

# Glucose-Driven Fuel Cell Constructed from Enzymes and Filter Paper

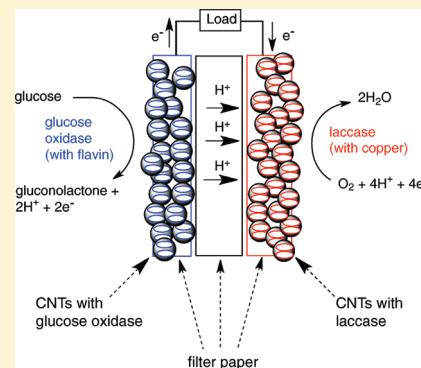
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 Supporting Information

**ABSTRACT:** A glucose-driven enzymatic filter-paper fuel cell is described. A strip of filter paper coated with carbon nanotubes and the glucose oxidase enzyme functions as the anode of the enzyme fuel cell. Another strip of filter paper coated with carbon nanotubes and the laccase enzyme functions as the cathode. Between the anode and the cathode, a third strip of filter paper is placed that holds the glucose, which is the fuel, and that allows the transport of ions. The design of the cell is simple, and all the materials used for the construction are readily available and biocompatible. The cell utilizes the oxidation of glucose to generate electricity and is useful to demonstrate how chemical energy can be converted to electrical energy.

**KEYWORDS:** First-Year Undergraduate/General, High School/Introductory Chemistry, Demonstrations, Physical Chemistry, Hands-On Learning/Manipulatives, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Enzymes, Laboratory Equipment/Apparatus



Human life is powered by glucose metabolism.<sup>1</sup> A simple device that converts the oxidation energy of glucose to electricity is described. It is constructed with readily available enzymes using strips of filter paper. Given the interest in portable energy sources, this device makes an appealing demonstration or laboratory project that illustrates many chemical principles for beginning chemistry students.

A fuel cell is a device that generates electrical energy from a chemical reaction. As with most commercial batteries, the fuel is dissipated in the discharge process. The fuel cell can be recharged only by supplying fresh fuel. An enzyme fuel cell uses enzymes at the electrodes to catalyze the chemical reaction. In principle, any substance that can be metabolized by an organism could be regarded as a potential fuel for an enzyme fuel cell. Conventional fuel cells use inorganic catalysts and tend to operate at elevated temperatures, often in excess of 100 °C.<sup>3</sup> In contrast, an enzyme fuel cell can operate at room temperature. Because of the substrate specificity of enzymes, the design can be simplified by removing expensive membranes that separate the anode and cathode. In addition, enzyme fuel cells are biocompatible and offer the possibility of being implanted.<sup>4</sup>

An easy-to-make enzyme fuel cell fabricated from filter paper is described (Figure 1). A strip of filter paper is coated with carbon nanotubes (CNTs) and with the glucose oxidase enzyme, which catalyzes the oxidation of glucose to gluconolactone.<sup>5</sup> This strip functions as the anode of the enzyme fuel cell. Another strip of filter paper is coated with CNTs and the laccase enzyme, which catalyzes the reduction of molecular oxygen in air to water.<sup>6</sup> This strip functions as the cathode. Between the anode and the cathode of the enzyme fuel cell, a third strip of filter paper is placed that holds the glucose, which is the fuel, and allows the

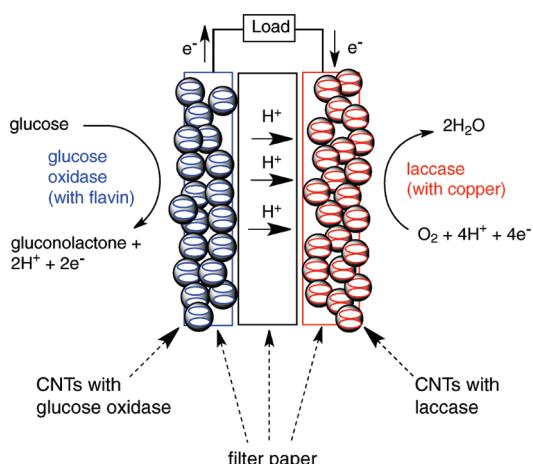
transport of ions. In practice, several strips of filter paper could be used in the middle to increase the fuel capacity. The chemical reactions occurring in the fuel cell are shown in Scheme 1.

