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Hydrogen production in a microbial electrolysis cell: the influence of operational parameters

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Abstract In the present study two identical two-chamber microbial electrolysis cells (MECs), fed with an acetate synthetic medium, were used for hydrogen production, using different anodic materials, i.e. commercial carbon fiber paper (CP) and graphite granules (GG). The effects of the applied voltage (i.e. 0.7 and 0.9 V) and of the acclimation procedure (direct potentiostatic operation as MEC or galvanostatic as microbial fuel cell, MFC) were assessed and the performance of both MECs was compared in terms of their biochemical and electrochemical characteristics.

Keywords: Microbial Electrolysis Cell (MEC), hydrogen, applied voltage, anode.

1. Introduction

Microbial Electrolysis Cells (MECs) are bio-electrochemical systems producing biohydrogen while simultaneously accomplish wastewater treatment (Logan et al., 2009). The concept of MECs originated in 2005, with the key feature being the use of an external voltage in a typical microbial fuel cell (MFC) system to enable hydrogen gas evolution at the cathode, through reduction of protons. Similarly to any other electrochemical system, a MEC consists of two electrodes (anode / cathode), typically separated by a membrane. At the anode, microorganisms forming an electro-active biofilm, catalyze the oxidation of organic substrates, using the electrode as direct electron acceptor. The electrons pass, via an external circuit, to the cathode, which plays the role of an electron donor, and there they combine with protons (migrated from the anode) and get reduced to form hydrogen gas, under the influence of a small applied voltage (at least 0.2–0.25 V), which is necessary since the reaction is not favored thermodynamically (i.e., is not spontaneous). In practice, external cell voltages for inducing hydrogen evolution in MEC range from 0.6 to 1.0 V, being much lower than the 1.8–2.0 V used in traditional water electrolysis (Logan et al., 2008). The aim of the study was to assess the effect of operational parameters such as the applied voltage and the acclimation mode, on hydrogen production and electrochemical performance of two MECs, equipped with different anode materials, i.e the two-dimensional commercial carbon fiber paper (CP) and and the 3-dimensional graphite granules (GG).

2. Materials and Methods

2.1. MECs

Two identical two-chamber MECs, MEC1 and MEC2 consisted of two bottles, filled to 250 mL and connected via a glass tube, separated by a proton exchange membrane (Nafion). The anode electrode of MEC1 was made of CP, while the empty bed volume of the anode chamber of MEC2 was filled with graphite granules, pretreated with HCl as described in Antonopoulou et al. (2019) and connected to the circuit using a graphite rod. For both MECs, the cathode (counter) electrode was made of carbon cloth coated with a Pt catalyst (ETEK, 0.5 mg/cm^2) (dimensions of 3 cm x 3 cm). Titanium wires were used to connect the cell to the external circuit.

Voltage of 0.7 or 0.9 V was initially supplied to the MECs using a power source (DC supply), in series to a 10 Ω resistor (resistance decade box), while the MECs potential was monitored and recorded using a data acquisition system (ADAM-4017).

The solutions in both bottles were mixed using magnetic stirrers and their temperature was kept constant at 30^{o}C, by placemen in a constant temperature box. The anode compartments were filled with a buffer solution (3.4472 g/ L$^-$ $Na_2HPO_4 \cdot 2H_2O$, 3.668 g /L $NaH_2PO_4 \cdot 2H_2O$), alkalinity (5 g /L $NaHCO_3$), a synthetic medium based on acetate (0.8 g COD /L), KCl (0.16 g/L) and a solution of trace elements (Antonopoulou et al., 2019). The cathode compartments were filled with the buffer solution and KCl.

During the acclimation phase, either the MECs operated directly potentiostatically at the elevated voltage (0.7 V) (directly as MEC) for two cycles of operation or galvanostatically, as MFCs, under close circuit

conditions (R=100 Ω), for five successive cycles. Inoculation was performed by using anaerobic sludge (10% v/v) along with the acetate-based medium, while the anode chamber operated as a batch reactor. At the end of each cycle, i.e. after the consumption of the chemical oxygen demand (COD), the liquid contents were emptied and the anode chamber was refilled with fresh culture medium (nutrients solutions and microbial inoculum), while the cathode was refilled only with the nutrient solution.

