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1

12 **Abstract**

13 Biogas upgrading to natural gas quality is essential for the efficient use of biogas in various

14 applications. Carbon dioxide (CO_2) which constitutes a major part of the biogas is generally removed

15 by physicochemical methods. However, most of the methods are expensive and often present

16 environmental challenges. In this study, an innovative microbial electrolytic system was developed to

17 capture, separate and regenerate CO_2 for biogas upgrading without external supply of chemicals, and

18 potentially to treat wastewater. The new system was operated at varied biogas flow rates and external

19 applied voltages. CO_2 was effectively separated from the raw biogas and the CH_4 content in the outlet

20 reached as high as 97.0±0.2% at the external voltage of 1.2 V and gas flow rate of 19.6 mL/h.

21 Regeneration of CO_2 was also achieved in the regeneration chamber with low pH (1.34±0.04). The

22 relatively low electric energy consumption (≤0.15 kWh/m^3) along with the H_2 production which can

23 contribute to the energy input makes the overall energy need of the system low, and thereby makes the

24 technology promising. This work provides the first attempt for development of a sustainable biogas

25 upgrading technology and potentially expands the application of microbial electrochemical

26 technologies.

27 Keywords: Biogas upgrading; Microbial electrolytic system; Bipolar membrane; Biomethane; CO_2

28 capture and regeneration; Wastewater treatment

29

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Introduction

Biogas as an alternative energy source could contribute to the reduction of fossil fuel utilization and greenhouse gas emissions, and thus, is ge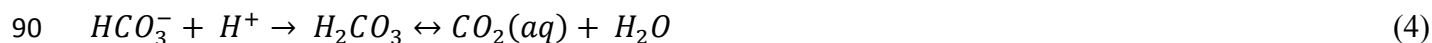tting increased attention worldwide (especially in Denmark).[1] Biogas is primarily composed of 60-70% v/v methane (CH_4), 30-40% v/v carbon dioxide (CO_2), and some trace gases such as hydrogen sulfide (H_2S).[2] Raw biogas with CO_2 presence exhibits a significantly low Wobbe index, heating value and may adversely affect the engine performance.[3] Thus, those unwanted impurities especially CO_2 need to be removed from biogas before used as vehicle fuel or injected to natural gas grids. The conventional technologies for CO_2 removal are water scrubbing[4], pressure swing adsorption, chemical absorption[5, 6], amine scrubbing, membrane separation[7], etc. Some of them have several limitations such as high energy requirement, difficulty in recovery of CO_2, corrosion or clogging problems. Among them, alkaline absorption is characterized of high efficiency, low working pressure, high selectivity and high reaction capacity.[6] However, the technology still encounters several challenges. In addition to alkali, acids may also be required for further regeneration of CO_2 to reuse/recover the captured CO_2 for subsequent sequestration or synthesis of biofuels and commodity chemicals. Currently, alkali and acids are mainly produced through electrolysis of salt solutions termed chlor-alkali process, which consumes a lot of electrical energy and the transportation to the biogas upgrading plants increases the cost.[8] Therefore, the high cost of chemicals and safety issues associated with the transportation and storage of chemicals may affect the application of the technology.

In the past years, microbial electrochemical technologies (METs) have gained increasing attention as potentially sustainable approaches for the production of electricity, biofuels or chemicals, and water treatment with low energy investment.[9, 10] Recently, one of METs, namely microbial electrolysis

3

53   desalination and chemical production cell (MEDCC), has been demonstrated as an efficient and cost-

54   effective method for water desalination, acid and alkali production.[11] With an external applied voltage

55   up to 1.2 V, pH of 0.68 and 12.9 was achieved in the acid-production chamber and cathode chamber,

56   respectively. Notably, the production cost of alkali in MEDCC was much lower than the market price.

57   Latterly, the feasibility of using the acid and alkali solutions produced by a MEDCC for mineral

58   carbonation and CO_2 sequestration in an external reactor was successfully investigated.[12] However,

59   similar systems, which produce alkali and acids for simultaneous biogas upgrading and CO_2 recovery

60   through absorption and regeneration process, have never been reported. Moreover, a more simplified

61   microbial electrochemical system which could take the advantages of the MEDCC for alkali and acid

62   production should be pursued to reduce the construction costs. Furthermore, the energy intensive

63   aeration associated with the alkali synthesis in cathode (e.g., in MEDCC-like reactor) could be further

64   replaced with energy-gained process such as hydrogen evolution.

65   In this study, an innovative microbial electrolytic capture, separation and regeneration cell (MESC)

66   was developed as an alternative, efficient and cost-effective approach to realize simultaneous biogas

67   upgrading, CO_2 recovery and wastewater treatment. Such a system consists of an anode chamber, a

68   regeneration chamber and a cathode chamber, separated by a bipolar membrane (BPM) and an anion

69   exchange membrane (AEM), respectively. With an external applied voltage, electrons derived from

70   bacterial oxidation of organic matter transfer from the anode to cathode where H_2 evolution and OH^-

71   accumulation occur. Meanwhile, H^+ and OH^- are produced in the BPM through water dissociation,

72   resulting in an acidic environment in the regeneration chamber and neutralization of OH^- with H^+

73   released from substrate oxidation in the anode chamber. Beside prevention of dramatic pH drop in the

74   anode for better bacterial growth, BPM has the proven potential of more efficient and cost-effective

75   production of acid and alkali in (bio)electrolytic process compared to conventional anion and cation

4

76   exchange membranes.[12, 13] In our system, inlet CO_2 from the biogas is initially captured as HCO_3^- and

77   CO_3^{2-} by the alkali solution produced in the cathode (Equation 1 and 2). Because of the potential

78   difference between the middle and cathode chambers, HCO_3^- and CO_3^{2-} subsequently transport through

79   AEM to the regeneration chamber where they combine with H^+ to form CO_2 again (Equation 3 and 4).

80   Therefore, through such process biogas upgrading, CO_2 recovery, wastewater treatment and H_2

81   production could be achieved simultaneously. The aim of the present study is to demonstrate the

82   feasibility of such novel technology by varying the biogas flow rates as well as the external voltages.

