Evaluation of catalysts and membranes for high yield biohydrogen production via electrohydrogenesis in microbial electrolysis cells (MECs)
Shaoan Cheng and Bruce E. Logan

ABSTRACT

Hydrogen gas can be produced from fermentation end products such as acetic acid through the electrohydrogenesis process in microbial electrolysis cells (MECs). In many MEC reactors, precious metal catalysts and expensive cation exchange membranes are often used. Here we examine Co- and FeCo-based alternatives to Pt, and compare the performance of an anion exchange membrane with that of a cation exchange membrane (Nafion® 117). It is found that these alternative catalysts have 40–80% better performance than uncatalysed surfaces, but they do not equal the performance of Pt based on our electrochemical tests using cyclic voltammetry. It was also found that the anion exchange membrane (AEM) performance was equal to that of cation exchange membrane (CEM) at applied voltages of 600 mV or less in MEC tests, but that it exceeded performance of the CEM at voltages above 600 mV. These results demonstrate choosing catalysts will require both analysis of performance and materials costs, but that performance is improved for producing H₂ gas in MECs using AEMs.

Key words | BEAMR, biohydrogen, bioreactors, catalysts, electrolysis, hydrogen, membranes

INTRODUCTION

Conventional wastewater treatment is needed to avoid water pollution and to protect human health, but it is not sustainable as advanced treatment technologies are very energy-demanding. Methanogenesis is a very useful process to capture energy from organic matter in the form of methane, but it is less effective for low strength wastewaters or in colder climates. Two new processes being developed to accomplish wastewater treatment that produce a net amount of energy in a useful form are called electrogensis and electrohydrogenesis, using a nomenclature scheme that follows that used for methanogenesis (Logan 2007). In the electrogensis process, exoelectrogenic bacteria are able to release electrons exogeneously (outside the cell) to solid substrates (i.e. a carbon electrode), allowing electricity to be produced in a reactor called a microbial fuel cell (MFC). The oxidation reaction generated by the bacteria at the anode is sustained through the production of water at the cathode from electrons and protons released by the bacteria, and oxygen. The electrohydrogenesis process is similar except that a small potential must be added into the circuit and no oxygen is used at the cathode. As a result of these changes, hydrogen gas is evolved at the cathode in a reactor called a microbial electrolysis cell (MEC). The process has also been referred to as a bacterial electrolysis cell (BEC) and a bioelectrochemically assisted microbial reactor (BEAMR) (Liu et al. 2005c; Rozendal & Buisman 2005; Rozendal et al. 2006a). The hydrogen gas that is generated can be collected and used in combustion or fuel cell type system for power generation, or stored and sold as a merchant gas to offset treatment costs.

One limitation of the process is that the precious metal Pt is used on the cathode to enhance the efficiency and rate of hydrogen production. In addition to being expensive, the worldwide supplies of Pt are limited and it is doubtful that
supplies would be sufficient to meet the needs of high surface-area processes for wastewater treatment. In MFC research, it has been shown that non-precious metal catalysts, such as Co and Fe-based materials, can be used instead of Pt (Zhao et al. 2005; Cheng et al. 2006). Thus, we wondered if these materials could be used in MECs as less expensive alternatives to Pt. Another limitation of MECs is that a membrane is used to separate the anode and cathode chambers so that hydrogen produced at the cathode does not diffuse back into the anode chamber and get consumed by bacteria. Various types of membranes have been used in MFC tests, including the cation exchange membrane Nafion developed for hydrogen fuel cells and water electrolyzers (Liu et al. 2005a; Rozendal et al. 2006a; Ditzig et al. 2007), and ion exchange membranes including both cation and anion exchange materials (Rozendal et al. 2007). The yields of hydrogen and the current densities produced in these studies varied over a large range, and thus it is not possible to determine to what extent the membrane affected these performance parameters compared to other reactor differences such as electrode materials, system architecture or materials. In this study we analysed the electrochemical performance of two Co- and FeC-based catalysts, and compared their performance to Pt and plain carbon electrodes. In addition, we conducted MEC tests with two different membranes under exactly the same conditions to determine whether the type of membrane limited system performance.

