Critical Review

# Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter

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*Received June 5, 2008. Revised manuscript received September 19, 2008. Accepted September 25, 2008.*

The use of electrochemically active bacteria to break down organic matter, combined with the addition of a small voltage (>0.2 V in practice) in specially designed microbial electrolysis cells (MECs), can result in a high yield of hydrogen gas. While microbial electrolysis was invented only a few years ago, rapid developments have led to hydrogen yields approaching 100%, energy yields based on electrical energy input many times greater than that possible by water electrolysis, and increased gas production rates. MECs used to make hydrogen gas are similar in design to microbial fuel cells (MFCs) that produce electricity, but there are important differences in architecture and analytical methods used to evaluate performance. We review here the materials, architectures, performance, and energy efficiencies of these MEC systems that show promise as a method for renewable and sustainable energy production, and wastewater treatment.

## 1. Introduction

Most hydrogen gas produced in the world today is made from fossil fuels, resulting in the uncontrolled release of carbon dioxide that contributes to climate change. Renewable hydrogen production is possible by water electrolysis using energy gained from renewable sources such as wind, solar or biomass, but the energy requirements are high (5.6 kWh/$m^3H_2$) and typical electrolyzer energy efficiencies are only 56−73% (*1*). Algae and photosynthetic bacteria can use sunlight to autotrophically make hydrogen gas from water, but efficiencies are currently low and most experts believe the process may never be feasible because of the large surface area requirements for the process (*2*). Carbohydrates, such as glucose and polysaccharides such as starch and cellulose, can be fermented by certain bacteria to hydrogen gas at average rates of 2.5 ± 4.3 $m^3/m^3d$ (*3*). However, hydrogen yields usually vary from 0.57−2.2 mol $H_2$/mol hexose and have a theoretical upper limit of 4 mol $H_2$/mol hexose despite a stoichiometric potential of 12 mol $H_2$/mol hexose (*3*). Fermentation results in a variety of soluble organic byproducts. Conversion of these byproducts to useful amounts of hydrogen requires endothermic reactions, and thus these molecules cannot be further converted to hydrogen without an external energy input. One method used by bacteria depends on sunlight (*2*). Phototrophic hydrogen production from volatile acids has been extensively reviewed by others (*4*). Disadvantages of phototrophic hydrogen production, however, are similar to those observed for algae and photosynthetic bacteria, i.e., low solar efficiencies and high costs associated with the large surface areas that are required.

It was independently discovered by two different research groups a few years ago that bacteria could be used to make hydrogen gas in an electrolysis-type process based on microbial fuel cells (MFCs) (*5*–*7*). In an MFC, bacteria oxidize organic matter and release carbon dioxide and protons into solution and electrons to an electrode (anode) (*8*). The electrons flow from the anode through an electrical circuit to the counter electrode (cathode) where they are consumed in the reduction of oxygen. When oxygen is present at the cathode, current can be produced, but without oxygen, current generation is not spontaneous. However, if current generation is forced in this situation by applying a small voltage (>0.2 V in practice) between the anode and the cathode, hydrogen gas is produced at the cathode through the reduction of protons (Figure 1). Different nomenclatures for the process, microorganisms, and the reactor have been used. Here, we modify the scheme used for methane production (methanogenesis, methanogens, and anaerobic digestors). We call the process electrohydrogenesis or microbial electrolysis, the bacteria are exoelectrogens, as they release electrons instead of hydrogen in this process, and the reactors are called microbial electrolysis cells (MECs) (*9*–*11*). The MEC has previously also been referred to as a biocatalyzed electrolysis cell (BEC) or a bioelectrochemically assisted microbial reactor (BEAMR) (*5, 7, 12*–*15*). We define the process as electrohydrogenesis or microbial electrolysis to emphasize that in an MEC there is an electrically driven hydrogen evolution process that is distinct from fermentation.

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10.1021/es801553z CCC: $40.75

Published on Web 11/01/2008

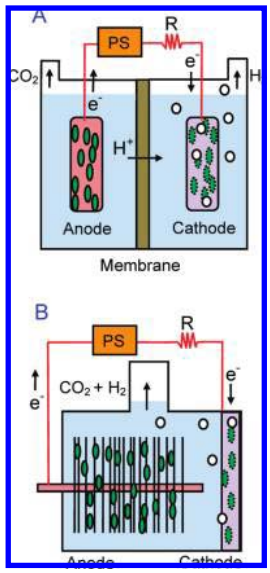


**FIGURE 1. Schematics of (A) two-chamber (flat anode) and (B) single-chamber membraneless (brush anode) MECs. Bacteria (green ovals) grow on the anode and donate electrons but can also function as the biocatalyst on the cathode (dotted green ovals). In a two-chambered MEC, $CO_2$ is collected in the anode chamber headspace and $H_2$ in the cathode headspace. In a single-chamber configuration, both gases are collected in the same headspace. Power supply (PS) for applying voltage to the cell, with an optional external resistor (R) for determining the current.**

The MEC is an *electrolysis* reactor that produces hydrogen, while an MFC is a *fuel cell* that produces electricity (*15*).

MECs are a new technology, and thus many researchers may be unfamiliar with the construction of these reactors and factors that can affect performance. MECs share many attributes with MFCs because the design of the anodes and the electrogenic reactions occurring there are similar. A previous review of MFCs provides a good background on the construction and operation of these electricity-producing systems (*8*). Hydrogen evolution at the cathode in an MEC results in many design and operational differences compared to an MFC. For example, air is not needed in an MEC. This simplifies cathode design, but since the product is a gas rather than electricity, the architecture must be modified for collecting this gas. While oxygen diffusion into an anode chamber can substantially reduce recovery of electrons from substrate as current (Coulombic efficiency, $C_E$) in an MFC, the lack of oxygen in an MEC results, on average, in greater electron recoveries (*8, 15*). Growth of strict anaerobes is better enabled in a fully anoxic MEC, but a lack of exposure of the microorganisms to oxygen will enhance the likelihood for methanogenesis, which can lower hydrogen recoveries (*7, 11*). In this review, we focus on these unique aspects of MEC designs, attributes, and performance, paying particular attention to the factors that make them distinct from MFCs.

## 2. MEC Systems

**2.1. Microorganisms.** Compared to MFCs, little is known about the composition of the microbial communities in MECs. The only study of a community analysis of an MEC found that *Pseudomonas* spp. and *Shewanella* spp. were present on the anode (*16*), consistent with some findings for MFCs (*17*). Microorganisms are observed to be attached to the cathode in an MEC, but to what extent they affect the function of the MEC is not clear. It was shown that enrichment of microorganisms on a graphite felt cathode achieved hydrogen evolution at rates similar to that of a Pt-catalyzed cathode, but the microbial community of this cathode was not examined (*18*).

Both MFCs and MECs enhance the growth of exoelectrogenic bacteria. However, MFCs usually have air-cathodes which results in oxygen diffusion into the anode chamber. The presence of oxygen can inhibit the growth of obligate anaerobic microorganisms. MECs operate under completely anaerobic conditions and therefore promote the growth of obligate anaerobic bacteria such as exoelectrogenic *Geobacter* spp., as well as nonexoelectrogenic fermentative or methanogenic microorganisms. Thus, microbial communities in MECs may be different from those in MFCs.

