A complete tattoo-based wireless biofuel cell using lactate directly from sweat as fuel

R.A. Escalona-Villalpando, E. Ortiz-Ortega, J. P. Bocanegra-Ugalde, S. D. Minteer, L.G. Arriaga, J. Ledesma-García

1Centro de Investigación y Desarrollo Tecnológico, MÉXICO and 2Universidad Autónoma de Querétaro, MÉXICO and 3University of Utah, USA.

janet.ledesma@uaq.mx

Abstract. In this work, an enzymatic type wireless biofuel cell (BFC) has been implemented. The bioanode consisted in the immobilization of the enzyme lactate oxidase (LOx) with the dimethylferrocene-modified redox polymer linear polyethylenimine LPEI (FcM₂-LPEI) and 5 % EDGE at a volumetric ratio of 56/24/3 and thoroughly mixed. The biocathodes were prepared immobilizing bilirubin oxidase (BOx) mixed with 7.5 mg of multi-walled carbon nanotubes MWCNT modified with anthracene and TBAB-Nafion by successive vortex mixing/sonication steps and the paste was deposited qualitatively on flexible Toray carbon (TC-PTFE) using a brush. The cyclic voltammetry results of the bioanode and biocathode show an enzymatic activity in the lactate oxidation and oxygen reduction reactions in PBS and human sweat respectively. The evaluation of BFC tattoo was performed in different parts of the body under conditions of exercise by a healthy volunteer, finding that located on the chest, was obtained the greatest current (96 μA) with 0.55 V of OCP monitoring the system using a potentiostat and a wireless controlled device.

1. Introduction

Besides glucose, there are other metabolites present in biological fluids (mainly sweat) to be quantified by biosensors and to generate energy, such as lactic acid or lactate. In energy generation, besides its high theoretical energy density, it is found in a high concentration in sweat, around 15 mM and up to 70 mM. Its application is in self-powered lactate biosensors, drug release systems, energy storage, and for providing power for low energy consumption devices [1].

Sweat is a hypotonic biofluid produced by the eccrine and apocrine glands in the epidermis. It is acidic in a pH range of 4.0 – 6.8 and is composed mainly by water; ions such as sodium, chloride and potassium; other electrolytes such as urea pyruvate and lactate; in small concentrations proteins, peptides, amines, aminocoids, antigens, antibiotics and a variety of xenobiotics such as drugs, cosmetics, and ethanol, mainly [2]. Its main function is to form a protective barrier that covers the skin and prevents dehydration [3].

The relevance of the development and implementation of flexible or elastic devices in their application mainly in healthcare devices such as biosensors [4] requires the devices to not have external connections. Therefore, research has expanded in the field of “wireless” devices, developing systems
that can be incorporated close or inside the body that obtain their energy from the piezoelectric effect [5], solar [6], body heat [7] and biofluids, specially sweat [8]. In this work, the incorporation of the LOx and BOx enzymes in a enzymatic BFC type tattoo was achieved and the construction of a wireless device for the production of energy in vivo from the lactate present in the sweat was achieved.

2. Experimental

2.1 Electrode preparation

LOx (Aerococcus viridans) and BOx (Myrothecium verrucaria) were used as catalysts at the anode and cathode, respectively. LOx (100 U mL⁻¹ in pH 5.6) was immobilized with the redox polymer FcM₂-LPEI, a dimethylferrocene-modified linear polyethylenimine in a concentration of 10 mg ml⁻¹ in deionized water and was mixed with 5 % EDGE crosslinking agent in deionized water at a volumetric ratio of 56/24/3 and thoroughly mixed. This solution was added to hydroxylated MWCNTs in a ratio of 0.5:1 W/W with respect to LOx. This suspension was vortex-mixed for 2 min. Afterwards, 50 μL were pipetted onto flexible Toray carbon (TC-PTFE) and allowed to dry overnight. The biocathodes were prepared mixing BOx (1.5 mg in PBS at pH 5.6) with 7.5 mg of MWCNT modified with anthracene [30] by successive vortex mixing/sonication steps. TBAB-Nafion (25 μL) was added and one more vortex/sonication mixing was performed; the paste was deposited qualitatively on TC-PTFE using a brush.

