Biogas upgrading through the hydrogen production and CO_2 removal in a microbial electrolysis cell (MEC)

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1. Introduction

Biogas upgrading consists in the production of biomethane from the anaerobic digestion biogas through the selective CO_2 removal from the gas mixture. The biogas upgrading process usually involves a purification step which is devoted to the impurity removal (H_2S, NH_3, siloxane) while the selective CO_2 removal from the gas mixture is named upgrading (Sun et al 2015). Besides physical chemical processes, which exploits the different solubility of CO_2 and CH_4, an attractive perspective for biomethane production is represented by the biological CO_2 methanation (Angelidaki et al 2018). Biological methanation represents an attractive approach for biogas upgrading due to the capability of methanogens to convert CO_2 into methane in the presence of hydrogen, with this latter being conveniently produced using renewable energy sources. Moreover, the use of renewable electricity for hydrogen production also represents a viable strategy for the storage of the surplus renewable electricity into a stable chemical molecule (i.e., hydrogen gas). An innovative strategy to supply reducing power to microorganisms is offered by bioelectrochemical systems in which an electrode can be used by electroactive microorganisms as electron acceptor or donor in their metabolisms. In a microbial electrolysis cell (MEC), a graphite-based electrode can be used as electron donor to supply the reducing power to electro-active microorganisms for methane production, also known as bioelectromethanogenesis reaction. Moreover, in a biocathode, the alkalinity generated in the cathodic chamber by the phenomenon of the pH split allowed for a considerable increase in CO_2 removal, which results adsorbed as bicarbonate ion (Zeppilli et al 2016). The pH split phenomenon in bioelectrochemical systems consists in the progressive anode acidification and cathode alkalization due to the transport of ionic species different from protons and hydroxyls through the ion exchange membranes (Zeppilli et al 2021). The synergy between bioelectromethanogenesis reaction and the alkalinity generation in the biocathode allows to boost the CO_2 removal capacity of the biocathode allowing a comparable energy consumption of the bioelectrochemical process with full scale technologies.

In the present study a microbial electrolysis cell has been adopted for the sustainable hydrogen production and contemporary CO_2 removal from a synthetic biogas using the energy supplied by a bioanode. Indeed, the reducing power produced by the COD oxidation in the anodic chamber was transferred to the abiotic cathodic chamber in which a stainless-steel plate reduces protons into hydrogen. Moreover, in the MEC configuration involved in the present study, an external CO_2 sorption chamber was placed in the MEC to promote CO_2 sorption into bicarbonate in the catholyte continuously recirculated between the cathode and the sorption chamber. The study described the main performances of the lab scale system by the utilization of mass electrons and energy balances which allowed for the characterization of the biological and abiotic processes involved in the MEC operation.

2. Material and methods

The microbial electrolysis cells (MEC) consisted of two identical Plexiglas frames, with internal dimensions of 17 cm× 17 cm×3 cm and an empty volume of 0.86 L, bolted together between two Plexiglas plates. A Nafion 117 proton exchange membrane (PEM) was used as separator between anode and cathode chambers (Figure 1). The anodic chamber was filled with graphite granules with a diameter between 2 and 6 mm, graphite granules constituted both the electrodic material and the physical support for the electroactive biofilm formation. The anodic chamber of the MEC has been inoculated with an activated sludge from a full-scale wastewater treatment plant. Cathode chamber was fille with polypropylene plastic filling material while the electrodic material was a stainless-steel plate connected to the potentiostat by a titanium wire. An Ag/AgCl reference electrode (KCl 3 M +0.199 V vs. standard hydrogen electrode, SHE) (Amel s.r.l., Milan, Italy) was placed in each MEC chamber to control the potential by a IVIUM-N-STAT potentiostat (Ivium, - The Netherlands) and to measure the potential of each chamber. A glass chamber, equipped with sampling ports sealed with butyl rubber stoppers and aluminum crimps, was placed in the outlet of each compartment to sample the headspace and the liquid phase of both the anolyte and catholyte. In the latter case, the cathodic glass chamber was connected to a milliGas counter (Ritter, Germany), which permit the measure of the volumetric gas mixture flow rate in cathode chamber outlet. The external sorption chamber dedicated to CO_2 sorption consisted of a borosilicate glass 1,2 L reactor filled with 1 L of catholyte which was continuously recirculated between the cathodic chamber and the sorption chamber with a peristaltic pump. In the sorption chamber, a gas mixture of N_2/CO_2 (30-70 % v/v) was continuously flushed.

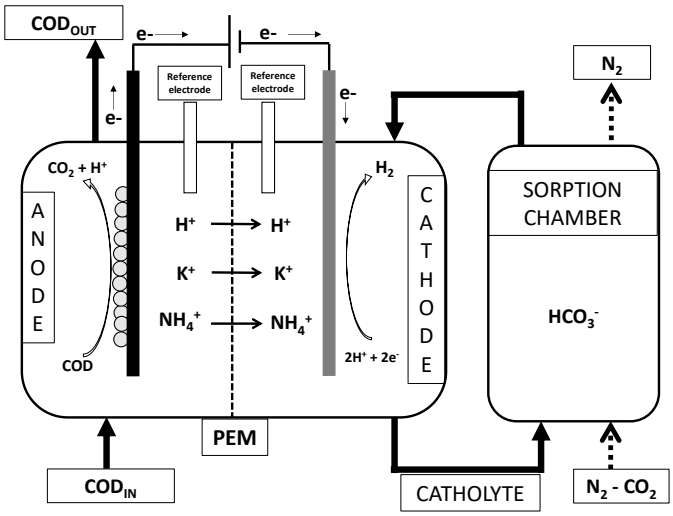

Figure 1. Schematic representation of the Microbial Electrolysis Cell equipped with the external CO_2 sorption chamber

3. Results and discussions

The continuous operation of the MEC was conducted by a peristaltic pump with an average flow rate of 1.56 L/d which corresponded to an HRT of 0.55 d (considering the empty volume of the anodic chamber). Table 1 resume the main performances of the MEC during its continuous operation under the anodic polarization at +0.2 V vs SHE. The anodic chamber removed mgCOD/Ld from the synthetic feeding solution which contained a mixture of soluble organic substrates at an average concentration of 1.35 gCOD/L. Considering an average current production of 77 ± 7 mA, the anodic chamber allowed for a coulombic efficiency, of 59 ± 6 %, which represents the capability of the anodic chamber to transfer the electrons from the substrate to the external circuit. On the other hand, the cathodic chamber produced a gas mixture with a hydrogen content of 85 % with an average hydrogen production rate of 31 ± 8 meq/Ld, the cathodic coulombic efficiency, i.e., the conversion efficiency of current into hydrogen of the stainless-steel cathode resulted on average 49 ± 6 %. The energetic consumption of the process for hydrogen production was estimated by considering the cell voltage and the average current, i.e. an average consumption of 7.54 kWh/m^{3}H$_2$ was obtained, a higher energy consumption with respect the 4.5 kWh/m^{3}H$_2$ (Wang et al 2014) reported for industrial water electrolysers. Considering the CO_2 removal obtained in the external sorption chamber, an average removal of 110 mmolC/d were obtained during the operation of the MEC in combination with the external chamber.

Table 1. Main performances of the MEC polarized at +0.2 V vs SHE

COD removal (mgCOD/Ld)	Anodic Coulombic Efficiency (%)	Hydrogen production rate (meq/Ld)	Cathodic Coulombic Efficiency (%)	CO2 removal (mmolC/Ld)
991 ± 45	59 ± 6	31 ± 8	49 ± 6	110 ± 14

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