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Paper-based enzymatic microfluidic fuel cell: From a two-stream flow device to a single-stream lateral flow strip

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HIGHLIGHTS

- A Biofuel Cell in which fluid transport is based on capillary action is presented.
- The paper-based fuel cell is able to produce the same power output as one operated with an external syringe pump.
- The system is simplified by evolving a two-stream flow device to a single-stream format.
- The single stream fuel cell has the potential of powering a real application.

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ABSTRACT

This work presents a first approach towards the development of a cost-effective enzymatic paper-based glucose/O_2 microfluidic fuel cell in which fluid transport is based on capillary action. A first fuel cell configuration consists of a Y-shaped paper device with the fuel and the oxidant flowing in parallel over carbon paper electrodes modified with bioelectrocatalytic enzymes. The anode consists of a ferrocenium-based polyethyleneimine polymer linked to glucose oxidase (GOx/Fc-C_6-LPEI), while the cathode contains a mixture of laccase, anthracene-modified multiwall carbon nanotubes, and tetrabutylammonium bromide-modified Nafion (MWCNTs/laccase/TBAB-Nafion). Subsequently, the Y-shaped configuration is improved to use a single solution containing both, the anolyte and the catholyte. Thus, the electrolytes pHs of the fuel and the oxidant solutions are adapted to an intermediate pH of 5.5. Finally, the fuel cell is run with this single solution obtaining a maximum open circuit of 0.55 ± 0.04 V and a maximum current and power density of 225 ± 17 μA cm^{-2} and 24 ± 5 μW cm^{-2}, respectively. Hence, a power source closer to a commercial application (similar to conventional lateral flow test strips) is developed and successfully operated. This system can be used to supply the energy required to power microelectronics demanding low power consumption.

1. Introduction

Since their first appearance in the literature, microfluidic fuel cells have shown their potential for supplying power to small portable electronic devices. They are simple to operate provided that an external pressure system is coupled to the device to maintain separate flow between the anode and cathode reactants without mixing. This avoids the need for a separation membrane, typically Nafion, reduces internal ohmic losses [1], and allows for the use of different pHs at the anolyte and catholyte streams with little reagent crossover issues [2,3]. However, the need for external pressure sources, like pumps, limits their portability and miniaturization severely [4]. Furthermore, these external pumps represent an extra energy consumption associated with the fuel cell. Although the first generation of microfluidic fuel cells was

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fabricated with MEMS-related technologies, it has been demonstrated in the last years that they can also be easily made in glass or plastic [1,5–7] using rapid prototyping techniques. Moreover, the need for external pumping has been recently overcome with the emergence of microfluidic paper devices [8–13]. These devices substitute classical microfabricated channels by a paper matrix, which provides important benefits. Paper possesses the ability to move fluids via capillary action, allowing passive liquid transport [14]. As a result, no ancillary devices are needed to supply pumping functions. Furthermore, paper presents good compatibility with a high number of chemicals/biochemicals and can be combined with other low cost materials, such as plastics, to provide extra mechanical support.

For many years, paper has been widely employed as a substrate to develop point of care (POC) diagnostics devices [15]. Among them, the most broadly used POC diagnostic devices are paper-based dipsticks (urinalysis dipsticks) and lateral-flow immunoassays (pregnancy tests) [16–19]. Lately, materials used in lateral flow devices have been adapted and reconfigured into 2D or 3D paper matrices. This has led to the creation of new and exciting components, for example valves, mixers and separators [20]. In this way, the capabilities of complex microfluidic functions and the simplicity of diagnostic tests strips have been combined to originate a new generation of paper-based analytical devices (μPADs) [21–25]. These systems have been identified as especially suitable for point of care purposes in the field of home health-care settings and at medical points of care in developing countries [10,12,26,27]. This is because they promise to accomplish the ASSURED criteria; they are affordable, sensitive, specific, user-friendly, rapid and robust, equipment free and deliverable to those who need it [21,25,28]. Nevertheless, the quantification of the results of a test requires the use of a hand-held reader which, in certain scenarios, is not a cost effective solution. This has brought the idea of developing low cost disposable readers; however, examples in the literature are still very scarce. To realize this vision, the search for a new generation of power sources that satisfy the requirements such as high power density, low cost and disposability with minimum environmental impact has attracted a lot of attention. In the last few years, paper has been used as a substrate to develop different kinds of power sources [29], for instance (i) fuel cells [8,9], (ii) biofuel cells, such as microbial [30,31] and enzymatic fuel cells [32,33], (iii) electrochemical batteries [10,34,35], (iv) lithium-ion batteries [36], (v) supercapacitors [37,38] and (vi) nanogenerators [39]. Among these, biofuel cells [40], and specifically enzymatic fuel cells, appear to be one of the most suitable power sources for paper-based μPADs in terms of environmental impact. This is because they use biological catalysts (enzymes) to convert organic fuels (commonly glucose) and oxygen into electrons, CO_2, water and/or oxidized fuel by-products [41–44]. For these reasons, enzymatic fuel cells are considered extremely cost-effective and a promising future alternative source of sustainable electrical energy for small electronic devices [42,45–48].

