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Microbial electrochemical separation of CO₂ for biogas upgrading

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. [‡]These authors contributed equally.

Abstract

Biogas upgrading to natural gas quality has been under focus the recent years for increasing the utilization potential of biogas. Conventional methods for CO₂ removal are expensive and have environmental challenges, such as increased emissions of methane in the atmosphere with serious greenhouse impact. In this study, an innovative microbial electrochemical separation cell (MESC) was developed to *in-situ* separate and regenerate CO₂ via alkali and acid regeneration. The MESC was tested under different applied voltages, inlet biogas rates and electrolyte concentrations. Pure biomethane was obtained at 1.2 V, inlet biogas rate of 0.088 mL/h/mL reactor and NaCl concentration of 100 mM at a 5-day operation. Meanwhile, the organic matter of the domestic wastewater in the anode was almost completely removed at the end. The study demonstrated a new sustainable way to simultaneously upgrade biogas and treat wastewater which can be used as proof of concept for further investigation.

Keywords: Biogas upgrading; Microbial electrochemical technologies; CO₂; Separation and Regeneration; Acid and alkali generation; Wastewater

1. Introduction

The increasing emissions of carbon dioxide (CO_2) to the atmosphere mainly due to the combustion of fossil fuels have accelerated the urge of non-petroleum-based substitutes (Lee et al., 2006; Zhu et al., 2014). Biogas is a renewable energy carrier that derives from the anaerobic digestion of organic waste (Bo et al., 2014; Chen et al., 2013; Andriani et al., 2014). It is composed of 40-75% methane (CH_4), 25-60% carbon dioxide (CO_2) and some trace gases such as hydrogen sulfide (H_2S) (Chen et al., 2013; Andriani et al., 2014). Upgrading through CO_2 removal besides increasing the calorific value of the gas, also expands its applications routes, such as vehicle fuel or injection to the natural gas grid (Andriani et al., 2014; Petersson and Wellinger, 2009; Ryckebosch et al., 2011). The definition “biomethane” is used when the upgraded biogas contains 95-97% CH_4 and 1-3% CO_2 . Some used biogas upgrading techniques are pressure swing adsorption, physical or chemical CO_2 absorption and membrane separation (Ryckebosch et al., 2011).

The separation of CO_2 from gases usually happens in two steps: capture and regeneration. In the capture step, the CO_2 gas source contacts with an absorber/adsorber into a solid or liquid and CO_2 gets captured physically or chemically. During regeneration, the CO_2 is separated from the absorber/adsorber by usually combining thermal, chemical or electrical methods and therefore, CO_2 gas is released (Eisaman et al., 2011). The regenerated CO_2 gas can be used for subsequent sequestration or reaction to synthetic hydrocarbons and their products (Jiang et al., 2010).

Alkali solutions such as sodium, potassium and calcium hydroxide are typically used for the chemical absorption of CO_2 (Eisaman et al., 2011; Zhao et al., 2010; Stolaroff et al., 2008). The caustic solvents convert CO_2 into carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) (Eisaman et al., 2011), whereas for the consequent regeneration of CO_2 the CO_3^{2-} and HCO_3^- can react with acids

such as hydrogen chloride and phosphoric acids. Currently, the production of alkali and acids is mainly based on the chlor-alkali process through electrolysis of salt solutions, which has very high electrical energy consumption (IPPC 2001).

Bipolar membrane electrodialysis (BMED), which enables the dissociation of water into H^+ and OH^- when electric field is applied, is an alternative mean to *in-situ* produce acids and bases from neutral salts. A bipolar membrane is made of an anion-exchange layer, a cation-exchange layer and a hydrophilic interface at their junction (Bazinet et al., 1998). Research has suggested that the production of acids and bases with application of BMED can be considered as cost-effective and be applied in large-scale systems (Davis et al., 2015). Thus, BMED has potential for an innovative biogas upgrading method. Nevertheless, the energy consumption still needs to be reduced before industrial application. Therefore, a cost-effective and efficient technology, which takes the advantages of the BMED, needs to be pursued.

Microbial electrochemical systems (MESs), as a potentially sustainable technology, have intensively been investigated over the recent years (Du et al., 2007; Hallenbeck et al., 2014; Huggins et al., 2013). Almost all the MESs share the same principle for the anode; electrochemically active microbes consume organic and inorganic electron donors and generate electrons through microbial oxidation (Wang and Ren, 2013; Logan et al., 2006; Han et al., 2013). The electrons are transferred to the cathode for multiple applications, such as direct capture of current, production of value-added chemicals such as H_2 and CH_4 , or desalination (Lu et al., 2015). It has been recently demonstrated that MESs can be integrated with BMED for efficient and cost-effective production of acid and alkali. With an applied voltage of 1.0 V, the pH reached to 0.68 and 12.9 in the acid-production chamber and cathode chamber after 18 h, respectively (Chen et al., 2012). Thus, a MES-BMED integrated system could fulfill the requirement for biogas upgrading through CO_2 separation (i.e., via absorption and regeneration),

which has never been reported. Especially, how to *in-situ* utilize the alkali and acid solutions in such integrated system for CO₂ absorption and regeneration is still unknown.

In this study, we developed an innovative microbial electrochemical separation cell (MESC) for a brand new application with respect to biogas upgrading via simultaneous CO₂ absorption and regeneration. This concept has never been suggested and implemented before and demonstrates a new avenue for biogas upgrading through microbial electrochemical separation of CO₂.