It is not clear to what extent the operation of an MEC is affected by the inoculum source. Wastewater has a high concentration of bacteria and is used as the inoculum in most studies (*5, 7, 14*). In one study, a soil inoculum was found to provide a good source of microorganisms capable of cellulose degradation (*10*). A common practice for enriching a bacterial community for an MEC is to operate an MFC and then transfer the anode into and MEC (*5, 11*). This procedure ensures biofilm formation on the anode and preselects an exoelectrogenic community for MEC operation. Alternatively, the effluent from an MFC/MEC containing exoelectrogenic bacteria (presumably displaced from the anode) can be used as an inoculum (*10, 19, 20*), or biofilm can be scraped from the anode and transferred to a new electrode. Some reactors can operate as either an MFC or MEC based on whether air is added to the cathode chamber and thus can be switched between these two modes of operation (*6, 14*). It is not clear at this time if there are advantages or disadvantages in developing the biofilm first in an MFC or just directly adding an inoculum to the MEC.

Methanogenesis can be a problem in MECs (*11, 21*). High concentrations of hydrogen gas favors the growth of methanogens, which reduces hydrogen gas production and contaminates the gas with methane. Rozendal et al. (*18*) found that use of a bicarbonate buffer with a biocathode encouraged the growth of hydrogenotrophic methanogens that used the buffer as a carbon source. By removing this buffer from the medium, they greatly reduced conversion of hydrogen to methane by microbes on the cathode. Oxygen exposure is another method used to inhibit methanogens. Call and Logan (*11*) showed in a membrane-less MEC, at an applied voltage ($E_{ap}$) of 0.6 V, that exposing the electrodes to air in between batch cycles reduced methane concentrations to <1% in the product gas and did not impact current densities. In contrast, a lack of air exposure at the same applied voltage resulted in methane concentrations of 3.4% or more. Long operation cycles needed for a low applied voltage ($E_{ap}$ = 0.2 V) also stimulated methane production (methane concentration >28%) and resulted in poor reactor performance for hydrogen generation. Exposure of the reactor biofilms to air may be useful in some cases, but strictly anaerobic conditions may be needed for certain substrates (e.g., cellulose). Furthermore, aeration of a reactor containing hydrogen could create the potential for explosive mixtures of hydrogen and oxygen. Other techniques for controlling the growth of methanogens in MECs need to be investigated, such as lowering pH, heat shocking of the inoculum, and operation at short retention times (*3, 22*). Alternatively, an MEC can be combined with an anaerobic digestor to obtain a product gas rich in both hydrogen and methane (*23*).

**2.2. MEC Materials.** *Anode.* The same materials used for anodes in MFCs can also be used in MECs (*8*). Anode materials used in MECs include carbon cloth (*5*), carbon paper (*14*), graphite felt (*7, 19*), graphite granules (*10, 14*), and graphite brushes (*11*). Suppliers of carbon materials include E-TEK (Somerset, NJ), Graphite Electrode Sales (USA), FMI Composites Ltd. (UK), National Electrical Carbon BV (The Netherlands), and Alfa Aesar (Germany). When graphite

**TABLE 1. Performance of MECs Reported in Various Studies**

| study | total reactor liquid volume (L) | substrate | applied voltage, $E_{ap}$ (V) | $H_2$ production rate, $Q$ ($m^3/m^3$day) | overall $H_2$ Yield, $Y_{H2,th}$ (%) | energy input (kW h/$m^3$) |
|---|---|---|---|---|---|---|
| Liu et al. (*5*) | 0.03 | acetate | 0.45 | 0.37 | 61 | 1.0 |
| Rozendal et al. (*7*) | 6.6 | acetate | 0.5 | 0.02 | 53 | 1.9 |
| Ditzig et al. (*14*) | 0.58 | wastewater | 0.5 | 0.01 | 9.8 | 2.5 |
| Cheng and Logan (*10*) | 0.04 | acetate | 0.6 | 1.1 | 88 | 1.3 |
| Hu et al. (*32*) | 0.3 | acetate | 0.6 | 0.69 | 64 | 1.4 |
| Call and Logan (*11*) | 0.03 | acetate | 0.8 | 3.12 | 93 | 1.7 |
| Rozendal et al. (*19*) | 3.3 | acetate | 1 | 0.3 | 23 | 2.2 |

granules are used, a graphite rod is inserted into the bed of granules as a current collector. For a graphite brush, the two twisted wires of a conductive and noncorrosive metal (such as titanium or stainless steel) holding the cut carbon fibers form the anode (*24*). For the other materials, the electrode is pressed (or glued using epoxy) to an insulated wire.

To increase the anode performance, these carbon materials can be pretreated with a high temperature ammonia gas process (*25*). Ammonia gas treatment results in a faster start-up and increased current densities in MFCs, which is thought to be caused by the more favorable adhesion of microorganisms to the positively charged anode and to improved electron transfer to the chemically modified surface.

*Cathode.* Hydrogen production in an MEC occurs at the cathode. The hydrogen evolution reaction (HER) on plain carbon electrodes is very slow, requiring a high overpotential to drive hydrogen production. To reduce this overpotential, platinum is usually used as the catalyst. Platinum catalyzed electrodes are commercially available (e.g., E-TEK, USA; Magneto Special Anodes, The Netherlands; Alfa Aesar, Germany) but are also easily prepared in the laboratory (*26, 27*) by mixing commercially available platinum (e.g., 10 wt % Pt/C, E-TEK) with a chemical binder (5% Nafion solution or 2% PTFE solution). This forms a paste that is applied to one side of the cathode, such as carbon paper, and then dried (24 h) at room temperature before being used. The platinum loading can be varied by changing the mass of Pt in the paste.

There are many disadvantages to using platinum, including the high cost and the negative environmental impacts incurred during mining/extraction (*28*). Furthermore, platinum can be poisoned by chemicals such as sulfide, which is a common constituent of wastewater. It was recently discovered that the HER can be catalyzed by bacteria (i.e., in the absence of an inorganic metal catalyst) (*18*). Optimal methods to develop this "biocathode" have not been thoroughly investigated. The approach used by Rozendal et al. (*18*) was to first develop an electrochemically active culture by enriching a biofilm of hydrogen-oxidizing bacteria on the anode. By reversing the polarity of the electrode, they then obtained an active biocathode for hydrogen production. A second biocathode was inoculated using the effluent of the active biocathode, producing a similar current density. The use of biocathodes in MECs needs to be further investigated. The low cost and good performance may make a biocathode a viable replacement of platinum.

*Membrane.* Most MECs contain a membrane, although it is possible to develop a single-chamber membrane-less architecture (see below). A membrane is used to create a chamber where the microorganisms can degrade a substrate that is kept separated from the cathode (where the hydrogen is evolved). This configuration minimizes hydrogen losses to microbes on the anode and in the liquid and prevents mixing of the hydrogen product gas with carbon dioxide from the anode. In most MECs the cathode is immersed in solution to facilitate proton transfer to the electrode, creating a two-chamber system. The first MECs used a cation exchange membrane (CEM) such as Nafion 117 (Ion Power Inc., New Castle, DE) or Fumasep FKE (FuMA-Tech GmbH, Germany). During operation, however, cation species other than protons are responsible for the positive charge transport through the cation exchange membrane (*29–31*) because concentrations of $Na^+$, $K^+$, $NH_4^+$, and $Ca^{2+}$ in wastewaters (~pH 7) are typically present at concentrations 10 (*5*) times higher than the protons. As a result, protons consumed at the cathode are not replenished by protons generated at the anode. This leads to a pH increase at the cathode and a pH decrease in the anode chamber, resulting in a loss of voltage consistent with the Nernst equation. Other types of membranes examined include anion exchange membranes (AEMs; Fumasep FAB, FuMA-Tech GmbH, Germany; AMI, Membranes International, Glen Rock, NJ), a bipolar membrane (BPM; FumaSep FBM, FuMA-Tech GmbH, Germany), and a charge mosaic membrane (CMM; Dainichiseika Color&Chemicals, Co. Ltd., Japan) (*10, 19, 20*). The use of an AEM was recently found to substantially increase MEC performance (*10*), as it allows for the transport of negatively charged chemical buffers, such as phosphate and bicarbonate alkalinity, across the membrane. This transport helps to buffer pH changes in the two chambers (*31*). Using an AEM and a graphite granule anode, hydrogen was produced at a rate of 1.1 $m^3$ $H_2/m^3$ d ($E_{ap}$ = 0.6 V) (Table 1) (*10*).

