Sustainable and efficient biohydrogen production via electrohydrogenesis

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Hydrogen gas has tremendous potential as an environmentally acceptable energy carrier for vehicles, but most hydrogen is generated from nonrenewable fossil fuels such as natural gas. Here, we show that efficient and sustainable hydrogen production is possible from any type of biodegradable organic matter by electrohydrogenesis. In this process, protons and electrons released by exoelectrogenic bacteria in specially designed reactors (based on modifying microbial fuel cells) are catalyzed to form hydrogen gas through the addition of a small voltage to the circuit. By improving the materials and reactor architecture, hydrogen gas was produced at yields of 2.01–3.95 mol/mol (50–99% of the theoretical maximum) at applied voltages of 0.2 to 0.8 V using acetic acid, a typical dead-end product of glucose or cellulose fermentation. At an applied voltage of 0.6 V, the overall energy efficiency of the process was 288% based solely on electricity applied, and 82% when the heat of combustion of acetic acid was included in the energy balance, at a gas production rate of 1.1 m³ of H₂ per cubic meter of reactor per day. Direct high-yield hydrogen gas production was further demonstrated by using glucose, several volatile acids (acetic, butyric, lactic, propionic, and valeric), and cellulose at maximum stoichiometric yields of 54–91%, and overall energy efficiencies of 64–82%. This electrohydrogenic process thus provides a highly efficient route for producing hydrogen gas from renewable and carbon-neutral biomass resources.

Results and Discussion

Hydrogen gas production from acetic acid, the predominant volatile acid produced from glucose or cellulose fermentation, was possible at applied voltages of >0.13 V, with the production rate increasing from 0.03 to 1.5 m³d⁻¹m⁻³H₂ (total reactor volume; up to 10.5 m³d⁻¹m⁻³H₂ based only on the anode liquid volume) at applied voltages of 0.2–0.8 V (Fig. 1). Increased production rates reduced the time needed for a complete batch cycle from 30 to 3 h. A reduction in cycle time accounts in part for the increased yields from 3.03 to 3.95 mol/mol H₂ at applied voltages of 0.3–0.8 V. At 0.2 V, the yield decreased to 2.01 mol/mol, suggesting that hydrogen losses through the membrane and tubing became appreciable relative to low H₂ production rates. The gas was nearly pure hydrogen (>99.5%) with only trace amounts of CO₂ and CH₄ in all experiments.

The energy efficiency ranged from ηₚ = 681–243% when evaluated in terms of only the voltage addition (0.2–0.8 V) as a result of energy contributed by bacterial oxidation of the acetate. In comparison, hydrogen produced by water electrolysis can never exceed 100%, and it typically has efficiencies of 50–70%. The external power needed for electrohydrogenesis could be obtained in practice by using MFCs, a hydrogen fuel cell, or other

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Abbreviation: MFC, microbial fuel cell.

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The electrohydrogenic process produced hydrogen at high yields from a variety of substrates (Table 1). Hydrogen was produced directly from cellulose particles with an overall hydrogen recovery of 68% and an energy recovery of 63%. The production rate of 0.11 m$^3$-d$^{-1}$-m$^{-3}$ from cellulose was less than that of acetate when the two substrates were added at the same concentration (1 g/liter) likely because of the slow hydrolysis rate of the cellulose particles (13). Hydrogen production rates could be improved by increasing the rate that volatile acids are produced from cellulose through further enrichment of cellulytic microorganisms to obtain cultures with higher intrinsic hydrolysis rates. Alternatively, adding a higher cellulose concentration would increase the overall production of volatile acids per volume of reactor and thus better match volatile acid production from cellulose with volatile acid consumption for electrohydrogenesis.

Glucose was converted to hydrogen gas at a rate (1.23 m$^3$-d$^{-1}$-m$^{-3}$) similar to that of acetate but at a lower overall recovery of 71% (8.55 mol/mol) (Table 1). This recovery is 4- to 5-times larger, however, than typically achieved through cellulose fermentation (14). The predominant acids produced by glucose fermentation include acetic, butyric, lactic, propionic, and valeric, all of which were successfully used to generate hydrogen gas in the electrohydrogenic process at energy recoveries of 66–82% (Table 1). Hydrogen production rates for lactic acid (1.04 m$^3$-d$^{-1}$-m$^{-3}$) were similar to those obtained with acetic acid, whereas the lowest rate was measured using valeric acid (0.14 m$^3$-d$^{-1}$-m$^{-3}$). Stoichiometric conversion efficiencies of these four volatile acids ranged from 67–90% (Table 1). The rate of mass transfer of acetic acid through the anion exchange membrane used here is low (12), suggesting that diffusive losses of volatile acids from the anode chamber through the membrane were minimal. These same volatile acids also are produced by fermentation of different types of organic matter; thus, the process developed here could be used with virtually any organic matter source as a method of high energy yield and high production rates of hydrogen.

