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Direct utilization of fermentation products in an alcohol fuel cell

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HIGHLIGHTS

► Used fermented sugar in a passive DAFC; only solids >0.2 μm removed from fermentate.
► DAFC performance on fermentate can be comparable to that of aqueous ethanol.
► Ionic strength and ethanol concentration of the fermentate had the largest effects.

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ABSTRACT

Due to energy demands and environmental concerns there has been a great interest in searching out renewable energy sources as an alternative to fossil hydrocarbons. These must also be environmentally sustainable and convenient to implement. Glucose has been proposed as a renewable energy source for several reasons including its energy density, safety, sustainability, and the ability to be scavenged from native ecosystems or from waste streams. Here we describe the use of a bio-hybrid fuel cell to oxidize the glucose to ethanol and limit parasitic power losses by using the fermented alcohol with minimal preparation in a direct alcohol fuel cell. Moving from using dilute alcohol in deionized water to the complex matrices of fermented media raises many questions about the performance and lifetime of the fuel cell and its components. These questions include but are not limited to the effects of starting materials and byproducts of the fermentations and the performance of the catalytic oxidation of ethanol at metal catalysts in batch mode. This study examines the effects of multiple components such as ionic strength, cation size, buffering strength, alcohol concentration, fermentation/fuel cell byproducts, and interfering organics on fuel cell operation.

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1. Introduction

Due to energy demands and environmental concerns there has been a great interest in searching out renewable energy sources as an alternative to fossil hydrocarbons. These must also be environmentally sustainable and convenient to implement. There have been decades of research and development in the area of proton exchange membrane (PEM) fuel cells to provide clean, quiet power generation [1–3]. However, the traditional renewable fuels for PEM fuel cells, hydrogen and methanol, have significant hazards of flammability and toxicity. These hazards impose additional logistics burdens, in addition to safety issues for the end user.

Glucose has been proposed as a renewable energy source for several reasons. It has an energy density of 16 MJ kg^{-1}, lower than ethanol (30 MJ kg^{-1}) or gasoline (47 MJ kg^{-1}), but still quite high [4]. Unlike more traditional fuels, however, glucose is completely safe, being non-flammable and non-toxic, making it easier to store and transport, especially in many areas of the world without a fuel pipeline infrastructure. Provided glucose is kept dry, it is entirely inert, subject neither to evaporation nor to decay. Glucose can be produced simply, in an environmentally sustainable manner, and in many areas of the world. In addition, glucose can be scavenged locally from native ecosystems or from waste streams, an important consideration for minimizing logistics.

While glucose has some significant advantages there are some significant challenges in how it should be best utilized. It is not compatible with traditional PEM fuel cell technologies. Two options commonly suggested for electrochemical power generation from glucose are enzymatic or microbial fuel cells.

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Enzymatic fuel cells have shown promise, but complete oxidation of glucose is necessary to gain full advantage of its high energy density. This is only possible if a cascade of enzymes is designed, all of which need to be stable in the same operational environment. Designing these cascades is an active area of research [5] but if one enzyme in a cascade losses activity it cannot be easily replaced, thus eventually causing the fuel cell to fail.

Microbial fuel cells (MFCs) utilize micro-organisms' natural enzyme cascades for effectively extracting energy from glucose. The microbes automatically detect and replace any inactive enzymes. The coulombic efficiency of MFCs is high, reaching 65% [6]. Unfortunately MFCs suffer significantly from low power density. The problem is that whole microbes serve as the catalysts. This limits the scale of the electrode materials to single micron dimensions because, for the highest electron transfer efficiency, the microbes need to be in direct contact with the electrode surface. These systems are limited to power densities of single W m^{-2} [6,7]. Attempts to get around this limitation of MFCs by using soluble electron mediators (which in theory would relieve the microbes of the necessity for direct electrode contact) have so far failed due to diffusion limitations. The power densities are not increased by the orders of magnitude that are required, and many soluble electron mediators are toxic or have proven to be unstable [8].

There have been demonstrations in the literature of using bio-derived alcohols in direct alcohol fuel cells (DAFCs) [9–12]. Performance is good – very much what one would expect from a PEM fuel cell. However, to date this has been accomplished by producing the alcohol, purifying it, and then diluting it in purified water to run in the DAFC. In this process, not only the energy from the oxidation of the glucose to alcohol is lost but also the purification steps are energy intensive, causing further energy loss. For real-life applications these parasitic losses must be minimized, yet in analyses of DAFC efficiency they are often overlooked. In a review of the literature, certain aspects of DAFCs have been explored in depth, such as the effects of utilizing ethanol as opposed to methanol [11–13], but parasitic loss has been mostly ignored.