83   The system performance was evaluated in terms of the current output, chemical oxygen demand (COD)

84   removal efficiency, quality of the outlet gas and energy input. This work is among the first attempts to

85   provide proof of concept for a new and value-added microbial electrochemical platform technology for

86   biogas upgrading.

87    $$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^- \tag{1}$$

88    $$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{2}$$

89    $$CO_3^{2-} + H^+ \rightarrow HCO_3^- \tag{3}$$

90    $$HCO_3^- + H^+ \rightarrow H_2CO_3 \leftrightarrow CO_2(aq) + H_2O \tag{4}$$

91

92   **Material and methods**

93

94   **The Setup and Operation of the MESC.** A three-chamber reactor made of nonconductive

95   polycarbonate plates was consisted of the anode chamber, regeneration chamber and cathode chamber

96   which were separated by a BPM (fumasep FBM, FuMA-Tech GmbH, Germany) and an AEM (AMI

97   7001, Membrane international, NJ), respectively. The working area of both membranes was 25 cm^2

5

98   (5×5 cm). The working volume of the three chambers was 50, 50 and 100 mL, for the anode,

99   regeneration and cathode chamber, respectively. The reactor was tightened using rubber gaskets and

100 screws to avoid leakage. The anodic electrode is made of carbon brush (5.0 cm in diameter, 5.0 cm in

101 length, Mill-Rose, USA). The cathode electrode is a titanium woven wire mesh (4×5 cm, 0.15 mm

102 aperture, William Gregor Limited, London) coated with 0.5 mg/cm^2 Pt. A power supply (HQ PS3003,

103 Helmholt Elektronik A/S, Denmark) was used to provide an additional voltage to the circuit with a 10

104 Ω external resistance.

105   The anode electrode was originally pre-acclimated in a two-chamber microbial fuel cell and

106 inoculated with a mixed bacterial culture from domestic wastewater collected from a primary clarifier

107 (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). When stable voltage was obtained

108 around 0.5 V with a 1000 Ω resistance for several cycles, the electrode was transferred into the

109 microbial electrolytic reactor. The anolyte was circulated over a 250 mL recirculation bottle with a

110 peristaltic pump at a flow rate of 25 mL/min. The total anolyte volume was 250 mL. The system was

111 then operated in a batch mode and a continuous mode. The batch experiment lasted for 7 days. During

112 the batch experiment, the recirculation bottle was filled with 250 mL wastewater from the same

113 primary clarifier mentioned before and 5 mL (1 M) sodium acetate was dosed to achieve a COD

114 concentration approximately 2000 mg/L. The regeneration and cathode chambers were filled with 0.05

115 M sodium chloride solution. Prior to each batch run, all chambers and the recirculation bottle were

116 purged with N_2 for 15 min to ensure anaerobic conditions. The synthetic biogas (60% CH_4 and 40%

117 CO_2) was introduced to the bottom of the cathode chamber by a column diffuser (pore diameters 0.5-

118 1.0 μm, Maltbazaren ApS, Denmark) via a peristaltic pump at varying gas flow rates. The gas retention

119 time in the chamber was between 3.6-7.5 h according to different gas flow rates. The upgraded biogas

120 was collected from the cathode with a gas bag. The collected gas was recirculated through the cathode

6

121   at the same gas flow rate of the raw biogas to enhance the mixing and increase CO_2 absorption. A

122   control experiment without external applied voltage was also operated in the batch mode at 19.6 mL/h

123   gas flow rate. In the continuous mode, the medium in the anodic recirculation bottle was renewed when

124   the current density decreased below 0.8 A/m^2 while the solution in the regeneration and cathode was

125   not refilled throughout the whole period. The reactor was operated for 40 days with 19.6 mL/h gas flow

126   rate. The external voltage was 1.2 V at the beginning and then increased to 1.4 V and further to 1.5 V at

127   the end. The experiments were carried out at least in triplicate and at room temperature (22±2°C). All

128   chemicals utilized were of reagent grade without purification.

129   **Electrochemical Analyses and Calculations.** Voltage drop across the 10 Ω resistance was

130   measured and voltage readings were taken every 30 mins by a digital multimeter (Model 2700,

131   Keithley Instruments, Inc.; Cleveland, OH, USA). Current was calculated according to ohm's law.

132   Current density was calculated as $i=I/A$, where I (A) is the current and A (m^2) is the project surface area

133   of the cathode electrode. Conductivity and pH were measured using a CDM 83 conductivity meter

134   (Radiometer) and a PHM 210 pH meter (Radiometer), respectively. Methane and carbon dioxide were

135   determined by a GC-TCD fitted with paralleled column of 1.1 m × 3/16 'Molsieve 137 and 0.7 m × 1/4'

136   with hydrogen as the carrier gas (MGC 82-12, Micolab A/S, Denmark). Hydrogen was analyzed by a

137   GC-TCD fitted with a 4.5 m × 3 mms-m stainless column packed with Molsieve SA (10/80). Cl$^-$ was

138   detected via Flame atomic absorptions spectrophotometer (FAAS, Shimadzu). Total inorganic carbon

139   (TIC) was determined by a TC-2000 (Shimadzu, Kyoto, Japan). COD was analyzed according to

140   APHA. Coulombic efficiency (*CE*), current efficiency (*CTE*), electric energy consumption by the

141   power source (W_E) and the energy efficiency (η_E) relative to the ratio of produced H$_2$ energy to the

142   electricity input were calculated as previously described [14] and equations are shown in the supporting

143 information. Methane loss was calculated as well and the formula is shown in the supporting

144 information.