**METHODS**

**Electrochemical reactors and catalysts**

A three-chambered electrochemical cell containing a working electrode (cathode electrode with 0.64 cm² projected surface area), a counter electrode (platinum plate with a projected surface area of 2 cm²), and an Ag/AgCl reference electrode (EE009 no leak electrode, Cypress Systems) as previously described (Cheng et al. 2006). Pt-containing cathodes were made using a commercial Pt catalyst (10 wt % Pt/C, E-TEK) and the same Nafion® binder to form a paste (7 µL of binder per mg of Pt/C catalyst). The paste was applied to one side of the wet-proofed carbon cloth (50 wt %, type B, E-TEK), and dried at room temperature for 24 h. Cobalt tetramethylphenylporphyrin (CoTMPP) was dissolved in chloroform (0.001 M) and mixed with Vulcan XC-72 carbon (320 mg per 100 mL) as previously described (Cheng et al. 2006). Iron cobalt tetramethyl-phenylporphyrin (FeCoTMPP) on carbon was made by adding ferricyanide into the above solution. The mixtures were air dried and then heated in an inert-gas atmosphere at 800°C for 1 hour. The materials (~0.6 mg cm⁻² metal TMPP loading) were applied to carbon cloth using a Nafion binder by the same method described above for the Pt catalyst cathode. Commercially available cathodes containing Pt were also tested as a positive control (A3EFCG/Std phosphoric Acid Fuel Cell Electrode). A cathode containing only carbon powder (Vulcan XC-72) was prepared as a non-catalyst control.

The cyclic voltammograms were obtained in a potential region of −1.8 to 0.2 V at a scan rate of 20 mV/s in a nutrient medium containing (g/L in deionised water, all at pH = 7): NH₄Cl (0.31), KCl (0.13), NaH₂PO₄·H₂O (2.69), Na₃HPO₄ (4.33). Before cyclic voltammetry was conducted the chambers were sparged with ultra-pure nitrogen gas (99.998%) to remove the dissolved oxygen in the solution.

**MECs and membranes**

A two-chamber cube-type MFC previously used to examine the effect of membranes on electricity generation and internal resistance (Kim et al. 2007) was modified for use as an MEC. The MECs consisted of two plastic (Plexiglas) cylindrical chambers each 2 cm long by 3 cm in diameter (each 14 mL liquid volume) separated by a membrane. The anode chamber was filled with graphite granules 2–6 mm in diameter (El Carb 100, Graphite Sales, Inc., USA; specific surface area of \( A_s = 1,320 \text{ m}^2/\text{m}^3 \), calculated as \( A_s = 6u/d \), where \( d = 4 \text{ mm} \) is the average particle diameter and \( u = 0.53 \) is the bed porosity). Granules were treated with a high-temperature ammonia gas process that increases current densities and reduces reactor acclimation times (Cheng & Logan 2007). A graphite rod (diameter 6.15 mm, Alfa Aesar, Ward Hill, MA, USA) was inserted into the bed of granules, producing a final liquid volume of 6 mL. The cathode (1 cm²) was made of carbon cloth and a Pt catalyst (0.5 mg Pt/cm², prepared as previously described (Cheng et al. 2006)); and was placed in the cathode chamber close
to the membrane and connected to the external circuit using a titanium wire (0.68 mm in diameter, Alfa Aesar, Ward Hill, MA, USA). The cation exchange membrane (CEM; Nafion™ 117, Dupont Co., DE) was pretreated by boiling in H$_2$O$_2$ (30% v/v) and deionised water, followed by soaking in 0.5 M H$_2$SO$_4$ and then deionised water, each for 1 hour. It was stored in deionised water prior to use. The anion exchange membrane (AEM; AMI-7001, Membrane International Inc., NJ) was preconditioned by immersion in a 50 mm phosphate buffer solution (pH 7) to allow for good ion conductivity.

The reactors were inoculated using anaerobic sludge (10 mL) and acetate (20 mM) in a nutrient medium containing (g/L in deionised water, pH 7): NH$_4$Cl (0.31), KCl (0.13), NaH$_2$PO$_4$·H$_2$O (2.69), Na$_2$HPO$_4$ (4.33), and a trace mineral and vitamin solution (Liu et al. 2005a,b). Both chambers were sparged with ultra-pure nitrogen gas (99.998%) for 30 min before the voltage was applied to the reactor. A positive voltage was applied to the circuit by connecting the negative pole of the power supply (3645A, Circuit Specialists Inc.) to the cathode, and the positive pole to the anode. The reactors were operated in fed batch mode until sustainable cycles of hydrogen production were obtained. All MEC tests were conducted in a temperature controlled room (30°C).

RESULTS AND DISCUSSION
Evaluation of cathode catalysts

The performance of the catalysts was evaluated in terms of two factors. The first was the voltage needed to initiate hydrogen production, as indicated by the flow of current, as shown by point $V_e$ in Figure 1a. The smaller the value of $V_e$, the lower the overpotential and thus the more effective the catalyst at driving hydrogen production. The second factor was the slope of the voltammogram when current was produced. As shown in Figure 1b, the catalyst with a steeper slope will more effectively catalyse the production of hydrogen gas by allowing a greater current per applied voltage.