The first enzyme fuel cell appears to have been reported by Yahiro et al.<sup>7</sup> in 1964. This cell contained platinum foil electrodes immersed in phosphate buffer in both the anode and cathode compartments, which were separated by a membrane. The cell utilized glucose as the fuel and employed glucose oxidase in the buffer solution to catalyze its oxidation. Since then, other enzyme fuel cells have been reported,<sup>4</sup> but none to our knowledge that uses filter paper. The topic of biofuel cells utilizing glucose is being actively researched<sup>8,9</sup> as one of the promising alternative renewable energy sources. We describe the construction and performance of a glucose-driven filter-paper fuel cell that is well suited for use as a lecture demonstration or an undergraduate laboratory experiment.

## MATERIALS AND METHODS

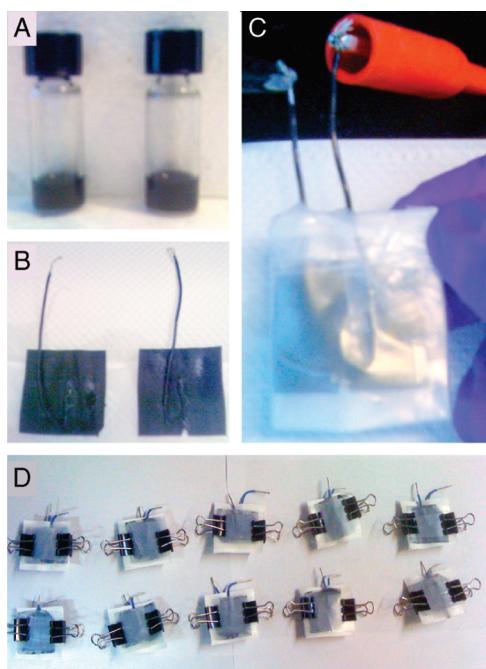
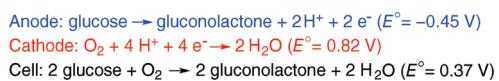
All chemicals are obtained from Sigma-Aldrich (St. Louis, MO) or are readily available from the chemistry department stockroom. There are several steps to fabricate the enzymatic filter-paper fuel cell: the preparation of the enzyme-containing conductive “inks”, their application to filter paper, and the assembly of the filter paper strips into a working fuel cell. To prepare the conductive ink, multiwalled carbon nanotubes (CNTs; product number 576808) and sodium dodecylbenzenesulfonate were dispersed in water at concentrations of 20 and 10 mg/mL, respectively, followed by probe-sonication for 1 min.

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**Figure 1.** Schematic illustration of the glucose-driven filter-paper fuel cell.

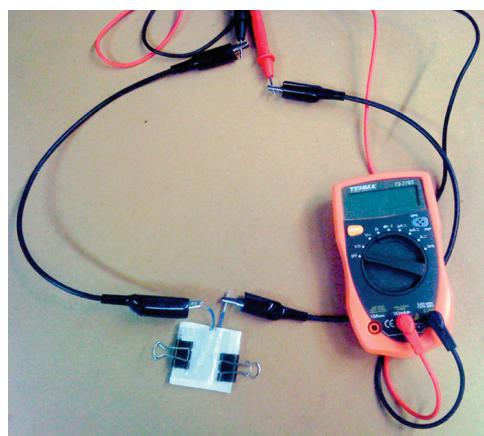
### Scheme 1. Chemical Reactions in the Enzymatic Fuel Cell



**Figure 2.** Components of the enzymatic filter-paper fuel cell: (A) the enzyme-containing conductive inks; (B) the anode and cathode made from filter paper coated with the conductive inks to which copper wires have been attached by conductive glue; and (C) the assembled structure, which contains a middle strip of filter paper that holds the glucose fuel. (D) Ten sets of the paper fuel cells.