2. Materials and methods

2.1. Set-up of the bipolar membrane electro dialysis system (MESC)

Figure 1a illustrates a schematic of the experimental set-up. Thanks to the application of external voltage on an alternating stack of two bipolar membranes (BPM) and one anion exchange membrane (AEM), the inlet CO₂ was initially captured by sodium hydroxide (NaOH) in an absorption chamber, thus forming a CO₃²⁻ and HCO₃⁻ solution. Then, the CO₃²⁻ and HCO₃⁻ anions moved to a regeneration chamber to form CO₂ again. As CO₂ was separated from the inlet biogas, treated biogas was released from the absorption chamber. The objective of this study was to investigate the MESC performance by varying operational parameters such as applied voltage, inlet biogas rate and electrolyte concentration. Moreover, the treatment of the domestic wastewater in the anode was an important sub-objective.

2.2. Reactor set-up

The MESC consisted of four successive chambers: anode, regeneration chamber, absorption chamber and cathode with corresponding working volumes of 50, 40, 40 and 40 mL (Figure 1b). The compartments were made of polycarbonate plate (BrønnumPlast A/S, Denmark) and respectively separated with: bipolar membrane (fumasep FBM, FuMA-Tech GmbH, Germany),

anion exchange membrane (AMI 7001, Membrane international, NJ) and bipolar membrane. The working area of the membranes was approximately 25 cm². Holes were made on the top of the chambers for sampling activities and connection to peristaltic pumps and sealed air bags. The peristaltic pumps (OLE DICH Instrumentmakers ApS, Denmark) were used for wastewater recirculation in the anode and supply of untreated biogas and air to the absorption chamber and cathode respectively. The inlet and upgraded biogas as well as the regenerated CO₂ gas were collected in the sealed air bags.

The anodic electrode was made by a carbon fiber brush (5.0 cm diameter, 5.0 cm length, Mill-Rose, USA), pretreated at 450 °C for 30 minutes. Before use, it was pre-acclimated with electrochemically active biofilm in an MFC operated with domestic wastewater. The cathodic electrode was a stainless steel woven mesh (v4.0 x 4.0 cm, 0.24 mm wire diameter, 1.57 mm aperture, The Mesh Company, United Kingdom). A stainless steel diffuser (2 micrometers cavity diameter, M alt Bazaar ApS, Denmark) was used to diffuse the inlet biogas. The negative and positive lead of the power supply were connected to the cathode and anode respectively. A 10 resistance was set between the positive lead and the anode.

2.3. Operation

Domestic wastewater from a primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark) was selected as anodic substrate. The composition of volatile fatty acids (VFA) was 0.3 mg/L ethanol, 28 mg/L acetate, 13.4 mg/L propionate, 3.8 mg/L isobutyrate and 4.2 mg/L butyrate. Before being loaded, the wastewater was enriched with acetate with concentration of 1 g COD-acetate/L and flushed with N₂ for 15 minutes to ensure anoxic conditions (Alatraktchi et al., 2014; Velasquez-Orta et al., 2011). The extra acetate along with the existing sCOD of the wastewater led a total initial sCOD concentration of 1174 mg/L. During

operation the anodic solution was constantly stirring in a feed reservoir (250 mL) and recirculating through the anode with a rate of 25 mL/min.

The regeneration chamber, absorption chamber and cathode were filled manually with the same NaCl solution, which was previously flushed with N₂ for at least 5 minutes. The air supply to the cathode was 25 mL/min. The untreated gas mixture (Aga Gas AB) contained 60% CH₄ and 40% CO₂, which belongs to the range of the typical biogas composition.

When external voltage was applied, OH⁻ and H⁺ were generated due to water dissociation by the bipolar membranes. In the absorption chamber, OH⁻ reacted with the dissociated Na⁺ to form NaOH, which successively absorbed the diffused CO₂ and transformed it into CO₃²⁻ and HCO₃⁻. The CO₃²⁻ and HCO₃⁻ penetrated the anion exchange membrane and moved to the regeneration chamber, where the environment was acidic due to the formation of HCl. In that low pH, CO₂ could be reformed. The continuous water dissociation maintained the regeneration chamber and absorption chamber respectively acidic and basic throughout the operation.

This research intended to elucidate the influence of the inlet biogas rate, applied voltage and NaCl concentration on the MESC performance. The operation started with inlet biogas rate of 0.088 mL/h/mL reactor, applied voltage of 1.2 V and NaCl concentration of 100 mM. Afterwards, one parameter changed while the others remained same, in order to observe the impact of each one individually. The addition tested parameters levels were for the inlet biogas rate 0.138 mL/h/mL reactor; applied voltage 0.8, 1.0 and 1.4 V; NaCl concentration 5 mM. The MESC was operated in batch mode for 5 days at room temperature. At the end of every batch, the medium in all the chambers was replaced with new one. The experiments were carried out in duplicate.

The control experiments were performed as abiotic electrochemical systems, merely modifying the anode. The anode electrode was replaced with a fresh one without biofilm. The anodic substrate was deionized water with Na_2SO_4 so as to keep similar conductivity and pH with the acetate modified domestic wastewater. The operational conditions were same as the first conducted experiments.