145

146 **Results and Discussion**

147

148 **The MESC reactor performance.** The microbial electrolytic reactor was first operated with 19.6

149 mL/h gas flow rate and 1.2 V external voltage. In the control experiment, the reactor was operated in

150 the open circuit at the same gas flow rate. Reactor performance in terms of the current generation, COD

151 removal, pH and conductivity profiles and gas contents was shown in Figure 2.

152 Figure 2a shows the current output and COD tendency along with the operation time. With 1.2 V

153 external voltage, the current density started at 1.7 A/m^2 and gradually decreased to 1.3 A/m^2 during the

154 first four days since COD in the anode decreased from 2341±320 to 420±79 mg/L. On day 5, when

155 COD concentration decreased to the level below 500 mg/L, the current density dropped significantly

156 below 0.8 A/m^2. Therefore, the concentration of organic matter can affect the circuit current by

157 affecting exoelectrogens.[15] Acetate amended domestic wastewater was used in this study as the anodic

158 substrate to proof the concept of the technology. Since METs can use nearly all kinds of organic wastes

159 as substrates, wastewater with high COD levels (e.g., industrial wastewaters and anaerobic

160 fermentation effluents) could be used for practical application of the technology. In the control

161 experiment, a similar COD removal efficiency of 94.4±1.3% was obtained indicating competitors to

162 exoelectrogens such as methanogen might prevail in the domestic wastewater. Indeed, CH$_4$ (17%) was

163 detected in the anode chamber for the control reactor. Lower amount of CH$_4$ (3%) was detected in the

164 closed circuit since exoelectrogens were dominant due to the anode potential[19]. Results show the

165 feasibility of the microbial electrolytic system for wastewater treatment. Figure 2b shows the pH

166   profile of the whole reactor. Initial pH of the wastewater and NaCl solution was 7.30±0.28 and

167   7.61±0.30, respectively. In the control experiment, pH in the anode and regeneration chambers changed

168   barely while that in the cathode chamber decreased a little from 7.61±0.30 to 6.32±0.21. This could be

169   due to CO_2 dissolving in water and the ionization of it to HCO_3^{-}[16]. When 1.2 V external voltage was

170   supplied to the reactor, pH in the regeneration chamber decreased below 2 which was contributed by

171   water dissociation between the BPM. Anodic pH was nearly stable during the experiment which was

172   due to the neutralization of H^+ from bacterial respiration with OH^- from water dissociation. Catholyte

173   pH first increased to maximum at 9.19±0.12 on the first day and then decreased gradually to 7.42±0.22

174   on the last day. The increase of the catholyte pH was probably due to the splitting of water for the

175   production of alkaline and H_2 at cathode, which was supported by the observed hydrogen production

176   (37±3 mL) at the end of the batch run. Catholyte pH decreased gradually since dissolved CO_2 reacted

177   with alkaline and generated HCO_3^- and CO_3^{2-} . On day 5 a sharp decrease was observed in catholyte pH

178   which was consistent with the remarkable decrease in the current output. The electrolysis process might

179   cease as organic matter was completely consumed.

180   The initial conductivity of wastewater and NaCl solution were 2.74±0.23 and 5.72±0.26 mS/cm,

181   respectively. As shown in Figure 2c, in the control experiment conductivity of the reactor fluctuated

182   insignificantly. With 1.2 V external voltage, conductivity in the regeneration chamber first increased

183   from 5.72±0.26 to 22.79±0.75 mS/cm on the second day and then decreased to 11.07±0.95 mS/cm in

184   the end. The increase of conductivity in the regeneration chamber could be explained by H^+ production

185   via the BPM. When pH in the regeneration chamber was 1.34, it could contribute 15.98 mS/cm in

186   conductivity (calculation was stated in Supporting Information). However, along with the decreasing of

187   current density from 1.7 to 0.8 A/m^2, the water dissociation efficiency decreased even to zero. In

188   Bauer's work[20], the water dissociation efficiency decreased from 70% to 0% as the current density drop

9

189   from 10 to 0 mA/cm^2. Another reason for the decrease of conductivity was that carbonate and

190   bicarbonate ions reacted with H$^+$ and CO_2 emission occurred. At the end of the experiment, 22±3 mL

191   CO_2 was collected from the regeneration chamber.

192   Alkaline absorption is an efficient way for biogas upgrading because of the large difference in the

193   solubility of CO_2 and CH_4.[14] As shown in Figure 2d, when no alkaline was produced in the control

194   experiment, the CH_4 concentration was kept around 85% and CO_2 concentration decrease from the

195   original 40% to approximately 15% due to dissolution in water. When 1.2 V voltage was supplied, CO_2

196   reacted with alkaline leading to a higher CO_2 removal from biogas. For example, the CO_2 concentration

197   was blow 8% during the whole period and even to 0.5±0.2% while the highest CH_4 content could be

198   97.0±1.3%. Therefore, the microbial electrolytic reactor was an efficient approach for biogas upgrading.

