A novel tubular microbial electrolysis cell for high rate hydrogen production

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HIGHLIGHTS

• A double-chamber tubular MEC with low internal resistance (0.33 Ω) was designed.
• The pleated SS felt anode enabled a high current density and a low energy loss.
• A hydrogen production rate (7.1 L L⁻¹ d⁻¹) was achieved with 1 V voltage.
• The reactor showed high hydrogen recovery/purity and excellent operational stability.

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Abstract

Practical application of microbial electrolysis cells (MECs) for hydrogen production requires scalable reactors with low internal resistance, high current density, and high hydrogen recovery. This work reports a liter scale tubular MEC approaching these requirements. The tubular cell components (a platinum-coated titanium mesh cathode, an anion exchange membrane, and a pleated stainless steel felt anode) were arranged in a concentric configuration. The reactor had a low internal resistance (0.325 Ω, 19.5 mΩ m²) due to the high conductivity of the electrodes, a compact reactor configuration, and proper mixing. With acetate as electron donor, the MEC achieved a volumetric current density of 654 ± 22 mA L⁻¹ (projected current density, 1.09 ± 0.04 mA cm⁻²) and a volumetric hydrogen production rate of 7.10 ± 0.01 L L⁻¹ d⁻¹ at an applied voltage of 1 V. The reactor also showed high hydrogen recovery (~100%), high hydrogen purity (>98%), and excellent operational stability during the 3 weeks of operation. These results demonstrated that high hydrogen production rate could be achieved on larger scale MEC and this tubular MEC holds great potential for scaling up.

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1. Introduction

The microbial electrolysis cell (MEC) is an emerging technology for hydrogen production from biodegradable organic matter. In a MEC, exoelectrogenic bacteria oxidize organic matter into CO₂, protons, and electrons at the anode, and hydrogen evolution reaction takes place abiotically at the cathode [1]. The low operational potential of the microbial anode allows the MEC to start producing hydrogen by applying a substantially smaller cell voltage (≥0.2 V in practice) than in traditional water electrolysis (≥1.6 V) [2]. The gain of energetic efficiency induced by the use of a microbial anode is unfortunately tarnished by low current densities (i.e. H₂ production rate) in comparison with abiotic electrolysers. Since the first reports on MEC [3,4], numerous studies have investigated electrode materials and reactor configurations to reduce the capital cost and improve the performance of the system [5,6]. To the best of our knowledge, the maximum hydrogen production rates (HPRs) of small-scale (volume < 100 mL) and middle-sized (100 mL < volume < 1 L) MECs have reached 50 L L⁻¹ d⁻¹ [7] and 2.8 L L⁻¹ d⁻¹ [8], respectively, while for those larger than 1 L the HPRs have not exceeded 1 L L⁻¹ d⁻¹ [9]. The poor performance of larger MECs is largely attributed to the low electrode surface to reactor volume ratio, large internal resistances caused by the high resistance of carbon electrodes, and poor mass transfer in the larger reactor [10].

Based on the presence of a separating membrane, MEC reactors can be divided into double-chamber and single-chamber MECs. Most of the first designs included a membrane to favour high hydrogen recovery (i.e. faradaic efficiency) and hydrogen purity. However, these systems require a higher applied voltage to reach substantial current density because of their high internal resistance.
and pH difference across the membrane [3,11]. Removing the membrane could not only solve these issues but also simplify the reactor design and reduce the capital cost [12]. Hence, a variety of single-chamber MECs have been designed. However, a major drawback of single-chamber MECs is the hydrogen consumption by microorganisms such as methanogens [13,14], electrogens [15] and homoacetogens [16,17], especially for long-term operation. For example, methane rather than hydrogen dominated the gas production in a pilot single-chamber MEC [18]. Therefore, a membrane appears necessary to achieve a high production rate of pure hydrogen in MECs.

In order to reduce the internal resistance and the mass transfer limitations in a scalable double-chamber MECs, we have designed a novel tubular MEC reactor (total working volume 1 L). The tubular configuration allows to optimize the ratio of membrane and electrode surface area to reactor volume. In addition, a pleated and tubular stainless steel (SS) fiber felt was fabricated as the anode. We assumed this 3D-structured electrode would improve the volumetric current density of the MEC. Furthermore, it is also expected that the excellent conductivity of the SS felt could also reduce the ohmic resistance of the system. Our results demonstrated that these novel electrode and reactor design dramatically enhances the HPR and hydrogen recovery.

