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Anion vs cation exchange membrane strongly affect mechanisms and yield of CO_2 fixation in a microbial electrolysis cell

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HIGHLIGHTS

- Microbial electrolysis cell (MEC) couple COD oxidation and CO_2 reduction and removal.
- CO_2 adsorption in a MEC cathode is driven by net alkalinity generation.
- Alkalinity generation is due to selective ion transport across separation membranes.
- Anion exchange membrane allows a higher CO_2 removal due to HCO_3^- transport from cathode to anode.
- Proton exchange membrane allows a higher COD oxidation and methane production.

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ABSTRACT

The CO_2 removal from a concentrated gas stream (simulating biogas) has been investigated by using two identical fully bio-catalyzed microbial electrolysis cell (MEC), equipped with either a proton exchange membrane (PEM-MEC) or an anion exchange membrane (AEM-MEC). The equivalents deriving from the anodic oxidation of the organic matter were mainly converted into current, with an average coulombic efficiency between 53 ± 9% and 85 ± 15%, resulting in a little microbial growth (with an observed growth yield between 0.17 and 0.18 gCOD/gCOD). The cathode compartment was continuously bubbled with a gas mixture containing CO_2 (30% v/v, N_2 balance) and the presence of an hydrogenophilic autotrophic culture allowed for CO_2 reduction into CH_4, with a cathode capture efficiency between 47 ± 2% and 80 ± 1%, respectively. In both systems, the first mechanisms of CO_2 removal was its sorption as bicarbonate ion at high concentration in the MEC cathode, which was supported by alkalinity generation, needed by electroneutrality maintenance. However, in the AEM-MEC, 5.4 g/Ld of CO_2 were removed by crossing the membrane (which was due to both molecular diffusion and ionic transport) whereas in the PEM-MEC only 3.2 g/Ld of CO_2 were removed (through the osmotic overflow which was spilled from the cathodic liquid phase). Moreover, PEM-MEC showed higher COD removal efficiency (78 ± 7%) and methane production rate (83 ± 24 meq/Ld) than AEM-MEC but showed a higher energy demand per unit of removed CO_2 (2.36 vs 0.78 vs kWh/Nm^3 $CO_{2removed}$). It is noteworthy that AEM-MEC energy demand was lower than full scale processes for biogas upgrading such as water scrubbing.

1. Introduction

The rapidly developing microbial electrochemical technology represents an innovative route to stimulate and control microbial metabolism [1]. In a microbial electrolysis cell (MEC), as an example, provided the addition of an external power supply it is possible to convert CO_2 into methane and the process is commonly referred to as "bio-electromethanogenesis" [2]. The latter occurs at a biocathode, where the reducing power necessary for CO_2 reduction is given by a solid state electrode [3] through microorganism-electrode interactions. Two main mechanisms underlying these interactions have been identified over the last years, which are based on a direct contact between the cathode and microorganisms [4], or on an hydrogen mediated electron exchange [5]. Also, a direct interspecies electron transfer (DIET) has been recently found to drive the synthrophic interactions between methanogens and other microbial species involved in the anaerobic digestion process [6], giving new insights in the understanding of bio-electromethanogenesis. However, regardless the mechanism involved, the utilization of mixed autothrophic methanogenic bacteria as sustainable and renewable bio-catalysts for CO_2

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reduction offers several advantages over chemical catalysis, which typically requires noble and heavy metals as well as the need to operate at high temperature and pressure, as occurs for the reaction of CO_2 methanation, also known as the Sabatier reaction [7].

The biocatalysis could offer an efficient route to enhance the environmental sustainability of the CO_2 reduction process. Furthermore, the utilization of no cost inocula (i.e. mixed cultures of anaerobic sludge) brings the economic advantage to avoid sterilization and to operate at neutral pH, low pressure and low temperature. A key aspect of the bio-electromethanogenesis reaction is the possibility to offer a new approach for energy storage from the surplus of electricity production deriving from renewable energy sources (e.g. photovoltaic, eolic, etc.), since this energy surplus can be exploited to reduce CO_2 into methane, a well storable energy vector which can be easily distributed to the grid or used in automotive engines [8]. In this frame, a rich renewable source of CO_2 is offered by the biogas that is the product of the anaerobic digestion process (AD) [9]. Biogas is a gas mixture mainly composed of CH_4 (50–70%) and CO_2 (50–30%) besides other impurities, such as H_2S, NH_3, siloxane, and H_2O, and the final percentage of each component depends on the composition of the raw materials used as feedstock. Biogas has been for decades considered as a byproduct but, over the last years, it has become the main target product of the AD process. Indeed, thanks to the development of mini and micronized combined heat power (CHP) units [10], the produced raw biogas can be used for the in situ energy recovery, especially in small plants (mainly used to treat agro-zootechnical effluents). Moreover, upon purification and upgrading, biogas can be turned into biomethane (BM), that is a carbon neutral footprint substitute of compressed natural gas (CNG) originated from fossil resources with an added value on the market higher than biogas. In particular, while the biogas purification step is aimed at eliminating impurities from the gas mixture in order to avoid corrosion or other problems related to downstream applications [11], the biogas upgrading process consists of an efficient CO_2 removal with a consequent significant increase of the methane content up to, at least, 95% [12]. Technologies mainly based on a physical chemical separation of CO_2, such as the water scrubbing (WS) and the pressure swing adsorption (PSA), are typically used at industrial scale for biogas upgrading [13]. From an economical point of view, however, CO_2 removal is feasible only for biogas produced in large-plants unless novel low cost upgrading approaches are developed. In this context, microbial electrochemical technology has been recently proposed as an innovative and promising tool to upgrade the AD biogas [14–17].

