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Short communication

# Glucose oxidase bioanodes for glucose conversion and $H_2O_2$ production for horseradish peroxidase biocathodes in a flow through glucose biofuel cell design

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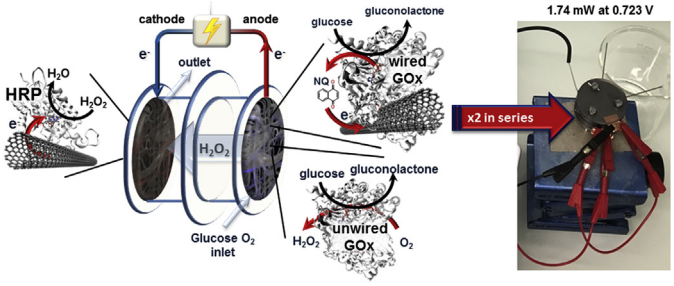
## HIGHLIGHTS

- A Glucose/$H_2O_2$ biofuel cell is presented where $H_2O_2$ is produced at the bioanode.
- $H_2O_2$ is then conducted and consumed at the biocathode in a flow through setup.
- This biofuel cell has an OCV of 0.6 V and generates 0.7 mW at 0.41 V.
- 290μW h (1.04 J) is produced during 48 h.
- The design allows the connection in parallel and in series doubling the power output.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Bioelectrocatalytic carbon nanotube pellets comprising glucose oxidase (GOx) at the anode and horseradish peroxidase (HRP) at the cathode were integrated in a glucose/$H_2O_2$ flow-through fuel cell setup. The porous bioelectrodes, separated with a cellulose membrane, were assembled in a design allowing the fuel/electrolyte flow through the entire fuel cell with controlled direction. An air saturated 5 mmol $L^{-1}$ glucose solution was directed through the anode where glucose is used for power conversion and for the enzymatic generation of hydrogen peroxide supplying the HRP biocathode with its substrate. This configuration showed an open circuit voltage (OCV) of 0.6 V and provided 0.7 ± 0.035 mW at 0.41 V. Furthermore, different charge/discharge cycles at 500 Ω and 3 kΩ were applied to show the long term stability of this setup producing 290 μW h (1.04 J) of energy after 48 h. The biofuel cell design further allows a convenient assembly of several glucose biofuel cells in reduced volumes and its connection in parallel or in series.

## 1. Introduction

Enzymatic glucose biofuel cells became famous for the conversion of energy to power electronic devices in a living body due to the high specificity of bocatalysts [1]. GOx is one of the most widely used enzymes for the anodic glucose oxidation of glucose-$O_2$ biofuel cells [2] due to its stable activity and life time over several pH values [3]. GOx consists of two identical subunits (homodimer) wherein the organic

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redox cofactor flavin adenine dinucleotide (FAD) is protected by a thick glycosylated protein shell [4,5].

The GOx catalyzes with high selectivity the oxidation of β-D-glucose to gluconolactone by a 2 $e^-$ and 2 $H^+$ process and usually regenerates itself by reducing oxygen to hydrogen peroxide [6] which can typically serve as electrochemical probe for glucose biosensor applications [7]. However, this byproduct is generally considered as disadvantage in biofuel cell applications due to its toxicity and denaturation of proteins [8]. Furthermore, the electrons used for oxygen reduction are not transferred to the electrodes and thus, do not contribute to the power conversion.

An efficient way to improve the performances of GOx bioanodes and to reduce the production of $H_2O_2$ is to use redox active molecules with appropriate potentials which play the role of electron shuttles from GOx to the electrode material [9]. The Adam Heller group realized pioneering work in tunable osmium hydrogels for efficient mediated electron transfer using GOx as biocatalyst [10–13] with steadily improved glucose biofuels cell performances [14–16]. Beside metal organic complexes, quinones became a prominent alternative due to improved current stabilities and life-time of the bioanodes [17–19]. An elegant approach to clearly reduce the side reaction producing $H_2O_2$ is to confine the enzyme in a redox hydrogel where the surface layer consumes oxygen thus providing for the inner layers an anaerobic environment with improved electron transfer rates [20,21]. However, even when very efficient wiring strategies could be developed, the production of $H_2O_2$ still remains an issue with GOx as anodic biocatalyst. The introduction of the enzyme catalase which consumes the produced $H_2O_2$ forming oxygen and water [22] can further reduce this issue but not totally eliminate it.

Nonetheless, an original approach was demonstrated taking advantage of this $H_2O_2$ production by GOx for the development of biocathodes using a bi-enzymatic system with HRP as catalysts for the reduction of hydrogen peroxide [23–25]. In this setup, GOx reduces oxygen to $H_2O_2$ which is then further reduced to water by HRP. This small enzyme has an easily accessible heme function enabling facilitated direct electron transfer [26].

