Anion vs cation exchange membrane strongly affect mechanisms and yield of CO₂ fixation in a microbial electrolysis cell

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HIGHLIGHTS
- Microbial electrolysis cell (MEC) couple COD oxidation and CO₂ reduction and removal.
- CO₂ 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 CO₂ removal due to HCO₃⁻ transport from cathode to anode.
- Proton exchange membrane allows a higher COD oxidation and methane production.

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ABSTRACT
The CO₂ 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 CO₂ (30% v/v, N₂ balance) and the presence of an hydrogenophilic autotrophic culture allowed for CO₂ reduction into CH₄, with a cathode capture efficiency between 47 ± 2% and 80 ± 1%, respectively. In both systems, the first mechanisms of CO₂ 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 only 3.2 g/Ld of CO₂ 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 CO₂ (2.36 vs 0.78 vs kWh/Nm³ CO₂ removed). 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 CO₂ into methane and the process is commonly referred to as “bio-electromethanogenesis” [2]. The latter occurs at a bio-cathode, where the reducing power necessary for CO₂ 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 autotrophic methanogenic bacteria as sustainable and renewable bio-catalysts for CO₂

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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$_2$S, NH$_3$, siloxane, and H$_2$O, 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 output 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$_4$Cl (0.125 g/L); MgCl$_2$ 6H$_2$O (0.1 g/L); K$_2$HPO$_4$ (4.0 g/L; CaCl$_2$ 2H$_2$O (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
Fig. 1. Schematic representation of the overall inorganic carbon mass balance and photographic view of the MEC.
recirculated at a flow rate of 60 mL/min and it was inoculated with an anaerobic sludge (digestate with a volatile suspended solids concentration of 8.24 g/L) enriched in hydrogenophilic bacteria in a fill and draw reactor (with a hydraulic and sludge retention time of 32 d). Particularly, in the PEM-MEC equipped a daily spill of the cathodic liquid phase (on average 0.103 L/d) was necessary in order to counterbalance the osmotic diffusion phenomena occurring from the anode to the cathode compartment. On the contrary, in the AEM-MEC configuration, a liquid spill from the cathode compartment was not necessary since the osmotic diffusion, occurring at a minor extent than in presence of the PEM, was directed from the cathode to the anode compartment (on average 0.01 L/d).

Throughout the study, the MEC was operated by controlling the potential of the anode at +0.2 or −0.1 V with respect to the standard hydrogen electrode (SHE) and all voltages are hereby reported with respect to SHE.

2.2. Batch diffusion tests

Batch tests in H-type electrochemical cells equipped whith either an AEM or a PEM were carried out in order to determine the diffusion coefficient of the bicarbonate ion. The H-type cells consisted of two gaslight borosilicate glass chambers [5] separated by a membrane with a surface area of 2.26 cm². The two chambers were kept under vigorous magnetic stirring and were filled with 0.2 L of the same mineral medium solution except for bicarbonate content. The difference of concentration in the two compartment was sufficiently high in order to keep constant the gradient of bicarbonate during the three days experiment. The first Fick’s law was used to determine the diffusion coefficient of the bicarbonate ion (Df, cm²/d) across both membranes:

\[ N_A = -D_f x \frac{\Delta C}{\Delta x} \]

Were \( N_A \) (g/d) was calculated by the linear regression of the detected concentration of bicarbonate ion in the cell chamber with an initial lower concentration; \( A \) (cm²) was the membrane surface area, \( \Delta C \) (g/cm³) was the concentration gradient between the two chambers and \( \Delta x \) was the thickness of the membrane (0.010 and 0.018 cm for the AEM and PEM, respectively). The diffusion tests were carried out both in the presence and absence of an applied current between the two chambers (elettrodifussion tests). More specifically, during the galvanostatic electrode processes, a fixed current was imposed in the cell in a two electrode configuration with the counter electrode (cathode) being kept at higher bicarbonate concentration. The value of the current was normalized by the surface area of the membrane, in order to establish similar conditions as in the MEC conditions.

