An enzymatic glucose biofuel cell based on Au nano-electrode array

Tanmay Kulkarni, Deepa Gupta and Gymama Slaughter
University of Maryland Baltimore County and Bioelectronics Laboratory
Department of Computer Science and Electrical Engineering
1000 Hilltop Circle, Baltimore, MD 21250, USA
E-mail address: gslaught@umbc.edu

***Abstract*— Herein a glucose biofuel cell capable of producing micro-watts power has been presented. The bioanode and the biocathode were fabricated using glucose oxidase and oxygen reducing laccase, respectively immobilized on a 4 x 4 Au nanotip pyramidal electrode array having a tip diameter of ~62 nm with an electroactive surface area of 0.04 cm². The power generating capability of the glucose biofuel cell was characterized in the presence of 5 mM, 10 mM and 20 mM glucose solution (pH 7) at 37° C to mimic the physiologic conditions. An open circuit voltage of 562.1 mV with a maximum power density of 112.21 μW cm^{-2} at a cell voltage of 270.4 mV was delivered by the glucose biofuel cell operating in 20 mM glucose. The use for the 4 x 4 Au nanotip pyramidal electrode array provides a novel approach to improve the electroactive surface area for enzyme immobilization, in addition to enabling the electrochemical energy generation via direct electron transfer. The as-fabricated glucose biofuel cell has a great potential to be employed in powering low-power implantable bioelectronic devices.**

Keywords— biofuel cell; buckypaper; nanotip pyramidal electrode array

I. INTRODUCTION

Recent improvements in implantable bioelectronic devices have opened up a new research field of energy generation and harvesting devices capable of generating micro-watts power. These power supplies must be environmental friendly, cheap, easily renewable, less bulky and reliable due to the implantation constraints. Currently, the micro-electronic bio-implantable devices are battery powered, which have limited stored chemical energy. As a result, the battery must be replaced or recharged once all the stored chemical energy is depleted and there is a considerable risk to a patient's life undergoing repeated surgery for battery replacement, in addition to the cost of surgery. To overcome the aforementioned problems, significant research has been conducted in the area of energy harvesting using alternative power sources.

Abiotic and microbial fuel cells and biofuel cells are receiving significant attention due to their potential applications as alternative 'green' energy sources and advantages over batteries. Although abiotic fuel cells can produce higher power density, a major drawback is the use of precious noble metals [1], which are costly, non-renewable and sometimes produce poisonous metal oxides [2] affecting the fuel cell's durability. Microbial fuel cells, on the other hand, use mixed bacterial culture to produce energy [3, 4]. This approach may prove to be harmful from bio-implantable perspective, although they have been shown to last up to five years [5]. These drawbacks of abiotic and microbial fuel cells has diverted the focus of research to enzymatic biofuel cells that rely on the use of naturally occurring enzymes that are renewable, economical and environment friendly to harvest energy [6]. Enzymatic glucose biofuel cell is ideal for bio-implantable power source since it uses the glucose present in the blood as a fuel to produce power. Glucose selective enzymes like glucose oxidase (GOx) [7], glucose dehydrogenase [8], are employed to oxidize glucose fuel to release electrons thus, generating electric power. The redox reactions involved in a typical glucose biofuel cell utilizing glucose oxidase and laccase as the anodic and cathodic enzymes, respectively are as follows:

$$Anode: \quad 4Glucose \rightarrow 4Gluconolatone + 4H^+ + 4e^-$$

$$Cathode: \; O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$Overall: \; 4Glucose + O_2 \rightarrow 4Gluconolactone + 2H_2O$$

Furthermore, enzyme's ability of bioelectrocatalysis depends upon direct electron transfer (DET) and mediated electron transfer (MET). In DET, the redox reactions between the enzymes and the fuel results in the direct electron transfer of electrons from the enzyme to the substrate, whereas in MET, a redox active species referred to as the mediator is incorporated to enable the electron transfer from the enzyme to the substrate. Moreover, most glucose biofuel cells are employing carbon nanotubes as the substrate due to their high surface area and their ability to mediate electron transfer [9-11]. Several of these biofuel cells reported an open circuit voltage around 500 mV [12, 13]. The largest recorded open circuit voltage of 780 mV was observed by Mano et al., under non-physiological conditions [14]. The urge for high power density and stable current operation is essential for powering bio-implantable micro-electronic devices.

In this study, we present a novel technique for improving the electroactive surface area of the bio-electrodes by fabricating a polyimide-based three dimensional 4 x 4 gold nanotip pyramidal electrode array bioanode and biocathode as an effective way to maximize the electroactive surface area available for enzyme immobilization and thus, improving the power density produced. We demonstrate the ability of the biofuel cell comprising of flexible glucose oxidase and laccase gold nanotip electrode arrays to generate sufficient electrical