Hydrogen Production in a Single Chamber Microbial Electrolysis Cell Lacking a Membrane

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Hydrogen gas can be produced by electrohydrogenesis in microbial electrolysis cells (MECs) at greater yields than fermentation and at greater energy efficiencies than water electrolysis. It has been assumed that a membrane is needed in an MEC to avoid hydrogen losses due to bacterial consumption of the product gas. However, high cathodic hydrogen recoveries (78 ± 1% to 96 ± 1%) were achieved in an MEC despite the absence of a membrane between the electrodes (applied voltages of 0.3–0.6 V). Through the use of a membrane-less system, a graphite fiber brush anode, and close electrode spacing, hydrogen production rates reached a maximum of 3.12 ± 0.02 m³ H₂/m³ day (292 ± 1 A/m³) at an applied voltage of Ε̂_{ap} = 0.8 V. This production rate is more than double that obtained in previous MEC studies. The energy efficiency relative to the electrical input decreased with applied voltage from 406 ± 6% (Ε̂_{ap} = 0.3 V) to 194 ± 2% (Ε̂_{ap} = 0.8 V). Overall energy efficiency relative to both Ε̂_{ap} and energy of the substrate averaged 78 ± 4%, with a maximum of 86 ± 2% (1.02 ± 0.05 m³ H₂/m³ day, Ε̂_{ap} = 0.4 V). At Ε̂_{ap} = 0.2 V, the hydrogen recovery substantially decreased, and methane concentrations increased from an average of 1.9 ± 1.3% (Ε̂_{ap} = 0.3–0.8 V) to 28 ± 0% of the gas, due to the long cycle time of the reactor. Increasing the solution conductivity to 20 mS/cm increased hydrogen production rates for Ε̂_{ap} = 0.3–0.6 V, but consistent reactor performance could not be obtained in the high conductivity solution at Ε̂_{ap} > 0.6 V. These results demonstrate that high hydrogen recovery and production rates are possible in a single chamber MEC without a membrane, potentially reducing the costs of these systems and allowing for new and simpler designs.

Introduction

Electrohydrogenesis is a recently developed electrolysis method for directly converting biodegradable material into hydrogen using modified microbial fuel cells (MFCs) (1–7). In an MFC, microorganisms called exoelectrogens oxidize organic matter and transfer electrons to an anode (8, 9). The electrons travel through an external resistance and combine at the cathode with protons and oxygen to produce water. A microbial electrolysis cell (MEC) operates in a manner similar to an MFC except that the cathode is sealed to exclude oxygen, and an additional voltage is added to the circuit (1, 2). A voltage must be applied because hydrogen formation using acetate as a substrate is not spontaneous under standard conditions. The anode open circuit potential with bacteria is around −0.300 V (0.8 g/L acetate, vs NHE) (10). A cathode potential of −0.414 V is required in order to produce hydrogen (1–3). Thus, an applied voltage of Ε̂_{ap} = 0.114 V is theoretically needed, but in practice, Ε̂_{ap} > 0.130 V is required to produce hydrogen due to electrode overpotentials (voltage losses) (1).

Membranes are used in water electrolyzers to prevent oxygen and hydrogen gases from combining and reacting. Membranes have been used in MECs as well, presumably to ensure high hydrogen concentrations and to eliminate hydrogen utilization by bacteria in the anode chamber. Some researchers have noted, however, that the hydrogen gas produced at the cathode is contaminated by other gases (such as carbon dioxide) produced at the anode even when a membrane is used (1, 3). The presence of a membrane also does not prohibit hydrogen diffusion back into the anode chamber (5, 11). In one MFC study, low energy recoveries were attributed to an estimated 43% loss of the produced hydrogen due to diffusion through the membrane into the anode chamber (3). Membranes also hinder proton diffusion between the electrodes and can create substantial pH differences between the anode and cathode chambers (12, 13). Rozental et al. (4) calculated that the pH gradient across the membrane accounted for the largest potential loss in the system (38% using a cation exchange membrane (CEM)), and concluded that improvement of the system was largely dependent on eliminating this pH gradient.

