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Perspective use of direct human blood as an energy source in air-breathing hybrid microfluidic fuel cells

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HIGHLIGHTS

- A microfluidic fuel cell operated under biological conditions is presented.
- Glucose oxidase, glutaraldehyde and carbon nanotubes are used as bioanode.
- The micro-device integrates an air-exposed electrode (Pt/C) as cathode.
- Glucose is obtained from synthetic solutions, human serum and blood as fuel.
- A maximum power density of 0.20 mW cm^{-2} was obtained using blood as fuel.

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ABSTRACT

This work presents a flexible and light air-breathing hybrid microfluidic fuel cell (HμFC) operated under biological conditions. A mixture of glucose oxidase, glutaraldehyde, multi-walled carbon nanotubes and vulcan carbon (GOx/VC-MWCNT-GA) was used as the bioanode. Meanwhile, integrating an air-exposed electrode (Pt/C) as the cathode enabled direct oxygen delivery from air. The microfluidic fuel cell performance was evaluated using glucose obtained from three different sources as the fuel: 5 mM glucose in phosphate buffer, human serum and human blood. For the last fuel, an open circuit voltage and maximum power density of 0.52 V and 0.20 mW cm^{-2} (at 0.38 V) were obtained respectively; meanwhile the maximum current density was 1.1 mA cm^{-2}. Furthermore, the stability of the device was measured in terms of recovery after several polarization curves, showing excellent results. Although this air-breathing HμFC requires technological improvements before being tested in a biomedical device, it represents the best performance to date for a microfluidic fuel cell using human blood as glucose source.

1. Introduction

The recently developed glucose enzymatic biofuel cells (BFC's) could become an important alternative for producing energy to power either biomedical devices or active sensors [1,2]. Nevertheless, the currently developed glucose biofuel cells still yield low current and power densities and poor stability with a short lifetime mainly due to inefficient immobilization [3,4]. Hybrid fuel cell (HFC) systems are an alternative studied based on an enzymatic catalyst and an abiotic material, combining the best properties of both types of catalysts and assuming that abiotic material works properly under physiological conditions (pH 7, 37 °C) [5]. Furthermore, to become implantable, the glucose bio or hybrid fuel cells must solve others issues: biomaterial use, on-chip fabrication and the ability to operate at the glucose and oxygen concentrations available in blood or other bodily fluids. In this context, glucose oxidase (GOx) has been used to fabricate the bioanode due to its high catalytic activity and selectivity for β-D-glucose under physiological conditions [6]. Pt has been selected as an abiotic catalyst for the cathode due to its high oxygen reduction activity. Pt is also biocompatible and operates efficiently in the human body [7,8]. Furthermore, using an abiotic catalyst reduces the catalytic

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inactivity to ions or organic molecules relative to enzymes such as bilirubin oxidase or laccase that are usually used in the cathode [9].

Some relevant works evaluating glucose enzymatic biofuel cells under physiological conditions are listed in Table 1. The maximum performance was reported by Pan Caofeng et al. [10] at 0.03 mW cm^{-2} using phosphate-buffered saline (PBS) as the electrolyte; nevertheless, the same work found a critical power decrease when the BFC was tested using human blood (0.0056 mW cm^{-2}). Similar behaviour had already been presented by Xiaoju Wang et al., [11] who performed an additional test using plasma. An improved performance was achieved [12–14] and primarily corresponded to the enrichment of glucose to 10 mM in the solutions, which is not a natural concentration for blood or human serum (3–5 mM). However, substituting human serum with bovine serum [5,6,12] lowered the performance. The work presented in Refs. [13,15] evaluated BFCs under quiet conditions in non-human media, which neglects the fluid dyamics of the human body, an important challenge to overcome. Additionally, using mediators [16] is typical when evaluating BFCs which is an important limitation for implantation.

The use of microfluidic platforms to build electrochemical microdevices for energy conversion transfers the operating principles of HFCs to a novel membraneless fuel cell technology, sometimes called a microfluidic fuel cell, for building implantable on-chip power sources. The following work reports a hybrid air-breathing microfluidic fuel cell (HμFC) composed by microfabricated components that incorporate a bioanode and an abiotic cathode as electrodes. The performance of the hybrid device is evaluated in the presence of glucose as fuel, which is obtained from three sources: phosphate buffer, human serum and human blood; and oxygen taken directly from air as oxidant which is a great advantage to increase the limiting reagent normally found in these micro fuel cells. The encouraging results obtained make this easily constructed microdevice a promising candidate for use as a power supply for *in vivo* applications due to its high performance.

2. Experimental

2.1. Electrode fabrication

The bioanode was constructed from two important elements: a biocompatible substrate made of ARcare®8890 (Adhesives Research Inc) covered by 0.66 cm^2 of adhesive graphite paper (Fig. 1a–a′) and a double deposit of GOx/VC-MWCNT-GA.