2.4. Analysis

The voltage across the resistor was monitored by a data acquisition system (Model 2700, Keithley Instruments, Inc., Cleveland, OH) every 30 minutes. The volume of the upgraded biogas and regenerated CO_2 gas was measured manually by emptying the sealed air bags with a syringe and the composition of the gases was measured by a gas chromatograph coupled with thermo conductivity detector (GC Biogas TCD, Mikrolab, Aarhus, Denmark). The total inorganic carbon contained in the regeneration chamber, absorption chamber and cathode was detected with a TOC analyzer (SHIMADZU TOC-VWP, Holm and Halby). The pH was measured by pH meter (PHM 92, Radiometer, Copenhagen or FiveEasy Plus, METTLER TOLEDO) and the conductivity by a microprocessor conductivity meter (LF 539, MOBRO INSTRUMENTERING). A standard method was followed to measure the chemical oxygen demand (COD) and soluble COD (sCOD) of the collected domestic wastewater and the sCOD of the anodic samples. The collected wastewater was primarily filtered with a $0.45\ \mu\text{m}$ membrane before the sCOD analysis (Feng et al., 2008). The anodic samples got centrifuged (Eppendorf Minispin) at 13.400 rpm for 10 minutes and the supernatant was later used for the sCOD analysis.

3. Results and discussion

3.1. The biogas upgrading performance of MESC

The first experiments were conducted as proof of concept. The conditions were: inlet biogas rate of 0.088 mL/h/mL reactor, applied voltage of 1.2 V and NaCl concentration of 100 mM. There was a direct relation between current density drop and sCOD consumption, which happens because the bacteria need organic matter in order to generate electrons through their metabolic paths. The current density started at 1.11 A/m² and significantly decreased during the first two days since the sCOD decreased from 1174 to 344 mg/L. However, in the next days, the current density became almost constant, ranging between 0.32-0.39 A/m², due to low presence of substrate. That result was consistent with previous observation that the current depends on the substrate consumption (Baudler et al., 2015). Meanwhile, the current density in the control experiment, as independent of the anode, displayed low values, between 0.19-0.08 A/m², with less significant variations. The microorganisms exhibited high sCOD removal rates under considerable quantity of organic matter. These microorganisms came from the recirculating wastewater as well as the biofilm of the pre-acclimated in domestic wastewater electrode. The sCOD removal rate ranged from 34 to 52% until the 4th day, but dropped to 9% the last day because the added acetate and the organic matter of the wastewater had nearly been utilized. Other types of wastewater can also be used efficiently if the anode has been acclimated to wastewater (Zhang et al., 2015). The acetate was used here as additional carbon source in order to exclude the substrate effect on the system performance and also to make it be easily comparable to previous studies using the same substrate. An alternative substrate in anode could be industrial effluents high in COD (Passos et al., 2016). That option could probably be more cost efficient in a potential industrial implementation of the method.

The treated biogas could be characterized as biomethane, since it contained 99-100% CH₄ (Figure 2a). On the other hand, the upgraded biogas in the control experiments included 78-84% CH₄, verifying the significance of microorganisms as catalyst in the anode.

Figure 2b shows that the MESC was provided with 230 mL CH₄ and 153 mL CO₂ during the batch. 210 mL CH₄ were collected back in the upgraded biogas, giving approximately 9% losses of CH₄ into the system, probably due to the sampling activities. From the supplied CO₂ only 0.32 mL was detected in the treated biogas. Consequently, the results evidently demonstrate the feasibility of MESC for biogas upgrading.

Figure 3a demonstrates the changes of the pH after the procedure began and the bipolar membranes forwarded the water dissociation. The initial pH of the NaCl solution was 5.6. The cathode became alkaline due to the oxygen reduction and its pH increased gradually to 9.1 during the experiment. The pH in the absorption chamber increased highly to 11.7 at the 1st day, and afterwards, it progressively decreased to 10. The pH values in the regeneration chamber were between 1.5 and 1.7, thus confirming that the mechanism of CO₂ reformation worked out. At pH lower than 4.4 only free CO₂ is present (Buecker, 1997). The buffering capacity of the released OH⁻ from the water dissociation maintained the pH of the anode between 7.7 and 8, which was close to the initial value of the acetate modified wastewater (pH 7.6).

Figure 3b illustrates the variations of conductivity at the end of the batch. The conductivity in the regeneration chamber had increased by 73%. That change was attributed to the transfer of CO₃²⁻, HCO₃⁻ and Cl⁻ from the absorption chamber, where consequently, the conductivity decreased by 8.8%, intensifying the internal resistance. The conductivity in the cathode raised by 13.5%. Besides the fact, that the cathode was open to the air, it is also possible that the bipolar membrane may have been anion permeable and let anions diffuse from the absorption chamber, which can also explain the gradual pH drop in the absorption chamber. That might also reduce a little the CO₂ absorption efficiency.

3.2. Effects of inlet biogas rate on biogas upgrading

A higher inlet biogas rate of 0.138 mL/h/mL reactor was tested. The CH₄ percentage in the upgraded biogas started at 93% and dropped to 87% throughout the operation. Therefore, the increase of the inlet biogas rate had a reverse effect on the quality of the generated biogas. This indicates that the capacity of the MES-C for CO₂ absorption needs to be further improved in order to enhance the gas treatment. The current density across the circuit started at 0.76 to decrease to 0.3 A/m² during the experiment, following a similar tendency to the current density with the inlet biogas rate of 0.088 mL/h/mL reactor.