We hypothesized that membranes were not needed for MECs, and that high hydrogen recoveries were possible in such single-chamber systems for several reasons. First, oxygen is not produced in an MEC like it is in a water electrolyzer, and thus there is no need to keep the gas produced at the cathode separated from the anode. Second, although hydrogen gas produced in the reactor could be consumed by microorganisms, we reasoned that if hydrogen gas production rates were sufficiently high, then the low solubility of the hydrogen gas in water would allow high recoveries. Third, we assumed a lack of a membrane in an MEC would not adversely affect current densities based on reports that MFCs lacking a membrane have equal or higher current densities compared to those containing cation, anion, or ultrafiltration membranes (13, 14). Finally, we reasoned that even if some hydrogen gas was lost, the reduced cost of the system due to the lack of a membrane might reduce the overall system cost and simplify reactor architecture. Therefore, we designed an MEC that lacked a membrane and included into this new system design recent features that have increased power density in MFCs, including: using graphite brush electrodes; using an ammonia treatment on the anodes (15, 16); spacing the electrodes as closely as possible to each other (17); and varying the solution conductivity to improve performance (18). We demonstrate here that this newly designed system is capable of both high hydrogen recoveries and improved hydrogen production rates.

Materials and Methods

Reactor Construction. The MEC was constructed from polycarbonate cut to produce a cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL) (Figure 1). The anode was an ammonia treated graphite brush (25 mm diameter × 25 mm length; 0.22 m² surface area; fiber type: PANEX 33 160K, ZOLTEK), with a specific surface area of 18 200 m²/m³ and a porosity of 95%, placed into the center of the chamber (15, 16). The cathode was wet-proofed (30%)

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carbon cloth (type B; E-TEK), with a surface area of 7 cm² and a Pt catalyst (0.5 mg/cm²), placed on the opposite side of the chamber. Gas produced at the cathode in the MEC bubbled into the reactor solution and was collected using an anaerobic tube (1.6 cm inner diameter and total headspace volume of 15 mL) glued to the top of the reactor above an opening 1.6 cm in diameter. The top of the tube was sealed with a butyl rubber stopper and an aluminum crimp top. All reactors were covered with aluminum foil to exclude light.

**Startup and Operation.** The brush anodes were first enriched in a cube-type MFC with a flat cathode (16). The MFC was inoculated with suspended bacteria from an acetate-fed MFC reactor that had been operating for about 11 months (16). The MFCs were fed a 50:50 mixture of the inoculum and sodium acetate (1 g/L; J.T. Baker) in a buffer (50 mM phosphate buffer, PBS; Na₂HPO₄, 4.58 g/L; and NaH₂PO₄·H₂O, 2.45 g/L, pH = 7.0) and nutrient solution (NH₄Cl, 0.31 g/L; KCl, 0.13 g/L; trace nutrient medium) (19). Once a reactor produced >0.100 V during a fed-batch cycle, the inoculum was omitted. When a reproducible maximum voltage was obtained for at least three batch cycles, the anode was considered fully acclimated and was transferred to an MEC.

MEC reactors were fed the same substrate (1 g/L sodium acetate) and trace nutrient solution and were operated in duplicate using a 50 mM PBS buffer (γ = 7.5 mS/cm), except as noted when 200 mM PBS (γ = 20 mS/cm) was used in order to examine the effect of solution ionic conductivity on reactor performance. After each batch cycle, the crimp tops were removed, the contents drained, and the reactors were left exposed to air for 30–45 min in order to inhibit the growth of methanogens. After adding the medium and rescaling the anaerobic tube, the reactor liquid was sparged using ultra high purity (UHP) nitrogen (99.998%) for 20 min. All batch tests were conducted in a constant temperature room (30 °C).