2. Materials and methods

2.1. Reactor design and construction

The MEC design can be seen in Fig. 1, photos of each reactor component are provided in the Supporting Information (Fig. S1). The MEC consisted of a jacketed glass vessel (inner diameter (ID) 9 cm, height 17 cm, working volume 1 L), a tubular anion exchange membrane (diameter 6 cm, height 15 cm, AMI-7001T, Membranes International, USA), and a custom-made Perspex reactor cap. The anode was made of 316L stainless steel fiber felt (SS felt, 40 cm × 15 cm × 1 mm, 100 μm filtering rate, Lier Filter Ltd, China). To fit in the reactor, the felt was folded into a pleated configuration with 40 layers (1 cm per fold along the length) and rolled into a tube (outer diameter (OD) 8.5 cm, ID 7.5 cm, height 15 cm). To further improve the mass transfer, 11 macro holes (5 mm diameter) were evenly drilled on each SS felt layer. The SS felt tube was finally treated in a Muffle furnace at 600 °C for 5 min under air as described before to improve its bio-compatibility toward electro-active biofilm [19]. The tubular membrane was plugged onto the central tube (OD 6 cm, ID 5 cm) of the reactor cap and the joint area (height 1 cm) was sealed by butyl tape. The other end of the tubular membrane was closed by a Perspex closing cap (height 1 cm, OD 6 cm), leaving the effective membrane height and surface area of 13 cm and 245 cm², respectively. The cathode was a platinum coated titanium mesh tube (OD 5 cm, height 15 cm, mesh thickness 1.2 mm, mesh hole size 3 mm × 6 mm, platinum coating thickness 1 μm). The reactor cap and the glass vessel were clamped together with a rubber O-ring in between as the sealing material. Four openings on the reactor cap were used for the reference electrode (RE, Ag/AgCl, 3M KCl), the pH probe, the anolyte inlet, and the anolyte outlet. All potentials reported are referred to the Ag/AgCl RE. The top opening of the cathode chamber was closed by a rubber stopper. A glass tube passing through the center of the stopper was used to collect the gas produced.

2.2. Startup and operation

The medium used in this study was a modified M9 medium which contains 6 g L⁻¹ Na₂HPO₄, 3 g L⁻¹ KH₂PO₄, 0.5 g L⁻¹ NH₄Cl, 0.5 g L⁻¹ NaCl, 0.1 g L⁻¹ MgSO₄·7H₂O, 14.6 mg L⁻¹ CaCl₂, and 1 mL L⁻¹ of a mixed trace element solution [20]. The medium was

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Fig. 1. Schematic sectional view (a) and top view (b) of the tubular MEC.
sparged with nitrogen gas for 30 min and adjusted to pH 8 before use. The anodic chamber was filled with 600 mL of medium with 4 g L\(^{-1}\) (48 mM) sodium acetate as the electron donor for the electroactive bacteria, and the cathodic chamber was filled with 350 mL of the same medium without adding acetate. The anodic chamber was inoculated with 50 mL (8 vol%) fresh anodic effluent of an existing acetate-fed bioelectrochemical system dominated by *Geobacter* spp. A magnetic stirrer was used to mix the anolyte continuously at a speed of 350 rpm. The internal temperature was controlled at 35 °C by hot water recirculation in the heating jacket. The potential of the anode was initially set at −0.2 V vs. Ag/AgCl and the current generation was recorded by a VSP Potentiostat (Bio-logic, France). When the current of the reactor exceeded the limit of the potential (400 mA), the reactor was controlled by a power supply (LABPS3005D, Velleman, Belgium) with an applied voltage of 1 V unless otherwise stated. The current was then recorded by the software of the power supply (LABPS3005D PC software V2.5) and the operating potential of each electrode was simultaneously collected by the potentiostat in open circuit potential mode. The reactor was run in fed-batch mode. Once the current decreased below −10% of the previous maximum current because of acetate depletion, 20 mL of medium with 200 g L\(^{-1}\) sodium acetate was added to the anodic chamber. Small volumes of medium were periodically added to the cathodic chamber to compensate for the water consumption induced by hydrogen evolution and hydroyde migration to the anodic compartment.

### 2.2. Analyses

The gas production rate was measured with a water displacement column (filled with pH 2 H\(_2\)SO\(_4\) solution). The gas composition was analyzed on a Compact GC (Global Analyser Solutions, Breda, The Netherlands), equipped with a Molsieve 5A pre-column and Porabond column (CH\(_4\), O\(_2\), H\(_2\) and N\(_2\)) and a RT-Q-bond pre-column and column (CO\(_2\), N\(_2\)O and H\(_2\)S). Concentrations of gases were determined by means of a thermal conductivity detector. The carrier gases were N\(_2\) for H\(_2\) channel and He for all other gases. The detection limit for these gases was 100 ppmv.