2.2. Analytical methods

The measurements of dissolved COD, pH and hydrogen content were performed as described in Antonopoulou et al. (2020). Cyclic voltammetry analysis was performed using an Autolab PGSTAT204 (0.4 A/20 V) potentiostat – galvanostat, controlled by the NOVA 2.1 software package. Cyclic voltammographs (CVs) were received in a potential range -1 to 1 V by scanning the applied potential with a rate of 50 mV /s. The anodic electrode was used as working, a Ag/AgCl was used as reference electrode and the cathodic electrode was acting as counter.

2.3. Calculations

The amount of hydrogen produced from acetate on a molar basis, was calculated as:

$$Y_{H2} = n_{H2}/n_S \quad \text{(Eq. 1)}$$

where n_{H2} is the moles of hydrogen produced and n_S is the moles of substrate consumed. The hydrogen yield for a specific substrate can also be compared to the theoretical maximal production (n_{th}), usually on a percent basis as:

$$Y_{H2,th}=(n_{H2}/n_{th})\,100\%. \quad \text{(Eq. 2)}$$

The value of n_{th} based on COD is calculated:

$$n_{th} = \frac{2\Delta COD}{M_{O2}} \quad \text{(Eq. 3)}$$

where MO_2 (32 g/mol) is the molecular weight of oxygen.

The moles of hydrogen that could be recovered based on the measured current, n_{CE}, is:

$$n_{CE} = \frac{\int_{t=0}^{t} I dt}{2F} \quad \text{(Eq.4)}$$

where dt (s) is the interval over which data are collected, F the Faraday constant and 2 is used to convert moles of electrons to moles of hydrogen.

This recovery is related to the Coulombic efficiency:

$$C_E = \frac{n_{CE}}{n_{th}} \quad \text{(Eq. 5)}$$

The moles of hydrogen actually recovered at the cathode, compared to the moles that theoretically could have been produced from the current, is the cathodic hydrogen recovery:

$$r_{cat} = \frac{n_{H2}}{n_{CE}} \quad \text{(Eq. 6)}$$

The overall hydrogen recovery is:

$$r_{H2} = C_E\, r_{cat}. \quad \text{(Eq. 7)}$$

3. Results and Discussion

3.1. Operation at 0.7 V and potentiostatic biofilm acclimation (directly as MEC)

During the whole operation, both MECs operated with a power supply of 0.7 V. Acclimation was performed potentiostatically, for two successive cycles, using anaerobic sludge and sodium acetate as substrate, in order to achieve enrichment of the anodes with electrochemically active bacteria. After the acclimation period, the MECs operated without addition of microorganisms in the anodic compartments, since it was supposed that the anodes were already enriched with electrochemically active bacteria. COD consumption and hydrogen production are presented in Figure 1 and the main characteristics of both MECs determining their performance in Table 1.

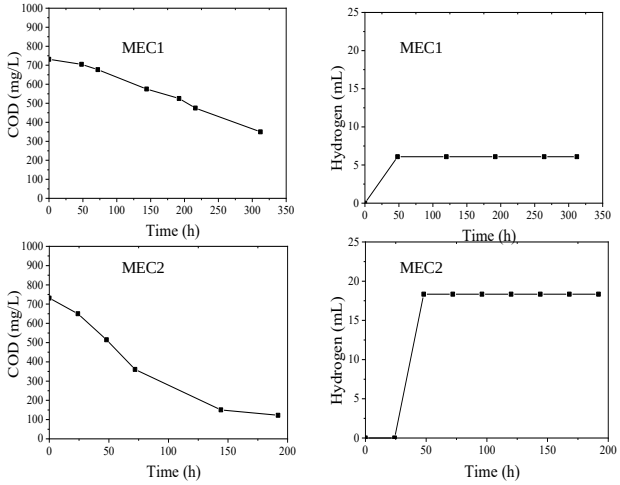

Figure 1. COD and hydrogen of MECs (MEC1 with CP and MEC2 with GG) under 0.7 V (potentiostatic biofilm acclimation at 0.7 V)

Table 1. Performance of MECs (MEC1 with CP and MEC2 with GG) under 0.7 V (potentiostatic biofilm acclimation at 0.7 V)