Continuous gas production was recorded using a respirometer (AER-200; Challenge Environmental) by inserting a needle connected to the collection tubing into the stopper of the anaerobic tube on the reactor top (5). Prior to each test, each flow cell used to measure gas production was sparged with 3 volumes (0.3 L) of UHP nitrogen and then vacuum sealed.

A fixed voltage (E_R) was added to the reactor circuit using a power source (model 3645A; Circuit Specialists, Inc.). A resistor (10 Ω) was connected in series with the power supply, and the voltage across the resistor was measured using a multimeter (model 2700; Keithley Instruments, Inc.) to calculate the current. The positive lead of the power source was connected to the anode, and the negative lead was connected to the resistor in the circuit connecting the electrodes. An Ag/AgCl reference electrode (RE-5B; BASi) was placed in the reactor, and the anode potential was recorded using the multimeter.

Total chemical oxygen demand (COD) analysis of the solution was performed at the beginning and end of each batch cycle by following a standard method (TNTplus COD Reagent; HACH Company). Internal resistance data were recorded by electrochemical impedance spectroscopy (EIS) using a potentiostat (model PC4/750, Gamry Instruments Inc.) (18).

**Gas Analysis.** After each batch cycle, the gas composition in both the anaerobic tube headspace and gas bag was analyzed by gas chromatography using a gas tight syringe (250 μL, Hamilton Samplelock Syringe). The concentrations of H₂, N₂, and CH₄ were analyzed with one gas chromatograph (GC) (argon carrier gas; model 2610B; SRI Instruments), and the concentration of CO₂ was analyzed with a separate GC (helium carrier gas; model 310, SRI Instruments). Because nitrogen served as a dilution gas, it was removed from the calculations in order to find the concentrations of H₂, CO₂, and CH₄ produced in the system.

**Hydrogen Yield and Production.** Reactor performance was evaluated in terms of hydrogen recovery, energy recovery, volumetric density, and hydrogen production rate. The total theoretical number of moles produced based on COD removal, nₜ, is given by eq 1,

$$n_{th} = \frac{b_{H_2}/s \cdot \int_{0}^{t} I dt}{M_S}$$

where \(b_{H_2}/s = 4 \text{ mol/mol} \) is the maximum stoichiometric hydrogen production possible from the substrate, \(n_{th} = 28 \text{ mL} \) is the volume of liquid in the reactor, \(\Delta S \) (g COD/L) is the change in substrate concentration over a batch cycle, and \(M_S = 82 \text{ g/mol} \) is the substrate molecular weight. To convert the COD (g COD/L) to moles of acetate, a conversion factor of 0.78 g COD/g sodium acetate was used. The moles of hydrogen that can be recovered based on the measured current, \(n_{CE} \), is given by eq 2,

$$n_{CE} = \frac{\int_{0}^{t} I dt}{2F}$$

where \(I = V/R_{th} \) is the current (A) calculated from the voltage across the resistor (10 Ω), \(2 \) is used to convert moles of electrons to moles of hydrogen, \(F = 96 485 \text{ C/mol e}^- \) is Faraday’s constant, and \(dt \) (s) is the interval (20 min) over which data were collected. The Coulombic hydrogen recovery is given by eq 3,

$$r_{CE} = \frac{n_{CE}}{n_{th}} = C_E$$

where \(C_E \) is the Coulombic efficiency (2). The moles of hydrogen recovered relative to that possible based on the measured current is the cathodic hydrogen recovery (\(r_{ce} \)), calculated as
substrate is given by eq 7,

\[ r_{\text{Cat}} = \frac{n_{\text{H}_2}}{n_{\text{CE}}} \]  

(4)

where \( n_{\text{H}_2} \) is the number of moles of hydrogen recovered during a batch cycle.

