Bioelectromethanogenesis reaction in a tubular Microbial Electrolysis Cell (MEC) for biogas upgrading

Marco Zeppilli, Edoardo dell'Armi, Lorenzo Cristiani, Mauro Majone

Department of Chemistry "Sapienza" University of Rome, piazzale Aldo Moro 5, 00185, Roma

marco.zeppilli@uniroma1.it

7th International Conference on Sustainable Solid Waste Management, 26-29 June 2019,Heraklion, Crete, Greece

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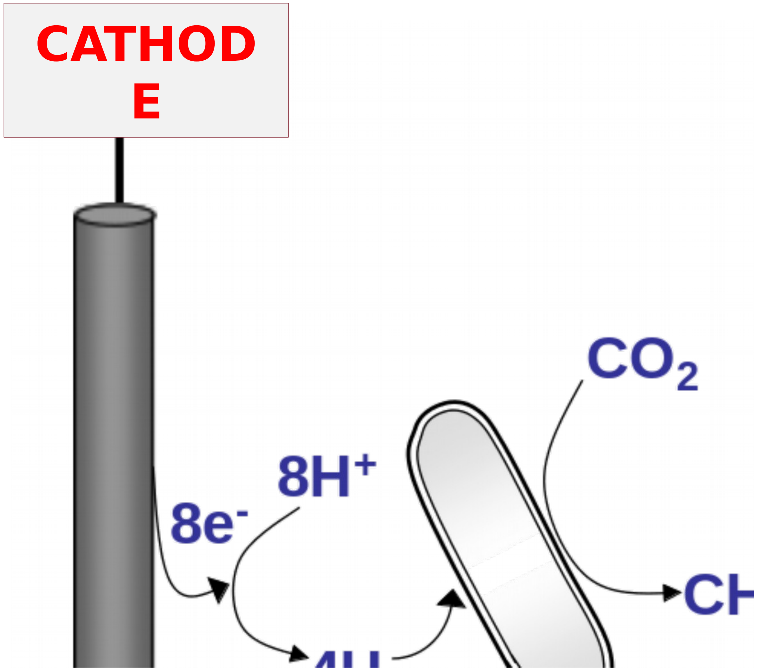
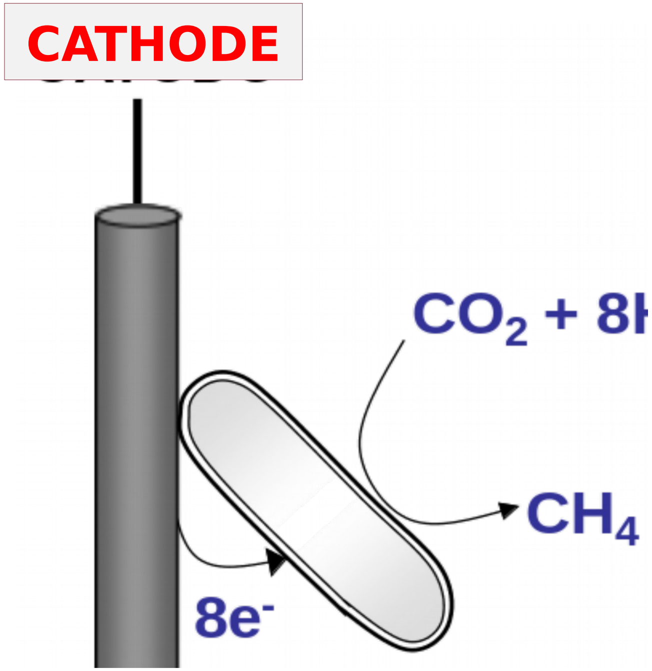
The Bioelectromethanogenesis Reaction

- In a bioelectrochemical system (BES) the reducing power for CO_2 reduction can be supply by an electrode (usually graphite based) controlling the potential of an electrode,



☐ Hydrogen mediated electron transfer

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
$$\Delta G^{0'} = 188 \text{ kJ/mol}$$

