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Short communication

Practical electricity generation from a paper based biofuel cell powered by glucose in ubiquitous liquids

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ABSTRACT

This paper introduces a novel enzymatic fuel cell design that employs cellulose paper-based quasi-2D microfluidic system to supply biofuel to the enzymatic layer. The state of the art nanoarchitectural design, employing carbon nanotube-based papers for the bioelectrodes, allows a single cell to maintain 400 mV for 16 days of continuous operation in glucose solution and reach 1 mA of current output. Stacks of cells connected in series show successful performance using glucose in Gatorade® resulting in stack-cell potential of 1.8 V, employed to power a digital clock for 36 h, continuously. These designs open the possibility for obtaining enzymatic fuel cells that can run small portable devices on easily available ubiquitous liquids while addressing environmental concerns that are prevalent in traditional fuel cells.

1. Introduction

Enzyme-based biofuel cells (EFCs) offer several advantages such as high theoretical efficiency, high specificity, ease of synthesis, not employing high cost precious metal catalyst or leaving toxic residues, and workability at room temperature unlike several conventional fuel cells [1,2]. Although EFCs offer numerous advantages, they are marred with issues related to the enzyme stability over time outside its natural environment, poor transport characteristics, and partial oxidation of most fuels resulting in overall low output of electrons. Efficient EFCs can be achieved by tuning the parameters such as: (1) immobilization techniques to enhance enzyme stability while maintaining kinetic activity (2) electrode materials' properties (conductivity, surface area and porosity) to achieve high energy density, higher enzyme loading and optimum fuel diffusion [3–16] and finally (3) improve transport of fuels, electrolytes and products to obtain optimum power density, and also accomplish manufacturability requirements such as mechanical stability, prolonged time at operating conditions and long-life time in storage.

In this paper, we addressed those critical challenges to improve biofuel cell performance. First, we addressed the transport of biofuel (e.g. glucose) to anode and oxygen to cathode, respectively. We uniquely employ a quasi-2D microfluidic system fabricated from filter paper that also serves as a structural mechanical support, proton exchange membrane and separator of the anodic and cathodic systems. Second, we improved the structure of the catalytic layers for enhanced enzyme loading and stability with improved electron transfer by employing multi-walled carbon nanotube (MWCNT)-based materials (bucky papers). Third, we employed glucose in a commercial beverage, Gatorade®, to demonstrate feasible conversion of chemical energy into electric energy by mimicking a physiological process observed in small and large organisms. These novel design and immobilization procedures allow us to run a clock for an extended period of time.

2. Experimental

2.1. Design of electrodes

Methylene green (MG) is electro-polymerized by cyclic voltammetry at a scan rate of 50 mV s^{-1} between −0.5 V and 1.3 V [17] on the bucky paper-based anode [18–20] and it reversibly re-oxidizes NADH to NAD^+ at a potential of app. −50 mV (vs. Ag/AgCl). MG was used as it demonstrates high performance. GDH was immobilized using

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standard procedures [21,22]. Typically 3 mg GDH is dissolved in 150 μl chitosan and left to dry overnight at 4 °C. GDH was used as it generates higher current density than glucose oxidase in our design.

The dual-layered cathode was fabricated by pressing teflonized carbon black on perforated Toray® paper [23] and, a thin layer of Vulcan XC-72 carbon black. The XC-72 catalytic layer is submerged in a bilirubin oxidase (BOx) solution (10 mg/ml) [24]. The surface area of the cathode reaction zone was ~2.5 cm^2, and the anode ~4.5 cm^2 as the current density is generally lower than that of cathode.

2.2. Biofuel cell assembly

Both bioelectrodes were assembled on a quasi-2D microfluidic system fabricated from a filter paper. A specific 'fan'-shape device (a 2 cm × 9.5 cm rectangle appended to a 270°-circular section of 15 cm of diameter, Fig. 1 (left)) was used for this study. Bioelectrodes were assembled to the upper part of a rectangular zone of the paper-'fan'. Lamination of anode was achieved with regular scotch tape and the cathode gas-diffusion layer was exposed to air (Fig. 1). Carbon yarn, and carbon and silver inks were used to establish series connection. Two and three cells connected in series were stacked in a 'fan'-shape of 180°-semicircular section of 24 cm diameter with rectangular sections of 2 cm ×9.5 cm and 1.7 cm × 8.5 cm, respectively (Fig. 1 (right)). External connections were made using carbon yarn. Later, the 'rectangular portion of the paper fan' of the setup is immersed in 1) glucose 0.1 M, NAD^+ 1 mM, or 2) Gatorade®, NAD^+ 1 mM biofuel solutions at pH 7.3 (physiological pH).

2.3. Electrochemical experiments

The performance of half-cells and full cell was analyzed by open circuit potential (OCP) measurements and chronoamperometry at 25 °C. The cells were tested in either phosphate buffer (PB) containing 0.1 M glucose as biofuel (0.1 M PB, 0.1 M KCl, 50 mM NAD^+, pH 7.3) or Gatorade® with 50 mM NAD^+ with addition of 0.1 M PB to buffer at pH 7 (neutral).