Here, mechanisms involved in CO_2 removal in a fully biocatalyzed MEC have been deeply analyzed. The MEC was assessed to couple the bio-anodic COD oxidation to CO_2 removal and methane generation at the cathode and two configurations with either an anion or a proton exchange membrane were assembled in order to test the effect of ionic transport phenomena on the overall process performance.

Based on literature, MEC can be used to convert CO_2 into methane so offering a way to both purify and upgrade biogas from anaerobic digestion. The MEC effectiveness is improved by the alkalinity generation in the cathodic chamber, due to ion transport across separation membranes which is needed to counterbalance the external electron flow, in order to maintain system electroneutrality [18–21]. This mechanism is strongly depending on the separation membrane (either anionic vs protonic) which establishes type and ratio of transported ions. As an additional consideration, alkalinity generation is in turn sustained by the bio-anode exploitation of the chemical energy contained in the COD source and in the electron scavenging due to biological reduction of CO_2 into methane, which both contribute to lower the energy demand of the overall process. Thus, MEC performance is a complex function of several mechanisms, which include anodic and cathodic biological reactions as well as mass and ion transfer phenomena.

This study aims to give a complete and quantitative picture of all relevant mechanisms of CO_2 removal in an MEC bio-cathode, and to compare their relative importance as function of different separation membranes (protonic vs anionic). Main reference is given to the role of ionic mobility and membrane-related transport phenomena on overall CO_2 sorption and removal. The study also includes the determination of the mass and energy balance of the process as determined by different membrane types.

2. Materials and methods

2.1. Microbial electrolysis cell design and setup

Throughout the study, two identical microbial electrolysis cells (MEC) were set up. Each MEC consisted of two identical Plexiglas frames, with internal dimensions of 17 cm × 17 cm × 3 cm, bolted together between two Plexiglas plates. A Nafion® 117 proton exchange membrane (PEM) or a Fumasep FAD anion exchange membrane (AEM) was placed between the frames (Fig. 1). Prior to being used, both PEM and AEM were pretreated as reported elsewhere [22]. The total empty volume of each frame (i.e., of the anodic and cathodic compartment) was 0.86 L. The anodic and cathodic compartments were filled with around 800 g of graphite granules with a diameter between 2 and 6 mm (El Carb 100, Graphite Sales, Inc, USA), giving a bed porosity of 0.48. Graphite granules were pretreated in order to remove impurities on graphite surface [23]. External electrical connections were guaranteed by inserting graphite rod current collectors (5 mm diameter, Sigma–Aldrich, Italy) in each compartment. An Ag/AgCl reference electrode (+0.199 V vs. standard hydrogen electrode, SHE) (Amel s.r.l., Milan, Italy) was also placed in each compartment in order to control the potential of the MEC anode by means of a potentiostat (Bio-Logic). A glass chamber, equipped with sampling ports sealed with butyl rubber stoppers and aluminum crimps, was placed in the outlet of each compartment in order to sample the headspace and the liquid phase of both the anolyte and catholyte.

Moreover, the cathodic chamber was continuously fed with CO_2 in large excess, by bubbling a N_2/CO_2 (70/30%, v/v) gas mixture, in order to simulate the typical CO_2 content of an influent biogas from an anaerobic digestion process. The gas outcome was flowing through the sampling glass chamber and then connected to a milliGas counter (Ritter, Germany), which allowed to measure its volumetric flow rate. The anode compartment of both MECs was inoculated with an activated sludge from the Roma Nord full-scale wastewater treatment plant. Particularly, 0.2 L of activated sludge (having a volatile suspended solids concentration of 3.2 g/L) was inoculated in each anode compartment. During the initial start up period, the anode compartment in both MEC configurations was operated with the liquid phase being continuously recirculated at a flow rate of 60 mL/min and acetate was spiked as carbon source in order to enhance the formation of electroactive biofilms on the graphite granules. Acetate consumption was linked to current generation and once acetate was completely depleted the anode operation was switched in a continuous mode at a flow rate of 1.34 and 1.57 L/d respectively for AEM and PEM configuration. The feeding consisted of a synthetic organic mixture made of (g/L): peptone (0.138), yeast extract (0.075 g/L), sodium acetate (0.088 g/L), glucose (0.34 g/L). The feeding solution also contained NH_4Cl (0.125 g/L); $MgCl_2$ $6H_2O$ (0.1 g/L); K_2HPO_4 (4.0 g/L); $CaCl_2{\cdot}2H_2O$ (0.05 g/L), 10 mL/L of a trace metal solution [24,25]; and 1 mL/L of vitamin solution [26]. The cathode compartment was operated with the liquid phase being continuously