### 2.4. Calculations

The performance of the MEC was evaluated with different parameters (details of calculation provided in SI):

- **volumetric current density** \(j_v\), mA L\(^{-1}\): the current normalized by the total reactor volume (1 L);
- **projected current density** \(j_{pr}\), mA cm\(^{-2}\): chosen as the current normalized by the projected surface area of the anode before folding (600 cm\(^2\));
- **volumetric HPR** \(Q_{\text{HPR}}\), L L\(^{-1}\) d\(^{-1}\): the HPR normalized by the total reactor volume (1 L);
- **hydrogen recovery** \(r_{H_2}\), %, or faradaic efficiency: the amount of H\(_2\) actually recovered from the cathodic compartment divided by the amount of H\(_2\) which is theoretically possible to produce (for a specific amount of charge crossing the MEC);
- **electrical energy recovery** (EER, %): the ratio of the energy content of the hydrogen produced (based on its heat of combustion) to the electrical energy required for its generation;
- **total energy recovery** (TER, %): the energy content of the hydrogen produced divided by the sum of the electrical energy required and the energy content (heat of combustion) in the acetate consumed.

The cell internal resistance and the uncompensated resistances between the reference electrode and the anode (or cathode) were assessed by the current interrupt method with 10 successive current steps of 200 mA/OCV at a frequency of 10 Hz. The internal resistance was reported in both apparent internal resistance \(R_{\text{apparent}}, \Omega\) and normalized internal resistance \(R_{\text{normalized}}, \Omega \cdot \text{m}^2\), where \(R_{\text{normalized}}\) was the product of \(R_{\text{apparent}}\) and the projected surface area of the anode (600 cm\(^2\)). The actual anode/cathode potential \(E_{\text{measured}}\) was calculated by removing the ohmic drop contribution to the measured anode/cathode potential \(E_{\text{real}}\). The electrode surface overpotential \(\eta\) at a specific current was the potential difference (in absolute value) between the \(E_{\text{real}}\) and the open circuit potential (OCP) [21]. Details of the calculations are provided in the Supplementary data (S-1).

### 3. Results and discussion

#### 3.1. Current and hydrogen production

Fig. 2 shows the current production of the MEC over a period of one month. The reactor was firstly controlled by the potentiostat with an applied anode potential of −0.2 V vs. Ag/AgCl. The current of the reactor gradually increased in the first week and exceeded the current limit of the potentiostat (400 mA) on day 7. Then, the reactor was controlled by a power supply at an applied voltage of 1 V until the end of the experiment except between day 14 and day 17 while the impact of voltage on the current was tested. After 3 fed-batch cycles, the reactor produced reproducible maximum current densities averaging at 654 ± 22 mA L\(^{-1}\) (1.09 ± 0.04 mA cm\(^{-2}\), \(n = 12\) batches) during the following two weeks. During the intervals of maximal current, the HPR reached a maximum of 7.06 ± 0.24 L L\(^{-1}\) d\(^{-1}\) at an applied voltage of 1 V. The maximum current density of the reactor slightly decreased in the last week of operation to 536 ± 26 mA L\(^{-1}\) (0.89 ± 0.04 mA cm\(^{-2}\), \(n = 5\) batches). Consequently, the maximum HPR decreased to 5.78 ± 0.28 L L\(^{-1}\) d\(^{-1}\) in the last four days of operation. The purity of the hydrogen gas was always higher that 98%. The remaining 2% were nitrogen and oxygen likely introduced during the sampling and measuring process. The decrease and stabilization of the current has been observed on this type micro-porous microbial anode [22]. It is also found in our long-term running MEC with the same SS felt anode that partially brushing out a fraction of biofilm from the anode allows the MEC to recover its current density (data not shown). Therefore, the decrease of the current in the end of the operational period could be attributed to the partial clogging of the micro-pores by the biofilm, hindering good mass transfer of substrate and products. The pore dimension of the material could be optimized to limit the impact of this phenomenon. The impact of pore dimension on the current density and hydrogen production rate should also be studied. Moreover, during long-term operation, nutrient limitation (e.g. nitrogen source limitation) could also be used to inhibit the overgrowth of biofilm.