199   **Influence of other ionic species on HCO_3^-/CO_3^{2-} transportation**. To achieve efficient CO_2

200   separation and capture, the key point is to drive HCO_3^- and CO_3^{2-} ions through the membrane to the

201   regeneration chamber. However, the cathode was filled with 0.05 M NaCl solution and alkali was

202   produced during H$_2$ evolution. Cl$^-$ and OH$^-$ might also move through the membrane and thereby are

203   competing with HCO_3^- and CO_3^{2-} for transportation. Therefore, pH and Cl$^-$ concentration in the cathode

204   and regeneration chambers were measured along with the operation time. The profile of Cl$^-$

205   concentration is shown in Figure 3. When catholyte pH increased to 9.2, the OH$^-$ concentration was as

206   low as 1.58×10^{-5} M and therefore would have insignificant effect on electron flux balance. As shown in

207   Figure 3 and Table S2, no significant changes in Cl$^-$ concentrations were observed in the regeneration

208   chamber and cathode chamber in the open circuit. On the first day of the closed circuit operation, when

209   current densities were the highest and HCO_3^- concentration was the minimum, the Cl$^-$ concentration

210   reached the maximum of 2404±50 mg/L followed by a slightly decrease in the regeneration chamber.

211   In the cathode, the Cl$^-$ concentration decreased to 1040±40 mg/L to compensate the flux of electron

212   which was consistent with the slightly lower conductivity (4.69±0.17 mS/cm) on the first day.

213   Subsequently, the slight transfer of Cl⁻ from the regeneration chamber to cathode chamber occurred due

214   to back diffusion or ion exchange with HCO_3^-/CO_3^{2-}. The final Cl⁻ concentrations in the regeneration

215   and cathode chamber in the closed circuit were 0.053 and 0.045 M, respectively. Results indicated the

216   final flux of Cl⁻ transported from the cathode to the regeneration chamber was limited ($\leq$10%). It has

217   been reported that ion transfer can be prevented due to similar ion concentrations in both compartments

218   separated by the membrane[17, 18]. According to the C balance shown in Figure 5, at the end of the batch

219   test 0.261 g of TIC was detected in the regeneration chamber in closed circuit which equals equivalent

220   of 0.022 mol HCO_3^-. A current efficiency of 81% could be achieved during the whole period meaning

221   that the transfer of every mol of electrons to the cathode was accompanied by 0.81 mol HCO_3^-

222   transportation. Thus, the HCO_3^- transportation would not be adversely affected by Cl⁻ and OH⁻.

223   **Effects of the gas flow rate and applied voltage on the system performance.** The influence of

224   biogas flow rate on the system performance was investigated at the external voltage of 1.2 V. The gas

225   flow rate was control by the peristaltic pump from 13.4 to 27.7 mL/h. The summary of current outputs,

226   pH and conductivity profiles, and outlet gas composition during the experiment is shown in Figure 4.

227   Under different gas flow rates, the current density showed similar trend along with the operation

228   time (Fig. 4a). The current density fluctuated around 1.6 A/m² and significantly dropped below 0.8

229   A/m² after the fourth day due to the substrate consumption and high polarization resistance of the BPM.

230   The current output was mainly influenced by the microorganism community and the substrate

231   concentration. However, with 13.4 mL/h gas flow rate, the reactor produced relatively lower current

232   densities. Since gas introduction to the catholyte might function as mixing and enhance the mass

233   transfer. Relatively low gas flow rate and recirculation rate resulted in small disturbances and slow

234   mass transfer which was adverse to the cathodic hydrogen evolution.

235   In Fig 4b, cathodic pH was in the rage of 7 to 10 while pH in the regeneration chamber was

236   between 1.5 and 4. With the gas flow rate increasing, cathodic pH decreased obviously indicating the

237   enhanced CO_2 absorption in the alkaline solution. With 13.4 mL/h gas flow rate, it was found that

238   cathodic pH reached the highest value around 10 on the second day. It is because relatively less CO_2

239   reacted and consumed OH^-. In Fig. 4c, the maximum conductivity in the regeneration chamber

240   increased from 14.08±0.75 to 22.79±0.75 mS/cm along with the increasing of gas flow rate from 13.4

241   to 19.6 mL/h. When the gas flow rate went up further, conductivity did not increase further.

242   Correspondingly, when the gas flow rate was below 20 mL/h, CH_4 composition kept above 90% and

243   could reach to maximum at 98.1±0.2%. CO_2 was removed effectively and could be lower than 2%

244   during the first 4 days when the gas flow rate was below 20 mL/h. When the gas flow rate increased

245   from 25.3 to 27.7 mL/h, CH_4 composition dropped from 88% to 84% as average during the whole

246   period. Therefore, a proper feeding gas flow rate is crucial to improve the system performance. When

247   the gas flow rate was low, the biogas upgrading capacity might decrease while high flow rates might

248   decrease the purity of CH_4. Further strategies for the improvement of biogas flow rate are thus required

249   in future studies for accelerating the commercialization.

250   The effect of external voltage on the CO_2 removal efficiency and CH_4 enrichment was studied. The

251   system performance was compared at external voltage of 0, 1.0, 1.2 and 1.4 V which are shown in

252   Figure S1 and S2. When the gas flow rate was the same but the external voltage elevated, the maximum

253   catholyte pH was increased from 6.44±0.05 (0 V, 19.6 mL/h), 7.37±0.12 (1.0 V, 19.2 mL/h) to

254   9.19±0.11 (1.2 V, 19.6 mL/h) and from 7.38±0.08 (1.2 V, 27.7 mL/h) to 7.52±0.10 (1.4 V, 28.0 mL/h)

255   as well as the volume of generated H_2 from 0 mL (0 V, 19.6 mL/h), 22±2 mL (1.0 V, 19.2 mL/h) to

256   37±3 mL (1.2, 19.6 mL/h V) and from 37±3 mL (1.2 V, 27.7 mL/h) to 40±3 mL (1.4 V, 28.0 mL/h),

257   respectively. The applied voltage would induce fast electron transfer kinetic and compensate the

258   electrode overpotential, which could also enhance the substrate consumption by anode respiring

259   bacteria[21] and favorite the electrolysis process. When the applied voltage was changed from 0, 1.0 to

260   1.2 V at around 19.6 mL/h gas flow rate, the maximum CH_4 content of the output gas increased from

261   85.5±0.3%, 89.2±0.4% to 97.0±0.2%. However, when the gas flow rate was higher than 25.3 mL/h, the

262   concentration of CH_4 could not be improved further with even higher applied voltage (1.4 V). The

263   biogas upgrading capacity probably has a threshold and the system performance might be determined

264   by other limiting factors.

