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Microbial Electrolysis Cells for High-yield Biohydrogen Production from Fermentable Substrates

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A microbial fuel cell (MFC) can be used to generate electrical current from the breakdown of organic matter by bacteria. Bacteria on the anode oxidize the organic matter, releasing electrons to the anode. Current flows to the cathode, where electrons combine with protons in the water and oxygen to form water. The voltage that is generated is about 0.5 V. The reaction is thermodynamically favourable, and so far a variety of biodegradable substrates have been used to generate electrical power, including pure compounds such as acetate and glucose [1, 2], as well as complex wastewaters from humans, animals and industry [3-5].

A microbial electrolysis cell (MEC) is a modified microbial fuel cell that can produce hydrogen gas at the cathode from the current generated by bacteria during the breakdown of organic matter [6]. Using an MEC it is possible to produce hydrogen gas at much higher yields than that possible by fermentation.

We conducted experiments here using a cube-shaped reactor consisting of a 4-cm long cylindrical chamber formed in a solid block of Lexan, with a liquid volume of 28 mL [7], as shown in Figure 1. The anodes used in these MECs were graphite fiber brush electrodes [8] pre-treated using an ammonia gas process [9]. Cathodes were flat carbon cloth containing a Pt catalyst (10% Pt/C) on the anode-facing side of the electrode. Gas produced in the reactor is collected in a glass anaerobic tube cut at the bottom and sealed to the top of the reactor. The top of the tube contains a thick rubber stopper and an aluminum crimp top. A needle pierces the stopper, allowing gas to leave through tubing, flowing through a respirometer for gas measurement.

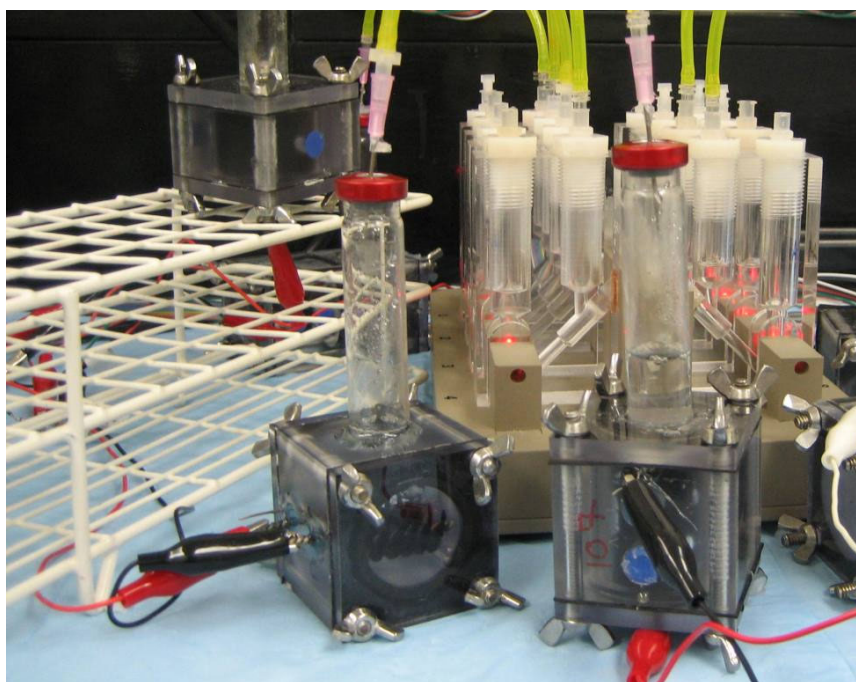


Figure 1: MEC reactor shown with tubing and bubble meters used to measure gas production in the reactor.

MEC tests with glycerol and glucose. Tests were conducted with two different fermentable substrates. In one set of tests we examined the use of glycerol, which is a side product of biodiesel fuel production. The production of 10 liters of biodiesel fuel results in the production of 1 liter of glycerol, and thus the production of useful products from glycerol is needed to make biodiesel production more economically viable as a renewable fuel. Tests were run using glucose as a positive control for hydrogen production from an easily fermentable substrate.

Dark fermentation tests were initially conducted to determine the amount of hydrogen that could be produced without the MEC. In fermentation tests, we achieved from glycerol a total of 0.28 mol-H₂/mol-glycerol, or only 4% of that possible by stoichiometric conversion of glycerol to hydrogen gas (a maximum of 7 mol/mol) [10]. With glucose we obtained 1.06 mol/mol compared to a maximum of 12 mol/mol.

In MEC tests using glycerol, we obtained 3.9 mol-H₂/mol-glycerol (56% of the maximum theoretical yield) [11]. This was comparable to that obtained with glucose, where we obtained 7.2 mol-H₂/mol-glucose (59% of the theoretical maximum). These percentage yields are both lower than those obtained with non-fermentable substrates such as acetate, where we can obtain up to 98% of the theoretical yields using an MEC [12]. To increase hydrogen yields it should be possible to use a two-stage process, where we can have fermentation in the first stage in order to maximize hydrogen production by fermentation, followed by a second stage using the MEC as described below.

Cellobiose and lignocellulose. Tests were conducted using a two stage process with cellobiose and lignocellulose. With cellobiose, we obtained in the first stage 1.64 mol H₂/mol-hexose-equivalent using *Clostridium thermocellum* for cellobiose fermentation [13]. In the

second stage, we achieved the equivalent of 2.9 mol H₂/mol for the mixture of the specific substrates in the feed using an MEC, or the equivalent of 8.31 mol H₂/mol for the MEC based on the starting substrate. Taken together, this is equivalent to 9.95 mol/mol overall for the two-stage process with cellobiose. Hydrogen yields and production rates using an actual fermentation effluents with lignocellulose were 750 ± 180 mL/g-COD and 1.00 ± 0.19 L/L-d (lignocellulose) [13]. These results show a two-stage system is a promising approach for biohydrogen production using fermentable substrates.



Figure 2: Photograph of a 1000-liter MEC being tested for hydrogen production using wastewater from a winery.

Field tests. The next step in development of this process is to examine the performance of larger scale systems. A 1000 liter reactor was recently constructed using graphite fiber brush anodes. The cathodes were made of stainless steel, based on our findings that stainless steel was able to catalyze hydrogen evolution at the cathode, and recent successes in using high surface area cathodes. Results for the field test will be presented at this meeting.

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