The maximum volumetric hydrogen production rate \( (Q) \) measured in m\(^3\) H\(_2\)/m\(^3\) of reactor per day (m\(^3\) H\(_2\)/m\(^3\) d) is given by eq 5,

\[ Q = \frac{43.2 I r_{\text{Cat}}}{c_g(T)} \]  

(5)

where \( I \) (A/m\(^3\)) is the volumetric current density averaged over a 4 h period of maximum current production for each batch cycle (see Supporting Information) normalized by the liquid volume, \( c_g \) is the concentration of gas at a temperature \( T \) calculated using the ideal gas law, and 43.2 is for unit conversion.

**Energy Recovery.** The amount of energy added to the circuit by the power source, adjusted for losses across the resistor \( (W_e) \) is given by eq 6,

\[ W_e = \sum_{i=1}^{n} \left( E_{\text{ap}} \Delta t - I^2 R_{\text{ext}} \Delta t \right) \]  

(6)

where \( E_{\text{ap}} \) (V) is the voltage applied using the power source, \( \Delta t \) (s) is the time increment for \( n \) data points measured during a batch cycle, and \( R_{\text{ext}} = 10 \Omega \) is the external resistor. Energy balances based on heats of combustion are commonly used for electrolyzers \((20)\) and for estimating the energy content of organic matter \((21)\). They have also been used in a previous MEC study; therefore, the same approach was used here \((1)\). The amount of energy added by the substrate is given by eq 7.

\[ W_s = \Delta H_s n_s \]  

(7)

where \( \Delta H_s = 870.28 \) kJ/mol is the heat of combustion of the substrate, and \( n_s \) is the number of moles of substrate consumed during a batch cycle based on COD removal. The energy efficiency 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

\[ \eta_e = \frac{n_{\text{H}_2} \Delta H_{\text{H}_2}}{W_e} \]  

(8)

where \( \Delta H_{\text{H}_2} = 285.83 \) kJ/mol is the energy content of hydrogen based on the heat of combustion \((\text{upper heating value})\) and \( W_{\text{H}_2} = n_{\text{H}_2} \Delta H_{\text{H}_2} \). The efficiency relative to the added substrate \( (\eta_s) \) is given by eq 9.

\[ \eta_s = \frac{W_{\text{H}_2}}{W_s} \]  

(9)

The overall energy recovery based on both the electricity and substrate inputs \( (\eta_{E+S}) \) is given by eq 10.

\[ \eta_{E+S} = \frac{W_{\text{H}_2}}{W_e + W_s} \]  

(10)

The percentages of energy contributed by the power source \( (\varepsilon_e) \) and substrate \( (\varepsilon_s) \) were calculated as

\[ \varepsilon_e = \frac{W_e}{W_e + W_s} \]  

(11)

\[ \varepsilon_s = \frac{W_s}{W_e + W_s} \]  

(12)

**Results**

**Hydrogen Production.** Hydrogen production rates increased with the applied potential \((\text{ANOVA}; p < 0.05)\) to a maximum of \(3.12 \pm 0.02 \) m\(^3\) H\(_2\)/m\(^3\) d at \( E_{\text{ap}} = 0.8 \) V \((\gamma = 7.5 \text{ mS/cm}; \text{Figure 2})\). Increasing the conductivity to 20 mS/cm increased the hydrogen production rate for applied voltages of \( E_{\text{ap}} = 0.3-0.6 \) V. The hydrogen production rate at 20 mS/cm was \(2.61 \pm 0.1 \) m\(^3\) H\(_2\)/m\(^3\) d \((E_{\text{ap}} = 0.6 \text{ V})\), and at 7.5 mS/cm the production was \(1.99 \pm 0.07 \) m\(^3\) H\(_2\)/m\(^3\) d. The production rate increased with the higher conductivity solution in part due to a decreased internal resistance of \(10 \pm 2 \Omega\) at \( \gamma = 20 \text{ mS/cm}, \text{compared to } 20 \pm 3 \Omega \text{ at } \gamma = 7.5 \text{ mS/cm}\).