2.3. Inorganic carbon mass balance

The two forms of inorganic carbon were CO2 in the gase phase and the bicarbonate ion (HCO3⁻), the latter being prevalent in the liquid phase due to the operational pH value between 6.5 and 7.5 in both the anodic and cathodic compartments of the MEC. The inorganic carbon mass balance was performed with reference to the cathode compartment or to the overall reactor.

As for the cathode inorganic mass balance, the daily amount of removed CO2 (\( \Delta CO_2 \), mmol/d) was assessed by the following equation:

\[ \Delta CO_2 = Q_{cat_{in}} * CO_2_{in} - Q_{cat_{out}} * CO_2_{out} \]

in which \( Q_{cat_{in}} \) (L/d) and \( Q_{cat_{out}} \) (L/d) are the influent and effluent gas flow rate in the cathode compartment respectively; whereas \( CO_2_{in} \) and \( CO_2_{out} \) (mmol/L) are the corresponding CO2 concentration in the influent and effluent gaseous cathodic streams.

By taking into account that CO2 was converted into methane and dissolved as bicarbonate ion at the cathode, \( \Delta CO_2 \) can also be expressed as follows:

\[ (r_{CH4}) \] and the concentration of the was possible to utilize the following expressions for the cathodic side of the PEM and AEM configurations.

\[ \Delta CO_2 = r_{CH4} + HCO_3^{\text{spilled}} \] (for the PEM configuration)

\[ \Delta CO_2 = r_{CH4} + HCO_3^{\text{transferred}} \] (for the AEM configuration)

where \( r_{CH4} \) (mmol/d) represents the rate of methane production; \( HCO_3^{\text{spilled}} \) (mmol/d) is the amount of bicarbonate ions daily spilled from the cathode of the PEM-equipped reactor (calculated as the product between the cathodic bicarbonate concentration and the average spill rate), and \( HCO_3^{\text{transferred}} \) is the amount of bicarbonate which daily diffused from the cathode to the anode compartment of the AEM-equipped MEC.

The overall inorganic mass balance was calculated according to Fig. 1 by using the following expression:

\[ Q_{cat_{in}} * CO_2_{in} + F_{in} * HCO_3_{in} \text{in} = Q_{cat_{out}} * (CO_2_{out}) + Q_{cat_{out}} * (CH_4_{out}) + Q_{an} * CO_2_{an} + F_{out} + HCO_3_{out} \] (for the AEM configuration)

\[ Q_{cat_{in}} * CO_2_{in} + F_{in} * HCO_3_{in} = Q_{cat_{out}} * (CO_2_{out}) + Q_{cat_{out}} * (CH_4_{out}) + Q_{an} * CO_2_{an} + F_{out} + HCO_3_{out} + F_{cat} + HCO_3_{cat} \] (for the PEM configuration)

where \( Q \) (L/d) are and \( F \) (L/d) are the volumetric flow rates of the gaseous and the liquid streams, respectively. For the mass balance referred to the overall MEC, the influent sources of inorganic carbon in the MEC were the gaseous CO2 in the cathodic chamber, and the HCO3⁻ contained in the anodic feeding solution; whereas the overall inorganic carbon effluents were the HCO3⁻ and the CO2 in the liquid and gaseous streams, respectively, of the anode compartment and CO2 and CH4 in the gaseous cathodic stream. Moreover, in the PEM-MEC, also the HCO3⁻ concentrated in the liquid phase of the cathode compartment was considered. A schematic representation of all involved parameters is reported in Fig. 1.

2.4. Calculations

The COD removal efficiency of the MEC was calculated according to the following equation:

\[ COD_{removal\ efficiency} = \frac{COD_{in} - COD_{out}}{COD_{in}} \]

in which \( COD_{in} \) (g/L) and \( COD_{out} \) (g/L) represent the COD concentration in the influent and effluent streams of the cathode compartment, respectively. The fraction of the oxidized COD which was converted into current, referred to as Coulombic Efficiency (CE, %), was calculated as the ratio between the cumulative electric charge transferred at the electrodes (meq) and the cumulative equivalents released from COD oxidation (meqCOD):

\[ CE = \frac{meq}{meq_{COD}} \]

In particular, \( meq \) was determined by integrating the current (A) over time and dividing by the value of the Faraday’s constant (F = 96,485 C/eq); whereas \( meq_{COD} \) was calculated by using a conversion factor of 4 meq/mmolCOD, deriving from the reaction of water oxidation.