3. Results and discussion

Fig. 1 (left) shows a fully assembled EFC. The cellulose paper-microfluidic system serves as a fuel transport medium for biofuel delivered continuously to GDH-anode. Within the 11 μm-diameter capillary of the cellulose paper grade 1, the capillary action generates a 1D-flow velocity profile of the biofuel governed by the Lucas–Washburn law, which explains the observed decrease in the flow velocity in the rectangular segment, initially. With given enough surface area of the half-circle and time of imbibition, evaporation of fluid from the circular portion becomes the sole driving force, resulting in a quasi-steady flow [25,26].

Similar setup was used to evaluate half-cells. The electrochemical tests on the half-cells (Fig. 2A) show that the BOx cathode has an OCP of 521 (±11) mV (vs. Ag/AgCl) in the presence of oxygen, which corresponds with literature data of 480 mV (vs. NHE, pH 5.3) [27]. The OCP of the anode −50 (±25) mV vs. Ag/AgCl corresponds to the redox potential of the mediator [28]. The measured full-cell voltage of cell is 621 (±24) mV. EFCs tested in the absence of glucose show high overpotential and rapid drop in current density as shown in Fig. 2A, Blank. The maximum current generated by the cell reaches values of 1 mA. This demonstrates the efficient transport of glucose to the anode through diffusion from the filter paper. Studies of the oxidation and reduction peaks by cyclic voltammetry have been performed on the bioelectrodes in electrolytic cell setup in previous research [22,24].

We tested a single cell under a constant load of 1.7 kΩ using glucose solution and maintaining steady voltage at 0.4 V for 16 days (Fig. 2B). This resistance loading was applied to analyze the cell behavior under condition of resistance found in real circuit components. The glucose solution needed to be refilled over steady intervals due to the evaporation of fluid ((ii) Fig. 2B). After continuous operation, the 'fan'-microfluidic device was changed because of saturation of the capillary channels of the paper with electrolytes, phosphate, remaining glucose and gluconolactone that obstruct the flow of fluid ((iii) Fig. 2B). The potential of the cell reaches 621 mV but it drops during continuous use reaching a potential of approximately 400 mV after the 6th day, which is observed up to the 16th day of continuous operation. We speculate that the potential-drop is due to partial denaturation of the 3D-structure of the

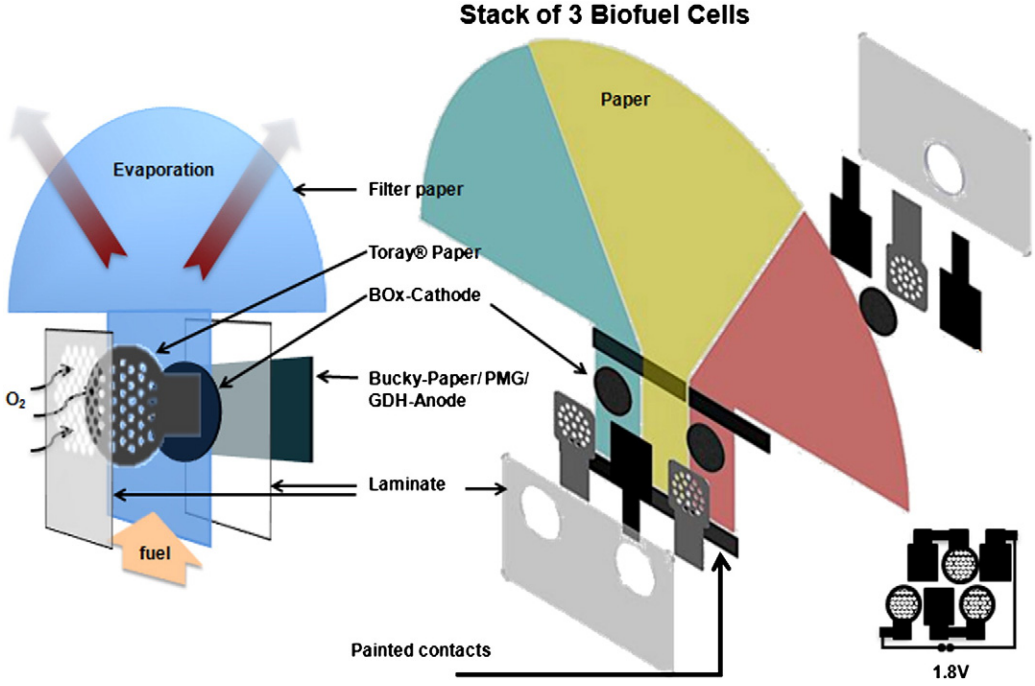

Fig. 1. Single paper based fuel cell with laminated 'leg' (left) and a 3 fuel-cell stack connected in series (right).