*Tubing and Gas Collection Systems.* Loss of hydrogen gas through tubing or seals can be a major problem in laboratory tests, as hydrogen is a small molecule that easily permeates through tubing and connections. Thus, it is very important that the reactor design is gastight and there are proper seals. All tubing will leak hydrogen gas to some extent, with typical hydrogen diffusivities of $10^{-12}$ $cm^2/s$ for Teflon and $10^{-13}$ $cm^2/s$ for Viton. Small amounts of hydrogen can also diffuse from the cathode to the anode through a membrane (if present). This diffusional hydrogen loss is dependent on the hydrogen concentration across the membrane, and it will have a maximum rate (i.e., at 100% hydrogen at the cathode and no hydrogen at the anode) which can be estimated (*15*). At higher hydrogen production rates this loss through the membrane is small compared to the total hydrogen production (*7*).

**2.3. MEC Architecture.** Several different architectures have been tested for hydrogen generation in MECs (Figure 2). The very first systems were designed only for "proof of concept" and thus were not optimized for performance (Figure 2A and 2E) (*5, 7*). For example, the reactor used by Liu et al. (*5*) was a simple H-type reactor consisting of two glass bottles separated by a CEM, with gas collection and release from the cathode bottle headspace (Figure 2A). H-type systems have a high internal resistance caused by the large anode to cathode distance and the small size of the CEM (*8*). Increasing the anode surface area using graphite granules, and reducing the electrode spacing, did not increase performance as a result of the small CEM used in a larger reactor (Figure 2B). Performance was improved by increasing the size of the membrane relative to the electrode-projected

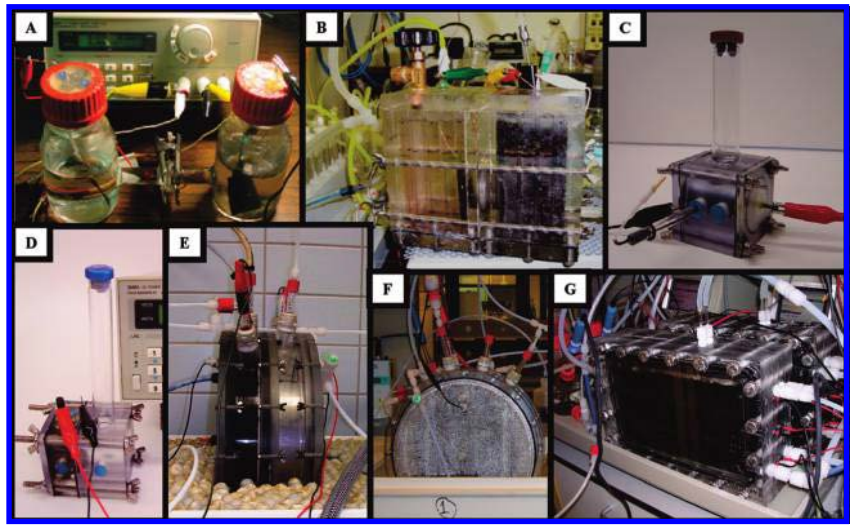


**FIGURE 2. MECs used in different studies. Four types used in fed-batch experiments: (A) H-type construction using two bottles (320 mL each) separated by a membrane (*5*); (B and D) two cube-type MECs (512 and 42 mL, respectively) where anode and cathode are separated by a membrane (*10, 14*); (C) cube-type single chamber (28 mL) MEC lacking a membrane (*11*). Three types used in continuous flow tests: (E) Disc-shaped two-chamber MEC (each chamber 3.3 L) (*7, 20*); (F) disk-shaped membrane electrode assembly MEC (3.3 L) with gas diffusion electrode (*19*); (G) rectangular-shaped MEC with serpentine-shaped flow channels through the reactor that allow the gas to be released at the top of each flow path (each chamber 280 mL) (*18*).**

surface areas (Figure 2D) (*10, 19*). Through combined use of graphite granules for the anode (high surface area), an anion exchange membrane (allowing charge transfer via phosphate buffer anions) in a cube-shaped reactor with a small electrode spacing resulted in a high current density and achieved increased hydrogen recovery and greatly improved performance (Figure 2D) (*10*).

The use of gas-diffusion electrodes in MFCs inspired Rozendal et al. (*19*) to examine an MEC design using a membrane electrode assembly. For this membrane electrode assembly (MEA) architecture, the membrane was integrated with the cathode and a platinum catalyst layer faced a gas collection chamber (Figure 2F) (*19*). This eliminated the liquid surrounding the cathode and reduced the reactor volume. An MEA was constructed using an electroless plating method developed by Millet et al. (*33*) to apply platinum (1.0 g/m$^2$) to one side of a CEM or AEM. Hydrogen was produced at a rate of 0.3 m$^3$ $H_2$/m$^3$ d ($E_{ap}$ = 1.0 V). The membrane pH effect was smaller with an AEM, but both membranes produced similar rates of hydrogen. The reactor was operated in continuous flow mode compared to batch mode in most other studies.

Another continuous flow reactor architecture was recently tested that had vertically orientated flow channels and a biocathode. The channels were designed so that the liquid flow followed the path of all flow channels and the produced hydrogen gas was collected from the headspace at the top of the flow channels (Figure 2G) (*18*). This architecture prevented development of stagnant areas on the electrode, where local pH increases could inhibit biocathode performance. At the same time, hydrogen was efficiently collected from the system without it accumulating in the channels.

An MEC can be operated without a membrane, resulting in a true single-chamber architecture that simplifies reactor design and can reduce capital costs (Figure 2C) (*11, 32*). While membranes and other types of separators are used in water electrolyzers to prevent the explosive mixtures of oxygen and hydrogen gases evolved from the electrodes, a membrane is not needed in an MEC because of a lack of oxygen evolution. Removing the membrane reduces Ohmic resistance and helps to reduce a bulk pH gradient in the liquid, but it does not prevent localized pH gradients at the electrodes. The main disadvantage of this design is hydrogen consumption by methanogens growing on the cathode or in the solution. Call and Logan (*11*) developed a membrane-less MEC with a graphite fiber brush anode to provide a high surface area for the bacteria, and a cathode placed in close proximity to the anode. The system design improved current densities, resulting in a maximum hydrogen production rate of 3.12 m$^3$ $H_2$/m$^3$ d at an applied voltage of 0.8 V over a fed-batch cycle time of 12 h. There was little methane in the product gas (1.9 ± 1.3%; average), $C_E$s were high ($C_E$ = 92 ± 6%; average), and cathodic hydrogen recoveries ranged from 78% to 96% at applied voltages of 0.3−0.8 V. Carbon dioxide was typically present in the product gas at 7−8% as a result of the single-chamber design, compared to <0.5% in MEC reactors using membranes. These results show that high $C_E$s and hydrogen recoveries can be obtained in an MEC lacking a membrane, but further work is needed to investigate the long-term stability of the system to avoid methane generation. The efficiency of this system on actual wastewaters that may contain high concentrations of hydrogen-consuming microorganisms also needs further evaluation. Furthermore, it is not known whether biocathodes can be effectively used in membraneless MECs.