With main reference to the cathode performance, the fraction of generated current diverted into methane is called Cathode Capture
Efficiency (CCE, %) and it was assessed as the ratio between the cumulative equivalents of produced methane (meqCH₄), calculated by considering the molar conversion factor of 8 meq/mmolCH₄ and the cumulative equivalents deriving from current:

\[
\text{CCE} = \frac{\text{meqCH}_4}{\text{meq}_i}
\]

The process energy efficiency (ηₑ) was calculated by taking into account the energy recovered from the produced methane (WCH₄) and the energy input added to the system (Wₚₑ), according to:

\[
\eta_E = \frac{W_{\text{CH}_4}}{W_{\text{pe}}}
\]

in which: \(W_{\text{CH}_4} = n_{\text{CH}_4} \times \Delta G_{\text{CH}_4}\) and \(W_{\text{pe}} = V \times C \times \Delta G_{\text{CH}_4}\), with \(\Delta G_{\text{CH}_4} (-817.97 \text{kJ/mol})\) and \(n_{\text{CH}_4} (\text{mmol})\) representing the molar Gibbs free energy for methane combustion and the amount of produced methane, respectively; whereas \(V\) is the average difference of potential established between the cathode and anode electrodes, and \(C\) represents the total Coulombs, calculated by integrating the current over time is the electric charge flowing in the reactor.

Another parameter to evaluate the MEC performance was the microbial growth yield (\(Y_{\text{obs}}\)) of biomass in the anode compartment, which was calculated according to:

\[
Y_{\text{obs}} = \frac{\Delta \text{COD}_{\text{biomass}}}{\Delta \text{COD}_{\text{removed}}}
\]

in which \(\Delta \text{COD}_{\text{biomass}} (\text{mgCOD/VSS/d})\) is the amount of daily produced biomass measured as the product between biomass concentration in the effluent stream of the anode (mg/L, as volatile suspended solids, VSS) and the effluent flow rate (L/d). Biomass concentration was converted into COD by using the conversion factor of 1.42 gCOD/gbiomass (obtained by considering the generic biomass composition as C₅H₇O₂N). \(\Delta \text{COD}_{\text{removed}} (\text{mg/d})\) was the amount of COD daily oxidized in the anode compartment.

Data concerning the MEC energy consumption were calculated considering the energy spent to operate the reactor, which takes into account both the generated current (I) and the external voltage (\(\Delta V\), which corresponds to the difference of potential established between the cathode and the anode) multiplied for 24 h of operation kWh = I * \(\Delta V\) * 24 h. The energy cost required for COD and CO₂ removal were calculated by dividing the energy consumption for the daily removed COD in each condition (kWh/kgCOD) or for the daily removed CO₂ (kWh/Nm³ CO₂), respectively. The latter being converted in volumetric unit under normal conditions (Pressure of 1 atm, Temperature of 0 °C).

2.5. Analytical

CO₂ and H₂ were analysed by injecting 50 μL of headspace sample into a Dani Master GC (Milan, Italy) gas chromatograph equipped with a thermal conductivity detector (TCD). Methane was analysed by injecting 100 μL of sample from the reactor headspace (with a gas-tight Hamilton syringe) into a Varian (Lake Forest, CA, USA) 3400 gas-chromatograph. Acetate was analysed by injecting 1 μL of filtered (0.22 μm porosity) aqueous sample into a Dani Master GC (Milan, Italy) gas chromatograph. Headspace concentrations were converted to aqueous-phase concentrations, by using Henry’s law constants (Green and Perry 2008). Measurements of the chemical oxygen demand (COD) content in the anode influent and effluent streams were assessed by using commercial COD cell test (Merck, Darmstadt, Germany). The inorganic carbon content was analyzed using a total carbon analyzer (TOC-V CSN Shimadzu), which allows to determine the concentration of both total and inorganic carbon contained in a sample. Ammonium nitrogen was spectrophotometrically (Shimadzu spectrophotometer UV-1800) measured at 410 nm by the direct Nessler colorimetric method [27]. The concentration of microorganisms in the anode effluent as well as in the cultures used to inoculate the MEC was determined as volatile suspended solids (VSS), according to standard methods [27].

