



Modeling Carbon Nanotube Connectivity and Surface Activity in a Contact Lens Biofuel Cell



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ABSTRACT

Biofuel cells are often limited by the current density produced by the cathode; this is especially true when such fuel cells are scaled down to fit a desired application. Herein, we created a computational model to examine the effects of carbon nanotube (CNT) connectivity and surface activity on the current density of a biofuel cell cathode. The model was motivated by the creation of a novel contact lens biofuel cell that, although more stable and biocompatible than previously reported designs, was cathode limited. The device produced a maximum current density of $22 \pm 4 \mu\text{A cm}^{-2}$, and a maximum power density of $2.4 \pm 0.9 \mu\text{W cm}^{-2}$ (at 0.163 V) with an open-circuit voltage of 0.44 ± 0.08 V. Computational results showed that in a Nafion film containing 1.6% CNTs by volume, less than 20% of the CNT fibers were connected to the electrode, assuming a planar electrode. The simulations predicted that a three-fold increase in CNT loading would lead to a roughly two-fold increase in total CNT connectivity. The simulations further estimated that for the CNTs connected to the electrode, only 21% of their sidewalls were contributing to cathodic current, meaning that the remaining surfaces were not electrochemically active. Given the low bilirubin oxidase (BOD) enzyme surface concentration, which was experimentally found to be $1.24 \times 10^{-13} \text{ mol cm}^{-2}$, it is likely that large portions of the CNT surfaces are not connected to enzymes. This result validates the push by the research community to increase BOD and laccase adsorption/orientation to CNT surfaces.

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1. Introduction

Enzymatic biofuel cells convert chemical energy to electricity using enzymatic catalysts. With origins in living systems, enzymatic catalysts operate well in physiological temperature and pH, which makes them an attractive option as a possible implantable power source [1–10]. Several examples of biofuel cells operating under such conditions have been reported, including some that operate in biological fluids [11–15]. The trends in power output and stability for biofuel cells are clearly positive, but operational stability remains a significant limitation.

Enzymatic biofuel cells are generally less stable than their transition metal counterparts due largely to thermal degradation of the biological catalyst. Many attempts have been made to improve biofuel cell stability; however, existing biofuel cells are still shy of the 5–10 year lifetime of common implantable devices such as pacemakers and implantable cardioverter defibrillators

(ICD) [16,17]. Meeting the stability requirements of fully implantable devices will continue to be a major goal for enzymatic biofuel cell research; however, an alternative approach involves the use of wearable biofuel cells that can be easily replaced on a regular basis. For example, wearable biofuel cells have recently been integrated into flexible textiles [18,19], iontophoresis patches [20], temporary tattoos [21], and contact lenses [22,23].

We recently reported a contact lens biofuel cell created using carbon paper comprised of carbon nanotubes (CNT), called buckypaper, electrodes modified with poly(methylene green), nicotinamide adenine dinucleotide (NAD^+), and lactate dehydrogenase (LDH) at the anode, and with anthracene-pyrene (An-pyr) and bilirubin oxidase (BOD) at the cathode [23]. However, the use of adsorbed NAD^+ as a cofactor results in inherent instability due to desorption of poly(methylene green) and adds significant complexity with respect to substrate and cofactor diffusion. As a potentially simpler alternative anode system, we recently reported [24] a high current density self-powered lactate sensor that utilizes a flavin adenine dinucleotide (FAD)-dependent lactate oxidase (LOx) that was “wired” to an electrode surface using a dimethylferrocene-modified linear poly(ethylenimine) ($\text{FcMe}_2\text{-LPEI}$) redox

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polymer, where the redox polymer simultaneously immobilizes the enzyme at the electrode surface and facilitates rapid electron transfer between the enzyme's active site and electrode. While using this system produced a simpler, more stable anode, the cathode continued to be problematic, requiring a high enzyme and CNT loading as well as a larger projected surface area to match the anodic current.

Enzymatic biofuel cells are commonly cathode-limited and this is currently an area of focused research [25]. The use of infused CNTs in an enzyme-immobilizing film is a highly effective method of increasing electrode surface area [26], yet only those CNTs that are electrically connected to the electrode surface contribute to electrocatalytic current. Additionally, only portions of the CNT surface may be electrochemically active [27–31]. Yet another important limitation is that not all the enzymes are able to communicate with or are “wired” to electrochemically active CNT sites. In a direct electron transfer (DET) system, limitations related to CNT connectivity, surface activity, and enzyme wiring are amplified compared to a mediated system, because the mediators increase the likelihood of electron transfer from enzymes to the current collector.

Analytical [32–35] and Numerical [36–44] modeling are useful, although arguably underutilized, tools for understanding enzymatic biofuel cell operational mechanisms. In an effort to better understand CNT-related limitations in enzymatic biofuel cell electrodes, especially those using DET, we built a series of prototypes and simulations that are reported herein. The first portion of this paper describes a contact lens biofuel cell prototype that was created as an experimental system to allow for computational analysis. It will be shown that cathode limitations were quite pronounced in the contact lens biofuel cell, so the second portion of this paper examines CNT-related factors contributing to low biocathode electrical current. CNT connectivity to the electrode was estimated using Monte Carlo simulation. The results were used in a COMSOL model to simulate current-potential data, which was fit to experimental data to estimate CNT electroactive/wired surface area. Although the modeling portion of this paper was performed with the contact lens biocathode specifically in mind, the results are applicable to any bioelectrode modified with a CNT-filled enzyme immobilizing polymer.