Pt was clearly the most effective catalyst in all tests, as shown in Figure 2, with the values of $V_e$ and $V_h$ summarised in Table 1. The initial voltage is the most critical of these two factors as this demonstrates the ability of the catalyst to reduce overpotential. A non-catalysed carbon electrode required a potential of 1.0 V for current flow, while the commercial Pt catalyst and our self-made cathode required only 0.65 V for current production. The Co-based catalysts required 0.83 or 0.85 V depending on Co-loading, while the Fe-based catalysts required 0.90 V. Thus, the Co-based catalysts performed better than the Fe-based catalysts in these tests. If we extrapolate the results obtained here in our electrochemical tests, this would imply that 0.20 V would be needed in an MEC for the Co-catalyst, and 0.35 V for a non-catalysed surface. In tests using non-catalysed surfaces, we found that 0.5 V was needed for H$_2$ evolution, providing reasonable agreement with these findings (data not shown).

The Co and FeCo catalysts were relatively more effective in increasing the current densities, as shown by values of $V_h$ only slightly less than those of the Pt catalysts. We expect that this increase in current density compared to the plain carbon cloth control is primarily a result of the slightly increased surface area resulting from application of the metal compounds. Indeed, the use of high surface area materials for the cathode could be expected to increase overall efficiency of current generation by increasing the current, if not the current density (i.e. the current normalized to the surface area of the electrode).

As a result of these tests, it was concluded that these alternative catalysts can be used to reduce the minimum overpotential needed for hydrogen evolution and that they increased current densities compared to non-catalysed surfaces. The reduction in the value of $V_e$ was 17% compared to a non-catalysed surface, and the improvement in $V_h$ was 136%. While these results are encouraging, it is
recommended that alternatives to Pt continue to be investigated in MECs in order to reduce overall costs of the system.

Performance of MEC with different membranes

At low applied potentials (200 to 600 mV), the H₂ production rates of the two membranes were similar with the AEM producing slightly more hydrogen than the CEM (Figure 3). At the higher applied voltages (>600 mV), the hydrogen production rate continued to increase using the AEM, but the rates did not increase using the CEM. The reasons for this lack of an increase in hydrogen production when using the CEM is not clear. However, it has been shown that Nafion will exchange cations other than protons (Rozendal et al. 2006b; Kim et al. 2007). This leads to changes in pH that can affect both bacteria in the anode chamber through decreased localised pHs, and performance of the cathode through elevated pH which can reduce the availability of protons and thus limit hydrogen evolution rates. The pH in both chambers at the start of the test were 7, but after a full cycle of operation the bulk pH in cathode chamber increased slightly to 7.1–7.2, and decreased in the anode chamber to 6.7–6.8. These bulk pH values, however, do not necessarily represent the pH values at the surfaces of the electrodes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$V_e$ (V)</th>
<th>$V_h$ (mA/cm² V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>−1.0</td>
<td>51.6</td>
</tr>
<tr>
<td>40% FeCoTMPP</td>
<td>−0.90</td>
<td>98.4</td>
</tr>
<tr>
<td>40% CoTMPP</td>
<td>−0.85</td>
<td>121.9</td>
</tr>
<tr>
<td>60% CoTMPP</td>
<td>−0.85</td>
<td>113.3</td>
</tr>
<tr>
<td>Pt (E-TEK)</td>
<td>−0.65</td>
<td>166.4</td>
</tr>
<tr>
<td>Pt (home-made)</td>
<td>−0.65</td>
<td>185.3</td>
</tr>
</tbody>
</table>
CONCLUSIONS

These results demonstrate that membranes designed to transfer anions can equal or exceed those based on cation exchange. Even though proton transfer from the anode to cathode is desired, CEMs often transfer positively charged species other than protons that can maintain charge balance, allowing pH to vary in the system. It has also been shown that Co and FeCo-based catalysts can improve hydrogen evolution rates compared to non-catalysed surfaces, but they are not as successful at reducing the minimum voltages needed compared to Pt. Thus, additional work is needed to find more suitable alternatives to Pt for MECs.

REFERENCES


Erratum

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Publisher’s note. We very much regret that in the course of production the correct version of Figure 2 of this article was replaced by a figure from another article. The correct version of Figure 2 is shown below.

Figure 2 | Cyclic voltamogram studies with different cathode catalysts for hydrogen evolution. The “cytochrome” catalyst is made by adsorbing enriched bacteria on carbon powder (Vulcan XC-72).