2.2 Development of enzymatic patch.

The device consisted of three parts. First, the bioelectrodes deposited over Ty-PTFE, in a “E” shape (1.14 cm²) for the biocathode and a “C” shape for the bioanode. These shapes were selected as to increase the surface area. The second part was the electrical connections to the copper wires, which were connected on the end of the bioelectrodes on the hydrophobic side of the Ty-PTFE using silver epoxy. The connection was electrically insulated with a non-conductive epoxy resin. The third part consisted of a biocompatible adhesive polymer (Tegaderm®) to which the electrodes are adhered. This flexible patch is then adhered to the skin (Figure 1).

![Diagram of the design and reactions in the different components of the tattoo-based biofuel cell.](image-url)

3. Results and discussion

The BFC was evaluated in a man and a woman to establish their comparative efficiency in two different volunteers. The evaluation of the BCC was performed in three different parts of the body of a male volunteer: lower back, upper back and chest, observing that the patch on the lower back obtained the highest voltage of 0.41 V ± 0.02 followed by the chest 0.35 V and upper back 0.32 V. On the other hand, the maximum current (measured at maximum power) and maximum power were obtained from the same regions. In the lower back, current and power were 30 ± 8.5 μA (0.25 V) and 7.5 μW respectively, while in the chest the current and power were 16.1 μA and 3.7 μW. On the other hand,
The patch stability was evaluated by amperometry for 30 min monitoring at 0.12 V, observing a decrease in current in the first minute of testing and later remaining constant in a range of 2 to 7.4 μA during the time of testing. Comparing the result with respect to the male volunteer, the OCP on a female volunteer was 0.16 V lower, while the current was about half as small and the results showed more dispersion (Figure 2).

![Figure 2](image2.png)

**Figure 2.** Incorporation of the dermal BCC adhered to the upper back in a female volunteer in exercise conditions and results of polarization, power and stability curves of the dermal BFC.

The open circuit voltage shows a slight increase in the voltage of 0.57 V when the patch is placed on the nape. This could be due to the pH found in that area where the bioanode could be favoured. Meanwhile, the OCP in the chest, arm and back is very similar between 0.5 and 0.55 V. On the other hand, the current and power were greater in the arm with values of 55.5 μA and 13.6 μW respectively, followed by the BFCs in the back and chest with values between 28 μA and 7 μW and finally in the neck. On the other hand, the stability of the dermal BFC in the different parts of the body was performed by amperometry for 30 continuous minutes at a constant potential of 0.12 V observing a very similar behaviour for the four cases, maintaining the current around 20 μA (Figure 3).

![Figure 3](image3.png)

**Figure 3.** Comparative polarization and power curves of the tattoo BFCs in different body parts: arm, chest, back and neck in a man at 5 mV s⁻¹ of linear discharge speed. B) Stabilities of the dermal BFC in different parts of the body at a potential of 0.12 V. Both experiments were performed using a potentiostat/galvanostat.

As can be seen in the Figure 4-A, the OCP was measured using the potentiostat obtaining a voltage of 0.58 V and was compared with that measured with a mobile phone using a wireless device coupled to
the BFC on the volunteer in exercise, obtaining 0.53 V of voltage. In this same sense, the current and power obtained in the wireless device shows a current near to 80 μA obtained from the variation of the resistances and read by the cell phone. Also, the power curve was built with the product between the measured voltage and the current. The result was compared with the measurement using the potentiostat as a control, showing a very similar result, indicating that the device is functional and provides measurements in real time, an achievement for wireless BFC (Figure 4-B).

![Figure 4. A) Comparative measurement of the OCP using the potentiostat and wireless device, B) Current and power polarization curve comparative performed using a potentiostat and wireless device.](image)

4. Conclusions
In this work, the immobilization of the LOx and BOx enzymes was achieved in the anode and cathode respectively; in both electrodes their catalytic activity was maintained in total sweat. Confirming the enzymatic activity towards their respective substrates, we achieved the construction of a tattoo-type BFC incorporating both electrodes in a BFC with a flexible carbon material on a biocompatible polymer. The evaluation of the BFC in two test volunteers using a potentiostat / galvanostat showed that the highest OCP and current were obtained in the male volunteer and were 0.58 V and 90 μA respectively. Finally, the incorporation of the BFC in a wireless device with variable resistances was achieved demonstrating its functionality in the test volunteer when compared with a potentiostat. This work demonstrates its importance in obtaining energy using a fully enzymatic tattoo type BFC and its stability.

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