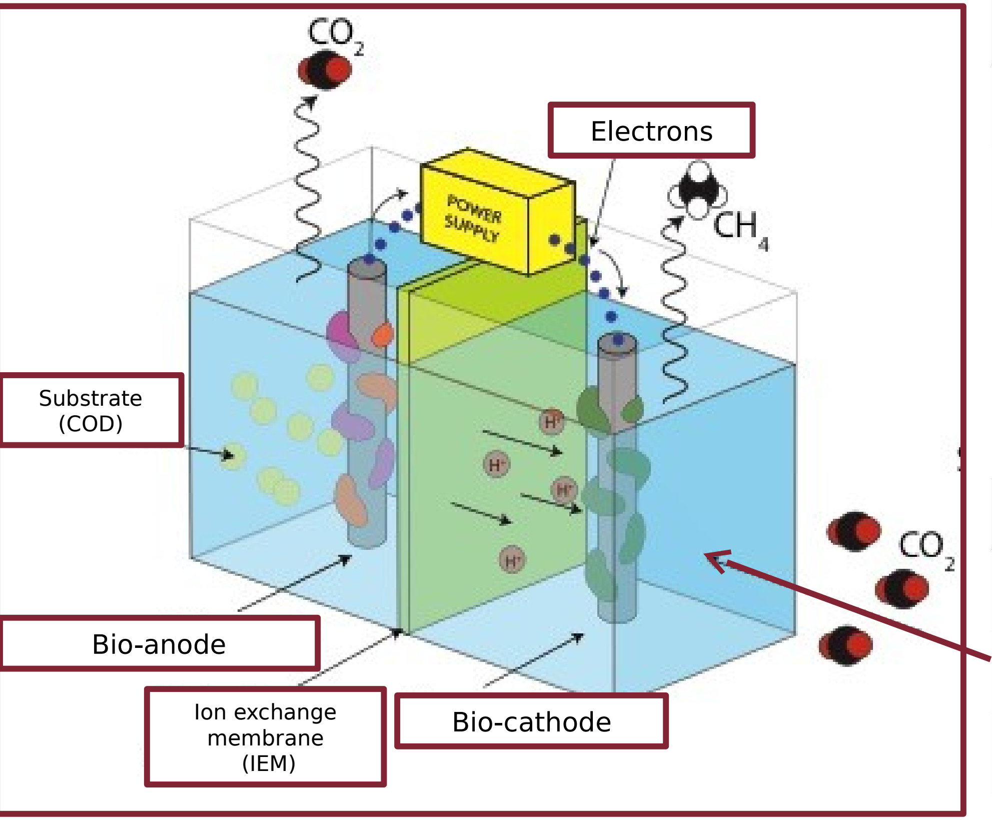


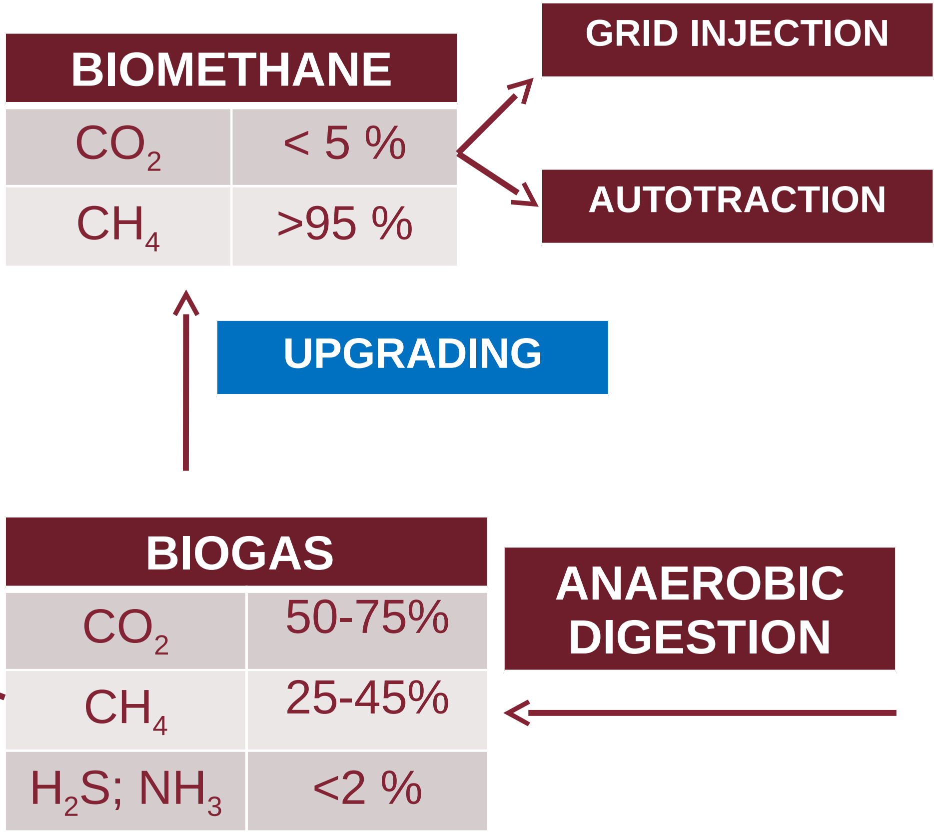
☐ Direct electron transfer

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$$
$$E^{0'} = -0.244 \text{ V}$$

BIOGAS UPGRADING THROUGH BIOELECTROMETHANOGENESIS

BIOANODE	BIOCATHODE
(64 gr) COD → $nCO_2 + 8H^+ + 8e^-$ COD oxidation	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ Electromethanogenesis