3. Results

3.1. MEC continuous operation with the anode poised at +0.2 V (vs SHE)

The two fully microbially-catalyzed MECs, equipped with either an AEM or a PEM, were operated under continuous feeding of the synthetic organic mixture with the potential of the anode poised at +0.2 V. The oxidation of the fed COD was linked in both configurations to current generation, indicating the capability of the anodic biomass to use the graphite granules as electron acceptors. The profile of COD concentration in the influent and effluent streams of the anode compartments is reported in Fig. 2. In particular, in the AEM-MEC on average 610 ± 51 mgCOD/d was removed and, by taking into account that current stabilized at 68 ± 7 mA, it can be calculated the amount of equivalents diverted into current (i.e. the coulombic efficiency, CE) which accounted for 80 ± 15%. With the PEM-MEC a slightly higher performance in terms of both COD removal and current generation was noticed, with an average value of 654 ± 83 mgCOD/d and 78 ± 1 mA respectively, which resulted in a lower CE value of 85 ± 14%.

As already detected in previous experiments [14], the conversion of the major part of the equivalents deriving from COD oxidation into current allowed for a little biomass formation at the MEC anode resulting in an observed growth yield (\(Y_{\text{obs}}\)) of 0.17 and 0.18 gCOD/gCOD for the AEM-MEC and PEM-MEC, respectively.

![Fig. 2. Trend of the influent and effluent COD concentration in the anode compartment during the continuous feeding operation of the MEC equipped with either the AEM (A) or the PEM (B).](image-url)
This evidence is likely due to different mechanism of electron transfer in these systems with respect to the common respiratory chain of aerobic bacteria, given the lower energetic level of the cytochromes or conductive proteins involved in the external electron transfer [28,29]. As a consequence the energy available to the microbial growth is lower than aerobic oxidation pathway [30], which indicates that bioelectrochemical systems have great potential as a strategy to minimize sludge production from wastewater treatment.

As for the performance of the cathode, the presence of an homoacetogenic activity was observed in both MEC configurations. This occurred also during the initial start up period (data not shown), causing a relevant acetate concentration in correspondence of day 0. The differences in the acetate concentration values detected in the two reactors were likely due to differences in the typology of the membrane used as separator of the anodic and cathodic compartments. Indeed, the AEM-MEC allowed for a higher diffusion of acetate from the cathode to the anode than the PEM-MEC which, in turn, resulted in a higher acetate concentration at the cathode. However, after about 25 and 35 days of operation methane became the predominant reduced cathodic product in the PEM-MEC and PEM-MEC (Fig. 3), respectively. With main regard to methane generation, a higher production rate was detected in the PEM-MEC than in the AEM-MEC (83 ± 24 versus 34 ± 1 meq/Ld, respectively) which, in turn, resulted in a higher cathode capture efficiency (i.e. the fraction of current diverted into the cathode) which accounted for 80 ± 1% and 47 ± 2% (for the PEM-MEC and PEM-MEC, respectively). Interestingly, in spite of the fact that both reactors were operated with the anode potential set at +0.2 V, the difference of potential established between the cathode and the anode (which corresponds to the external energy input to the system) was higher in the PEM-MEC than in the AEM-MEC with measured values of 1.67 ± 0.07 V and 1.13 ± 0.02 V, respectively. The ratio between the energy recovered as methane at the cathode and the external electrical energy input is referred to as the energy efficiency (\(\eta_E\)) which, due to the more than doubled methane production rate, was slightly higher in the PEM-MEC (51 ± 1%) than in the AEM-MEC (44 ± 2%) in spite of the higher energy input required.