## 3. Thermodynamics of $H_2$ Production

Many organic compounds are unsuitable as substrates for fermentative hydrogen production because of thermodynamic limitations, but they can be used for hydrogen production in MECs. Fermentation of glucose and cellulose produces "dead-end" fermentation products, which are different oxidized species (e.g., other volatile acids such as butyrate and propionate, and solvents such as butanol and ethanol) that are not broken down to produce hydrogen because bacteria cannot extract energy from those reactions. For any reaction to occur spontaneously, the Gibbs free energy of the reaction ($\Delta G_r$) must be negative, but the conversion of most of these organic compounds to hydrogen yields a positive $\Delta G_r$. For example, under standard biological conditions ($T$ = 25 °C, $P$ = 1 bar, pH = 7) the Gibbs free enery of reaction ($\Delta G_r^{\circ\prime}$) for acetate oxidation to hydrogen is (*34*):

$$CH_3COO^- + 4\,H_2O \rightarrow 2\,HCO_3^- + H^+ + 4H_2 \qquad (\Delta G_r^{\circ\prime} = +104.6\ \text{kJ/mol}) \quad (1)$$

This reaction has a positive $\Delta G_r^{\circ\prime}$, and therefore acetate

cannot be fermented to hydrogen. Additional energy has to be added to this system in order to overcome this thermodynamic limit for hydrogen evolution, and for an MEC the added voltage supplied by the power supply provides this extra energy input. To drive the microbial electrolysis process, the applied voltage needs to be at least larger than $\Delta G_r^{\circ'}/nF$, where $n$ is the amount of electrons involved in the reaction, and $F = 96\,485$ C/mol $e^-$ is Faraday's constant. This value is referred to as the equilibrium voltage, $E_{eq}$, which for acetate under standard biological conditions is:

$$E_{eq} = -\frac{\Delta G_r^{\circ'}}{nF} = -\frac{104.6\times10^3}{8\times96485} = -0.14\ \text{V} \quad (2)$$

The negative sign indicates that the reaction is not spontaneous and that a voltage has to be applied in order for the reaction to proceed.

$E_{eq}$ can also be calculated from the theoretical anode ($E_{an}$) and cathode potentials ($E_{cat}$) as

$$E_{eq} = E_{cat} - E_{an} \quad (3)$$

These potentials can be calculated from tabulated values under standard conditions by using the Nernst equation. For example, for acetate the anode potential can be found as

$$CH_3COO^- + 4\ H_2O \rightarrow 2\ HCO_3^- + 9\ H^+ + 8\ e^- \quad (4)$$

$$E_{an} = E_{an}^0 - \frac{RT}{8F}\ln\left(\frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9}\right) \quad (5)$$

with $E_{an}^0$ equal to 0.187 V, $R$ (8.314 J/K mol) is the ideal gas law constant, and $T$(K) is the absolute temperature (*8*). Under standard biological conditions, the anode potential is equal to −0.279 V. The theoretical cathode potential is determined from the Nernst equation as

$$2\ H^+ + 2\ e^- \rightarrow H_2 \quad (6)$$

$$E_{cat} = -\frac{RT}{2F}\ln\left(\frac{p_{H2}}{[H^+]^2}\right) \quad (7)$$

with $p_{H2}$ the hydrogen partial pressure. Under standard biological conditions, the cathode potential is equal to −0.414 V; therefore, the equilibrium voltage is

$$E_{eq} = (-0.414\ \text{V}) - (-0.279\ \text{V}) = -0.14\ \text{V} \quad (8)$$

This is the same value calculated with eq 2, which translates to a theoretical energy requirement of 0.29 kWh/m$^3$ $H_2$.

Equation 7 shows that the cathode potential, and thus $E_{eq}$, is dependent on the hydrogen partial pressure ($p_{H2}$). Every 10-fold increase of the hydrogen partial pressure increases $E_{eq}$ by 0.03 V. Consequently, producing hydrogen at a partial pressure of 10 or 100 bar, instead of 1 bar, theoretically requires only an additional voltage of 0.03 or 0.06 V, respectively, which is equal to an additional energy requirement of 0.06 and 0.13 kWh/m$^3$ $H_2$, respectively. This principle of electrochemical pressurization may make it possible to produce hydrogen at pressures much higher than atmospheric pressures; it also works in reverse and can reduce the needed voltage for lower hydrogen partial pressures (i.e., through gas flushing).

The electrode potentials, and consequently $E_{eq}$, are also dependent on pH (eq 5 and eq 7). This is particularly important when ion exchange membranes are used in an MEC (*19, 20, 30*). The presence of a membrane will typically result in a membrane pH gradient which reduces MEC performance. Every pH unit difference between the anode and the cathode chamber will increase $E_{eq}$ by 0.06 V, which corresponds to an additional energy requirement of about 0.13 kWh/m$^3$ $H_2$ per pH unit.

Under operating conditions the applied voltage ($E_{ap}$) will be always larger than $E_{eq}$ because of internal losses in the system. These losses are comparable to those observed for MFCs: anodic overpotential ($\varphi_a$; including bacterial metabolic losses), cathodic overpotential ($\varphi_c$; including bacterial metabolic losses in case of a biocathode), and Ohmic losses ($IR_\Omega$), which are all a function of the current. Therefore, $E_{ap}$ and $E_{eq}$ are related by:

$$E_{ap} = E_{eq} - \left(\sum \varphi_a + \left|\sum \varphi_c\right| + IR_\Omega\right) \quad (9)$$

In MECs the electrical energy input represented by the applied voltage is not completely lost in the systems because part of the invested energy is stored as chemical energy in the hydrogen product. The irreversible electrical energy loss is represented by the irreversible voltage loss, or $E_{loss} = -(\sum\varphi_a + |\sum\varphi_c| + IR_\Omega)$. Consequently, at currents approaching zero, the applied voltage should theoretically also approach to the equilibrium voltage, but when we increase the voltage, we increase the current and thus have an increased electrical energy loss. Because hydrogen production is directly linked to current (assuming all electrons to be converted into hydrogen), this means that the higher the applied voltage, the higher the electrical energy input per amount of hydrogen produced (kWh/m$^3$ $H_2$). Therefore, to reduce the hydrogen costs, it is important to minimize the irreversible energy losses as much as possible, while maintaining an acceptable hydrogen production rate. Experiments have shown that the microbial electrolysis reactions typically start to occur at applied voltages above 0.2 V, which corresponds to an energy requirement of 0.43 kWh/m$^3$ $H_2$ (at 100% cathodic hydrogen recovery).