BIOMETHANE

CO_2	< 5 %
CH_4	>95 %

BIOGAS

CO_2	50-75%
CH_4	25-45%
H_2S; NH_3	<2 %

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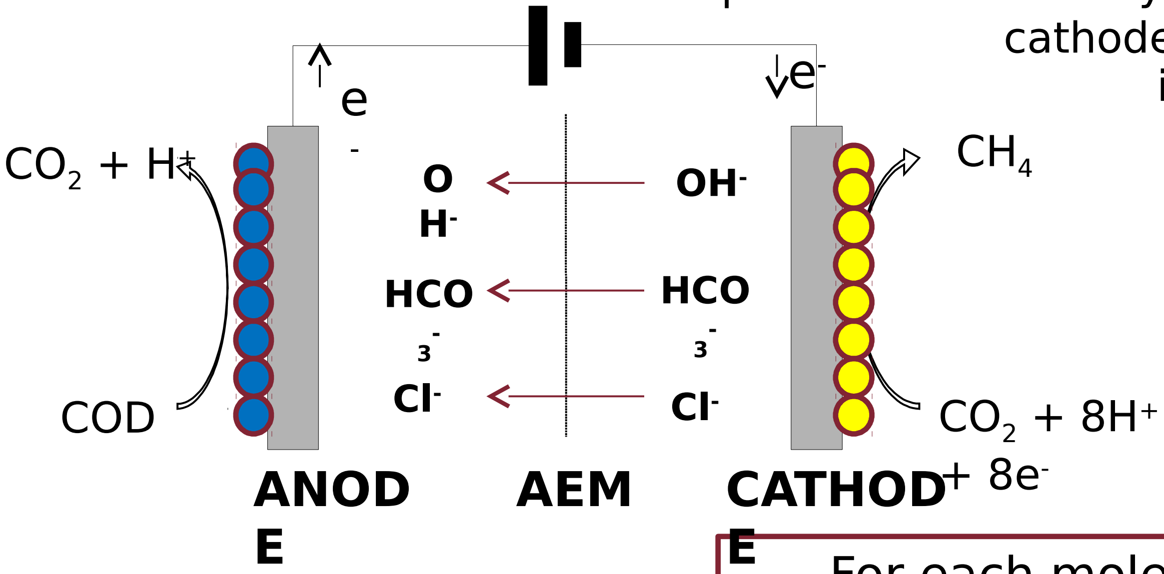
CO_2 removal mechanisms in a Biocathode

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O$$

For each mole of CH_4 produced, 8 moles of monovalent ions must be transported across the IEM to maintain electroneutrality, for each ionic charge transported by ionic species different from hydroxyls an equivalent of alkalinity is generated in the cathode