A gas mixture containing CO2 (30% v/v, N2 balance) was continuously bubbled in the MEC cathode and an average removal rate was calculated, which accounted for 5.4 gCO2/Ld and 3.2 gCO2/Ld in the AEM-MEC and PEM-MEC, respectively.

3.2. Determination of the diffusion coefficient of the bicarbonate ion

Prior to assess a mass balance concerning all mechanisms involved in the CO2 removal process, the determination of the bicarbonate diffusion coefficient was performed through short-term experiments in H-type electrochemical cells equipped with either the AEM or the PEM. These experiments were carried out in absence of microorganisms and under vigorous magnetic stirring. As expected, in the presence of the PEM to separate the anode and cathode compartments of the cell, a negligible diffusion of bicarbonate from the side with the higher to the lower bicarbonate concentration (i.e. from the cathode to the anode) occurred. This was likely due to the membrane material structure, i.e. sulfonated groups present on the chain of fluorocarbon structure, which by means of electrical repulsion did not allow the crossing of compounds with negative charge. On the contrary, when the AEM was used, bicarbonate diffusion from the cathode to the anode compartment of the cell occurred to a major extent and an average value of the diffusion coefficient of 0.033 cm2/d was estimated. Furthermore, in order to evaluate the occurrence of other transport phenomena, a similar experiment was carried out by controlling with a potentiotstat the current flowing in the electrochemical cell which was fixed at 0.380 mA/cm2. Importantly, under this galvanostatic condition, the value of the AEM bicarbonate diffusion coefficient increased to 0.058 cm2/d, indicating the presence of an active transport of the bicarbonate ion through the anion exchange membrane in order to maintain the cell electroneutrality (i.e. the cell charge balance). In particular, when current was flowing in the system, an increase of about 1.8 times in the value of the bicarbonate diffusion coefficient was obtained due to active transport of the bicarbonate ion across the membrane.

3.3. CO2 removal mechanisms

In order to characterize the different mechanisms involved in the CO2 removal process, a mass balance was performed by taking into account both the gaseous (CO2) and soluble (HCO3-) forms of inorganic carbon detected at the anode and cathode compartments of the PEM-MEC and the AEM-MEC. To accomplish this objective, measurements of the inlet and outlet gaseous streams of the cathode compartments as well as measurements of the cathode liquid phase and of the anode influent and effluent streams were daily performed. In particular, the trend of the concentration of the bicarbonate ion in the three different liquid streams of both reactors is reported in Fig. 4. As a main result, an accumulation of HCO3- at the cathode of the two reactor configurations was observed with an average value of 8.5 ± 0.2 gHCO3-/L and 26.7 ± 1.7 gHCO3-/L for AEM PEM-MEC and PEM-PMEC, respectively.

The formation of the bicarbonate anion was due to CO2 dissolution in the liquid phase driven by alkalinity generation in the cathodic compartment of both reactors. More in detail, the alkalinity generation was caused by the presence in the mineral medium of ion species other than protons and hydroxyl ions.
Anode in
Anode out
the bicarbonate ion did not contribute to the ionic transport since
the literature[31], can contribute to maintain electroneutrality in
(such as alkali cations and bicarbonate ion) which, as reported in
the system by means of transport across the membrane. As an
example, protons are generated at the anode from the oxidation
of organic matter and consumed at the cathode for the production
of reduced compounds. Protons required for cathodic reactions
can be transported across the membrane and/or generated by water
split in the cathode compartment which also causes the production
of hydroxyl ions. Therefore, for each equivalent of electric charge
not balanced by the transport of a proton or a hydroxyl ion
(flowing from the anode to the cathode in the PEM-MEC or from
the cathode to the anode in the AEM-MEC, respectively) across
the membrane, acidity (at the anode) and alkalinity (at the
cathode) are consequently generated. The latter is balanced by
the formation of the bicarbonate ion which, in turn, prevents pH
increase in the cathode compartment. In terms of concentration,
the different content of the bicarbonate ion at the cathode of
the AEM-MEC or the PEM-MEC was a direct consequence of the
different diffusion phenomena occurring across the membranes.
Indeed, in the AEM-MEC the bicarbonate ion was removed from
the cathode compartment by two different mechanisms: the
molecular diffusion induced by the establishment of a gradient of
concentration between the anode and cathode compartments
and the active transport due to the anionic flow from the cathode
to the anode. As a consequence, bicarbonate concentration in the
effluent stream was higher than that detected in the influent
stream of the anode compartment (Fig. 4A). As for the PEM-MEC,
the bicarbonate ion did not contribute to the ionic transport since
its diffusion was hindered by the functional sulfonated groups of
the membrane and it accumulated at high concentration in the
cathode compartment. However, since a constant volume of the
liquid phase (0.103 L) was daily removed from the cathodic liquid
phase, the cathodic bicarbonate concentration remained almost
stable over time (Fig. 4B).