Figure 4 shows that the initial pH of the anode was 8.1 and decreased slightly during operation, ranging between 7.6 and 8. The initial pH of the NaCl solution was 6.8. After the experiment commenced, the pH in cathode elevated to reach 9.4 at the 2nd day and then dropped gradually to 9 till the end of the experiment. Comparing to the results with the inlet biogas rate of 0.088 mL/h/mL reactor, the increasing amount of the supplied CO₂ led to a consequent pH reduction and pH raise in the absorption chamber and regeneration chamber respectively. The pH fluctuated from 7.6 to 8.3 in the absorption chamber. In the regeneration compartment the pH varied significantly, as firstly reduced to become 1.6 at the 2nd day, and afterwards, escalated to reach 3.7 at the last day.

3.3. Effects of applied voltage on biogas upgrading

The effect of the applied voltages of 0.8, 1, 1.2 and 1.4 V was investigated. As illustrated in Figure 5a, for 1.4 V, the current density started at 1.49 A/m² and decreased sharply to get values of 0.4-0.5 A/m² at the end of the 2nd day. Afterwards, the reduction became less abrupt to reach 0.27 A/m² at the end of the batch. The current density at 1.2 V showed a similar tendency, as explained before. On the contrary, the current density at 0.8 and 1.0 V started low, at 0.16 and 0.29 A/m² respectively, and did not decrease severely during operation. The total current density

drop was approximately 33%, 44%, 73% and 82% for the corresponding voltages of 0.8, 1.0, 1.2 and 1.4 V, proving that the microbes were more active at high voltages.

Figure 5b shows that the CH₄ percentage in the treated biogas was 92.3-96.5, 98.3-100, 99.4-100 and 91-95.6% at 0.8, 1, 1.2 and 1.4 V, correspondingly. The quality of upgraded biogas deteriorated during operation, since it was reliant on the sCOD removal (Figure 5c). However, the batch at 1.2 V constituted an exemption of that observation because biomethane was constantly generated, fact that renders 1.2 V as the most optimal voltage for the MESC operation under those conditions.

The lower CH₄ percentage in the treated biogas at 1.4 V occurred because the microorganisms exhibited higher activity then. As shown in Figure 5c, nearly 88% of the organic matter had already been removed at the 2nd day. However, if acetate was frequently added in the anode during operation, the biogas quality would enhance. The sCOD removal was similar under 0.8, 1 and 1.2 V; most of the organic matter had been utilized at the end of the experiments.

3.4. Effects of NaCl concentration on biogas upgrading

Table 1 presents the carbon mass balance with two different concentrations of NaCl as electrolyte solution. It was noticed that the carbon of the inlet CO₂ was distributed differently at each case. When the concentration of the NaCl solution was 100 mM, 76.7% of the carbon stayed in the absorption chamber. Only 15.4% moved to the regeneration chamber, where 2.2% remained in the liquid phase and 13.2% evolved to CO₂ gas. The amount of carbon in the generated biogas was minor.

When the concentration of the NaCl solution was reduced to 5 mM, the supplied carbon mainly moved to the regeneration chamber. More precisely, 40.7% of it stayed dissolved in the acidic phase, whereas, another 18.4% proceeded to CO₂ gas formation. In the absorption

chamber, 24.6% stayed dissolved, while, 16.6% formed CO_2 into the treated biogas. Therefore, it can be stated that the reduced NaCl concentration can endorse the transportation of CO_3^{2-} and HCO_3^- to the regeneration chamber.

The Cl^- concentration could be the most possible reason of that different distribution of carbon. In both experiments the amount of the inlet carbon was the same. However, in the first experiment, the Cl^- anions in the absorption chamber were 20 times more comparing to the second experiment. Consequently, these anions would also utilize more of the applied energy in order to move through the anion exchange membrane, rendering the transfer of CO_3^{2-} and HCO_3^- more difficult. Additionally to this, anion exchange membranes have also been described to have low ionic conductivity and chemical stability, mainly at the cationic site (Arges et al., 2010). Therefore, this challenge would probably require to limit the application to low Cl^- solutions. Research has indeed shown that water with low conductivity and hardness is necessary for ion-exchange experiments with acidification (Eisaman et al., 2012). Nevertheless, lower NaCl concentration may increase the internal resistance of the system, and thus, may have a negative impact on the quality of the upgraded biogas. Concerning the carbon mass balance of the CH_4 , the loses of carbon were less with 5 mM NaCl solution. The overall mass balance was 92% for 100 mM NaCl solution and 99.3% for 5 mM NaCl solution.

3.5 Practical significance and perspectives

This study demonstrated a state-of-the-art approach on biogas upgrading. The principle of the chemical separation (i.e., absorption and regeneration) of CO_2 was applied in a coupled system of MES and bipolar membrane electrodialysis (MESB). The main outcome was the *in-situ* production of upgraded biogas with the simultaneous treatment of domestic wastewater. The concept demonstrates various financial, but also environmental advantages. More particularly: 1)

the *in-situ* production of NaOH and HCl is integrated with the generation of upgraded gas. 2) It reduces the emissions of CH₄ to the atmosphere. 3) The reactor can possibly be used for the further treatment of the anaerobic digestion effluent or other types of wastewater. There are also savings comparing to a conventional wastewater treatment plant because aeration is not needed and less sludge is produced. 4) The CO₂, CO₃²⁻ and HCO₃⁻ may be further utilized for of high value-added products, e.g. glycerol carbonate. 5) The reactor has the potential of more advanced modifications. For instance, in another part of this research an MESC was operated with anaerobic cathode for additional biohydrogen generation.