Then, 5 mg/mL of glucose oxidase or laccase was dissolved in the unbuffered CNTs suspension to form the enzyme-containing conductive inks (Figure 2A).

For the fabrication of anode and cathode from the filter paper, the enzyme-containing conductive ink was applied to a strip of



**Figure 3.** An enzymatic filter-paper fuel cell is tested for its operating performance in air using a multimeter.

filter paper by a pipet. Typically, for each run, 100 μL of the enzyme-containing conductive ink was applied to a piece of filter paper cut to the size of 2 cm × 2 cm, followed by drying at room temperature for about 20 min. For each filter paper, the coating process is repeated five times to load multilayers of enzymes on the filter paper. Copper wires are attached to the anode and cathode filter paper strips using conductive glue (Electrodag 502, purchased from Ted Pella, Inc., Redding, CA) (Figure 2B). An untreated piece of filter paper is placed between the treated pieces of filter paper. The three strips of filter paper acting as anode, separator, and cathode are stacked closely together, wrapped with Parafilm, and clamped by two binder clips (Figure 2C). By this simple procedure, 10 sets of such filter-paper fuel cells are easily made with only 5 mL of “conductive inks” (Figure 2D).

### HAZARDS

Gloves and safety glasses are to be worn in carrying out the above procedure. Care should be taken to avoid inhalation or skin contact with these chemicals. When handling carbon nanotubes, avoid breathing dust and ensure adequate ventilation. The nanotube dust, sodium dodecylbenzenesulfonate, and glucose oxidase may cause irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled. Keep in suitable, closed containers for disposal.

### PERFORMANCE OF THE FUEL CELL IN GLUCOSE SOLUTION

The assembled fuel cell (wrapped in Parafilm) was placed in a beaker containing 10 mM air-saturated glucose solution (1× phosphate buffered saline, pH 7.4) to allow the filter paper to absorb the glucose. After 5 min, the fuel cell was removed from the solution and tested for its operating performance in air using a multimeter (Figure 3). Typically, the open-circuit voltage and the maximum current density of this filter-paper fuel cell were around 0.18 V and 20 μA/cm<sup>2</sup>, respectively. The time dependence of power density and current density of the fuel cell with a load in the circuit were tested immediately after removing it from the 10 mM glucose solution (Figure 4). The power and current density of the fuel cell were initially high owing to the sufficient supply of glucose as fuel. However, these density values gradually declined as the glucose was consumed. After 2 h, the power and current density

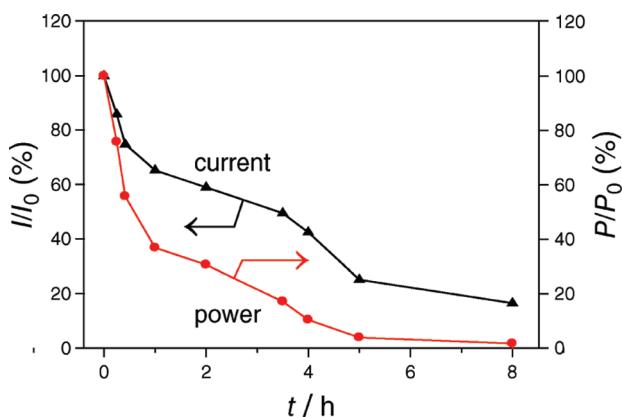


Figure 4. The time dependence of power density and current density of the enzymatic filter-paper fuel cell.