A mass balance of the inorganic carbon has been assessed by
taking into account the different mechanisms of CO2 removal at
the cathode of both reactors. Concerning methanation generation,
as summarized in Table 1, this represented about 4% and 15% of
the overall removed carbon dioxide for AEM-MEC and PEM-MEC,
respectively. Notably, most of the CO2 which was flushed at the
MEC cathode was dissolved in the liquid phase in the form of bicar-
bonate ion which was removed from the cathode compartment by
means of its transport across the AEM or due to a daily spill of the
cathode liquid phase in the case of a PEM. As a consequence,
the removal of the bicarbonate ion from the cathode compartment
contributed for about 94% (in the AEM-MEC) or 73% (in the
PEM-MEC) to the overall CO2 removal process. Therefore, CO2
dissolution represented an important additional mechanism of CO2
removal coupled to methanation generation, with an increase from
25 to 5 times in the CO2 removal due to the self generation of
alkalinity. With main reference to the AEM-MEC, although a small
amount (about 0.01 L/d) of liquid phase was diffused from the
cathode to the anode compartment of the MEC, the main detected
mechanisms of CO2 removal were the ionic transport and the
molecular diffusion of the bicarbonate anion across the membrane.
In particular, by using the molecular diffusion coefficient
(0.033 cm2/d) calculated through batch experiments and by taking
into account the membrane surface area of the reactor as well as
the concentration gradient of the bicarbonate ion established
between the anode and cathode compartments, a daily diffusion
of 49 mmol/d was estimated which accounted for 49% of the over-
all bicarbonate transported across the membrane (99 mmol/d).
Moreover, the active transport phenomena allowed for the addi-
tional removal of 50 mmol/d of bicarbonate ion. This mechanism
occurred in order to maintain electroneutrality in the reactor
and, specifically, the transport of bicarbonate ion (corresponding,
in terms of current, to 55 mA) counterbalanced about 81% of the
electron flow due to current generation (68 mA) in the system.

Finally, it has to be underlined that methanation generation
gave strong contribution to overall CO2 removal; indeed, although CO2
conversion into methane was low in terms of CO2 mass balance,
it was an important electron sink (8 mol of electrons per mole of
formed methane), which contributed significantly to current
generation, that in turn generated the driving force to transfer
bicarbonate across the AEM. Roughly speaking, each mole of CH4
formed was so responsible for up to 9 mol of CO2 removed from the
cathodic gas stream.

3.4. AEM operation at –0.1 V vs SHE

Based on the above described results, the AEM-MEC resulted in
a more efficient condition in terms of CO2 removal than the