However, there is still need for improvements and optimization. The optimal combination of the operational parameters has to be found to achieve simultaneously high-quality biogas and efficient CO₂ regeneration. Moreover, some parts of the equipment may be replaced or altered so as to enhance the mechanism of the carbon distribution. For instance, anion exchange membranes with higher anion permeability and selectivity, thicker bipolar membranes, or vacuum stripping in the regeneration chamber could be some suggestions. Finally, experiments under continuous mode would be interesting in order to observe the performance of the reactor till saturation.

A more solid conclusion about the energy requirements of the suggested technology could be drawn when these improvements will have been applied. The system is unique and not optimized yet and therefore, a direct comparison to lab scale and industrial biogas upgrading methods would be difficult. The majority of the needed energy comes from the voltage application. It is also true that the required power will decrease significantly with higher inlet biogas rates since the same amount of upgraded biogas will be produced in less time. Some estimation on the energy requirements for the production of 1 m³ upgraded biogas was proven very promising. This fact along with the benefits of the wastewater treatment and the opportunity to use the

cathode for various applications indicates that under the right modifications that system can be energy efficient.

4. Conclusion

This study proposes a new avenue on biogas upgrading by implementing the chemical absorption of CO₂ into a microbial electrochemical system. The MES operation can significantly contribute to enhanced biogas quality and effective wastewater treatment. The upgrading performance was affected by external applied voltages, inlet biogas rates and electrolyte concentrations. Pure biomethane was generated and almost complete removal of the organic matter in the wastewater was achieved at 1.2 V, inlet biogas rate of 0.088 mL/h/mL reactor and NaCl concentration of 100 mM at a 5-day operation.

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REFERENCES

1. Alatraktchi, F.A., Zhang, Y., Angelidaki, I., 2014. Nanomodification of the electrodes in microbial fuel cell: Impact of nanoparticle density on electricity production and microbial community. *Appl. Energy* 116, 216-222.
2. Andriani, D., Wresta, A., Atmaja, T.D., Saepudin, A., 2014. A review on optimization production and upgrading biogas through CO₂ removal using various techniques. *Appl. Biochem. Biotechnol.* 172(4), 1909-1928.
3. Arges, C., Ramani, V., Pintauro, P., 2010. The chalkboard: Anion exchange membrane fuel cells. *Electrochem. Soc. Interface.* 19, 31-35.
4. Baudler, A., Schmidt, I., Langner, M., Greiner, A., Schröder, U., 2015. Does it have to be carbon? Metal anodes in microbial fuel cells and related bioelectrochemical systems. *Energy Environ Sci.* 8, 2048-2055.
5. Bazinet, L., Lamarche, F., Ippersiel, D., 1998. Bipolar-membrane electro dialysis: Applications of electro dialysis in the food industry. *Trends Food Sci. Technol.* 9(3), 107-113.
6. Bo, T., Zhu, X., Zhang, L., Tao, Y., He, X., Li, D., Yan, Z., 2014. A new upgraded biogas production process: Coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. *Electrochem. Commun.* 45, 67-70.
7. Buecker, B., 1997. *Power Plant Water Chemistry: A Practical Guide*, PennWell Publishing Company, Oklahoma.
8. Chen, S., Liu, G., Zhang, R., Qin, B., Luo, Y., 2012. Development of the microbial electrolysis desalination and chemical-production cell for desalination as well as acid and alkali productions. *Environ. Sci. Technol.* 46(4), 2467-2472.

9. Chen, M., Zhang, F., Zhang, Y., Zeng, R.J., 2013. Alkali production from bipolar membrane electro dialysis powered by microbial fuel cell and application for biogas upgrading. *Appl. Energy* 103, 428-434.
10. Davis, J.R., Chen, Y., Baygents, J., Farrell, J., 2015. Production of acids and bases for ion exchange regeneration from dilute salt solutions using bipolar membrane electro dialysis. *ACS Sustain. Chem. Eng.* 3(9), 2337-2342.
11. Du, Z., Li, H., Gu, T., 2007. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. *Biotechnol. Adv.* 25(5), 464-482.
12. European IPPC Bureau, 2001. Reference document on best available techniques in the chlor-alkali manufacturing industry. *Integrated pollution prevention and control (IPPC)*.
13. Eisaman, M.D., Alvarado, L., Larner, D., Wang, P., Garg, B., Littau, K.A., 2011. CO₂ separation using bipolar membrane electro dialysis. *Energy Environ Sci.* 4, 1319-1328.
14. Eisaman, M.D., Parajuly, K., Tuganov, A., Eldershaw, C., Chang, N., Littau, K.A., 2012. CO₂ extraction from seawater using bipolar membrane electro dialysis. *Energy Environ Sci.* 5(6), 7346-7352.
15. Feng, H., Hu, L., Mahmood, Q., Qiu, C., Fang, C., Shen, D., 2008. Anaerobic domestic wastewater treatment with bamboo carrier anaerobic baffled reactor. *Int. Biodeter. Biodegr.* 62(3), 232-238.
16. Hallenbeck, P.C., Grogger, M., Veverka, D., 2014. Recent advances in microbial electrocatalysis. *Electrocatalysis* 5(4), 319-329.
17. Han, A., Hou, H., Li, L., Kim, H.S., de Figueiredo, P., 2013. Microfabricated devices in microbial bioenergy sciences. *Trends Biotechnol.* 31(4), 225-232.