265   Experimental results at various operation conditions are summarized in Table 1. As shown in

266   Figure 4a, with the fixed external voltage supply (1.2 V), the current density increased along with the

267   increasing of gas inflow rate since it enhanced the mixing and mass transfer. However, cathodic pH and

268   upgrading performance showed opposite trends (Figure 4b and 4d). It could be due to a change in

269   equilibria between alkali production capacity at cathode (expressed as pH) and the dissolving gasses. In

270   this case, the gases dissolution rate was higher than the OH^- generation rate. As expected, the current

271   density, cathodic pH and upgrading performance increased with the increasing external voltage supply

272   (Figure S1 and S2). However, the increase in those parameters turned to be limited when the gas inflow

273   rate was over a certain level. Thus, operational parameters applied such as voltage and gas inflow rate

274   need to be better adjusted to maintain equilibrium between cathodic pH and the dissolving gasses for

275   efficient upgrading. Considering the final pH and Cl^- concentration in the cathode (Table S2), the

276   changes in the transportation of other anions than HCO_3^- and CO_3^{2-} were not significant under the

277   tested conditions. The collected CO_2 increased with the current density since more HCO_3^- ions were

278   transported via the membrane driven by higher current and then CO_2 was formed at the lower pH.

279   Results indicate that both the applied voltage and biogas flow rate are crucial to the system

280   performance. Eligible CH_4 content (>90%) was obtained when the gas flow rate was in the range of

281   13.4 and 19.6 mL/h with 1.2 V applied voltage.

282   **Energy analysis and mass balance.** The electrical energy consumption for biogas upgrading

283   technologies is an important issue for the practical application. Our lab-scale system consumed

284   between 0.09 and 0.15 kWh of electrical energy for upgrading one m^3 raw biogas, which was quite

285   competitive compared with commercial technologies. For instance, the electricity demand for biogas

286   upgrading is about 0.2-0.32 kWh/Nm^3 raw gas with water scrubbing, 0.1-0.15 kWh/Nm^3 with chemical

287   absorption and 0.15-0.22 kWh/Nm^3 with membrane technology[3, 22]. It should be noted that the

288   electricity consumption is the sole "consumable cost" of microbial electrolytic system for biogas

289   upgrading while additional of chemicals (e.g., acids and alkali), high pressure or temperature are

290   required in most of the conventional methods. Since the microbial facilitated release of electrons stored

291   in organic matter from wastewater, the applied voltage was much lower than that used in the water

292   electrolysis process.[14] Moreover, an energy carrier (H_2) is produced in the cathode which could

293   substitute 21-27% of the electric energy input. Since the substrate was degraded and about 16-33% of

294   the chemical energy was converted to the electrical energy, the energy provided by the organic

295   substrate was 140-334 kJ/Nm^3 which was calculated according to the energy content of acetate based

296   on the heat combustion. The energy benefits could be even higher if energy savings for wastewater

297   treatment was considered. Besides operational and maintenance costs for in real scale application,

298   investment should also be considered. However, investment costs per m^3 raw biogas would decrease

299   with increasing capacity.

300   At the end of the batch run with and without 1.2 V external voltage at 19.6 mL/h gas flow rate,

301   carbon balance was performed to study the carbon capture mechanism. Rude biogas was introduced

302   into the reactor as the source of CO_2. In the cathode, CO_2 was converted to (bi)carbonate and

303 transported to the regeneration chamber. Then (bi)carbonate reacted with H^+ and CO_2 was regenerated.

304 Volume of initial CO_2 and regenerated CO_2 was measured and TIC of the solution was determined. The

305 carbon balance is shown in Fig. 5. In the control experiment, approximately 30% of the CO_2 was

306 remained and 16% of the CO_2 existed in the cathode chamber as the form of soluble $NaHCO_3$ and

307 Na_2CO_3. No CO_2 was collected from the regeneration chamber since acid was not produced. When an

308 external voltage of 1.2 V was supplied, carbon distribution was quite different. The remained CO_2 in

309 the outlet accounted for 15% of the total initial CO_2 and 37% existed as (bi)carbonate in the

310 regeneration chamber. The regenerated CO_2 and TIC in the cathode chamber shared 2% and 12% of

311 the initial carbon, respectively. The imbalance on CO_2 species could be due to diffusion to the anode

312 and measurement error.