<table>
<thead>
<tr>
<th>Ionic membrane</th>
<th>AEM (mmol/d)</th>
<th>Percentage</th>
<th>PEM (mmol/d)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removed CO2</td>
<td>105</td>
<td>100</td>
<td>62</td>
<td>100</td>
</tr>
<tr>
<td>CO2 reduced in CH4</td>
<td>4</td>
<td>4</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>HCO3 mechanism</td>
<td>Ionic transport across AEM</td>
<td>99</td>
<td>94</td>
<td>45</td>
</tr>
</tbody>
</table>
PEM-MEC. Therefore, in order to investigate the effect of the set anode potential on the overall process performance as already examined for a PEM-MEC [32], a further run of the AEM-MEC reactor was carried out with the anode potential controlled at −0.1 V (Fig. 5). Importantly, COD removal did not substantially change with respect to the run at +0.2 V and, on average, 572 ± 167 mgCOD/d were removed resulting in a COD removal efficiency between 60% and 80% (with the only exception for few data). As reported in Table 2, the average current decreased to a value of 42 ± 2 mA and, by taking into account both the generated current and the removed COD, a CE of 53 ± 9% was estimated. With respect to the cathode performance, the rate of methane production was not substantially affected by the shift in the anodic potential. Indeed, the cathodic potential stabilized at a value (−0.676 V) slightly lower to that detected in the reactor run at +0.2 V (−0.755 V) resulting in a similar rate of methane generation of 30 ± 2 meq/Ld but a higher CCE (68 ± 1%). As a consequence, the difference of potential established between the cathode and the anode (i.e. 0.73 ± 0.04 V) of the reactor as well as the no alteration in methane production resulted in a significant increase of the energy efficiency with the anode potential poised at −0.1 V with respect to that obtained with the anode potential at +0.2 V (99 ± 2% vs 44 ± 2%, respectively).

The obtained energy efficiency of about 100% indicates that the energy input required to operate the process is completely recovered through the generated methane which, in turn, corresponds to a theoretical zero energy cost of the process. On the other hand, concerning CO₂ removal at the cathode compartment, about 54 mmol/d of CO₂ were daily removed which is a value lower than that observed with the anode potential controlled at +0.2 V. This evidence could be attributed to a decrease in current generation in the system that probably affected the transport of the bicarbonate ion across the AEM. The latter remained the main mechanism of CO₂ removal and, on average, 50 mmol/d of bicarbonate ion were transported from the cathode to the anode compartment. More specifically, by using the diffusion coefficient determined for the AEM membrane with the anode potential controlled at −0.1 V, it was possible to assess that 37 mmol/d of bicarbonate were transported due to molecular diffusion phenomena and 13 mmol/d as a result of the active transport to maintain the system electroneutrality. The term of active transport corresponded to 35% of the overall current flowing in the reactor and, therefore, it substantially decreased with respect to the percentage (81%) calculated in the run with the anode potential at +0.2 V. However, it should be considered that the calculated fraction of bicarbonate ions transported across the AEM by molecular diffusion was probably overestimated since several factors, e.g. membrane fouling and/or other mass transfer process like entrapment or adsorption on biofilm as well as the heterogeneity of the granular bed, could decrease the molecular diffusion phenomena. This, in turn, would mirror in an increase of the contribute due to the active transport which, in principle, depends only on the generated current.

3.5. Overall process performance and energetic evaluation

A general overview of the MEC process operated under the different explored conditions has been assessed with main reference to the energy consumption associated with COD removal, methane generation and CO₂ abatement. To accomplish this objective, the MEC energy demand has been estimated by taking into account the electrical power consumption which depends on both the external applied voltage and the generated current. With respect to COD removal, the AEM-MEC with the anode potential controlled at +0.2 V resulted in an energy consumption required for COD removal further dropped down to 1 kWh/kgCODremoved lower than that estimated for the PEM-MEC at the same anodic potential (3.5 kWh/kgCODremoved and 5 kWh/kgCODremoved, respectively). However, when the anode potential of the AEM-MEC was shifted to −0.1 V, the value of the energy consumption for COD removal further dropped down to 1 kWh/kgCODremoved. Importantly, this value is even lower than reported in the literature [33] for the activated sludge process which accounts for 1.2 kWh/kgCODremoved. The latter consideration can be reasonable explained by taking into account the different mechanisms of COD removal involved in the activated sludge (AS) and in a MEC. In the AS, energy consumption depends on the request of oxygen per unit of produced biomass and the efficiency of the oxygen transfer rate (mainly depending of the adopted technology to supply oxygen) whereas in a MEC the energy demand derives from the need to boost electrons from the anode to the cathode and mostly depends on the efficiency of electric transfers and related overpotentials [34].