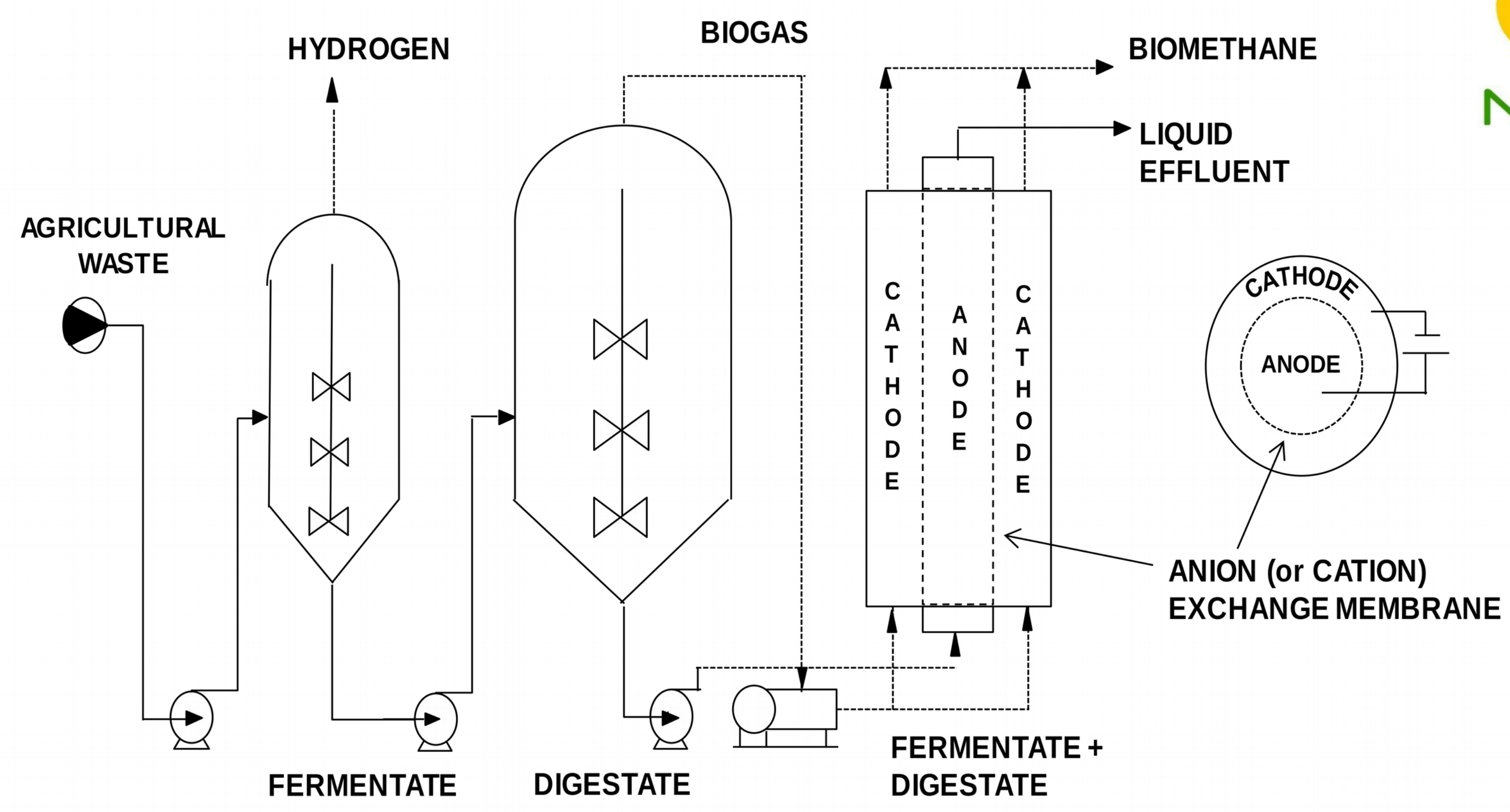


if 8 HCO_3^- are transported for electroneutrality maintenance

For each mole of CH_4 produced, a maximum of 9 mole of CO_2 could be removed

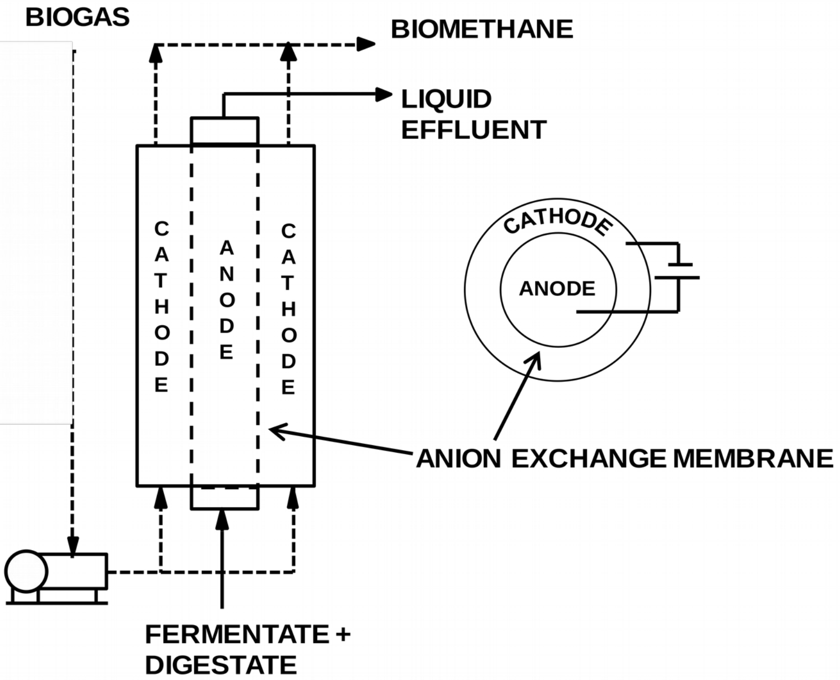
Zeppilli, M., A. Lai, M. Villano and M. Majone (2016). Chemical Engineering Journal 304: 10-19

Integration scheme of AD and MEC



- While the biogas can be refined in the cathodic chamber of the MEC, the COD contained in the liquid effluents can be oxidized by the anodic chamber and partially sustain the energy demand of the process

Tubular Microbial Electrolysis Cell Set up



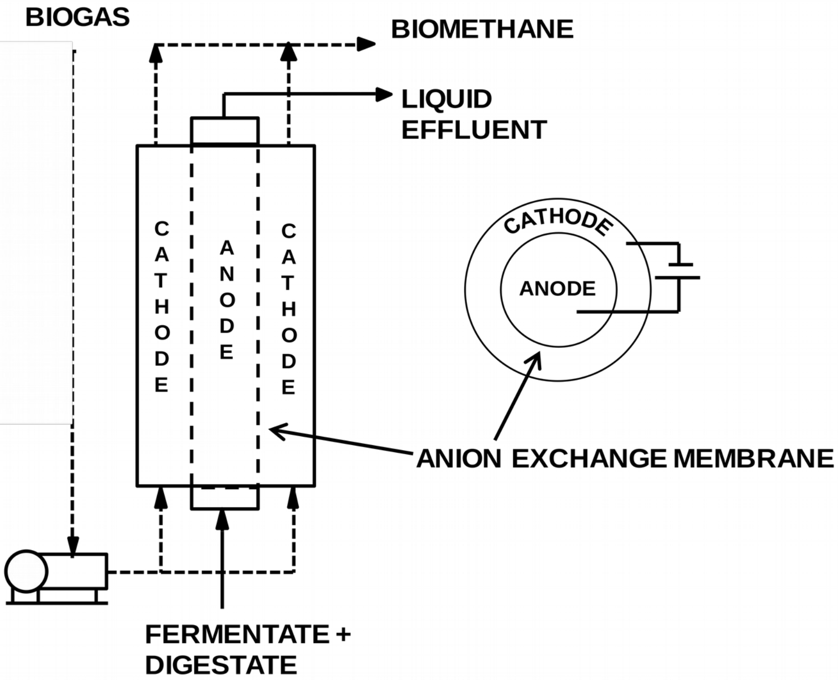
ANODIC CHAMBER

- Electrodic material: graphite granules
- Substrates: synthetic municipal wastewater
- Inoculum: activated sludge
- Volume: 3.14 L
- Porosity: 0.57