2. Experimental

2.1. Lens and Electrode Fabrication

A 3D-printed contact lens mold was created that had a concave, hand-polished, spherical surface, which defined contact lens curvature, and a sharp edge at the spherical surface's boundaries to control lens outer diameter. On the underside of the mold was a cylindrical protrusion used for centering the mold in a spin coater during lens curing. Fig. 1 shows CAD cross-sectional and isometric views.

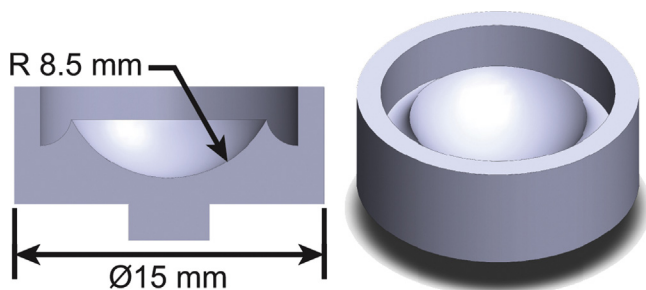


Fig. 1. CAD model of the contact lens mold showing dimensions that defined the contact lens; on the left is a cross-sectional view and on the right is a 3D isometric view.

views of the mold, including important mold dimensions defining the contact lens features. The electrode shapes were defined using a mask made from laser-cut vinyl tape (Gerber Instachange Removable Film). The mask was created in such a way so that the electrodes would have the correct size and shape and would be located around the perimeter of the lens once the mask was adhered to the cylindrical mold surface (Fig. 2).

The carbon paste used for the electrodes was based on a formulation reported by Sameenoi et al. [45], but with an increased wt. percentage of polydimethylsiloxane (PDMS) for additional mechanical stability. The carbon paste was a mixture of 45% (by weight) 12–15 μm graphite (Asbury Graphite, type 5601), 5% multi-walled CNT (MWCNT) (outer diameter: $\varnothing 25$ nm, length: 20 μm , Cheap Tubes, Inc.), 25% mineral oil (Mallinckrodt #6358), and 35% polydimethylsiloxane (PDMS) (Sylgard 184, 10:1 w/w base:cross-linker). The graphite and MWCNT were thoroughly mixed in a small tube, the mineral oil and PDMS were added, and the paste was mixed with a small spatula until the consistency was visually uniform (approximately one minute of mixing). With the electrode mask adhered to the mold, the carbon paste was applied over the mask with the spatula. Removing the mask left patterned carbon paste electrodes on the mold surface where the contact lens would be formed. Transparent UV-curable silicone rubber (Shin-Etsu product X-34-4184) base and cross linker was mixed in a 10:1 w/w base:cross-linker ratio and 110–115 mg was poured into the mold over the carbon paste electrodes. The amount of elastomer was important for achieving the desired final contact lens thickness (300–400 μm) and outer diameter ($\sim \varnothing 15$ mm). The mold was placed into a spin coater (Laurell, WS-400A-6NPP-LITE) with the lid up and spun at 400 rpm for 15–17 minutes while exposing it to a 100-Watt UV light source (Blak-Ray) placed roughly 3 inches from the mold. The cured lens was then carefully removed from the mold before the carbon paste was fully cured and placed in an oven at 60 $^{\circ}\text{C}$ for an hour to cure the carbon paste electrodes. Removing the lens from the mold before the carbon paste fully cured was important, because it sheared the carbon paste, leaving part of the paste on the mold, while removing the paste that had cured to the lens. This increased the electrode surface approximately 60 times (Fig. 4.2F) based on surface area measurements made using the electrochemically accessible surface area (EASA) method [46] and assuming a specific capacitance of 20 $\mu\text{F cm}^{-2}$. Small wires were attached to the electrodes using conductive silver epoxy (Electron Microscopy Sciences), which was then insulated with clear epoxy (5 Minute[®] Epoxy, Devcon). Not including electrode areas bonded to wire leads, the anode and cathode geometric surface areas were about 0.04 cm^2 and 0.2 cm^2 , respectively. The cathode was larger in an attempt to overcome cathode limitations.

2.2. Contact Lens Electrode Enzyme Immobilization

Fig. 3 schematically illustrates the enzymatic modifications made to the electrodes after the contact lens electrodes were fabricated. Anodic enzymes were immobilized in a previously reported dimethylferrocene-modified linear polyethyleneimine (FcMe₂-LPEI) redox polymer [47] that has proven to be very effective at mediating electron transfer for oxidation of glucose [47], fructose [48], ethanol [49], and lactate [24]. Anode-modifying solutions containing 70.5% v/v FcMe₂-LPEI (10 mg ml⁻¹ in deionized water), 26% v/v LOx from *Pediococcus* sp. (200 U/ml, Sigma-Aldrich), and 3.5% v/v ethylene glycol diglycidyl ether (EGDGE) (2.5 μl in 45 μl DI water, Polysciences, Inc.) were mixed thoroughly and 6 μl was pipetted onto the anode and allowed to dry overnight at room temperature.

On the cathode, a solution containing An-pyr modified CNT, BOD, and TBAB-modified Nafion was pipetted and allowed to dry

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