18. Huggins, T., Fallgren, P.H., Jin, S., Ren, Z.J., 2013. Energy and performance comparison of microbial fuel cell and conventional aeration treating of wastewater. *J. Microb. Biochem. Technol.* S6, 002.
19. Jiang, Z., Xiao, T., Kuznetsov, V.L., Edwards, P.P., 2010. Turning carbon dioxide into fuel. *Phil. Trans. R. Soc. A* 368, 3343–3364.
20. Lee, S.C., Choi, B.Y., Lee, T.J., Ryu, C.K., Soo, Y.S., Kim, J.C., 2006. CO₂ absorption and regeneration of alkali metal-based solid sorbents. *Catal. Today* 111(3-4), 385-390.
21. Logan, B.E., Hamelers, B., Rozendal, R., Schrorder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: Methodology and technology. *Environ. Sci. Technol.* 40(17), 5181-5192.
22. Lu, Y., Qin, M., Yuan, H., Abu-Reesh, I.M., He, Z., 2015. When bioelectrochemical systems meet forward osmosis: accomplishing wastewater treatment and reuse through synergy. *Water* 7(1), 38-50.
23. Passos, V.F., Neto, S.A., de Andrade, A.R., Reginatto, V., 2016. Energy generation in a Microbial Fuel Cell using anaerobic sludge from a wastewater treatment plant. *Sci. Agric.* 73(5), 424-428.
24. Petersson, A., Wellinger, A., 2009. Biogas upgrading technologies-developments and innovations. *IEA Bioenergy Task 37*, 1-20.
25. Ryckebosch, E., Drouillon, M., Veruaeren, H., 2011. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy* 35(5), 1633-1645.
26. Stolaroff, J.K., Keith, D.W., Lowry, G.V., 2008. Carbon dioxide capture from atmospheric air using sodium hydroxide spray. *Environ. Sci. Technol.* 42(8), 2728-2735.
27. Wang, H., Ren, Z.J., 2013. A comprehensive review of microbial electrochemical systems as a platform technology. *Biotechnol. Adv.* 31(8), 1796-1807.

28. Velasquez-Orta, S.B., Head, I.M., Curtis, T.P., Scott, K., 2011. Factors affecting current production in microbial fuel cells using different industrial wastewaters. *Bioresour. Technol.* 102(8), 5105-5112.
29. Zhang, X., He, W., Ren, L., Stager, J., Evans, P.J., Logan, B.E., 2015. COD removal characteristics in air-cathode microbial fuel cells. *Bioresour. Technol.* 176, 23-31.
30. Zhao, Q., Leonhardt, E., MacConnell, C., Frear, C., Chen, S., 2010. Purification technologies for biogas generated by anaerobic digestion. CSANR Research Report.
31. Zhu, X., Logan, B.E., 2014. Microbial electrolysis desalination and chemical-production cell for CO₂ sequestration. *Bioresour. Technol.* 159, 24-29.

Figure captions

Figure 1. Schematic of the experimental set-up (a) and photo of the reactor (b). Anode, regeneration chamber, absorption chamber and cathode are marked as 1, 2, 3 and 4 respectively.

Figure 2. Performance with applied voltage of 1.2 V, inlet biogas rate of 0.088 mL/h/mL reactor and NaCl concentration of 100 mM. Composition of upgraded biogas compared to control (a); Accumulative volume of CH₄ and CO₂ in inlet and upgraded biogas (b).

Figure 3. Performance with applied voltage of 1.2 V, inlet biogas rate of 0.088 mL/h/mL reactor and NaCl concentration of 100 mM. pH (a); Conductivity (b). Where RC: Regeneration chamber, AC: Absorption chamber.

Figure 4. pH for inlet biogas rate of 0.138 mL/h/mL reactor. Where RC: Regeneration chamber, AC: Absorption chamber.

Figure 5. Effects of applied voltage of 0.8, 1.0, 1.2 and 1.4 V. Current density (a); Composition of upgraded biogas (b); sCOD (c).