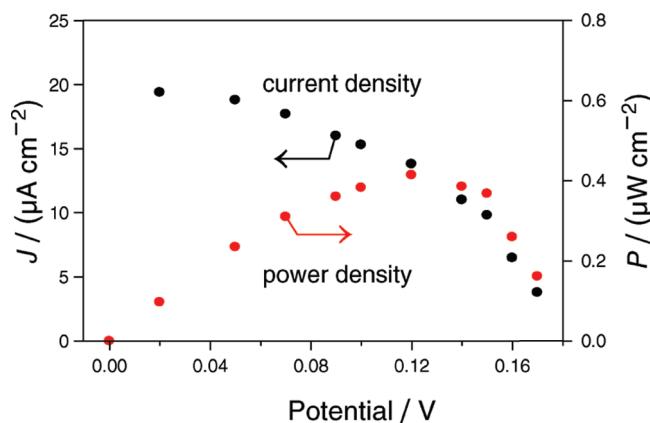


Figure 5. The dependence of power density,  $P$ , and current density,  $J$ , of the enzymatic filter-paper fuel cell on operating voltage.

dropped to 31% and 59% of their initial values, respectively. After 8 h, the fuel cell needed to be reloaded with fresh fuel.

The power density–voltage and current density–voltage behaviors of the fuel cell were tested by applying different external loads. To minimize the power loss caused by fuel depletion during the test, measurements under each load were restricted to 5 s. The power density–voltage and current density–voltage behaviors of the fuel cell are shown in Figure 5. The maximum power density was found to be  $0.4 \mu\text{W}/\text{cm}^2$ . In general, the open-circuit voltage of the enzymatic filter-paper fuel cell is comparable to other enzymatic fuel cells that use glucose oxidase and laccase.<sup>10</sup> However, the power density is lower, which might be caused by the higher resistance of filter paper compared to that of other conductive materials.

## ■ DISCUSSION

In this *Journal*, several studies discussed electrochemical principles and reactions involved in fuel cells<sup>11,12</sup> as well as several examples of fuel cells.<sup>13–15</sup> However, to the best of our knowledge, no enzyme fuel cells have been reported in this *Journal*. Compared to a conventional fuel cell, which utilizes a membrane to separate two compartments and allows only protons to pass, in the enzyme fuel cell described here, the enzymes are localized on the two outside filter papers owing to their high substrate affinity, which

obviates the need for a membrane.<sup>4</sup> In this filter-paper enzymatic fuel cell, the carbon nanotubes (CNTs) serve to promote conduction and to help immobilize the enzymes on the filter paper. As shown in Figure 4, the performance of the fuel cell drops quickly under ambient conditions. This behavior occurs because the enzymes often lack stabilities at temperatures and pH values commonly used, but could be improved by the choice of proper conditions.<sup>16</sup> Though laccases from fungi have optimal pH values in the region of 3–5,<sup>17</sup> our fuel cell was constructed to perform in human tissue and fluids, at the pH closer to neutrality. As shown in Figure 5, the dependence of the power density on the operating voltage exhibits the typical shape of a biofuel cell power curve with three regions corresponding to (i) the activation losses at low current density governed by the activation overpotential that arises from the kinetics of electron transfer reactions; (ii) the ohmic losses that arise from the resistance of biofuel cell, which depends on the materials used; and (iii) the concentration polarization at high current density that depends on mass transport.<sup>4</sup>

## ■ DEMONSTRATION

The pieces of filter paper impregnated with the enzyme-containing CNTs suspensions should be prepared before the demonstration. For the demonstration, the cell can be constructed, soaked in the glucose solution, and the current and power examined. Various glucose solutions may be used, including commercial drinks such as Red Bull that contain glucose, as well as blood.

Students can also construct the cell and gather the current and power data as a laboratory experiment. Detailed instructions for constructing the cell and a student handout are available in the Supporting Information. This material was used in a 4-h lab as part of the first-year chemistry course that was offered to 11 students. The fuel cell can be constructed rather rapidly but measurements of its characteristics take the majority of the lab time.

## ■ SUMMARY

The construction and demonstration of the glucose-driven enzymatic fuel cell can be used to illustrate several chemical principles: the important role chemistry plays in seeking alternative energy sources, the action of enzymes, how chemical energy can be converted to electrical energy, and the function of nanomaterials in electrochemistry.

## ■ ASSOCIATED CONTENT

### S Supporting Information

Instructions for constructing the cell and a student handout. This material is available via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

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