The advantage of such biocathodes is the lack of inhibition effects by chloride or urate present in body fluids which is a constant drawback for multi copper enzymes like laccase or bilirubin oxidase (BOD) which are often used as cathodic biocatalysts [27–30]. The disadvantage of such biocathodes is the need to combine two enzymes thus increasing the amount of protein to immobilize while only one will be connected. Another disadvantage is the possible depletion of the glucose concentration for the operation of the bioanode. Furthermore, the issue of contaminating $H_2O_2$ production at the bioanode is still not resolved. One example of a glucose/$H_2O_2$ biofuel cell using GOx as anodic and HRP as cathodic biocatalyst describes a two compartment setup with defined glucose and $H_2O_2$ concentrations in the respective compartment to reach 4.7 $\mu W cm^{-2}$ [31] without profiting from the natural production of hydrogen peroxide.

Here, we present a new approach that benefit from this $H_2O_2$ production of remaining unwired GOx at the bioanode. A mixture of GOx, naphthoquinone, and multi-walled carbon nanotubes (MWCNTs) were compressed in a Plexiglas housing to form the bioanode. The biocathode was made in the same way by using a mixture of HRP and MWCNTs. The bioelectrodes were integrated in a recently designed and adapted flow through setup [32,33]. Hydrogen peroxide is here conducted from the anode to a HRP base cathode supplying this enzyme with its natural substrate which is entirely consumed. This setup reduced diffusion issues of oxygen to the cathode and provides very satisfying power outputs and lifetimes.

## 2. Material and methods

All reagents, glucose oxidase (GOx) from *Aspergillus Niger* and peroxidase from *Horseradish* (HRP) enzymes were purchased from Aldrich, Saint-Quentin-Fallavier, France. MWCNTs were purchased from Nanocyl, Sambreville, Belgium (> 95% purity, 10 nm diameter, 1.5 μm length). It has to be noted that all experiments were conducted with the same batch of enzymes and MWCNTs to assure the reproducibility of our results and to avoid possible performance fluctuations related to batch-to-batch variations. The microporous gas diffusion layer (GDL) of 210 μm thick, 8 $m\Omega\,cm^2$ of through plane electrical resistance and through plane air permeability of 70 s, was purchased from Paxitech, Échirolles, France (FI2C6). Graphoil® was provided by Panasonic, Kadoma, Japan, with 0.07 mm thickness and 1 $kW\,m^{-1}\,K^{-1}$ thermal conductivity. The 100% cellulose membrane with 0.13 mm thickness and 64 $g\,m^{-2}$ was purchased from FiltraTech, Saran, france. Enzymes were stored at −20 °C. Distilled water was obtained by water purification to a resistivity of 15 MΩ cm using a Millipore, Burlington, Massachusetts, USA, Ultrapure system. Glucose solutions were left to mutarotate overnight to β-D-glucose prior to use.

For the electrochemical characterization of the biofuel cell, the anode was set as the working electrode while the cathode was plugged as the counter-reference electrode. All experiments were conducted in a glucose solution of 5 $mmol\,L^{-1}$ in McIlvaine, pH 7 unless otherwise mentioned. The biofuel cell was connected to a multichannel potentiostat Biologic®, Seyssinet-Pariset, France, VMP3 running EC-lab software 10.39. Polarization and power curves were recorded after 30-s discharge. All the experiments were done at room temperature.

### 2.1. Preparation of the bioelectrodes

The MWCNT pellets were obtained by soft grinding of an optimized mixture of 100 μL of distilled water, 5 mg of 1,4-naphthoquinone, 15 mg of GOx from *Aspergillus Niger* (174 $U\,mg^{-1}$) and 35 mg of MWCNTs as described in detail in Ref. [34]. Here, catalase which disproportionates $H_2O_2$ was not included providing optimal substrate production for the biocathode. The same procedure was employed for the biocathode using 15 mg of HRP from *Horseradish* (193 $U\,mg^{-1}$) and 35 mg of MWCNTs. Each of the obtained homogenous pastes is then compressed directly in a 3 mm thick Plexiglas housing with a hole of 1.3 cm diameter using a hydraulic press [33]. A graphoil disc is connected to one side of the pellet to permit the electrical connection.

### 2.2. Design of the biofuel cells

The biofuel cells were designed according a specific configuration depicted in Fig. 1 to allow the easy assembly of multiple biofuel cells using easy-to-handle in-house fabricated Plexiglas elements. A 3 mm thick Plexiglas slice was designed with a hole in the center of 13 mm in diameter. A microporous GDL was then placed at the backside of the Plexiglas to serve as the electron collector and assures simultaneously the diffusion of the glucose-oxygen solution. After compressing the MWCNT-enzyme pellet in the 13 mm hole of the Plexiglas slice with the GDL on the backside. The open side of the pellet was then covered with a cellulose sheet which served as electrolyte reservoir. A polytetrafluoroethylene (PTFE) sheet of 100 μm thickness with a 16 mm hole was inserted in between the bioanode and the biocathode as a separator and to prevent any leakage of the electrolyte. At the GDL backside of each bioelectrode, a graphoil sheet is placed to allow the electrical connection to an external circuit. To provide a constant glucose flow within the cells, a peristaltic pump or standard glucose perfusion bag, such as those found in hospitals, were used. The 0.2 $mL\,min^{-1}$ flow was oriented from the anode to the cathode.

## 3. Results and discussion

### 3.1. Design of the GBFC

Fig. 1 presents the glucose/$H_2O_2$ fuel cell and its device. The flow diffuses from the anode to the cathode to drive the produced hydrogen

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