Also, another important factor to be considered with respect to the activated sludge process is the observed growth yield which, in the MEC, was significantly lower (between 0.17 and 0.18 gCOD/gCOD) than data (0.50 gCOD/gCOD) typically reported for conventional activated sludge systems [35]. Regarding the methane production yield, which represents the amount of methane produced at the cathode with respect to the COD oxidized at the anode, data have been compared with a conventional anaerobic process [36], which is higher than values calculated in this study of 0.12 and 0.22 Nm³CH₄/kgCODremoved (for the AEM-MEC and PEM-MEC at +0.2 V vs SHE, respectively). In terms of energy consumption required for CO₂ removal, the MEC performance has been compared
with two major technologies typically utilized to remove CO₂ during the AD biogas upgrading process, namely the pressure swing adsorption (PSA) and the water scrubbing (WS). According to the literature [37,38] this energy consumption expressed as kWh/Nm³ CO₂removed has been calculated by assuming a complete removal of CO₂ from a model biogas made of methane (70%) and CO₂ (30%). Concerning the PSA and WS technologies, the estimated energy consumption is of 1.12 and 1.40 kWh/Nm³ CO₂removed respectively; and lower values were calculated with the AEM-MEC corresponding to 0.78 and 0.61 kWh/Nm³ CO₂removed (at +0.2 and –0.1 V, respectively). However, for the PEM-MEC, a value of 2.26 kWh/Nm³ CO₂removed was calculated, which is higher than data reported for conventional technologies. Importantly, all data referred to MEC have been determined under not CO₂-limiting conditions.

4. Conclusions

One of the most attractive features of the MEC technology is certainly represented by the possibility to couple several positive actions in one process (e.g. COD removal, methane generation, low microbial growth) and, in this study, the performance of an MEC equipped with either an AEM or a PEM has been deeply analyzed. In particular, most of equivalents deriving from COD oxidation at the anode were diverted into current with a CE between 53 ± 9% and 83 ± 15%, with only a little fraction being used for biomass growth. Indeed, the observed growth yield (between 0.17 and 0.21 gCOD/gCOD) was significantly reduced with respect to typical values (0.5 gCOD/gCOD) reported for active sludge processes. The generated current was mainly used at the cathode to convert CO₂ into CH₄, with a CCE between 47 and 80%. However, methane generation represented only a little fraction (4% and 15% in the AEM-MEC and PEM-MEC, respectively) of the overall CO₂ removal mechanism which was mainly attributed to alkalinity generation (between 73% and 94%), caused by the dissolution of the bicarbonate ion at high concentration in the MEC cathode compartment. Moreover, in a AEM-MEC, the dissolved bicarbonate was removed by means of molecular diffusion and ionic transport phenomena across the membrane, that accounted for 49% and 50% of the overall removed CO₂ (with the anode potential controlled at +0.2 V vs SHE), respectively. More in details, the main CO₂ removal mechanism was the sorption of CO₂ under slightly alkaline condition, the alkalinity being produced by ionic transport needed to electroneutrality maintenance. In this frame methane generation was an important electron sink that generated the driving force to transfer bicarbonate across the AEM.

Overall, in spite of the higher CO₂ removal in the AEM-MEC with respect to the PEM-MEC, the latter resulted in a higher performance in terms of both COD removal efficiency (654 ± 83 vs 572 ± 167 mgCOD/d) and methane production (83 ± 24 vs 34 ± 1 meq/Ld).

With respect to the energetic evaluation of the overall process, data obtained have been compared with conventional full scale processes. More in detail, the estimated energy consumption required for COD removal was comparable with values reported for the activated sludge process and, similarly, the methane production yield was even lower than values of anaerobic digestion process. The energy required for CO₂ removal was compared to the pressure swing adsorption and the water scrubbing technologies and, also in this case, the obtained results clearly indicate the great potential of the MEC technology for process scaling up. Particularly, the MEC technology is an attractive route for biogas upgrading and the possibility to upgrade the biogas at the cathode without its preliminary compression while treating at the anode real wastewater could be the main objective of future studies.

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