B) analysis to CH₄: ~ 440 mV vs Ag/AgCl; CO₂ to ethanol: ~ 510 mV vs Ag/AgCl.). The higher reductive current and peak current generation in CV analysis at applied voltage of 1.0 V can be correlated with high current transfer rate. This study was carried out with a research grant from National Research Foundation of Korea (Project number: No 2015R1D1A1A09059935).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.09.057.

References