CATHODIC CHAMBER

- Electrodic material: graphite granule
- Substrates: Synthetic biogas CO_2 (30 v/v)
- Inoculum: anaerobic sludge
- Volume: 8.83 L
- Porosity: 0.57

Tubular Microbial Electrolysis Cell Set up



POLARIZATION STRATEGIES

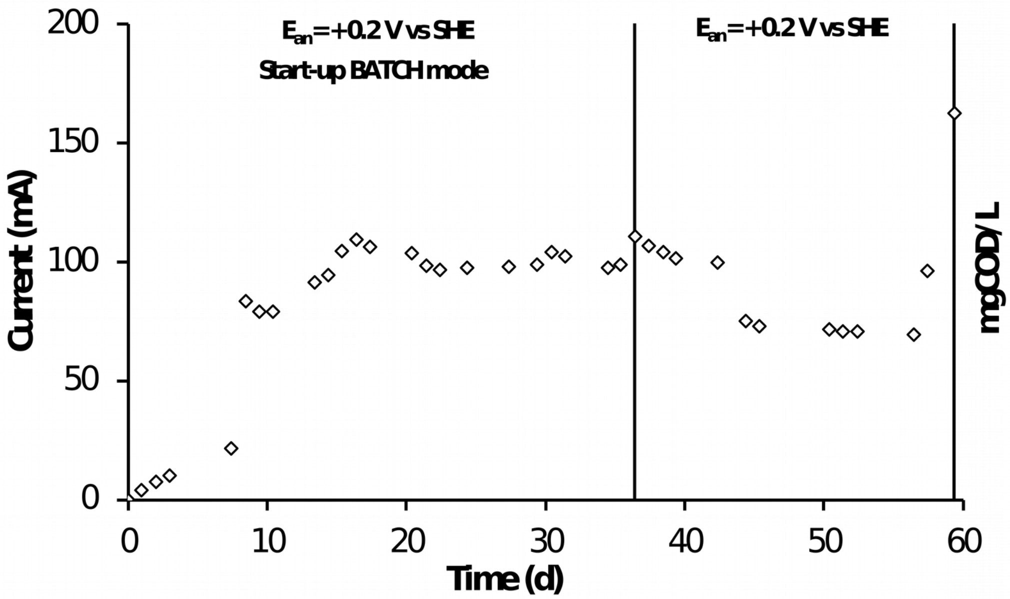
THREE ELECTRODE CONFIGURATION

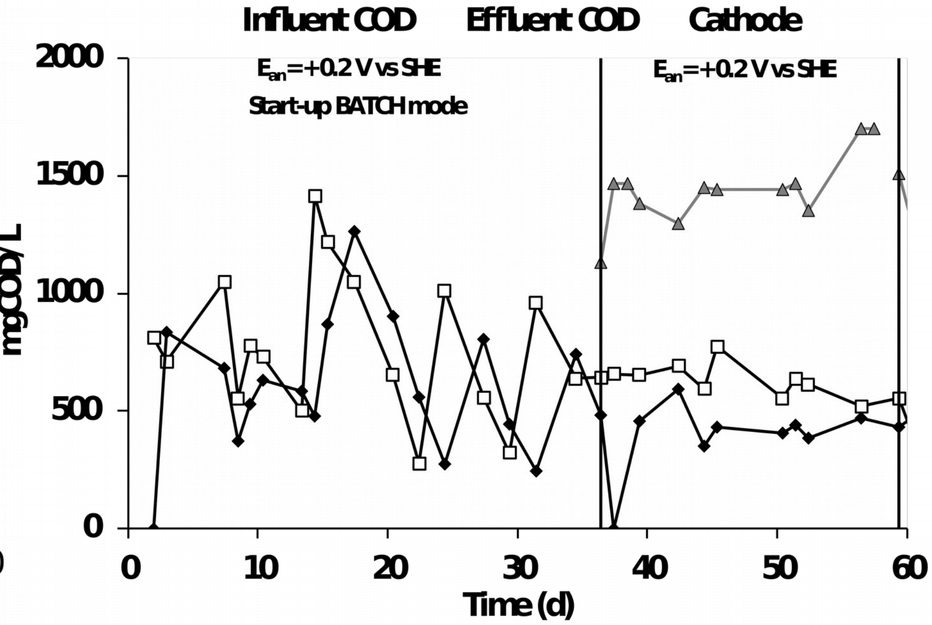
- AgAgCl reference electrode
- Control of the potential of one electrode, i.e. the anode or the cathode
- Potentiostat is needed

TWO ELECTRODE CONFIGURATION

- A potential difference is applied between anode and cathode
- DC power supplier