At an applied voltage of \( E_{\text{ap}} = 0.7 \) V, the hydrogen production rate in the high conductivity solution dropped appreciably, and we were unable to obtain reproducible hydrogen production data at this applied voltage \(\text{(see Supporting Information Table S1 for all data). Furthermore, once we had conducted a test at } E_{\text{ap}} = 0.7 \text{ V in the 20 mS/cm solution, the system produced poor performance at any other applied voltage, indicating irreversible damage to the bacteria in the biofilm. In contrast, results were reproducible when changing to any other applied potential for } E_{\text{ap}} < 0.6 \text{ V.} \)

Although anode potentials became less negative with the increased applied voltage in all tests (Figure 3), at an applied voltage of \( E_{\text{ap}} = 0.7 \) V in the higher conductivity solution there was a sharp increase in the anode potential. This indicates damage to the bacteria that could arise for a number of reasons, including a high applied potential, current density, and solution conductivity. High solution conductivity has been shown to adversely affect bacteria in MFC tests \((18, 22)\). Higher current densities alone are likely not the sole reason for the problem with performance at 0.7 V, as higher current densities obtained in MFC studies have not affected the bacteria \((15)\).

**Hydrogen Recoveries.** Coulombic efficiencies did not significantly vary with applied voltage and had an average \(\eta_e = 92 \pm 6\%\) (range: 79 \pm 3 to 98 \pm 0\%; Figure 4). These values demonstrate a high efficiency of capturing electrons.
from the substrate as current. The cathodic hydrogen recoveries from the generated current ranged from 78 ± 1 to 96 ± 1% (E<sub>ap</sub> = 0.3–0.8 V) (Figure 4). Cathodic hydrogen recoveries were slightly reduced using the high conductivity solution (γ = 20 mS/cm) for reasons not well understood.

At E<sub>ap</sub> = 0.2 V, an appreciable drop in hydrogen recovery occurred for both the high- and low-conductivity solutions. At this low applied voltage, the reaction time needed for a complete fed batch cycle (θ, defined as the time where the current dropped below 0.5 mA) increased to an average of 66 h, and increased methane concentrations using the 7.5 mS/cm solution (28 ± 0% at E<sub>ap</sub> = 0.2 V vs 4 ± 0% at E<sub>ap</sub> = 0.3 V) were measured in the produced gas (Figure 5). In contrast, at higher voltages hydrogen concentrations were greater than 87 ± 0% (7.5 mS/cm) and 86 ± 3% (20 mS/cm). Thus, it is concluded that at E<sub>ap</sub> = 0.2 V the low recovery of hydrogen was primarily due to the reduced cathodic hydrogen recovery, which resulted from an increase in methanogenesis at the increased reaction times.

Energy Recoveries. The energy recoveries ranged from η<sub>E=5</sub> = 75 ± 1 to 86 ± 2% for the 7.5 mS/cm solution, and from 66 ± 6 to 80 ± 4% for the 20 mS/cm solution at applied voltages >0.3 V (Figure 6). On average, energy recoveries were η<sub>E=5</sub> = 78 ± 4% for the 7.5 mS/cm solution and 72 ± 6% for the 20 mS/cm solution. Energy recoveries were not significantly correlated with applied voltage over this range (E<sub>ap</sub> = 0.3–0.8 V; ANOVA, p > 0.38). The energy recoveries decreased sharply at E<sub>ap</sub> = 0.2 V at both solution conductivities for reasons described above relative to hydrogen cathodic recoveries.

Energy and Substrate Efficiency. The efficiency relative to only the electrical input ranged from 194 ± 2% (E<sub>ap</sub> = 0.8 V) to 406 ± 6% (E<sub>ap</sub> = 0.3 V), and the substrate efficiency was always above 95 ± 2% within this range of applied voltages (Figure 7A). At the higher applied voltages within this range, a larger amount of energy was derived from the power source, whereas at the lower applied voltages the substrate had a greater contribution (Figure 7B). For example, at E<sub>ap</sub> = 0.4 V roughly 75% of the energy was derived from the substrate, whereas only 25% came from the power source. Decreasing the voltage to E<sub>ap</sub> = 0.2 V decreased the contribution of the power source to 12 ± 0%, and the substrate contributed 88 ± 0%.