## 4. MEC Experiments

**4.1. Applying a Voltage.** An external power source is used to provide the energy input required for driving the hydrogen production reactions of the microbial electrolysis process. Two different devices are used: a power supply unit or a potentiostat. When using a power supply unit (e.g., Circuit Specialists, Inc., (Mesa, AZ); Delta Elektronika B.V., The Netherlands) the positive lead is connected to the anode and the negative lead to the cathode. A low-resistance (1−10 Ω) resistor is included in one of the leads of the circuit so that the current can be calculated based on measuring the voltage across the resistor, $R_{ext}$, as $I = V/R_{ext}$. However, including a resistor results in an additional voltage loss in the system, and thus the actual applied voltage over the anode and cathode, $E_{ap}$, is smaller than the power source applied voltage, $E_{ps}$. The applied voltage can be corrected for this difference using

$$E_{ap} = E_{ps} - IR_{ext} \quad (10)$$

where $I = V/R_{ext}$ is the current (A) calculated from the voltage across the resistor. The energy added, $W_E$ (J), measured over each constant time increment $\Delta t$ (s) for $n$ data points in a batch cycle (or over a certain period of time in a continuous flow system), is

$$W_E = \sum_{i=1}^{n} (I_i E_{ps}\Delta t - I_i^2 R_{ext}\Delta t) \quad (11)$$

The voltage loss should be small and is often negligible. Some power supply units (e.g., Delta Electronics B.V., The Netherlands) can automatically adjust the actual voltage to achieve the applied voltage over the cell by making use of sensing leads that are also connected to the anode and cathode. These sensing leads continuously measure the voltage across the

MEC and adjust the output of the power supply unit to keep this voltage at the applied value regardless of the losses across the resistor. This internal correction makes an additional correction to the voltage or power unnecessary and is preferred over noncorrecting power supply units.

A voltage can also be applied with a potentiostat (Bank IC, Germany; Ecochemie, The Netherlands) by setting a positive cell potential, connecting the working electrode to the anode, and connecting both the counter electrode lead and the reference electrode lead to the cathode. Potentiostats can also be used to control anode or cathode potentials or to set a specific current (galvanostat mode). Setting an electrode potential can result in a highly variable applied voltage because the voltage is automatically adjusted to keep the electrode at its set potential. This type of operation is particularly useful when investigating a reaction occurring at the anode or cathode. Although the price of a potentiostat varies with software and other features, it is a relatively expensive method to set the voltage compared to a power supply unit (a few hundred vs several thousands of US dollars for a potentiostat).

**4.2. Measuring $H_2$ Production.** The volume of gas produced by an MEC is measured in laboratory experiments using various techniques developed for measuring gas evolution by fermenters or anaerobic digesters. These include an intermittent gas release method (Owen method) (*35*) and continuous gas release methods based on water displacement or volume measurements using various types of gas flow devices. If the Owen method is used, the vessel must be sufficiently durable and gastight to withstand the build up of gas pressure in the headspace. At the start of the test, the headspace volume ($V_h$) must be free of oxygen and its composition known, either through measurement or by flushing completely with ultrapure nitrogen (99.999%). The volume of gas produced ($V_m$) is measured by releasing the gas pressure into a glass syringe (for example 2, 20, or 50 mL capacity; Perfektum Syringe, Popper & Sons, Inc.) until pressure in the syringe equilibrates with atmospheric pressure (*5, 14, 36*). The syringe is removed, and the gas discarded. The volumetric fraction of hydrogen ($x_{H2}$) in the gas is determined by obtaining a very small sample from the headspace (~50 to 100 $\mu$L) using a gastight syringe, with composition measured using a gas chromatograph (SRI Instruments, Torrance, CA; Shimadzu, Japan). If the system was flushed with nitrogen prior to the experiment, the volume of hydrogen gas ($V_{H2}$) produced after the start of the experiment is calculated as $V_{H2} = x_{H2}(V_m + V_h)$. Otherwise, calculated hydrogen production at a certain sample time must take into account the change in the gas mixture, which is calculated from the mass balance equation (*36*)

$$V_{H2,t} = V_{H2,t-1} + x_{H2,t}(V_{m,t} - V_{m,t-1}) + V_h(x_{H2,t} - x_{H2,t-1}) \quad (12)$$

where $V_{H2,t}$ and $V_{H2,t-1}$ are cumulative hydrogen gas volumes at the current ($t$) and previous ($t-1$) time intervals, ($V_{m,t} - V_{m,t-1}$) the gas production during the time interval, and $x_{H2,t}$ and $x_{H2,t-1}$ the fraction of hydrogen gas in the current and previous intervals, respectively.

Continuous gas release methods have been shown to increase hydrogen yields in fermentation systems, as there is no inhibitory effect of accumulated hydrogen gas on production (*36*). The use of large lengths of tubing and fittings for continuous flow devices should be avoided, as these can result in substantial hydrogen gas losses, especially when gas production rates are low (*14*). Continuous gas production in MEC studies has been measured using an anaerobic respirometer system (AER-208; Challenge Environmental System, Fayetteville, AR) (*10*) or a flow meter (Milligascounter, Ritter, Germany) (*18, 19*). The hydrogen produced can be calculated using the above equation, but the hydrogen gas composition is sampled infrequently relative to the flow measurements and must therefore be estimated between sampling times, typically by assuming a linear change in concentration over the sampling interval (*19*), using:

$$V_{H2,t} = V_{H2,t-1} + (V_{m,t} - V_{m,t-1})\frac{(x_{H2,t} + x_{H2,t-1})}{2} + V_h(x_{H2,t} - x_{H2,t-1}) \quad (13)$$

An alternative approach to minimize the number of times the gas composition must be analyzed is to collect all of the gas produced over a complete cycle (or a desired time interval) in a gas bag (for example, a 0.1 L bag; Cali-5-Bond, Calibrated Instruments Inc.) (*11*). Using this approach, changes in the gas composition over the course of the experiment do not affect the final calculation of the hydrogen gas production. If the volume of gas collected in the bag ($V_b$) is assumed to be the volume of gas measured by the respirometer ($V_m$), then the volume of hydrogen gas produced is

$$V_{H2} = x_{H2,h}V_h + x_{H2,b}V_b \quad (14)$$

where $x_{H2,h}$ and $x_{H2,b}$ are the mole fractions of hydrogen in the headspace and gas bag, respectively. In a batch cycle test, the headspace and tubing must be flushed with nitrogen gas. However, some of the nitrogen gas from the tubing or headspace may enter the gas bag when the system is flushed because of extra pressure in the system. As a result, $V_b > V_m$ by the additional and unknown volume of nitrogen gas. To correct for this extra gas, the fraction of hydrogen gas in the bag ($f_{H2,b}$) is calculated on a *nitrogen gas-free basis* as

$$f_{H2,b} = \frac{x_{H2,b}}{x_{H2,b} + x_{C,b} + \ldots} \quad (15)$$

where the mole fractions in the denominator can include carbon dioxide ($x_{C,b}$) or other gases that may have been produced such as methane ($x_{M,b}$), but excludes nitrogen. Using this approach, the volume of hydrogen gas produced can be calculated as:

$$V_{H2} = x_{H2,h}V_h + f_{H2,b}(V_m - V_{hl}) \quad (16)$$

The measured gas volume is corrected using this equation for the amount of nitrogen gas that was lost from the headspace and was collected in the gas bag, as $V_{hl} = (1 - x_{N,h})V_h$, where $x_{N,h}$ is the mole fraction of nitrogen at the end of the sampling period in the headspace.

**4.3. Reporting Performance.** *Hydrogen Yield.* The amount of hydrogen produced from a substrate is the hydrogen yield. It is usually calculated for specific compounds on a molar basis, as $Y_{H2} = n_{H2}/n_S$, where $n_{H2}$ is the moles of hydrogen produced and $n_S$ is the moles of substrate consumed. The moles of hydrogen produced in an experiment is calculated from the volume of hydrogen produced and the ideal gas law as $n_{H2} = V_{H2}P/(RT)$, where P (bar) is the atmospheric pressure measured in the laboratory and R is 0.08314 L bar/K mol. The hydrogen yield for a specific chemical on a molar basis is therefore

$$Y_{H2}\left[\frac{\text{mol } H_2}{\text{mol S}}\right] = \frac{V_{H2}PM_S}{RT\Delta c_S} \quad (17)$$

where $\Delta c_S$ (g) is the substrate consumption over a set period of time and $M_S$ (g/mol) is the molecular weight of the substrate.