Characteristic	MEC1	MEC2
Volumetric hydrogen productivity, L/Ld	0.002	0.02
Y_{H2} yield, gH_2/gCOD	0.005	0.02
n_{th}, mmol	5.96	4.38
$Y_{H2,th,}$ %	4.17	17.14
Coulombic efficiency, %	70.60	44.77
Cathodic hydrogen recovery, %	5.90	38.00
Hydrogen recovery, %	4.16	17.14

The CV of MEC1 obtained using the anodic electrode as working, the Ag/AgCl as reference and the cathodic as counter, is presented in Figure 2. The oxidation peak is centered at ca. 0.4 V vs Ag/AgCl and the maximum current was ca. 15 mA.

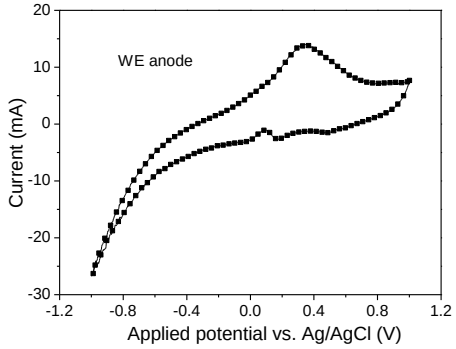

Figure 2. CV obtained for the MEC1, using Ag/AgCl as reference electrode (potentiostatic biofilm acclimation at 0.7 V)

3.2. Operation at 0.7 V and galvanostatic biofilm acclimation (as MFC)

In this set of experiments, the acclimation phase was performed galvanostatically as MFC, for three successive cycles, using anaerobic sludge and sodium acetate as substrate, in order to achieve enrichment of the anodes with electrochemically active bacteria. After the acclimation period, a voltage of 0.7 V was applied and the MECs operated without addition of microorganisms in the anodic compartments. COD consumption and hydrogen production are presented in Figure 3 and the main characteristics of both MECs in Table 2.

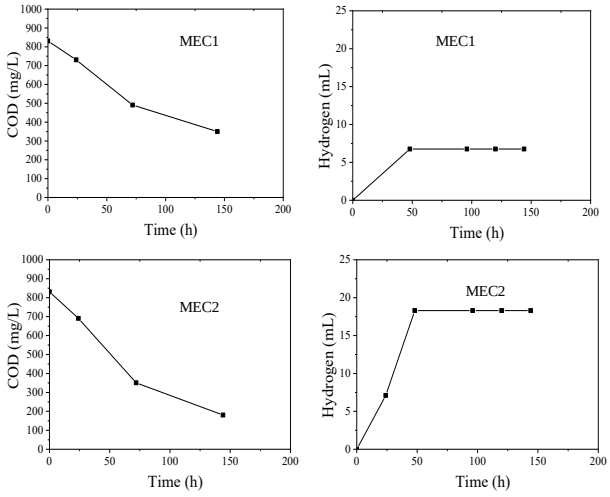

Figure 3. COD and hydrogen of MECs (MEC1 with CP and MEC2 with GG) under 0.7 V (galvanostatic acclimation as MFCs)

Table 2. Performance of MECs (MEC1 with CP and MEC2 with GG) under 0.7 V (galvanostatic acclimation as MFCs)

Characteristic	MEC1	MEC2
Volumetric hydrogen productivity, L/Ld	0.004	0.03
Y_{H2} yield, $gH_2/gCOD$	0.005	0.02
n_{th}, mmol	3.68	4.47
$Y_{H2,th,}$ %	3.69	16.8
Coulombic efficiency, %	29.5	35.3
Cathodic hydrogen recovery, %	12.5	47.4
Hydrogen recovery, %	3.7	16.7

The use of GG as anode materials seems to enhance hydrogen production rates and yields, as well as the electrocatalytic performance, compared to the use of CP. In addition, galvanostatic operation of MECs during the biofilm acclimation mode seems to be beneficial for the MECs.

The behavior of the CP anode was studied applying cyclic voltammetry, using the anodic electrode as working, a Ag/AgCl as reference and the cathodic electrode as counter electrode, respectively (Figure 4). The oxidation peak of the CV located at ca. 0.53 V vs. Ag/AgCl.