MEC with three electrode configuration: start up and continuous flow mode



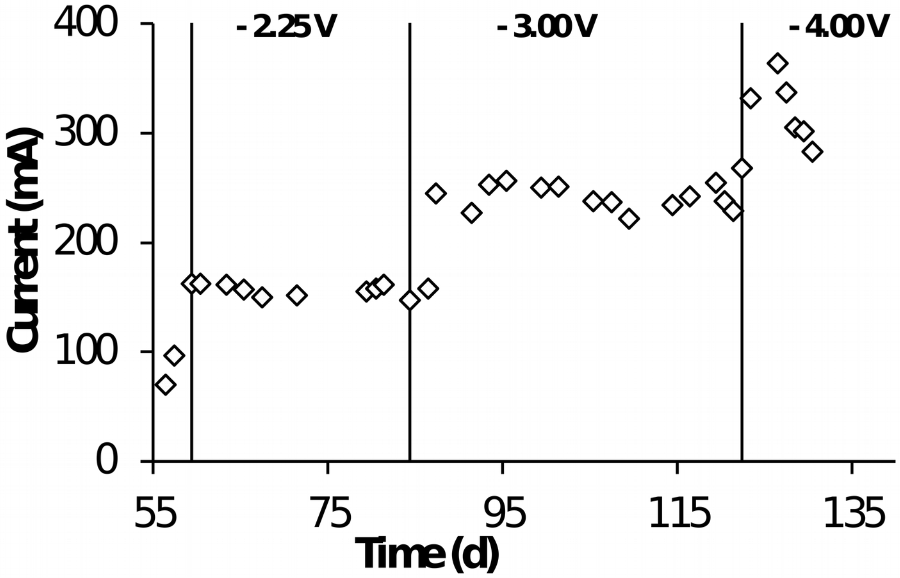


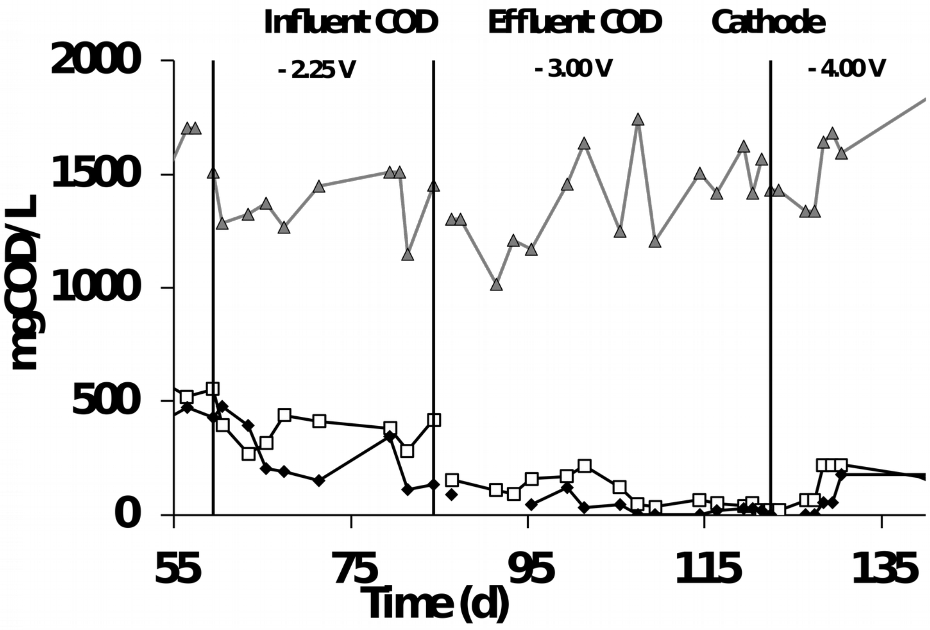
- ➢The start up phase showed the increase of the current during the first 20 days that corresponds to the formation of the anodic biofilm

- ➢A continuous flow condition was monitored for more than 20 days by maintaining the three electrode configuration at +0.2 V vs SHE

- ➢The COD profiles showed a high correlation of the COD concentration in the anodic and cathodic chamber, this evidence can be attributed to the diffusion of substrates across the AEM membrane