313 **Experiment under the continuous mode**. The microbial electrolytic system was then operated in

314 the continuous mode for 40 days. For the initial 26 days the system was operated with 1.2 V external

315 voltage and 19.6 mL/h raw biogas flow rate. The external voltage was increased to 1.4 V since day 26th

316 and enlarged further to 1.5 V from day 33rd to the end of the experiment at the same gas flow rate. CH_4,

317 H_2 and CO_2 contents in the outlet gas in the continuous mode are showed in Figure 6. During the first

318 six days, CH_4 content was above 90% and could reach 97.5±0.74% at maximum while CO_2 content

319 was below 5% and reached 1.0±0.48% at minimum. Subsequently, CH_4 and CO_2 content were kept

320 around 88.3% and 8.3%, respectively. During the whole period, H_2 was produced and the content was

321 around 3.8%. Approximately, 18.8 L rude biogas was treated and the energy consumption for per m^3

322 raw biogas was 0.18±0.01 kWh. During the 40 days operation, NaCl solution has not been changed and

323 the saturation state was not reached yet, which shows a huge absorption capacity of our system with

324 less maintenance. When the external voltage was increased to 1.4 V and 1.5 V, a peak occurred at the

325 corresponding CH_4 content. However, the enhancement on the biogas upgrading was limited which

326   indicated that there were probably other limiting factors dominating the system performance other than

327   external voltage in the continuous mode. Membranes were not cleaned or replaced during the whole

328   period which exhibits the tolerance of membranes.

329   This study for the first time demonstrated the proof of concept of a microbial electrolytic system

330   for simultaneous CO_2 capture, separation and regeneration, biogas upgrading and wastewater treatment.

331   Compared to commercial biogas upgrading technologies, the novel system developed here has several

332   merits. First, addition of chemicals is not needed since acid and alkaline are generated and utilized in

333   situ which saves the cost/risks for chemicals transportation and storage. Secondly, methane loss (e.g.,

334   due to dissolution) during the whole period is less than 1.4% while that in traditional biogas upgrading

335   technologies is about 2%[3, 23]. Low methane loss is beneficial for economic and environmental aspects.

336   Thirdly, separated CO_2 from rude biogas and the (bi)carbonate solution can be further used in other

337   industrial applications, such as the production of algal biomass and enhanced oil recovery.[3] Moreover,

338   the applied voltage to overcome the thermodynamic barrier of water splitting in our system is quite

339   lower than that used in the abiotic water electrolysis. It is because the chemical energy stored in the

340   organic matter was released with the help of bacteria to offset the difference. Organic substrates

341   provided energy to the system instead of consuming energy. However, it was not counted as energy

342   input since the wastewater has to be treated anyway. Therefore, the electrical energy consumption in

343   the system is quite low (0.09 kWh//Nm^3) and H_2 produced can even substitute part of the energy costs

344   (up to 27%). In addition, the MESC as biological system could meet the needs of sustainability and

345   circular economy. The simple configuration of the MESC makes the technology more competitive

346   compared to the traditional electrolysis processes and MEDCC for the purpose of biogas upgrading and

347   CO_2 recovery. However, for practical applications, several issues should be considered. For instance,

348   H_2S and other impurities in biogas should be removed (biogas pre-upgrade) in advance to eliminate the

349 risk for adverse effect on the microbial electrolytic system. Acetate amended real domestic wastewater

350 was used here to prove the concept. Many waste streams such as industrial wastewater or fermentation

351 effluent have high COD concentrations and can potentially be used for practical application of the

352 technology. Despite long term operation of the microbial electrochemical system with domestic

353 wastewater (emended with acetate), for more than half year, biofouling of the membranes was not

354 observed. Furthermore, NaCl as electrolyte in this study may add the operational costs. However, in

355 practical application, NaCl can be added once to start up the process rather than continuous addition.

356 Wastewater, which could support the conductivity in the liquid during continuous operation, may

357 substitute NaCl. Taking this into account, the energy costs could be further reduced, and thus, further

358 improvement such as appropriate material selection and chemicals refusal might be necessary. To

359 conclude, the concept is very challenging but also full of promises and is definitely going to make a

360 significant impact on relative research field.

361 **Acknowledgement**

366 **Supporting Information**

367   Calculation for Coulombic efficiency (CE), energy efficiency, current efficiency and methane loss.

368 Table S1, Table S2, Figure S1, and Figure S2 as noted in the text. This material is available free of

369 charge via the Internet at http://pubs.acs.org/

370 **Author Contributions**

371 [#]X.J. and Y.Z. contributed equally to the paper.

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427   **Table 1**. Experimental results at various operation conditions

Voltage V	0	1.0	1.2				1.4
Gas flow rate mL/h	19.6	19.2	13.4	19.6	25.3	27.7	28.0
pH_{max} in Cathode	6.44±0.05	7.37±0.12	10.03±0.07	9.19±0.11	8.59±0.10	7.38±0.08	7.52±0.10
pH_{min} in Regeneration	6.87±0.04	2.09±0.07	1.88±0.05	1.34±0.04	1.43±0.10	1.36±0.07	1.44±0.06
Max CH_4 %	85.5±0.3	85.9±0.4	98.1±0.2	97.0±0.2	90.3±0.3	86.0±0.3	86.1±0.2
CO_2 removal efficiency %	78.3±1.4	77.0±0.7	98.7±0.5	92.6±0.6	89.3±1.5	85.7±.04	81.3±1.1
COD removal efficiency %	94.4±1.3	80.4±2.7	78.7±3.5	98.2±2.6	91.9±2.8	93.4±4.7	86.5±5.9
CE %	-	16.3±1.4	20.0±1.3	26.0±2.1	22.7±1.7	32.6±1.3	17.5±1.8
CO_2 collected mL	-	6±3	10±3	22±3	18±2	24±2	25±2
H_2 mL	-	22±2	24±2	37±3	32±2	31±4	40±3
Electricity consumption kWh/m^3		0.09±0.004	0.15±0.003	0.15±0.003	0.10±0.003	0.11±0.002	0.13±0.004
Energy efficiency	-	26.8±1.2	24.2±1.7	26.5±0.8	26.7±1.4	20.6±1.7	22.4±2.2
CH_4 loss %	1.22±0.02	1.32±0.03	1.21±0.02	1.23±0.02	1.14±0.03	1.20±0.02	1.27±0.02

428   **Figure Caption**

429   **Figure 1**. The schematic diagram of MESC. BPM, bipolar membrane; AEM, anion exchange membrane.