If a complex source of organic matter is used, such as a wastewater, it is more useful to use yield based on mass, or

$Y_{H2} = m_{H2}/m_s$, where $m_{H2}$ is the total mass of hydrogen produced, and $m_S$ the mass of substrate consumed. For a measured change in COD over a batch cycle or a period of time in a continuous flow experiment, the hydrogen yield on a COD-mass basis is

$$Y_{H2}\left[\frac{\text{g H}_2}{\text{g COD}}\right] = \frac{V_{H2}PM_{H2}}{RT\Delta\text{COD}} \quad (18)$$

where ΔCOD(g) is the cumulative COD consumption over a set period of time, and $M_{H2}$ (2 g/mol) is the molecular weight of hydrogen.

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%. On a molar basis, the value of $n_{th}$ equals the moles of substrate converted $n_s$ multiplied by the stoichiometric production of hydrogen from 1 mol of substrate. The yield based on COD is easily calculated because each mole of COD removed could produce 2 mol of hydrogen. On a COD basis, $n_{th}$ is given by

$$n_{th} = \frac{2\Delta\text{COD}}{M_{O2}} \quad (19)$$

where $M_{O2}$ (32 g/mol) is the molecular weight of oxygen. For cellulose, the maximum molar yield is 12 mol $H_2$/mol hexose or 2 mol $H_2$/mol COD, or on a mass basis 0.133 g $H_2$/g hexose or 0.125 g $H_2$/g COD. In MECs, molar yields as high as 3.7 mol/mol (93%) have been reached using acetate ($E_{ap}$ = 0.8 V) (*11*), with values for 8.55 mol/mol (71%) for glucose and 8.71 mol/mol (73%) for cellulose (hexose equivalent; $E_{ap}$ = 0.6 V) (*10*).

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

$$n_{CE} = \frac{\int_{t=0}^{t} I\,dt}{2F} \quad (20)$$

where d$t$ (s) is the interval over which data are collected, and 2 is used to convert moles of electrons to moles of hydrogen. This recovery is related to the Coulombic efficiency $C_E$ by

$$C_E = \frac{n_{CE}}{n_{th}} \quad (21)$$

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 ($r_{cat}$),

$$r_{cat} = \frac{n_{H2}}{n_{CE}} \quad (22)$$

The overall hydrogen recovery is $r_{H2} = C_E\, r_{cat}$.

*Energy Yield.* The performance of the MEC in terms of energy recovery is based on the energy content of the hydrogen recovered, compared to (i) the energy input in only the electricity (which is useful for comparing performance to water electrolysis), (ii) the energy input in the substrate, or (iii) the energy in both the electricity and substrate. The energy content of a compound is expressed as either energy or work released upon combustion. The calculated performance is dependent on the choice of thermodynamic values for the energy content, i.e., Δ$G$ for Gibbs free energy (an exergy analysis), or Δ$H$ for heat of combustion. The electrical energy input into an MEC is 100% work and therefore equivalent to Gibbs free energy. From that perspective, it makes sense to calculate Gibbs free energy for efficiency calculations as the maximum energy efficiency based on the energy input of both the electricity and substrate is exactly equal to 100% (Table 2). The Gibbs free energy calculation should be made on the basis of the actual conditions in the reactor (i.e., concentrations, temperature, and partial pressures). For example for acetate oxidation, this means that bicarbonate is the end product (eq 1), and we have:

$$CH_3COO^- + 2\ O_2 \rightarrow 2\ HCO_3^- + H^+ \quad (23)$$

Energy balances for water electrolyzers are usually based on heats of combustion (*1, 37*). However, the end products used in this combustion energy calculation of Δ$H$ are assumed to be $CO_2$ and $H_2O$. The equation used for calculation of acetate oxidation based on combustion energy therefore is:

$$CH_3COOH + 2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O \quad (24)$$

Note that when combustion energy is used, the calculated maximum energy efficiency based on the energy input of both the electricity and substrate could be larger than 100% (Table 2). Because these two approaches for making energy balances are appropriate for different reasons, we include both Δ$H$ and Δ$G$ approaches here.

The amount of energy recovered in hydrogen over a batch cycle or over a set time in a continuous flow system based on combustion energy is $W_{H2} = n_{H2}\,\Delta H_{H2}$, where $n_{H2}$ is the moles of hydrogen produced, $\Delta H_{H2} = -285.8$ kJ/mol (*38*) is the energy content of hydrogen based on the heat of combustion (upper heating value). Energy recovery based on Gibbs free energy $W_{H2} = n_{H2}\,\Delta G_{H2}$ where $\Delta G_{H2} = -237.1$ kJ/mol is the Gibbs free energy content of hydrogen based on its oxidation by oxygen to water (*38*).

The energy yield relative to the electrical input, $\eta_E$, is the ratio of the energy content of the hydrogen produced to the input electrical energy required, or

$$\eta_E = \frac{-W_{H2}}{W_E} \quad (25)$$

The amount of energy added by the substrate is $W_S = n_S\Delta H_S$, where $\Delta H_S$ is the heat of combustion of the substrate, and $n_S$ is the moles of substrate consumed during a batch cycle. Based on Gibbs free energy, $W_S = n_S\Delta G_S$ where $\Delta G_S$ is the Gibbs free energy content of the substrate based on its oxidation by oxygen to bicarbonate and water. For example, for acetate $\Delta H_S = -874.3$ kJ/mol (eq 24) (*38*) and $\Delta G_S = -844.1$ kJ/mol (eq 23) (*39*). For wastewater, the energy content needs to be determined on a case by case basis. For example, for municipal wastewater it is has been determined that $\Delta H_S = -14.7$ kJ/g-COD (*40*). The energy yield relative to the added substrate, $\eta_S$, is

$$\eta_S = \frac{W_{H2}}{W_S} \quad (26)$$

The overall energy recovery based on both the electricity and substrate inputs, $\eta_{E+S}$, is

**TABLE 2. Theoretical Limits of the Different Types of Energy Recoveries for Hydrogen Production from Acetate in MECs under Standard Biological Conditions**

| energy recovery basis | based on Δ$G$, % | based on Δ$H$, %[a] |
|---|---|---|
| electricity ($\eta_E$) | 907 | 1094 |
| substrate ($\eta_S$) | 112 | 131 |
| electricity and substrate ($\eta_{E+S}$) | 100 | 117 |

[a] Based on the higher heating value of hydrogen gas.

