

Characterization of Microbial Electrolysis Cell's Bioanode Performances through Potentiostatic and Potentiodynamic Techniques

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Introduction

Among the various sustainable hydrogen production technologies under investigation, alkaline electrolysis appears to be the most promising, particularly when renewable electricity powers the process. Theoretically, water electrolysis requires an electromotive force of +1.23 V. Another promising approach appears in the production of hydrogen through Microbial Electrolysis Cells (MECs), offering significant advantages over conventional methods. Indeed, MECs use microorganisms to oxidize organic compounds at low energy, dramatically reducing the thermodynamic voltage required compared to water electrolysis. This electrochemical activity occurs at significantly lower redox potentials, leading to a substantial reduction in energy requirements (Roubaud et al., 2018). For example, when the acetate is used as the substrate, the electromotive force of the cell is only +0.187 V, representing an 85% reduction. This enables a more efficient hydrogen production process with lower energy consumption. Additionally, MECs can utilize organic waste and wastewater as substrates, helping to improve the energy balance in water treatment processes, making it an innovative and sustainable solution and an emerging technology for hydrogen production and waste management (Cristiani et al 2024a).

Material and methods

The laboratory scale MEC consisted of three identical Plexiglas chambers (0.86 L volume each) with internal dimensions of 17 cm × 17 cm × 3 cm, where the anode chamber was positioned centrally while two identical cathode chambers were arranged on either side, each divided by CMI International exchange membrane (Membrane International, USA) installed between the chambers, thus permitting the migration of protons. The cathode chamber consisted of two sheets of 316 stainless steel (RS components) each with a surface area of 176.46 cm², while granular graphite with a diameter < 4 mm (Faima srl, Milan) was used as filler for the bioanode. In particular, two different feeding solutions were used and compared, with a concentration equal to 1.2 gCOD/L for both. The carbon fraction of the synthetic solution was composed of glucose, 0.680 g/L, sodium acetate, 0.211 g/L, peptone, 0.276 g/L and yeast extract 0.150 g/L. While the real substrate, rich in volatile fatty acids (84% COD_{vfa}/COD_{tot}), was obtained from the acidogenic fermentation of organic waste. The pH of the feeding solution was maintained at around pH of 7.5 with a buffer solution of sodium bicarbonate. The cathodic chamber operated in batch configuration, where a daily spill of the catholyte was performed to compensate the water electro-osmotic diffusion through the CEM membrane. Cyclic voltammetry (CV) was employed to characterize the electrocatalytic activity of the bioanode after each starvation period. CVs were recorded at 4 different scan rates, namely 5, 20, 40, and 60 mV/min (Zeppilli et al., 2021), three CV cycles were performed in each routine (with vertex of E_i = +0.40 V and E_f = -0.40 V).

Results and discussion

The present study reports the utilization of potentiodynamic and potentiostatic techniques for the electrochemical characterization of the biofilm activity of a bioanode of different setups of microbial electrolysis cell. The adoption of potentiodynamic techniques, i.e. of cyclic voltammetry has been already applied as tool to monitor biofilm activity restoration after starvation periods (Cristiani et al 2024b), highlighting the possibility to monitor electroactive species re-activation and to characterize the biofilm electrocatalytic activity and to track the dynamics of biofilm.

In this study, biofilm activity at different organic load rates with a synthetic mixture a substrate and a real acidogenic fermentate has been monitored using cycle voltammetry's at different scan rates along with the application of potentiostatic polarization at different anodic potential obtaining the electricity/potential relationship under potentiostatic conditions. The data showed the applicability of these electrochemical techniques to monitor the biofilm activity of the bioanode under different operating conditions, particularly the cyclic voltammetry highlight the presence of a clear oxidation peak around -0.15 V vs SHE when an OLR of 1gCOD/Ld was applied to the anodic chamber with synthetic substrates (Figure 1-a). On the other hand the characterization of biofilm activity during the bioanode operation with the real substrate highlights the presence of soluble oxidable compounds which affected the current production for applied anodic potentials higher than +0.3 V vs SHE.

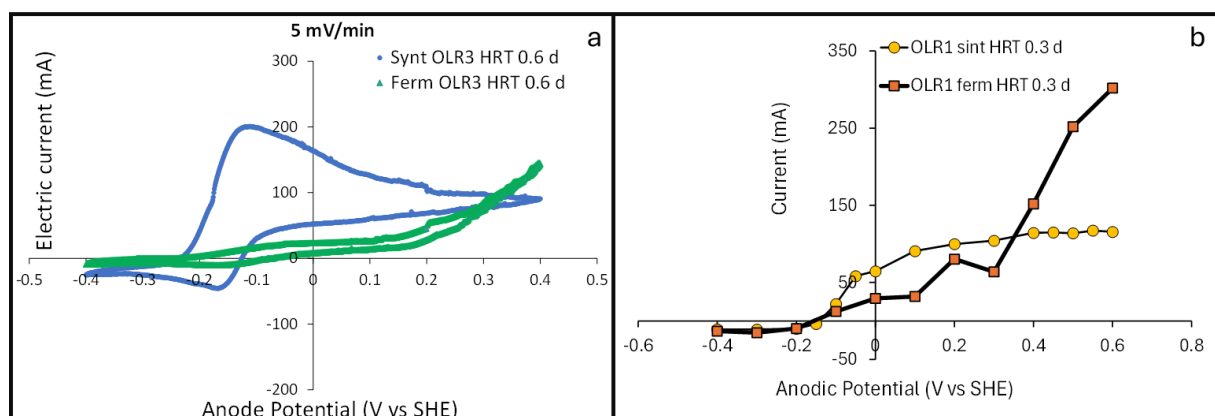


Fig. 1. Cyclic voltammetry scan at 5 mV/min using synthetic and real substrate (a), kinetic characterization of biofilm activity under potentiostatic conditions with synthetic and real substrates.

Conclusions

The present study highlighted the promising potential of Microbial Electrolysis Cells in integrating COD oxidation at the bioanode with green hydrogen production at the cathode within a single biobased process. Additionally, the use of CV to track biofilm performance and dynamics offers a non-destructive and precise method to monitor MEC operation. This could be integrated into regular monitoring protocols to ensure optimal performance and timely interventions if biofilm activity declines.

References

- Cristiani L, Zeppilli M, Fazi G, Marandola C, Villano M (2024a). Renewable gases production coupled to synthetic wastewater treatment through a microbial electrolysis cell. *Biochemical Engineering Journal*, 205: 109249
- Cristiani L, Zeppilli M, Brutti S, Puig S, Salvatori G, Petrangeli Papini M, Villano M (2024b). Impact of extended starvation conditions on bioelectrocatalytic activity of a methane-producing microbial electrolysis cell. *Bioresource Technology*, 413: 131491
- Roubaud E, Lacroix R, Da Silva S, Bergel A, Basséguy R, Erable B (2018). Catalysis of the hydrogen evolution reaction by hydrogen carbonate to decrease the voltage of microbial electrolysis cell fed with domestic wastewater. *Electrochimica Acta*, 275: 32-39
- Zeppilli M, Cristiani L, Villano M, Majone M (2021b). Carbon Dioxide Abatement and Biofilm Growth in MEC equipped with a packed bed adsorption column. *Chemical Engineering Transactions*, 86: 421-426