MEC with two electrode configuration: current profile and COD removal



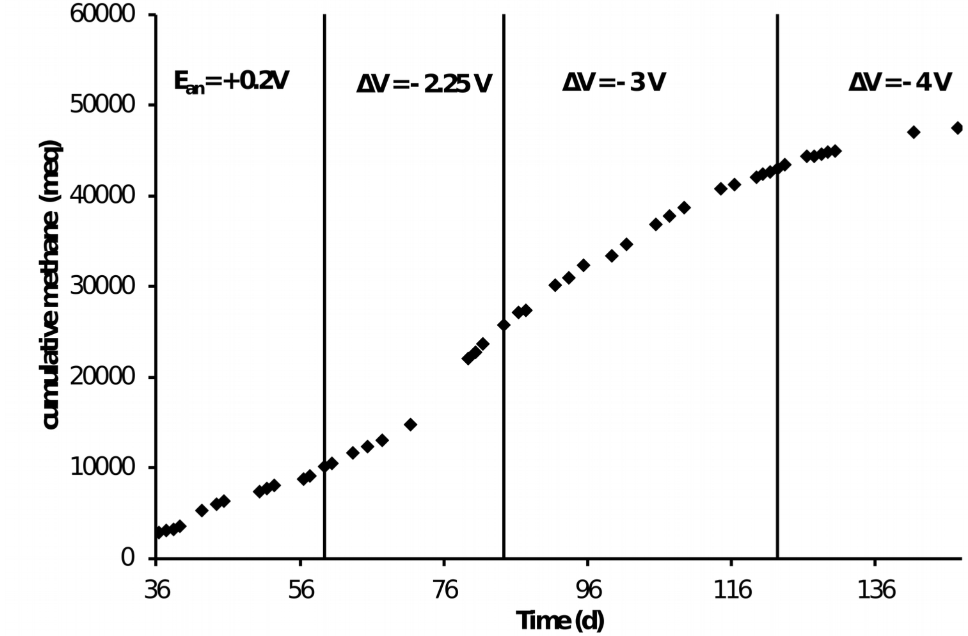


➢The increase of the applied voltage promote the increase of the current flowing in the circuit and of the COD removal in the anodic chamber

➢However, a very low conversion of COD into current (Coulombic Efficiency) have been obtained in all of the explored conditions

	+ 0.2 V vs SHE	- 2.25	- 3.00	- 4.00
Current (mA)	86	154	237	282
COD removed (mgCOD/d)	4850	5982	7631	8360
COD removal efficiency (%)	56	72	92	90
Coulombic Efficiency (CE, %)	13	18	22	24

MEC performances: methane production

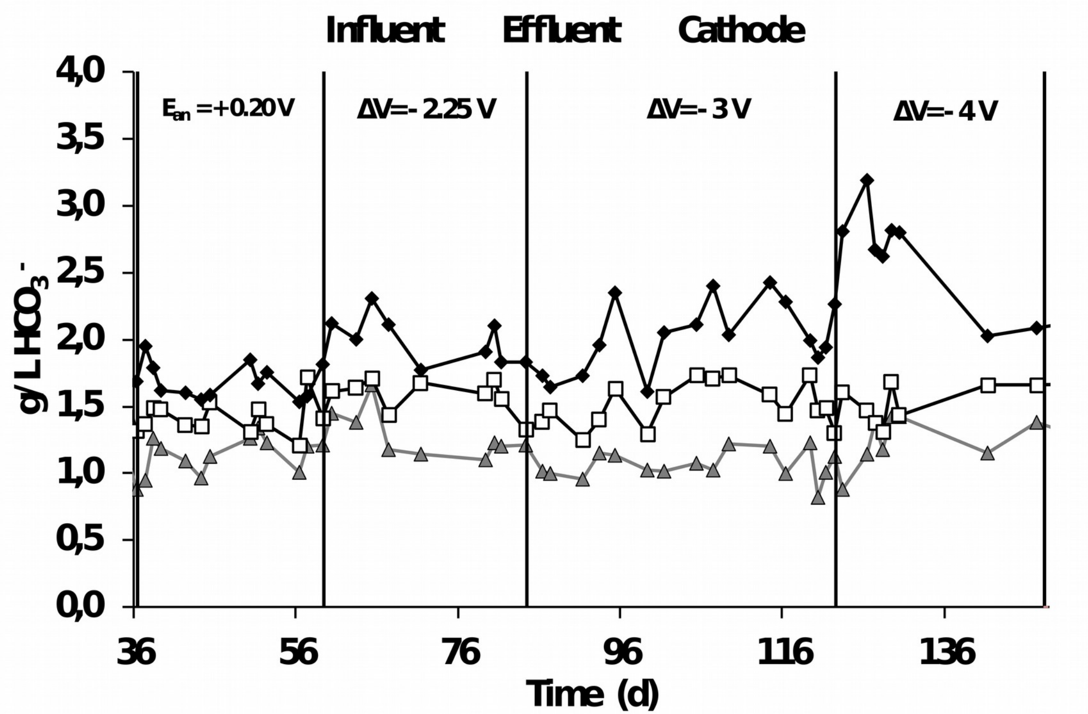


➢In all of the explored conditions the methane production resulted higher than the current available for the cathodic reduction another mechanisms of CH_4 production occurred

➢The efficiency of the cathodic (i.e. current diverted into methane) reaction resulted higher in all of the condition explored

	+ 0.2 V vs SHE	- 2.25	- 3.00	- 4.00
Current (mA)	86	154	237	282
Methane production (meq/d)	300	449	367	261
Cathode Capture Efficiency (CCE, %)	390	325	173	103