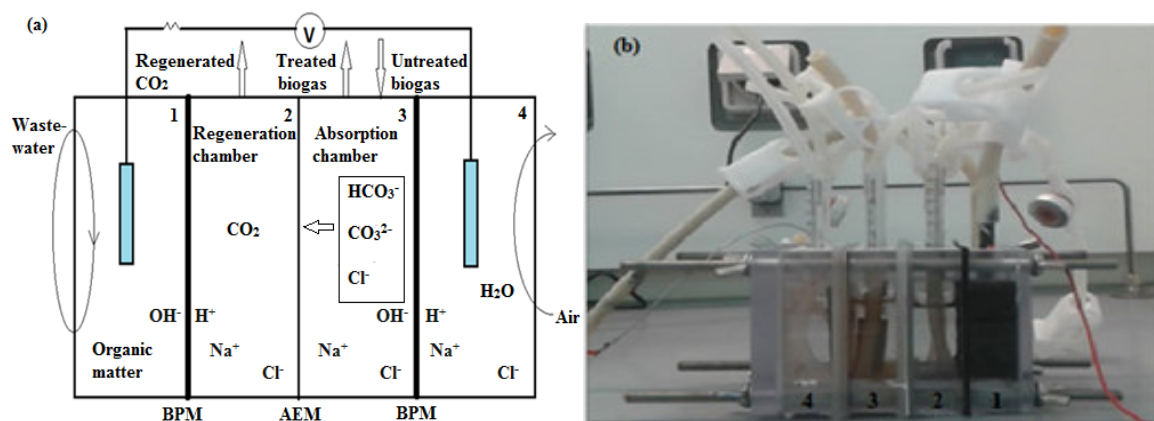


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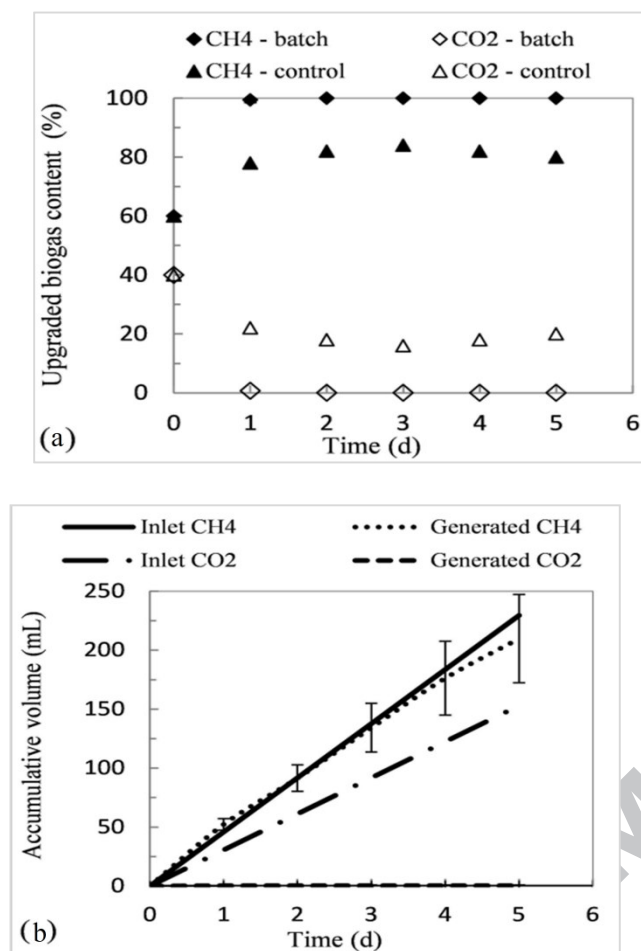


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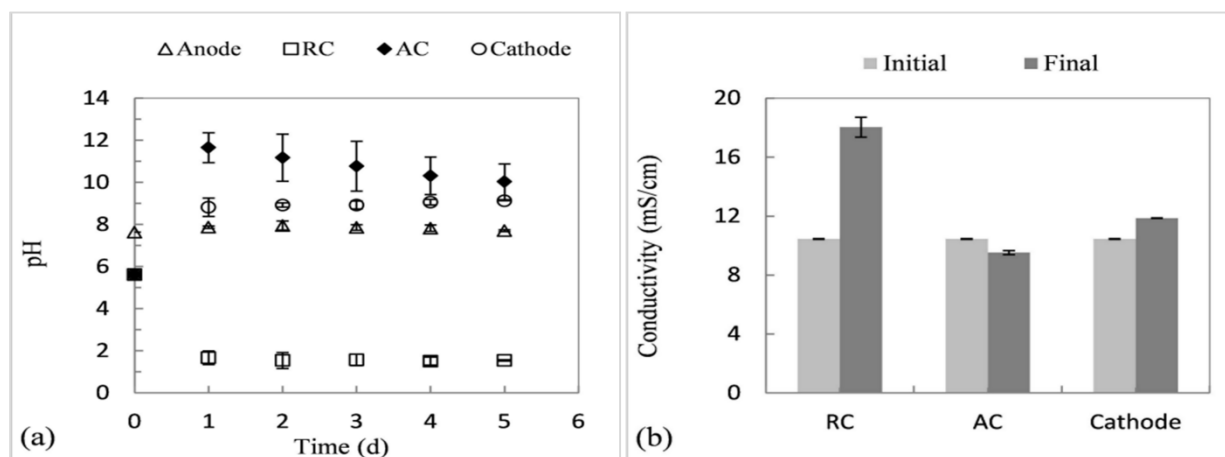


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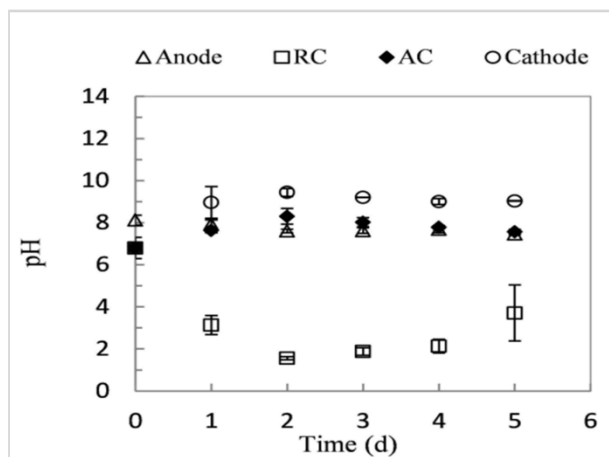