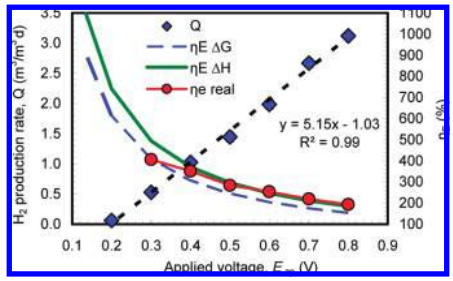


**FIGURE 3. Hydrogen production rate (*Q*) and energy efficiency calculated from the electricity input and hydrogen output as a function of the applied voltage using data from Call and Logan ($\eta_E \Delta H_{exp}$, based on heat of combustion) (*11*) and theoretical maximum energy efficiencies based on Gibbs free energy ($\eta_E \Delta G_{max}$) and heat of combustion ($\eta_E \Delta H_{max}$).**

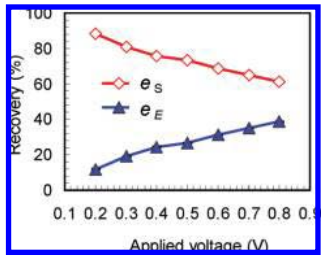


**FIGURE 4. Energy input of the power source and substrate relative to the total energy input as a function of applied voltage, with energies based on heat of combustion ($\Delta H$) (from Call and Logan (*11*)).**

$$\eta_{E+S} = \frac{-W_{H2}}{W_E - W_S} \tag{27}$$

A comparison of the $\Delta G$ and a $\Delta H$ approaches is summarized in Table 2 for acetate. We can see that the theoretical maximum efficiency is over 900% no matter which approach is used, and that combustion efficiencies over 100% based on $\Delta H$ are theoretically possible, although they have not been achieved. These maximum theoretical yields are compared to experimental data in Figure 3. The energy input of the power source ($e_E$) or the substrate ($e_S$) relative to the total energy input can be calculated as

$$e_E = \frac{W_E}{W_E - W_S} \tag{28}$$

$$e_S = \frac{-W_S}{W_E - W_S} \tag{29}$$

As the applied voltage is increased, more energy is derived from the electrical energy input compared to the energy in the substrate (Figure 4). Thus, to maximize renewable energy production, $W_E$ should be minimized.

*Current Density.* The hydrogen production rate can be expressed as a direct function of the volumetric current density (see below), and therefore current should be normalized to the reactor volume. In some cases, however, it may be useful to examine current normalized to the area of a single electrode or (if present) a membrane to better understand system performance. An engineering goal is to achieve the highest possible volumetric current density in order to minimize reactor volume. Nonoptimal working volumes may be chosen for laboratory experiments, however, to extend batch cycle time for researcher convenience (i.e., to fit a work day or week for a single cycle).

Current density increases with the applied voltage and thus there is no single value for current production in an MEC that would be analogous to the "maximum power" used to evaluate MFC performance (*8*). Current densities should be compared on the basis of similar applied voltages, using the lowest voltages that produced consistent reactor performance. Current densities often deviate from a linear response at applied voltages of <0.2 V (*7*) or produce little measurable hydrogen or have erratic performance below 0.3 V (*5, 11*). Applied voltages above 1 V make little sense as the energy input becomes so large that the microbial electrolysis process becomes closer to a water electrolysis process. Thus, it is recommended here that current densities be compared on the basis of a single voltage in the range of 0.4 to 0.8 V.

*Hydrogen Production Rates.* To minimize capital costs, one architectural goal of the MEC is to maximize hydrogen production per reactor volume. The maximum volumetric hydrogen production rate, $Q_{max}$ ($m^3$ $H_2$/$m^3$ d), is directly proportional to the current density,

$$Q_{max} = \frac{I_v(A/m^3) r_{cat}[(1C/s)/A](0.5 \text{ mol } H_2/\text{mol})(86400 \text{ s/d})}{F(9.65 \times 10^4 C/\text{mol}) c_g(\text{mol } H_2/L)(10^3 L/m^3)}$$

$$= \frac{43.2 I_v r_{cat}}{F c_g(T)} \tag{30}$$

where $I_v$ ($A/m^3$) is averaged over a specified time period (i.e., several hours of peak current production), $c_g$ (mol/L) is the molar density of gas at a standard temperature (298.15 K) and standard pressure (1 bar), and 43.2 results from the given units. Thus, when hydrogen is captured efficiently ($r_{cat} \rightarrow 1$), increasing the hydrogen production rate depends solely on increasing current. To date, MEC hydrogen production rates have reached 3.12 $m^3$ $H_2$/$m^3$ d ($E_{ap} = 0.8$ V), values which are in the same order as those of fermentation systems (*3*). So far, MEC systems have reached a maximum of $I_v = 186$ $A/m^3$ at the maximum recommended applied voltage of 0.6 V (*11*). These are much lower than those in the more-extensively studied MFCs (5600 $A/m^3$, 10 $A/m^2$) at maximum power densities of 1.55 kW/$m^3$ (2.77 W/$m^2$) (*41*), and thus it is likely that with additional research, higher current densities will be achieved in MECs in the future.

## 5. MEC Applications

**5.1. MECs for WWT.** MECs are a promising technology for wastewater treatment because (i) they provide energy in the form of hydrogen gas as a product, (ii) they can reduce solids production and in turn lower sludge handling costs, and (iii) they can possibly limit the release of odors. However, they need to be shown to be more cost-effective than existing wastewater treatment technologies (*9*). Since electrical energy is consumed in an MEC, sufficient hydrogen must be recovered from the wastewater to help make the process economical. The net amount of energy extracted depends largely on the applied voltage. MECs using acetate have required as little as 0.5 kWh/kg COD ($E_{ap} = 0.2$ V) and up to 1.74 kWh/kg COD ($E_{ap} = 0.6$ V) (*11*). These energy requirements are similar to those needed for aerators in activated sludge (AS) systems which require 0.7 to 2 kWh/kg COD (*42*) (Table 3). Full-scale MEC systems are expected to require ca. 1 kWh/$m^3$ $H_2$ and to produce 10 $m^3$ $H_2$/$m^3$ d (*19*). With a 100% overall hydrogen recovery efficiency, this is an energy consumption of 1.5 kWh/kg COD, a value within the typical range for activated sludge. Actual wastewater has only been tested in one MEC study, but the design used was not efficient in terms of current density (4.1 $A/m^3$) (*14*) compared to more recent systems (186 $A/m^3$; $E_{ap} = 0.6$ V) (*11*), and as a result there was relatively little net hydrogen produced (*14*). Slow degradation of complex substrates (*43, 44*) and low conductivities of real wastewaters (0.8 − 2 mS/cm, based on domestic wastewater in State College, PA, and ref (*45*)) have been shown to decrease performance of MFCs compared to tests under optimal laboratory conditions (*46*). Thus, ad-

**TABLE 3. Energy Requirements and Production for Wastewater Treatment Processes**

| WWT process | volumetric loading rate (kg COD/$m^3$/day) | sludge production | nutrient removal | energy consumption (kWh/kg COD) | energy production |
|---|---|---|---|---|---|
| activated sludge | 0.5−2 (8) | high | yes | 0.7−2 (42) | no |
| anaerobic digestion (*42*) | 8−20 | low | no | low | yes, $CH_4$ |
| microbial electrolysis | ~6.5 (19) | low (expected) | possibly | 0.5−2.4 (11) | yes, $H_2$ |

ditional studies are needed using MECs with nonamended wastewaters (without nutrients or buffers). Moreover, to properly compare the performance of MECs (or MFCs) among different studies it is essential to report the conductivities of synthetic media or the wastewater.

The MEC process can be compared to anaerobic digesters (ADs) that produce methane gas for energy efficiency. ADs do not require any significant electrical energy input and produce a valuable product (methane). Some of the product gas is needed for heating the reactor to the high temperatures needed for efficient methanogenesis, so these systems are only economical for high-strength wastewaters. Compared to AD, microbial electrolysis has the advantage that from the same amount of COD, the gas produced is more valuable ($ 0.75/kg $H_2$ COD vs $ 0.11/kg $CH_4$ COD; calculated from (*47*)). As MECs are only recently invented, there is a great need for further research into process engineering aspects such as design rules for scale-up, reactor control, and operation strategies. These are not trivial issues, as the underlying process of microbial electron transfer is only recently discovered and no mathematical models are available to guide design. Additional research and pilot tests are needed to determine if the higher value of the product gas can compensate for the electrical energy costs and the inherently more complex design of MECs compared to ADs (*9*). Also, research is needed on whether MEC systems will be capable of stand-alone operation or if they will require aerobic effluent polishing (as commonly is the case for ADs).