#### 3.2. Impact of the applied voltage on the performance

Fig. 3 displays the impact of the cell voltage on the volumetric current density, the recorded potential of the electrode (i.e. including the ohmic drop contribution), the HPR, and the hydrogen recovery. The data reported here were recorded during two time intervals when the current was maximal (acetate saturation for the microbial metabolism). These recordings are presented in Fig. S2 for the evolution of current and electrode potentials. The open circuit voltage of the cell was recorded at 0.465 V. The minimum voltage required for generating substantial current production (0.01 mA cm\(^{-2}\)) was −0.55 V. The current density increased quickly with the applied voltage and reached a
maximum of 658 ± 4 mA L⁻¹ (1.10 ± 0.01 mA cm⁻², n = 2) for the maximum voltage (1 V). The evolution of the recorded potentials of the anode and cathode with the voltage are also presented on Fig. 3a. At a voltage of 1.0 V, the recorded anode potential was −0.38 ± 0.01 V. This value is close to the apparent midpoint potential E₁/₂ of the redox cofactors (c-type cytochromes, −0.35 V) involved in the charge transfer from anodic electroactive biofilms to solid-state electrodes [23,24]. This electron transfer is quasi-reversible implying that the current generated at an electrode potential E = E₁/₂ is approximately half of the maximum one that can be generated (typically reached for E ≥ −0.2 V [19]). This means that at 1 V, the reactor is approximately at half of its maximum capacity in term of microbially-driven current production. However, considering the loss of the energy efficiency (vide infra) when increasing voltage, no voltage higher than 1.0 V was applied to the reactor.

The HPR increased almost linearly with the current (Fig. 3b). From 0.55 V to 1 V, it increased from 0.05 ± 0.01 L L⁻¹ d⁻¹ to 7.10 ± 0.01 L L⁻¹ d⁻¹. To the extent of our knowledge, this is the first time that a MEC reactor of a liter-scale reaches a HPR that is higher than 1 L L⁻¹ d⁻¹ at a voltage not exceeding 1 V. The hydrogen recovery increased from 77.6 ± 1.7% to 99.5 ± 0.2% when the applied voltage increased from 0.55 V to 0.7 V. Under higher voltages, the hydrogen recovery was steady around 100%. These results demonstrate that the tubular double chamber MEC allows high hydrogen product rate at maximum hydrogen recovery.

3.3. Energy recovery

Fig. 4 shows the impact of the applied voltage on the electrical energy recovery (EER) and total energy recovery (TER). The EER decreased from 209 ± 5% to 149 ± 1% as the voltage increased from 0.55 V to 1.0 V. However, the TER firstly increased from 69 ± 1% to 81 ± 0% when the voltage increased from 0.55 V to 0.7 V and then decreased to 70 ± 0% when the voltage further increased to 1.0 V.
An applied voltage of 0.7 V corresponds to an electrical energy cost of 1.56 kWh m\(^{-3}\) \(\text{H}_2\), which is far below the typical values required by abiotic water electrolysis (~5 kWh m\(^{-3}\) \(\text{H}_2\)) [25]. However, running at this lower voltage would dramatically decrease the HPR, so the reactor was still running at 1.0 V after day 17 and the rest of the operational period (2.23 kWh m\(^{-3}\) \(\text{H}_2\)).

In this study, the power consumption of the mixing (magnetic stirrer) was close to the power consumption of the electrolysis (~6.5 W). This power consumption is already much lower than recirculating the electrolyte with a pump, but if this part of energy was taken into account in the calculation, the energy recovery of the MEC will be reduced by half. It was observed in the experiment that failure of the stirring caused about 30% loss of the current density, which indicates that the continuous stirring is crucial to maintain the high current density. Therefore, to scale up this reactor design for practical application, more energy-saving mixing methods need to be introduced.

3.4. Voltage distribution

The OCV of this tubular reactor (0.465 V) is much higher than those typically reported for single-chamber MECs (normally ~0.114 V [12]). The higher OCV of the two-compartment reactor is caused by the large pH difference across the membrane (4 pH unit, accounting for an extra voltage of 0.244 V at 35 °C according to the Nernst equation). A substantial junction potential across the membrane is unexpected since the ionic compositions of the anolyte and catholyte are similar. Current interruption measurements indicated that the ohmic resistance between anode and RE (\(R_{\text{anode}}\)) was 0.075 \(\Omega\) (4.5 m\(\Omega\) m\(^2\)), and that between RE and cathode (\(R_{\text{cathode}}\)) was 0.25 \(\Omega\) (15 m\(\Omega\) m\(^2\)). Hence, the reactor total internal resistance (\(R_{\text{total}}\)) was 0.325 \(\Omega\) (19.5 m\(\Omega\) m\(^2\)) (Fig. S3). The low internal resistance can be attributed to the high conductivity of the electrode materials, the compact reactor design. Based on these values, the actual electrode potentials, electrode surface overpotentials, and the ohmic voltage loss were calculated. Details of the calculations can be seen in the Supplementary data (S-1).