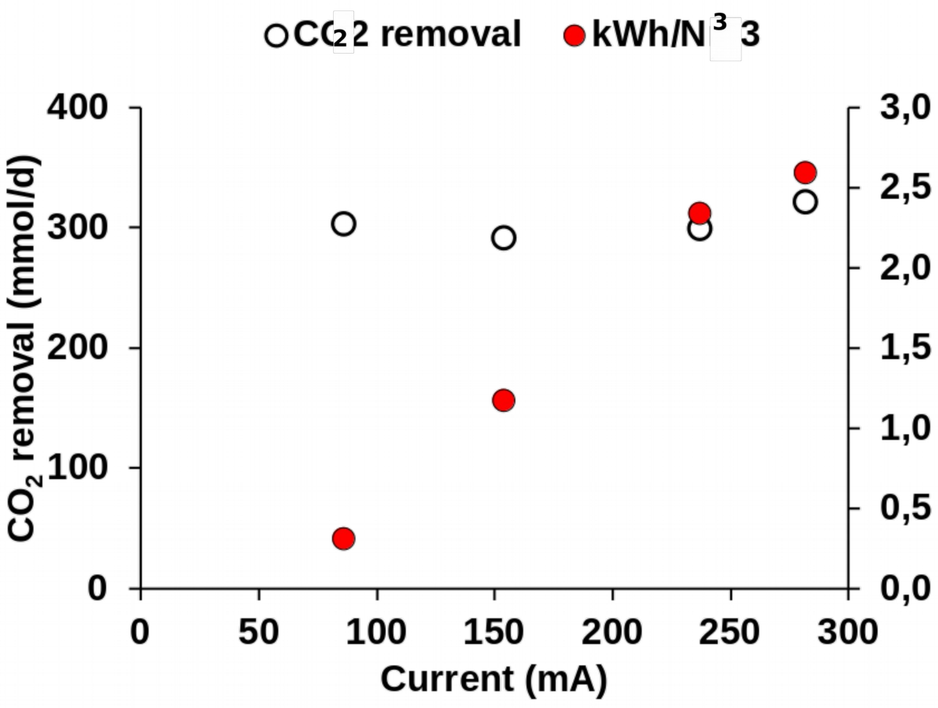
CO_2 removal and Bicarbonate migration

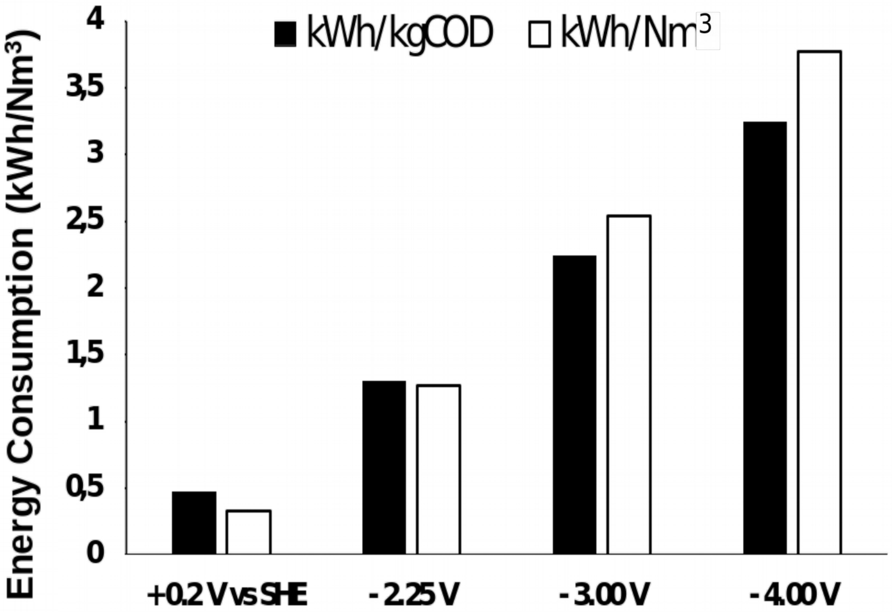


- ➢The cathodic HCO_3^- concentration resulted higher than the anodic in all of the condition explored CO_2 sorption due to alkalinity generation
- ➢The HCO_3^- concentration in the anodic effluent indicated the HCO_3^- transport

	+ 0.2 V vs SHE	- 2.25	- 3.00	- 4.00
CO_2 removal (mmol/d)	303	292	299	321
rCH_4 (mmol/d)	38	56	46	33
$HCO^-_{3\ transf}$ (mmol/d)	30	33	43	38

Energetic Evaluation





	+ 0.2 V vs SHE	- 2.25 V	- 3.00 V	- 4.00 V
kWh/Nm^{3}CO$_2$	0.33	1.27	2.54	3.77
kWh/kgCOD	0.47	1.39	2.24	3.24

Conclusions

- The tubular MEC was successfully operated for the first time showing the capability to remove both COD and CO_2 from synthetic substrates

- The COD shortcut from the anode to the cathode resulted in a loss of coulombic efficiency of the reactions

- Even if the two electrode configuration don’t permit the strictly control of the electrodic potentials of the electrodes, it resulted a more feasible approach for the operation of the process

- The three electrode configuration resulted the most efficient in terms of energy consumption for the COD and CO_2 removal

Acknowledgment

This work has been carried out with the financial support of the project NoAw. “This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 688338”.

Thank you for your attention

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