Discussion

The MEC examined here produced a maximum overall energy recovery of 86 ± 2% at a hydrogen production rate of 1.02 ± 0.05 m<sup>3</sup>H<sub>2</sub>/m<sup>3</sup> d, with an applied voltage of E<sub>ap</sub> = 0.4 V (7.5 mS/cm). Higher production rates could be achieved by increasing the applied voltage (3.12 ± 0.02 m<sup>3</sup>H<sub>2</sub>/m<sup>3</sup>d at E<sub>ap</sub> = 0.8 V), although this resulted in a greater percentage of the recovered energy being contributed by the electrical power source. Increasing the solution conductivity improved hydrogen production rates (1.41 ± 0.07 m<sup>3</sup>H<sub>2</m<sup>3</sup>d at E<sub>ap</sub> = 0.4 V), but overall energy recoveries decreased due to lower cathodic hydrogen recoveries. Although increasing the ionic...
conductivity demonstrates how the performance of an MEC can be improved, solution conductivities of actual wastewaters may be lower than optimum, for example, 1.5–2 mS/cm for domestic wastewater in State College, PA. Hydrogen concentrations remained above 87 ± 0% for applied voltages $E_{ap} = 0.3–0.8$ V. At $E_{ap} = 0.2$ V, hydrogen concentrations decreased because of a longer reaction time that was favorable for methanogenic growth.

The energy recoveries reported here are based on heats of combustion ($\Delta H$), which are measures of the total (thermal) energy. We used this approach to be consistent with previous MEC studies and with other studies on water electrolysis that report recoveries based on $\Delta H$ (1, 2, 20, 23). An alternate approach is to calculate energy content Gibbs free energy ($\Delta G$), which indicates the total energy is less due to entropy losses. Using that approach lowers the calculated energy recoveries. For example, using the results from the $E_{ap} = 0.4$ V experiment to calculate the energy content of the produced hydrogen based on $\Delta G$, the overall recoveries are 21% lower (86% using $\Delta H$ vs 72% using $\Delta G$). Detailed calculations showing both approaches are included in the Supporting Information.

Compared to other studies that used a membrane in the MEC, these results show that it is possible to achieve similar or higher hydrogen recoveries when the membrane is omitted (Table 1). In addition, hydrogen production rates are higher than those reported in other studies, and energy recoveries are very high. Using a CEM and a 1:1 anode to cathode surface area, Rozendal et al. obtained an overall energy recovery of 53% at a hydrogen production rate of 0.02 m$^3$ H$_2$/m$^2$ d ($E_{ap} = 0.5$ V) (3). In a similar system, but using an anion exchange membrane (AEM), the overall energy recoveries were 23%, and the hydrogen production rate was ca. 0.3 m$^3$ H$_2$/m$^2$ d despite applying a higher voltage of $E_{ap} = 1.0$ V (4). By increasing the anode surface area using graphite granules, incorporating an AEM, and collecting gas using the same anaerobic tube used here in a two-chamber system, Cheng and Logan achieved an overall recovery of 82% at a production rate of 1.10 m$^3$ H$_2$/m$^2$ d for $E_{ap} = 0.6$ V (1). Although the overall recovery at the same applied voltage in this study was slightly less (80 ± 2%), the hydrogen production rate achieved here was about 84% larger than Cheng and Logan.