Here we describe the use of a bio-hybrid fuel cell where the starting fuel, glucose, is oxidized to ethanol and parasitic power losses are limited by using the fermented ethanol in the DAFC with minimal preparation. The fuel cells described here are also passive: no liquids or gases are pumped past either electrode, no chemicals are added to facilitate the process, and (except for fermentations) they are run on the laboratory benchtop. To limit the scope, we first perform batch fermentation of glucose to ethanol with yeast (a well-studied process), then operate a DAFC in batch mode using the product of the fermentation. The only purification step is to filter out solids. Moving from using dilute alcohol in deionized water to the complex matrices of fermented media raises many questions about the performance and lifetime of the fuel cell and its components. These questions include but are not limited to the starting materials and byproducts of the fermentations, and the performance of the catalytic oxidation of ethanol at metal catalysts in batch mode. Some of these components include the glucose feedstock and the known oxidation products acetaldehyde and acetate [10]. While this would be sufficient for chemically derived fuels, to support yeast fermentations the organisms need other essential components in order to thrive. Therefore, this study also examines the effects of multiple other components such as ionic strength, cation size, buffering strength, alcohol concentration, fermentation/fuel cell byproducts, and interfering organics in the microbial media's composition (i.e. salts, amino acids, protein concentration, etc.). It should also be kept in mind that conditions suitable for fermentation are not ideal for PEM fuel cell operation [9].

2. Experimental materials and methods

2.1. Chemicals

Control experiments are conducted in either deionized (DI) water or a yeast growth medium, both with a known amount of ethanol (molecular biology grade, absolute, Sigma–Aldrich) added. All DI water used in this study is from a deionized reverse osmosis source passed through a Barstead Nanopure water polisher. Similarly, the acetaldehyde, sodium acetate, acetic acid, glucose, KH_2PO_4, Na_2HPO_4, NaCl, $MgSO_4$, and KCl are research grade or better, and are obtained from Sigma–Aldrich or Fisher.

Yeast (Bakers' Yeast, *Saccharomyces cerevisiae Type II*, Sigma) fermentations use D-(+)-Glucose from Sigma Life Science (SigmaUltra, 99.5%). Sterile filters (0.2 μm nylon) used to remove organisms and solids from the fermented media are from various manufacturers. Yeast nitrogen base (YNB) growth medium is from Difco prepared as directed for 1× solution, with 4% glucose added, then sterile-filtered. M9 growth medium is prepared as follows: 3 g KH_2PO_4, 6 g Na_2HPO_4 (anhydrous), 5 g NaCl, and 1 mL of 1 M $MgSO_4$ (120.37 g) are dissolved in DI water to make 1 liter (L) of solution, and sterile-filtered.

The chloride salts used to determine sensitivity of the DAFC to cation size are LiCl (Fisher Scientific Co.), CsCl (Alfa Aesar, 99.9%), and KCl and NaCl (Sigma). The 5% v/v sulfuric acid (H_2SO_4) used to clean the DAFC between runs is prepared from 50% v/v stock (Fluka) and DI water.

2.2. Supplies and instruments

The DAFCs are purchased from fuelcellstore.com (SKU 1071041, H-Tec Ind., GmbH, single plate methanol/air PEMFC), and are intended by the manufacturer as direct methanol fuel cells. The current collectors are stainless steel mesh. These fuel cells were selected to be similar to those used in bio-hydrogen generation studies [14–16].

For electrical measurements (current vs. time and linear sweep voltammetry) we use an Electrochemical Workstation from CH Instruments (Austin, TX), either the 660A model with a single-potentiostat or the 760B model with a bi-potentiostat. High-performance liquid chromatography (HPLC) measurements are performed with an Agilent HPLC 1200 equipped with a refractive index detector. The HPLC column is an Aminex HPX-87H cation exchange column (300 mm × 7.8 mm i.d.; 9 μm polystyrene divinylbenzene beads) from Bio-Rad Laboratories.

2.3. Experimental procedures

In order to differentiate between the effects of media components and fermentation products on DAFC performance, the investigation is performed in three stages. In the initial stage, the performance of the DAFCs with aqueous ethanol is carefully evaluated to establish a baseline for comparison. In the second stage, media is prepared with 3% (v/v) ethanol, to fuel the DAFCs. In the third stage, media containing 4% (w/v) glucose is prepared, and fermented to completion with yeast (4 days at 40 °C). The fermentate is sterile-filtered, with no other processing, and fuels the DAFCs. The DAFC performance is evaluated via amperometric (current vs. time, I–t) curves poised at 200 mV (for 1800 s, unless otherwise stated), followed by linear sweep voltammetry (LSV) from 0 to 600 mV at a scan rate of 1 mV s^{-1}. The DAFC's cathode is utilized both as a pseudo-reference and as the counter electrode for the LSV and amperometric current vs. time (I–t) experiments, as is common practice in PEM fuel cell analysis.