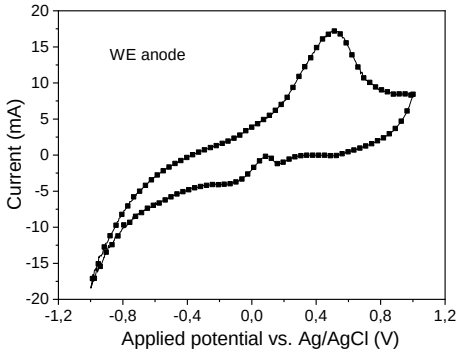

Figure 4. CV obtained for the MEC1, using Ag/AgCl as reference electrode 0.7V (galvanostatic acclimation as MFC).

3.3. Operation at 0.9 V and galvanostatic biofilm acclimation (as MFC)

In this set of experiments, the acclimation phase was performed galvanostatically, and the reactors operated as MFCs, for five successive cycles. After the acclimation period, a voltage of 0.9 V was applied and the operation of MECs was performed without addition of microorganisms. COD consumption and hydrogen production are presented in Figure 5 and the main characteristics of both MECs are given in Table 3.

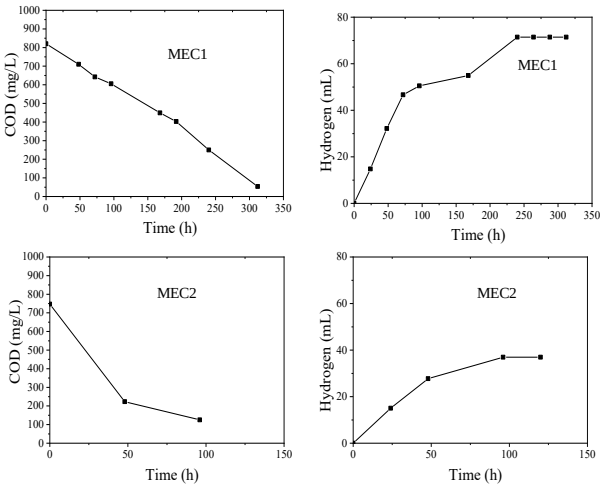

Figure 5. COD and hydrogen of MECs (MEC1 with CP and MEC2 with GG) under 0.9 V (galvanostatic acclimation as MFCs)

Table 3. Performance of MECs (MEC1 with CP and MEC2 with GG) under 0.9 V (galvanostatic acclimation as MFCs)

Characteristic	MEC1	MEC2
Volumetric hydrogen productivity, L/Ld	0.03	0.09
Y_{H2} yield, $gH_2/gCOD$	0.03	0.05
n_{th}, mmol	11.98	3.89
$Y_{H2,th,}$ %	24.4	38.89
Coulombic efficiency, %	50.8	65.3
Cathodic hydrogen recovery, %	48.0	59.6
Hydrogen recovery, %	24.4	38.9

The cyclic voltammogram received for the anodic electrode of MEC1 is presented in Figure 6. An oxidation peak is located at applied potential value ca. -0.17 V vs. Ag/AgCl whereas the maximum current value was ca. 6 mA.

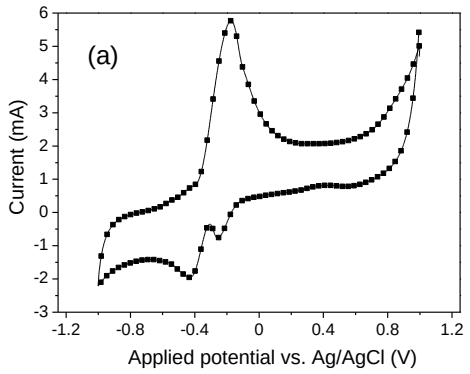

Figure 6. CV obtained for the MEC1, using Ag/AgCl as reference electrode- 0.9V (galvanostatic acclimation as MFC).

From all the above, it is obvious that biofilm acclimation phase is crucial for the MECs performance and specifically the galvanostatic operation (as MFC) for some successive cycles, enhances the electrocatalytic behavior of the MECs. In addition, operation at 0.9 V led to higher cathodic and overall hydrogen recovery, compared to 0.7 V. Finally, the use of GG is more effective for the overall MEC performance compared to the use of 2-Dimensional CP.

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