Sustainable Hydrogen Production in a Two-Chamber MEC: Effect of Synthetic and Real Substrate Feeding on System Performance

A. Marchetti[1], M. Villano[1], M. Zeppilli[1].
[1]Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro, Rome, 00185, Italy
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angela.marchetti@uniroma1.it

Introduction

Nowadays, even if hydrogen is considered a sustainable fuel because its combustion produces exclusively water and no other side-products, 96% of its production still relies on coal, petroleum, or natural gas via the steam reforming process that requires energy-intensive and results in considerable CO_2 emissions (Holladay et al., 2009). 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 (Khandaker et al., 2021). 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, making it an innovative and sustainable solution and an emerging technology for hydrogen production and waste management. Over the past two decades, various strategies have been implemented to increase system efficiency. In this view, this study focuses on achieving consistent anodic current generation, maintaining a stable anode overpotential and minimizing the cathode overvoltage. For this reason, a new configuration was developed, in which the intermediate anode chamber was flanked by two cathode chambers. The aim was to increase the quantitative conversion of the current produced by the bioanode into molecular hydrogen with higher energy efficiency. With this new configuration, by using two different substrates, one synthetic and one real obtained from the fermentation of organic waste, two steady states were characterized. The objective was to evaluate the performance of MECs for hydrogen production, also exploring the effect of using waste substrate as a feeding solution, in a view of developing a robust biobased process.

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 cm^2, while granular graphite with a diameter < 4 mm (Faima srl, Milan) was used as filler for the bioanode. The anodic chamber was operated with a continuous flow of 2.9 L/ d, working with an organic loading rate (OLR) equal to 4 gCOD/Ld and a hydraulic retention time (HRT) equal to 0.3 day. 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. A sampling glass chamber was placed above each chamber to sample both the liquid and gaseous phases. During the whole experimental period the temperature of the MEC was maintained at 25 ± 1 °C. To control and/or measure the potential of individual electrodes an Ag/AgCl reference electrode, immersed in a saturated KCl solution ($E°' = 199$ mV vs. SHE, Standard Hydrogen Electrode) was placed in each chamber of the MEC. Then, to connect the graphite granules to the electrical circuit, two graphite rods were dipped into the chambers using titanium wires and connected to a potentiostat, by means of which a potential, selected based on previous studies (Cristiani et al., 2024), equal to +0.2 V vs the Standard Hydrogen Electrode (SHE), was applied to the anode, configuring it as the working electrode.

Results and Discussion

After an initial period of biomass acclimatization, the MEC was operated for 10 and 13 days, by using synthetic and real feeding solution, respectively. The anodic parameters were maintained stable to focus the experiment on the cathodic performance. Through liquid sampling it was possible to determine the COD consumed daily from which the coulombic efficiency at the anode (CE) is determined. While, by means of gas phase analysis, it was possible to determine the gas flow rate out of the system, and thus the daily production. The latter, by a gas chromatographic analysis, was found to consist solely of hydrogen, with an average mixture percentage of around 100% H_2, throughout the entire period of reactor operation. Furthermore, by means of the daily current data, it was possible to define the coulombic efficiency at the cathode (CCE), from which the energy efficiency (ηE) of the process was defined. *Figure 1* shows the average percentage values of these parameters for both feeding cases. In particular, the electric current generated by the electroactive biofilm through COD oxidation was around 95 and 51 mA, corresponding to an average coulombic efficiency of 130 ± 30% and 141 ± 20%, by feeding the reactor with the synthetic and real substrate, respectively. While a CCE equal to 100 ± 9 % and 92 ± 2 % were obtained. Overall, MEC performance was better when applying OLR1_Synth, with higher efficiencies for higher values of daily current (around 100 mA) and lower ΔV (-1.35 V), with an ηE equal to 110 ± 11 %. While, when the real substrate was fed to the reactor an ηE equal to 55 ± 4 % was obtained. This was due to a lower conductivity of this substrate (1.0 mS/cm) compared with the conductivity of the synthetic one (6.1 mS/cm), thus increasing the system resistance (ΔV = -2.58 V). Nonetheless, the results obtained show and confirm that it is possible to produce sustainable hydrogen from wastewater, achieving high efficiencies with this new MEC configuration.

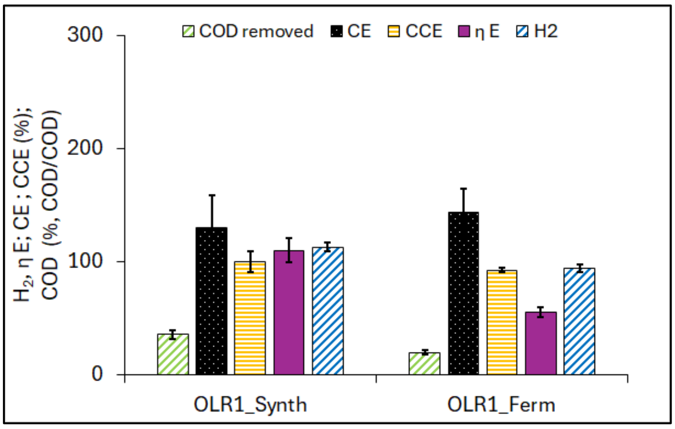

Fig. 1. Average values in terms of coulombic efficiency calculated at the anode and cathode, energy efficiency, hydrogen composition of the outlet gas flow and COD removed for the two feeding solutions.

Conclusions

The present study highlighted the promising potential of MEC system in integrating COD oxidation at the bioanode with green hydrogen production at the cathode within a single biobased process. Specifically, the bioanode consistently provides a stable electron source for the cathodic reaction, with good results for both steady state cases. In both, a composition of around 100% of hydrogen of outlet gas flow, with a CCE about 100%. These results show how the new configuration is energetically more efficient than the traditional single-chamber configuration. Furthermore, this study points out the possibility to achieve high efficiencies using waste substrates, making this system highly attractive also for their valorization from a sustainability viewpoint.

References

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