Operating strategies to improve performance and coulombic efficiency by selecting electrogens over methanogens in microbial fuel cells

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Abstract
The suppression of methanogens affects the performance of Microbial Fuel Cells (MFCs), but its degree of importance is application dependent. In terms of Coulombic Efficiency (CE), avoiding methanogenesis is essential for MFC type volatile fatty acid (VFA) sensors but less critical for scaled-up MFCs removing COD from real wastewater. To study the suppression of methanogenesis, different H-type MFCs were enriched with acetate, propionate and butyrate. These reactors were operated under different open ciruit (OC) and closed circuit (CC) regimes. During OC operation, significant CH_4 was produced but was inhibited when anodic media was replaced and operated in CC. The archeal communities on the electrode and in solution were compared after different OC/CC regimes, and clearly indicated the shift of some dominant species from electrode to the solution phase during OC operation. The results indicate gradual inhibition of methanogenesis during OC/CC operation and also complete inhibition after starving the MFC for a period of time.

Keywords
Bioelectochemical system; methanogenesis; coulombic efficiency; open/closed circuit

INTRODUCTION

Enhancing coulombic efficiency (CE) by suppressing methanogenesis is an ongoing issue in the area of bioelectrochemical systems (BES). This is almost regardless of their application, which may include scaled-up systems for treating industrial or municipal wastewaters; or small devices used as sensing elements. There are many parameters which adversely affect CE in MFCs, but the losses caused by methanogenic archaea are of considerable importance. Various studies have already reported on the inhibition of methanogens by using various inhibitors (Chae et al., 2010). These inhibitors suppress methanogens but also affect electrogens on the anode electrode (Chiu and Lee, 2001; Liu and Logan, 2004). In this study operational strategies to improve CE by inhibiting methanogenesis are presented.

MATERIALS AND METHODS

Six H-type MFCs in a set of three replicated reactors were constructed as previously described in (Kim et al., 2009) and enriched individually with acetate, propionate and butyrate. One set was continuously operated under CC mode for >1 year after initial open and CC operations. Another set was first operated in an OC mode and then CC for 10 days each and subsequently for one month. In addition, one H-type MFC was operated under maximum power point tracking (MPPT) control for 64 days prior to the measurement of CE. Also to determine the dependence of the CE on the organic loading rate (OLR), a longitudinal tubular reactor with four modules (V_{module} = 0.25 L) was

continuously fed with the effluent of a two stage biogas process, itself fed on wheat feed (Fradler et al., 2012). The reactor was built as previously described by (Kim et al., 2010; Kim et al., 2011). The CE was calculated as previously report (Logan, 2008). A *pseudo*-half saturation constant K_s was calculated by fitting Monod type kinetics to the plot of sCOD concentration (S [mg sCOD/L]) vs. average current (I [A]) in four MFC modules using SigmaPlot 10.0, according to the following function $\mathbf{I} = \mathbf{I_{max}} \frac{\mathbf{S}}{\mathbf{K_s + S}}$.

RESULTS AND DISCUSSION

Effect of OLR on Coulombic efficiencies when processing complex wastewater streams

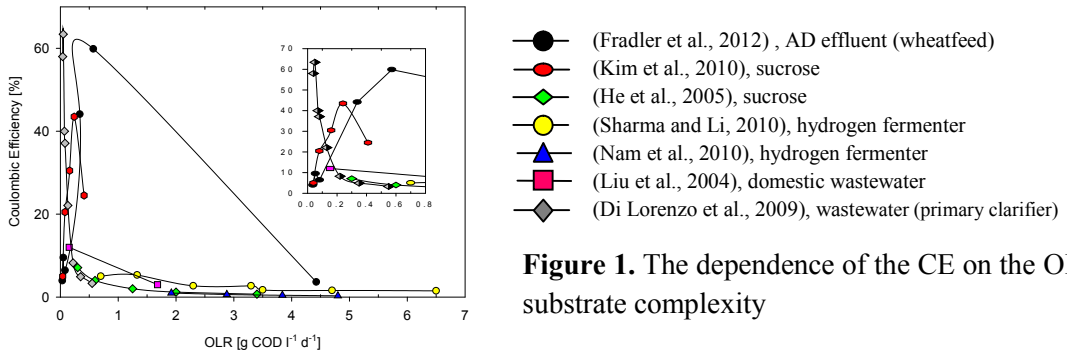

Figure 1. The dependence of the CE on the OLR and substrate complexity

Figure 1 indicates that high CEs can only be achieved at low OLRs (<0.6 g COD L^{-1} d^{-1}) and the maximum CE of different systems is restricted to a narrow range of organic loading rates. In particular, the results obtained from the tubular reactor with 4-modules hydraulically connected in series (Fradler et al., 2012) and in 2-module mode using sucrose as a feedstock (Kim et al., 2010), show that the CE increases to a maximum at very low organic loading. This might be attributed to mass transport limitations to and from the biofilm and/or might be due to the presence of methanogens in the fermented wastewater used in addition to other side reactions and oxygen diffusion. After the CE peak, the results from the tubular reactors correlate with the findings of other studies and decreases at higher OLRs most likely because more substrate becomes available for methanogenesis. To achieve high CE the concentration of substrate available for electrogens and their affinity towards this substrate is of great importance. The *pseudo*-half saturation concentration K_s gives an indication of the electrogen's substrate affinity, but only if substrate limitations are rate limiting (Rabaey et al., 2009). The fitted K_s for the 4-module tubular reactor on the AD effluent is 436.6 mg COD l^{-1} (R = 1000 Ω), which is significantly higher than the K_s value obtained with sucrose in a very similar tubular system (K_s = 50 mg COD l^{-1}; R = 150 Ω) (Kim et al., 2010). The higher half saturation concentration for the complex AD effluent might be attributed to the presence of VFAs in the AD effluent, different external loads and other system related parameters. The results obtained in the H-type bottles indicate, that methanogens can be outcompeted as electrogenic bacteria exhibit a higher substrate affinity towards VFAs than methanogens. Hence the availability of substrate with high affinity towards electrogens increases with the reactor length because complex organic compounds are degraded to lower carbohydrates and will therefore automatically increase the overall CE throughout the reactor.