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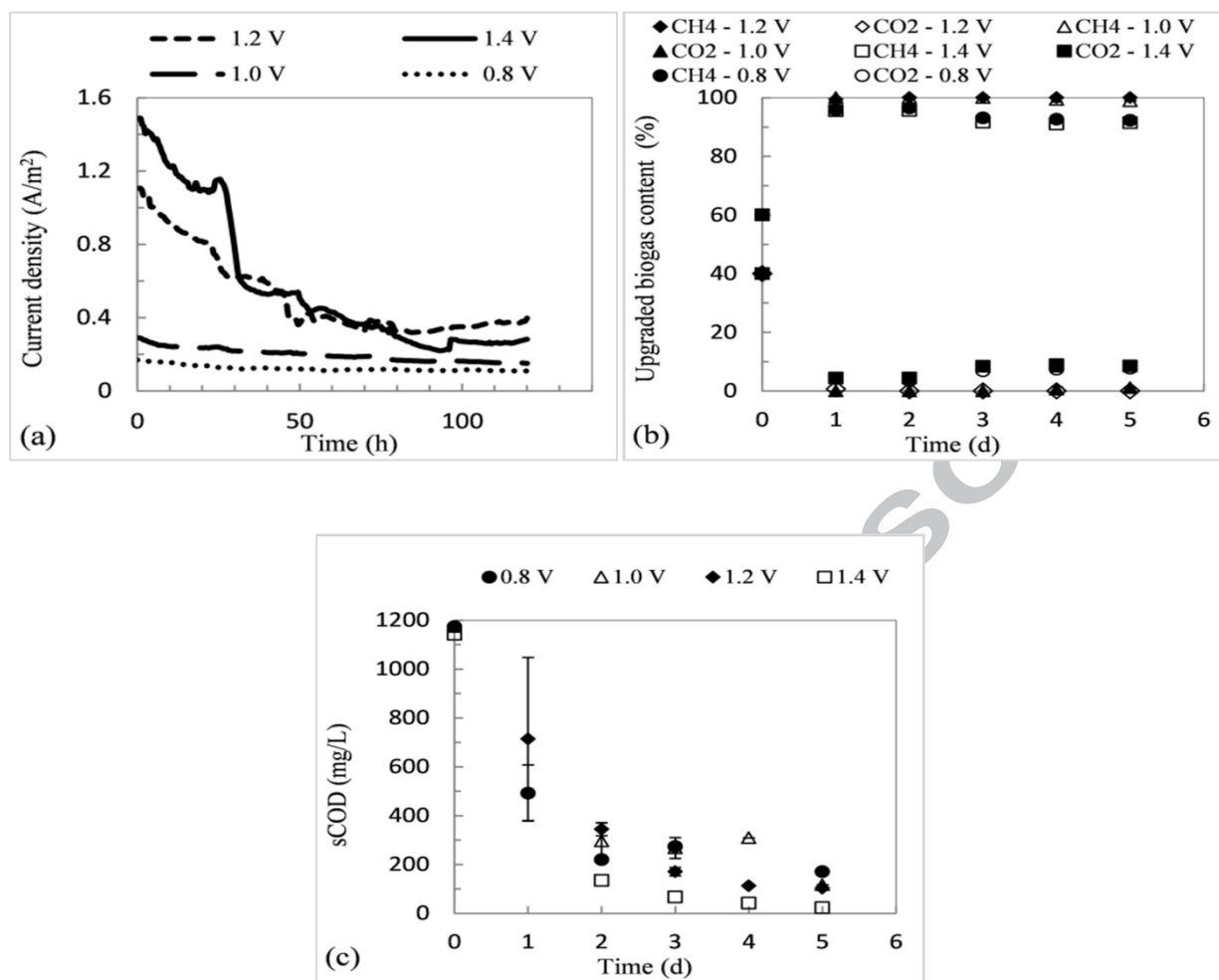


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Table 1. Mass balance on carbon with different concentration of NaCl as electrolyte^a.

NaCl solution (mM)	Chamber ^b	In (mg)			Out (mg)			Balance (%)
		CO ₂	CO ₃ ²⁻ / HCO ₃ ⁻ / H ₂ CO ₃	CH ₄	CO ₂	CO ₃ ²⁻ / HCO ₃ ⁻ / H ₂ CO ₃	CH ₄	
100	RC	0	0	0	39.8	6.8	0	92.0
	AC	300.8	0	164.1	0.6	230.8	149.9	
5	RC	0	0	0	55.4	122.5	0	99.3
	AC	300.8	0	164.1	49.9	74.0	159.7	

^a The mass balance was made based on RC and AC chamber, as the transfer of CO₂ and CH₄ from biogas to anode and cathode could be neglected.

^b Where RC: Regeneration chamber, AC: Absorption chamber.

- Innovative microbial electrochemical separation cell for biogas upgrading.
- In-situ separate and regenerate CO₂ without external supply of chemicals.
- Simultaneously biogas upgrading and wastewater treatment.
- Applied voltages, inlet biogas rates and electrolyte as key affecting factors.
- New avenue for biogas upgrading via microbial electrochemical separation of CO₂.

ACCEPTED MANUSCRIPT