Considerable attention is being focused on ethanol production from renewable biomass for use as a transportation fuel (15). However, the production of cellulose-derived ethanol presents substantial technical challenges because the cellulose must first be hydrolyzed and released as sugar. Ethanol production also is not practical from organic matter other than simple sugars. Moreover, fermentation-produced ethanol can only be separated from water by using highly energy demanding processes, and ethanol must be used in combustion engines that have low energy efficiencies compared with hydrogen oxidation in chemical fuel cells. Hydrogen production using electrohydrogenic reactors represents an immediate method for renewable energy production in the form of hydrogen gas for transportation. There are substantial infrastructure issues to be addressed in using hydrogen gas, but the environmental and energy-conversion efficiency benefits for hydrogen as a transportation fuel makes it worth addressing and solving these issues (16). Even if a hydrogen-based transportation system is never developed, sustainable hydrogen production from cellulose and fermentation end-products still is valuable as a sustainable method of hydrogen generation. One immediate application is for fertilizer production. Local production of fertilizers from cellulose-derived hydrogen gas could greatly reduce transportation costs for fertilizers and improve global agricultural yields and economics.

### Table 1. Hydrogen production using cellulose, glucose, or five different volatile acids at an applied voltage of 0.6 V

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$Y_{H_2}, \text{ mol of } H_2/\text{mol of substrate}$</th>
<th>Production rate, m$^3$-d$^{-1}$-m$^{-3}$</th>
<th>$\eta, %$</th>
<th>$\eta_{W+S}, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>8.55</td>
<td>1.23</td>
<td>266</td>
<td>64</td>
</tr>
<tr>
<td>Cellulose</td>
<td>8.20*</td>
<td>0.11</td>
<td>268</td>
<td>63</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3.65</td>
<td>1.10</td>
<td>261</td>
<td>82</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>8.01</td>
<td>0.45</td>
<td>285</td>
<td>77</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>5.45</td>
<td>1.04</td>
<td>283</td>
<td>82</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>6.25</td>
<td>0.72</td>
<td>248</td>
<td>79</td>
</tr>
<tr>
<td>Valeric acid</td>
<td>8.77</td>
<td>0.14</td>
<td>263</td>
<td>66</td>
</tr>
</tbody>
</table>

*Calculated per mole of hexose equivalent.
Materials and Methods

Reactor and Operation. The reactor was constructed by clamping an anion exchange membrane (AMI-7001; Membrane International, Glen Rock, NJ) between the anode (30 mm in diameter, 20 mm long; 14 ml) and cathode (40 mm long; 28 ml) chambers (12). The anode chamber was filled with graphite granules that were 2–6 mm in diameter (El Carb 100; Graphite Sales, Birmingham, AL) at a specific surface area of $A_s = 1.320 \text{ m}^2/\text{g}$, calculated as $A_s = 664d$, where $d = 4 \text{ mm}$ is the average particle diameter and $\theta = 53\%$ is the bed porosity. The granules were pretreated with a high-temperature ammonia gas process that increases current densities and reduces reactor acclimation times (10). A graphite rod (6.15 mm in diameter; Alfa Aesar, Ward Hill, MA) was inserted into the bed of granules, reducing the liquid volume to 6 ml. The cathode (1 cm²), made of carbon cloth and a Pt catalyst [0.5 mg/cm² Pt; prepared as previously described (17)], was placed in the cathode chamber close to the membrane and connected to the external circuit by a titanium wire (0.68 mm in diameter; Alfa Aesar). Hydrogen gas was collected by gluing the open bottom of a glass tube (80 mm long by 16.8 mm in diameter; empty bed volume of 18 ml) containing a crimp top with a thick rubber stopper to a hole cut into the top of the cathode chamber.

Bacteria derived from a soil (cellulose-fed reactor) or wastewater (all other substrates) were inoculated and enriched on a temperature ammonia gas process that increases current densities and reduces reactor acclimation times (10). A graphite rod (6.15 mm in diameter; Alfa Aesar, Ward Hill, MA) was inserted into the top of the cathode chamber. Reactor and Operation.

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