Gas Analyses during Starvation period and Open/Closed Circuit Operation

In all H-type reactors, during OC, percentage of CH_4 production was higher than in CC i.e. >10% and <3.0% resp. whereas very low (<0.1%) and no CH_4 was detected after one month of OC/CC operation and 1 year. Production of H_2 i.e. 0.48%, 1.1% and 16% resp. during CC operation indicates the inhibition of hydrogenotrophs on the electrode. Hydrogen and CH_4 were totally

replaced in the headspace, by high %CO_2 (value) due to wash out of the methanogenic community as well as some displacement of the bacterial community from the electrode. For MFCs under MPPT operation, CH_4 was being produced before starvation and increased from 0.65% to 1.68% with increasing substrate concentration (0.5 mM to 2 mM) while the coulombic efficiency was 61 – 87%. After starvation for 12 days, CH_4 was no longer detected but resulted in a lower CE (59.1%). This may be due to exo-electrogen biomass growth and biofilm recovery. Replacing media again with 5 mM and further long term operation, CE resumed to 86.98% without any CH_4 production. Lack of CH4 in the gas samples taken after starvation suggests that methanogens and hydrogenotrophs were eliminated by not supplying the substrate (carbon source).

Molecular Analyses

Samples from electrodes and solution were collected during and after OC/CC operation. DNA amount was measured in ng/µl from both electrode and liquid samples and is summarized in Table 1 this shows the movement of active biomass from electrode to the solution during OC.

Table 1. Electrode and liquid phase biomass total DNA concentrations in OC and CC operated MFCs

		DNA Concentration (Electrode) ng/µl			DNA Concentration (Solution) ng/µl	
Substrate	Time	Before	Open	Closed	Open	Closed
Acetate	10 days	326.5	172.1	136.5	102.0	42.0
	1 month	299.6	197.2	123.2	96.0	11.5
Propionate	10 days	373.5	296.6	210.5	211.0	59.0
	1 month	410.2	232.6	201.6	116.0	74.0
Butyrate	10 days	319.2	211.1	301.1	182.0	102.0
	1 month	317.0	288.3	320.7	152.0	110.0

The tendency of methanogens to leave electrodes during OC was found to be more pronounced compared to electrogens, which is supported by DGGE profiles obtained from open and CC operation.

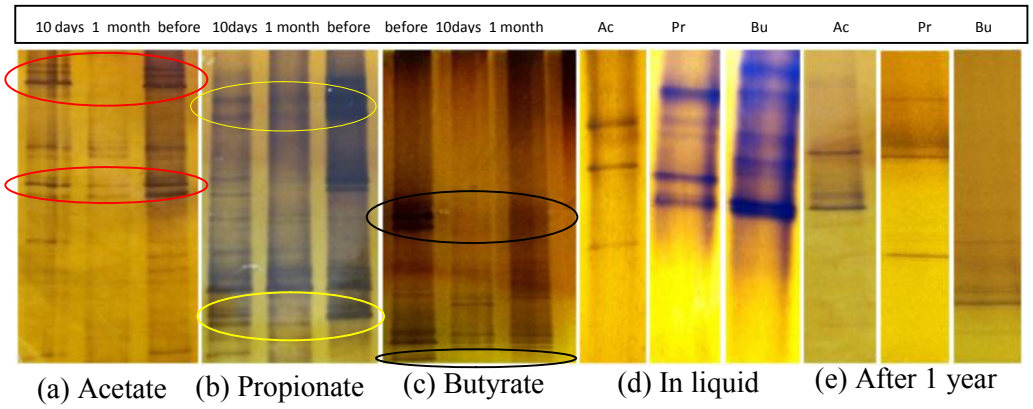

Figure 2. PCR-DGGE profiles of anode archeal communities obtained from the MFC after different OC/CC operation.

Figure 2 (a-c) is showing the difference of archeal DGGE profiles before OC/CC operation and after 10 days, 1 month and 1 year. These results indicate that after every OC/CC operation the

density of each methanogenic species is reduced. After one year's CC operation only few common dominant species were found on the electrode in all the reactors, which shows the inhibition of methanogens from the electrode with time (Figure 2e). DGGE profiles from the solution during OC operation also indicates the movement of some biomass, both electrogens as well as methanogens, to the solution as shown in Figure 2(d). Bacterial DGGE profiles were also studied and it has been found that there was not much difference in the profiles (data not shown) from both OC and CC, which indicates that OC/CC operation affects methanogens more, compared to electrogens.

CONCLUSION

The finding from this study shows that there are a number of ways to prevent methanogenesis in MFCs, but depending on their application, consideration should be given to whether it is essential, as in sensors or of less importance as in up-scaled MFC reactors. In a multi-modular tubular reactor the CE is adversely affected at high OLR but increases along the reactor length due to substrate degradation and increasing availability and affinity for electrogens. It is particularly important to inhibit methanogens in microbial fuel cell based VFA sensors, where methanogens might utilize the substrate and therefore the current response will not adequately represent the true concentration. A cross inhibiting method such as a period of starvation after OC operation, may lead to CH_4 inhibition and improved performance.

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