An MEC operates under completely anaerobic conditions, and therefore low sludge production is expected (*48*), but there have been no reports on solids production in these systems. There are tremendous potential savings for use of a treatment system that reduces sludge production. In a typical AS system, one-third to half of the operating costs are associated with solids handling and treatment (*49*). For domestic wastewater, approximately two-thirds of the energy content of wastewater may be removed by the primary clarifier (*15*). Thus, to substantially reduce solids production either the domestic wastewater would need to be treated without primary clarifiers (avoiding sludge production from the primary clarifiers) or the solids would need to be fermented and fed back into the main wastewater stream.

Another concern with wastewater treatment is preventing the release of odors. In AS processes, aeration can widely disperse odors but an MEC is a completely enclosed process and thus has the inherent advantage of complete containment of the wastewater odors during treatment. Although MFCs have been shown to remove chemicals associated with odors (*50*), this aspect of MECs has not yet been examined.

To function as a wastewater treatment plant, microbial electrolysis systems need to exhibit reasonable COD conversion rates. Assuming 10 $m^3$ $H_2$/$m^3$ d (*19*) and 100% hydrogen recovery, COD loading rates would be on the order of 6.5 kg COD/$m^3$ d, a range in between that for AS systems (0.5−2 kg COD/$m^3$ d) and high rate ADs (8−20 kg COD/$m^3$ d) (*8*). On the basis of these COD loading rates, MECs could therefore be competitive with other wastewater treatment technologies.

AS systems can be designed to remove nutrients such as nitrogen and phosphorus. ADs are not capable of removing nutrients, and nutrient removal in MECs has not been examined. Recent studies have shown that nitrate can be removed by a biocathode in MFCs (*51, 52*), but the fate of ammonia or nitrate in MECs has not yet been examined. Phosphorus removal has not been demonstrated in either MFC or MEC systems. Although phosphate is often used in laboratory tests as a buffer, it would not be practical to add phosphorus in practice because of the cost and effluent limitations in the order of 1 mg/L (*53*). Phosphate buffers and carbonate buffers have been shown to improve performance in an MFC (*41*). While buffer addition to any wastewater is not practical, the role of bicarbonate alkalinity MECs should be further explored, especially since it is a naturally occurring buffer system in most wastewaters.

**5.2. MECs for Renewable Energy Production.** Cellulose is the most abundant biopolymer in the world. The DOE concluded that in the US it is possible to obtain 1.34 billion dry tons of biomass per year, which could produce up to 200 billion kg $H_2$/year (100% conversion and recovery) (*54*). Chitin is the second most abundant biopolymer, but like cellulose and many biomass waste materials, these substrates are particulate and not soluble. Particulate substrates have not been well studied in either MECs or MFCs, and thus much work is needed to optimize these systems for practical applications. It is likely that the process in either MECs or MFCs will require separate microorganisms or microbial communities to accomplish particle hydrolysis and subsequent current generation. Fortunately, many strains of microorganisms, such as *Clostridia* spp., readily ferment cellulose to hydrogen, volatile fatty acids, and other typical fermentation end products (*55*). Power generation from these end-products in MFCs has been shown by mixed communities and by a coculture of fermentative and exoelectrogenic bacteria (*43, 44, 56*) as well as current generation in MECs (*10*).

Hydrogen production from cellulose was recently demonstrated in a two-chamber MEC at hydrogen yields (63%) similar to that obtained with glucose (64%) but less than that of acetic acid (82%), suggesting that hydrogen recovery was not achieved for the fermentation step in the process (*10*). Producing 1 kg of $H_2$ (roughly equivalent to the energy content of a gallon of gasoline) would take 7.5 kg (16.5 lb) of cellulose at 100% yield. Hydrogen production rates were much lower from cellulose (0.11 $m^3$/$m^3$ d) than glucose (1.23 $m^3$/$m^3$ d), indicating that the rates of hydrolysis and fermentation were not well matched to those possible by electrohydrogenesis in this system (*10*). These fermentation and electrohydrogenesis rates will need to be better matched, either through feeding strategies or a two-stage process, using reactors especially designed to handle particulate substrates.

## 6. Outlook

MECs efficiently convert a wide range of organic matter into hydrogen and are therefore a promising technology for renewable and sustainable hydrogen gas production from organic feedstocks. MECs show high hydrogen yields and they need only a relatively small electrical energy input. Given these interesting properties, MECs could become viable technology to produce renewable hydrogen, provided a clean and renewable electricity input is used.

Renewable hydrogen has many applications, the most prominent ones being for transportation and industry.

Transportation fuels are currently responsible for about 20 to 25% of the global fossil fuel consumption (*57*). Because of climate change, and instabilities in the fossil fuel market, there is great interest in hydrogen as a transportation fuel (i.e., the hydrogen economy). Moreover, even without a hydrogen economy, there exists a large hydrogen demand. In 2000, the global hydrogen consumption was already estimated to be 50 million tons per year, with about two-thirds used by the petrochemical industry (*58*). This hydrogen is used for upgrading fossil fuels and synthesis of industrial chemicals such as ammonia and methanol. Other industries that consume significant amounts of hydrogen include the food industry (saturation of fats and oils) and the metal industry (as a reducing agent for metallic ores).

MECs can contribute significantly to these hydrogen demands by producing large quantities of hydrogen from renewable resources such as biomass and wastewaters. The MEC concept is now well proven, and significant advancements have been made with respect to the performance in only a few years since its discovery. To become a mature hydrogen production technology, however, several research questions still need to be addressed (*9*): (i) more experience is required with real organic feedstocks containing complex organic substrates such as polymeric and particulate substances; (ii) novel, more cost-effective chemical and/or biological cathodes need to be developed that show low potential losses and are not platinum based; (iii) membrane pH gradients need to be eliminated, or membranes should not be used in the reactor; (iv) methanogenic consumption of the hydrogen product needs to be prevented (in case of membrane-less MECs and/or MECs with a biocathode). The most critical need is to develop a cost-effective, scalable MEC design. Nevertheless, rapid advancements in MECs that are being helped by the developments in related MFCs, combined with additional funding and research into microbial electrolysis, should allow for rapid commercialization of this new biohydrogen technology.

## Acknowledgments

This review was supported by the following: the National Science Foundation (CBET-0730359) and Air Products and Chemicals, Inc. (B.E.L); the KAUST Global Research Partnership (BEL and S.C.); a National Defense Science and Engineering Graduate Fellowship, and the National Water Research Institute Ronald B. Linsky Fellowship (D.C.); SenterNovem (NEO Grant 0268-03-04-04-002) and the Australian Research Council (DP 0666927) (R.A.R). Wetsus is funded by the Dutch Ministry of Economic Affairs, the city of Leeuwarden, the Province of Fryslan, the European Union European Regional Development Fund, and the EZ-KOMPAS Program of the "Samenwerkingsverband Noord/Nederland". We thank the participants of the theme "Hydrogen" for their input and contributions: Shell, Paques bv, and Magneto Special Anodes bv.

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ES801553Z