The enzyme catalytic ink contained glucose oxidase (GOx) (5 mg mL^{-1}) dissolved in 0.1 M phosphate buffer (PB) at pH 7 and immobilised with 1% glutaraldehyde (GA) via cross-linking. In a parallel process, multi-walled carbon nanotubes (MWCNTs) were cleaned by refluxing in 9 M HNO_3 for 24 h before dispersing into isopropyl alcohol via ultra-sonication for one hour. Finally, the MWCNT solution was mixed with 10 mg mL^{-1} Vulcan carbon (Vulcan XC-72 from E-ETEK) and the GOx-GA solution and dispersed via sonication (Fig. 1a–b′). A 220-μL double deposit of GOx/VC-MWCNT-GA was physically adsorbed on the adhesive graphite electrode surface. This surface was then dried at room temperature for 14 h (Fig. 1a–c′). A schematic representation of the integral bioanode is shown in Fig. 1b.

On the other side, the air-breathing cathode was prepared on a piece of 20-micron-thick micro-porous Toray® carbon paper (Technoquip Co Inc TGPH-120) and covered with an ink containing 7 μL of Nafion® 5% (Sigma–Aldrich), 73 μL of isopropyl alcohol (J.T. Baker) and 1 mg of commercial Pt/C (30 wt. % on Vulcan XC-72 from E-TEK), which was deposited using an airbrush adapted to a mini CNC (computer numerical control) system to assure homogeneous deposition with a final metal loading of 1 mg cm^{-2} over the entire surface.

2.2. Glucose activity assay

The enzymatic activity was determined by measuring the amount of hydrogen peroxide produced using (3,3′,5,5′-tetrametilbenzidina) TMB as a co-substrate [17]. The reaction mixture

Table 1
Fuel cell performance for glucose in buffer at pH 7, serum and human blood.

Anode	Cathode	Solution	Operation period	OCV	J	P	Cell	Author, year, reference
				V	mA cm^{-2}	mW cm^{-2}	Type	
GDH-PolyBCB-SWNT	BOD-SWNT	40 mM Glucose PB pH 7	NS	0.73	0.120	0.0539 at 0.50 V	Vessel	Feng Gao et al.,
		Bovineserumalbumin		0.63	0.023	0.005 at 0.45 V	Vessel	2007, [13]
CtCDH/Au NP	MvBOx/AuNP	PB pH 7.4 5 mM Lactose	12 h	0.68	NS	0.0149 at 0.52 V	One-compartment	Xiaoju Wang et al.,
		Human blood	3 h	0.66	NS	0.0028 at 0.45 V	One-compartment	2012, [11]
		Human plasma	8 h	0.63	NS	0.003 at 0.37 V	One-compartment	
CtDH	MvBOx	PBS pH 7.4	6 h	0.62	NS	0.003 at 0.37 V	Non-compartmentalised	Coman et al., 2010, [20]
		Human serum	<2 h	0.58	NS	0.004 at 0.19 V	Non-compartmentalised	
GOx-CNTs	Lac	PBS pH 7.0	NS	0.23	0.388	0.03	NS	Pan Caofeng et al.,
		Human blood	NS	0.12	0.155	0.0056	NS	2010, [10]
Gox/DNA-wrapped-SWNTs	Lac/DNA-wrapped-SWNTs	Bovine Serum glucose 10 mM in O_2	Over 1 week	0.55	NS	0.190	Vessel	Jin Young Lee et al., 2011, [15]
GOx-PPy-FHFP-PQQ	Lac-PPy-SDP-RuPy	PB pH 7.4 10 mM glucose 37 °C	NS	0.51	0.003	0.0031	Non-compartmentalised	MalikaAmmam and Jan Fransaer, 2010, [12]
		Human Serum 37 °C	NS	0.38	0.0014	0.0016	Non-compartmentalised	
MWCNTs-GOx-PQQ	MWCNTs-Lac-ABTS	PB pH 7.4 10 mM glucose 37 °C	NS	NS	NS	0.11 at 0.167 V	Non-compartmentalised	MalikaAmmam and Jan Fransaer 2012, [16]
		Human Serum 5 mM glucose 37 °C	NS	NS	NS	0.069 at 0.151 V	Non-compartmentalised	
PPy-CNTs-Gox	PPy-ABTS-Lac	PB 10 mM glucose (37 °C)	15 mL Solution in cell	0.68	6.67	1.33 at 0.38 V	NS	Kim, Jihun Yoo and Kyung-Hwa, 2013, [14]
		Fetal bovine Serum + PBS (1:1 v/v) + glucose 10 mM	NS	0.65	2.9	0.64 at 0.34 V	NS	

NS: Not specified