Fig. 5 displays the evolution with the current of the voltage repartition between the minimal voltage requirements (OCV), the surface overpotentials (\(\eta_{\text{an}}\) and \(\eta_{\text{cat}}\)), and the ohmic drop. The ohmic drop logically increased with the current and maximally accounted for 21% of the total voltage at 1 V. Both the \(\eta_{\text{an}}\) and \(\eta_{\text{cat}}\) increased relatively sharply at the beginning of the current production (activation) and then slowly rose with the current in a similar manner. The maximum overpotentials (at 1 V) were reasonably low and similar for the anode (0.13 V) and cathode (0.14 V), reflecting a well-balanced electrochemical cell (no anodic or cathodic process strongly limiting). Introducing catholyte mixing or active \(\text{H}_2\) harvesting by vacuum [26] at the cathode might further improve the performance of the MEC by limiting \(\text{H}_2\) bubble accumulation on the electrode (and the subsequent extra resistance) and decreasing \(\text{H}_2\) partial pressure (favoring the thermodynamic of the process). Further optimization in the reactor design could improve the performances, such as decreasing the average cathode/anode distance or increasing the ratio of electrode surface area over reactor volume. Using a more conductive electrolyte would also reduce the ohmic loss. The most considerable bottleneck of the current setup is the high capital cost involved by the use of the platinum-containing cathode. However, it has been shown that nickel foam also present low hydrogen evolution overpotential at a much cheaper price while conserving good stability under alkaline conditions [7]. Thus, using nickel foam as cathode might further enhance the HPR and significantly reduce the capital cost of the system.

3.5. Comparison to other high-performance MECs

Table 1 lists the performances of the most efficient MECs currently reported. The majority of the MECs studies were conducted with reactor volumes below 100 mL. Table 1 shows the best performances reported so far for each reactor configuration. The highest HPR (50 L L\(^{-1}\) d\(^{-1}\)) was achieved on a 40 mL double chamber flow cell reactor [7], while the maximum HPR of MECs larger than 100 mL (2.8 L L\(^{-1}\) d\(^{-1}\)) was also obtained on a flow cell reactor with a reactor volume of 560 mL [8]. The high performance of these reactors can be attributed to the compact reactor design and vigorous flowing of the electrolyte through the electrode (e.g. enhanced mass transfer). The maximum HPR achieved in this study was 7.10 L L\(^{-1}\) d\(^{-1}\), which is about 2.5 times higher than that of the aforementioned 560 mL flow cell MEC reactor. This HPR is also more than 3.5 times higher than that of the reported best performance tubular MEC reactor (18 mL, 2.0 L L\(^{-1}\) d\(^{-1}\)) [27].

The operational temperature for this study (35 °C) was 5 °C higher than most studies presented in Table 1 (30 °C). However, it has been demonstrated that the current density of the anodic biofilm only decreased about 10% with decreasing temperature from 35 °C to 30 °C [40]. Thus, the good performance of this reactor can be mainly ascribed to the novel electrode and reactor designs. Compared to the existing tubular MEC designs, this novel tubular reactor design and the configuration of the modified SS felt anode allowed to achieve a higher electrode surface to reactor volume ratio (600 cm\(^2\)/L). The magnetic stirring and the macro-porous structure on the SS felt anode ensured a proper mixing in the anode chamber. The conductivity of the modified SS felt anode is much higher that traditional carbon-based anodes. Moreover, the average distance between the anode and cathode was reduced to 6 mm. The presence of the AEM membrane ensured a sterile environment of the cathode (due to high pH) and a high hydrogen recovery (100%). Therefore, extremely low internal resistance, high volumetric current density, and high hydrogen production rate were achieved on this new tubular MEC reactor. The reactor can be further scaled up by extending the length of the tubular components or by assembling series of tubular modules in a large tank. The capital cost of the reactor could be lowered by replacing the Pt-coated titanium mesh with nickel foam. In summary, this tubular MEC design holds great potential for practical application, more energy-saving mixing methods need to be introduced.
Another crucial step in the development of MECs is their efficiently good energetic efficiency. This study identified the best preforming MEC among all the MEC reactors larger than 100 mL and appears to be scalable. Further studies should be carried on to assess how to maintain long-term stability of the reactor performances. Further studies should also assess the ability of MECs to efficiently convert the energy contained in different organic waste stream rather than from ideal acetate solutions. Another crucial step in the development of MECs is their efficient upscaling at lower capital cost without jeopardizing their inherently good energetic efficiency.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.03.029.

References