430   **Figure 2**. MESC performance at 19.6 mL/h gas flow rate with 1.2 V and control experiement. A, anode chamber;

431   R, regeneration chamber; C, cathode chamber. The current density output and COD changes (a); pH

432   profiles in three chambers (b); conductivity profiles in three chambers (c); methane and carbon dioxide

433   contents in the outlet gas (d).

434   **Figure 3.** Profiles of Cl⁻ concentration in the regeneration chamber and cathode chamber along with the

435   operation time.

436   **Figure 4**. MESC performance with 1.2 V and varying gas low rates. The current density output (a); pH profiles

437   in the cathode (C) chmaber and the regeneration (R) chamber (b); conductivity profiles in the

438   regeneratioin chamber (c); methane and carbon dioxide contents in the outlet gas (d).

439   **Figure 5**. Carbon balance in MESC system with and without 1.2 V external voltage at 19.6 mL/h gas flow rate.
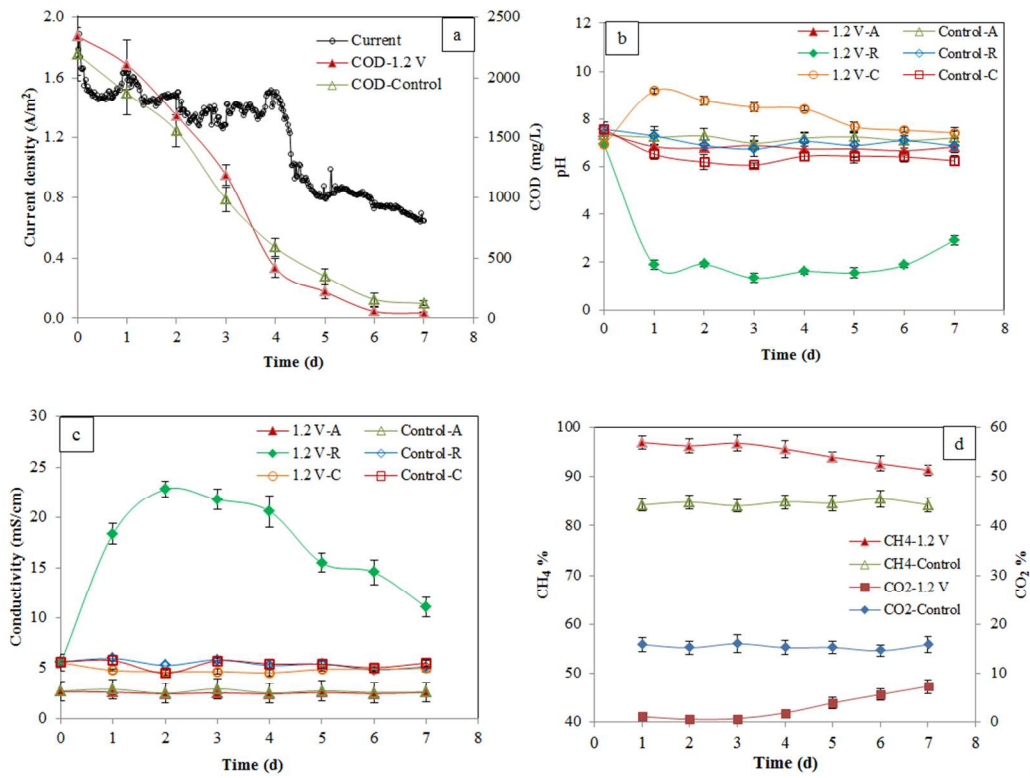
440   **Figure 6**. Methane, hydrogen and carbon dioxide contents in the outlet gas in the continuous mode.
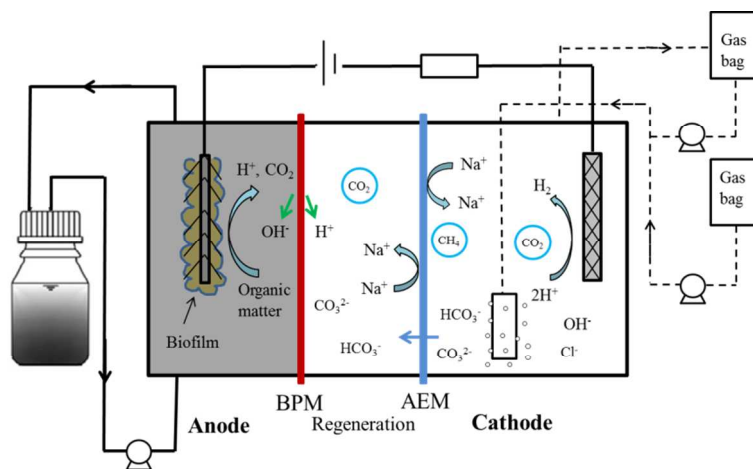
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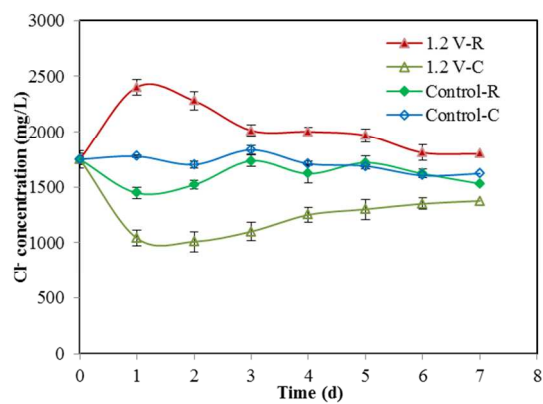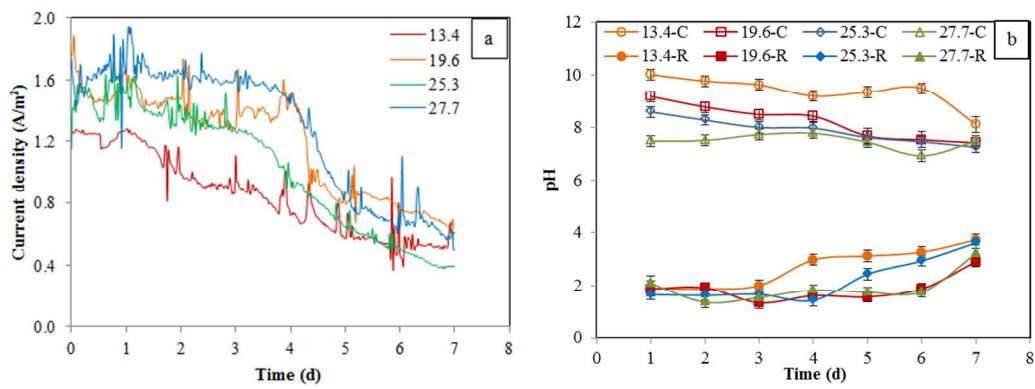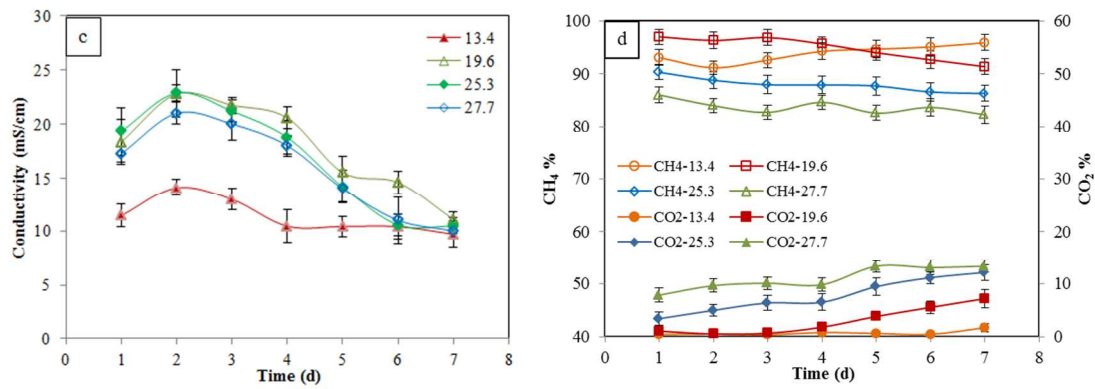442   **Figure 1**
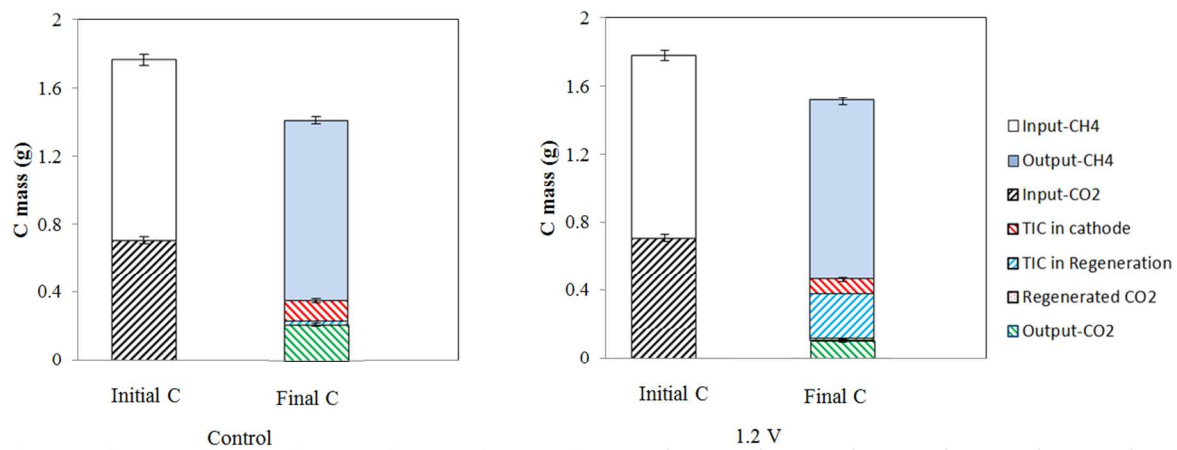
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445   **Figure 2**

448

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450   **Figure 4**

451   Control   1.2 V

452   **Figure 5**
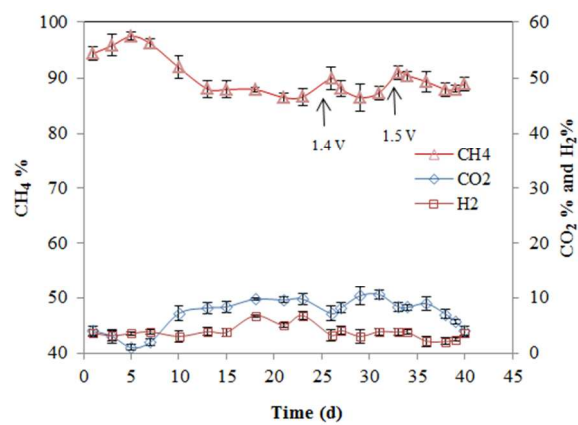
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454   **Figure 6**

455   **TOC art**

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