Operating a MEC without a membrane can potentially affect the purity of gas produced. It was found here that the produced gas was > 87% pure H$_2$ at applied potentials greater than 0.2 V and that methane concentrations at these applied potentials remained below 4.4 ± 0.3%. Part of the low rate of methanogenesis is due to the exposure of the reactor biofilm to air in between feeding cycles. When the reactors were operated under completely anaerobic conditions at $E_{ap} = 0.6$ V, the methane concentrations averaged 3.5 ± 0.2% (see Supporting Information). Exposing the reactors to air in between batch cycles, however, decreased the average methane concentrations to 0.9 ± 0.1% at $E_{ap} = 0.6$ V. These results suggest a strategy for controlling methanogenesis in these reactors based on either intermittent draining and air-exposure or perhaps in situ air-sparging of the liquid inside the reactor. Because facultative exoelectrogenic bacteria have been found in MFC systems (8, 24), exposing the biofilm to air may not be detrimental to electricity generation. However, air exposure could limit the growth of exoelectrogenic bacteria, such as Geobacter spp., which are strict anaerobes (25). Methods for reducing methanogenic consumption of hydrogen in a MEC need to be further investigated, such as continuous operation at a short reaction time, reducing the solution pH, and operating under carbon-limited conditions (7, 26, 27). Reaction time was shown to be important here as methane concentrations substantially increased to 28 ± 0% at the longest reaction time of $\theta = 66$ h ($E_{ap} = 0.2$ V), compared to <1% at $\theta = 17$ h ($E_{ap} = 0.6$ V).

The development of an MEC architecture that does not require a membrane and a reactor design that has high efficiencies are important steps in making electrohydrogenesis an economically viable process for producing hydrogen. Typical fermentation processes using glucose show conversion efficiencies of around 18–38% (28), whereas this study showed values in the range of 72–93% (see Supporting Information Table S1). Water electrolyzers typically have energy efficiencies in the range of 56–73% (23), yet the MEC in this study had efficiencies as high as 400% when compared on the same basis of electricity energy input. Furthermore, water electrolysis typically requires 5.6 KWh/m$^3$ H$_2$, but in this study the energy demand was only 0.9 KWh/m$^3$ H$_2$ at an applied voltage of $E_{ap} = 0.4$ V. This corresponds to an electrical energy input of 0.28 mol H$_2$ per mole of hydrogen produced (based on higher heating value). These energy demands translate into a cost of $3.80$/kg H$_2$ for water electrolysis and $0.62$/kg H$_2$ for the MEC based on the 2005 U.S. average industrial price of electricity (29). With the U.S. Department of Energy’s goal of reducing the cost of hydrogen to $2.00–$3.00/kg H$_2$, electrohydrogenesis could prove to be a viable method for achieving this target (30).

**Supporting Information Available**
Figures, tables, and sample calculations mentioned within the text are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

**Acknowledgments**
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**Literature Cited**

### Table 1. Electrical Efficiencies, Overall Energy Recoveries, Volumetric Current Densities, and Hydrogen Production Rates Reported in the Literature Versus Those Obtained in This Study

<table>
<thead>
<tr>
<th>Reactor System</th>
<th>$E_{ap}$ (V)</th>
<th>$\eta_e$ (%)</th>
<th>$\eta_{elv}$ (%)</th>
<th>$I_e$ (A/m$^2$)</th>
<th>$Q$ (m$^3$/m$^3$ d)</th>
<th>Source</th>
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<tr>
<td>gas diffusion membrane electrode</td>
<td>1.0</td>
<td>148</td>
<td>23</td>
<td>28</td>
<td>0.33</td>
<td>4</td>
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<tr>
<td>no membrane with brush anode</td>
<td>0.8</td>
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<td>75</td>
<td>292</td>
<td>3.12</td>
<td>this study</td>
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<td>no membrane with brush anode</td>
<td>0.6</td>
<td>254</td>
<td>80</td>
<td>186</td>
<td>1.99</td>
<td>this study</td>
</tr>
<tr>
<td>AEM with granule anode</td>
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<td>261</td>
<td>82</td>
<td>99</td>
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<td>Nafion membrane</td>
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