An intrinsic advantage of paper-based matrixes as substrates for microfluidic fuel cells is their capability of establishing laminar flow. This feature is important when considering microfluidic fuel cells as it means that, fuel and oxidant streams can flow in parallel without mixing.

In this work, we will show that the implementation of a microfluidic enzymatic fuel cell in paper allows us to eliminate the need for pumps without losing electrical performance. In order to gain simplicity in its use, the two inlets typically used in a Y-shaped fuel cell have been simplified into one inlet, so that the fuel and the electrolytes could be added together in a single step. This results in a fuel cell working with the simplicity of lateral flow test strips. This replaces the two parallel flow solutions by a single one that combines the anolyte and the catholyte components. In order to achieve this ease of use, the fuel cell has to work with a single electrolyte which required a compromise in the pH values between anolyte and catholyte solutions. Free from the size restrictions and power requirements of external equipment, the system presented in this paper can become an alternative for providing energy to power small single use point-of-care devices [49].

2. Experimental

2.1. Fuel cell design and fabrication

Two different microfluidic devices were constructed using paper, a Y-shaped and an I-shaped fuel cells. The paper selected as substrate for the systems was Whatman®, grade Fusion 5, due to its high wicking rate. The system was designed using Vectorworks 2012 student edition (Techlimits, Spain). The paper sheet was attached onto a flexible plastic carrier covered with a low-strength adhesive layer to provide mechanical support during the cutting process. The paper strips were cut using a Roland GX-24 cutter plotter with a force and speed of 30 g and 1 cm s^{-1}, respectively, and the cutting was performed in two passes in order to prevent any tearing of the paper [50]. The thickness of the Fusion 5 substrate (and consequently the height of the microfluidic channel) was 370 μm and the fuel cells had final dimensions of 45 × 5 mm^2. After cutting, the paper structures were released from the plastic support.

Carbon paper from Fuel Cell Earth (type TG-H-060) was used as the electrodes of the fuel cells. They were cut in a rectangular size of 5 × 15 mm^2 and positioned in parallel 2 cm downstream (from the reactant inlets) and separated 1 mm from each other. In this configuration, the active electrode area exposed to the microfluidic channel is 0.10 cm^2. A piece of a conducting copper tape (3M-1182) purchased from RS (Spain) was used to contact the outer part of the carbon paper electrodes. Fig. 1 (a) and (b) shows the pictures of the Y-shaped and the I-shaped paper strips together with the carbon paper electrodes.

2.2. Microfluidic device assembly

A holder made of poly(methyl methacrylate) - PMMA - was designed and made with a Roland MDX-40 milling machine (Roland DG, Spain). This component was fabricated to facilitate the connection of different elements of the measurement setup to the fuel cell. A pocket milled into the holder was used to hold the glass slide that supports de paper fuel cell. Two adhesive magnetic bands, placed on the sides of the PMMA block, allow fixing a PMMA bar with two fuel reservoirs at the paper inlets. Also the fuel cell wicking pad (an absorbent wipe from Kimtech Science) and the external electrical connections of the device are held by PMMA pieces. All of these plastic components host small magnets that keep them attached to the holder. For the external electrical connections, spring-loaded pins (Preci-Dip, Switzerland) were inserted in the PMMA plugs that at the same time were in contact with the copper foil over the electrodes.

2.3. Equipment and chemicals used in the enzymatic solutions

The salts acting as supporting electrolyte, the enzymes for the electrodes (Glucose oxidase from *Aspergillus niger* –EC 1.1.3.4, Type X-S, 175 units/mg of solid, 75% protein– and laccase from *Trametes Versicolor*), glucose, Nafion and solvents were purchased from Sigma Aldrich and used as received. The proton conducting binder was Nafion 5% by wt. in an alcoholic suspension EW1100. Hydroxylated MWCNTs (10–30 μm length, 1.6% –OH