Microscopic Imaging of Electrical Current Distribution at the Electrode-Electrolyte Interface

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***Abstract*—A method to directly visualize electrical current distribution at the electrode-electrolyte interface of a biopotential electrode is presented in this paper. A voltage-responsive florescent material is first coated on the surface of a bioelectrode. Then, an electric potential is used to activate the release of the florescent material while a camera acquires images at the electrode-electrolyte interface. This imaging method allows observation of microscopic electrical current distribution at the active area of the electrode, providing a new tool to optimize bioelectrode design. Our computational and experimental data demonstrate the feasibility of the florescent imaging method.**

I. Introduction

Biopotential electrodes have been widely utilized in various applications, such as deep brain stimulation, electroencephalography (EEG) and electrocardiography (ECG). The characteristics of interaction between the electrode and electrolyte within biological tissue are of paramount importance in determining the performance of the bioelectrode. Theoretical modeling and computational simulation are conventional methods to study the electrical properties at the interface. In order to ease analysis, the interface is usually modelled as a combination of circuit elements (e.g., resistors and capacitors), ignoring the size and structure of the bioelectrode [1, 2]. However, in order to obtain information regarding the interaction between electrode and electrolyte, the structure of the electrode and the effective contact area at the interface must be included in the modelling. Thus, finite element analysis was utilized to study both the electrical and structural properties of bioelectrodes [3-5]. Although the impedance spectroscopy provides a useful experimental measurement to validate circuit models and simulation results, this method does not provide detailed information about the interface within local structures of the bioelectrode. Imaging the electrical phenomena microscopically at the interface in addition to modelling and simulation still remains to be a challenging problem.

This paper presents a new method to image the current distribution at the electrode-electrolyte interface. The fluorescent microscopy is proposed as a powerful tool to observe the current distribution on the surface of the bioelectrode. We found that the distribution was non-uniform with high concentrations in local areas with certain geometric features.

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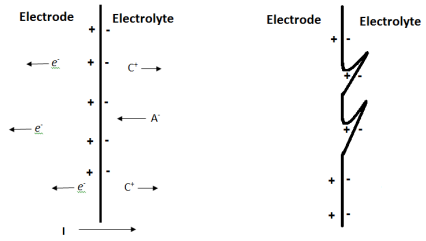
II. Electrode-Electrolyte Interface

The electrode-electrolyte interface is illustrated in Fig.1(a). The movements of electrons, cations and anions at the interface produce a static electrical potential at the resting state called the half-cell potential [2]. When a current is applied between the electrode and electrolyte, this potential is altered due to the polarization of the electrode. The difference caused by polarization is known as the overpotential. Based on the level of electric charges across the interface when a current is applied, bioelectrodes are usually classified into two categories: polarizable electrodes and nonpolarizable electrodes. When evaluating the performance of an electrode, the overpotential is usually assumed to be distributed uniformly at the interface and simplified as a capacitive component in the traditional models. However, this assumption does not hold if the microstructure of the interface is irregular (Fig. 1(b)). Cantrell et. al. studied the effects of geometric shape on the electrode-electrolyte interface using a finite element model [3]. But the assumption of uniformity was still utilized. How to study the electrode-electrolyte interface in irregularly shaped microstructures of a bioelectrode remains to be a highly significant, but unsolved problem.



(a) (b)

Figure 1. (a) Schematic illustration of the electrode-electrolyte interface. The current flows through the interface from left to right. The electrode consisted of metal C. The electrolyte contains cations of the electrode metal C^+ and anions A^-; (b) Illustration of an irregular electrode-electrolyte interface.

III. Methods

We propose a method to visualize the electrical current distribution at the electrode-electrolyte interface via controlled release of a fluorescent tracer. The electrode is first coated with a solution containing a florescent material using electrochemical deposition. When activated by an electric potential applied across the interface between the electrode and electrolyte, this material is released. A sequence of

images produced by the fluorescent microscopy captures the electric distribution at different time points. Modelling of the electrode-electrolyte interface and finite element analysis of the electric field are then conducted to validate the proposed method. In the following, we present details of our method.

A. Electrically Controlled Release of Fluorescent Tracer

In this work, the polypyrrole (PPy) film doped with fluorescein anions is used as a fluorescent tracer to image the electric distribution. The PPy film is deposited on the electrode by one-step electropolymerization [6]. In the presence of dopant fluorescein anions in the supporting electrolyte, the monomers become oxidized and polymerized. Because the polymer backbone is positively charged during oxidization, the counterion in the solution is incorporated into the PPy thin film to maintain charge neutrality. But the doped PPy film can be reversibly switched between an oxidized state and a reduced state under the stimulus of an electrical potential. The redox reaction is also accompanied by the movement of dopant ions in and out of the polymer film for charge balance. Therefore, upon the application of the electrical potential, incorporated fluorescein anions are expelled from the polymer film and are free to diffuse out to the immediate surrounding electrolyte. This property inspired us to develop a new tool capable of observing how current flows in or out of the electrode tip microscopically. Such an electrically-controlled mechanism has been used in drug delivery system to release drug upon stimulation [7, 8].

B. Finite Element Modeling and Simulation

In finite element analysis, the experimental setting and the electrical property of each component (e.g., the electrode and electrolyte) are first determined in the finite element model. Then, each component is divided into small building blocks called elements. Each element is used to describe its response to a given input locally, and the "sum" of all elements in the model produces the total response. In our study, each element is considered as a volume conductor, and the Laplace equation is used to characterize the electrical response of each element. Thus, the distribution of the electric potential within each element can be calculated by solving

$$\nabla \cdot \sigma \nabla \phi = 0, \quad (1)$$

where ϕ is the potential distribution, σ is the electrical conductivity, and ∇ is the gradient operator. The electrical current density, denoted by J, can be computed from

$$J = -\sigma \nabla \phi . \quad (2)$$

To solve the electrostatic problem with a finite element analysis, excitation and boundary conditions must be provided. In our case, voltage excitation at electrode is set to a constant value. A square vacuum region outside the study area is defined as the physical boundary and the current in or out this region across the boundary is assumed to be zero.

IV. Experimental Design

A. Electrode

A dry EEG electrode (called skin screw electrode), developed by our group, was used in this work (see Fig.2 (a)-(b)) [9, 10]. It is made of stainless steel, with a cylinder shape (diameter about 1cm). When this electrode is installed on human scalp for signal recording, the microteeth around its rim can penetrate the stratum corneum, which is the very top layer of the skin. The skin screw electrode hooks the stratum corneum so it can both grab the skin firmly and make a reliable electric connection without using an electrode paste. The shape of these teeth is specifically designed, shown in Fig. 2(c). When applied to the scalp, they extend horizontally, holding the electrode in place without penetrating too deeply into the skin. Since both the mechanical and electrical properties of the electrode depend on it structural design, imaging of the electric current distribution at the interface between the electrode and scalp helps us improve electrode performance.

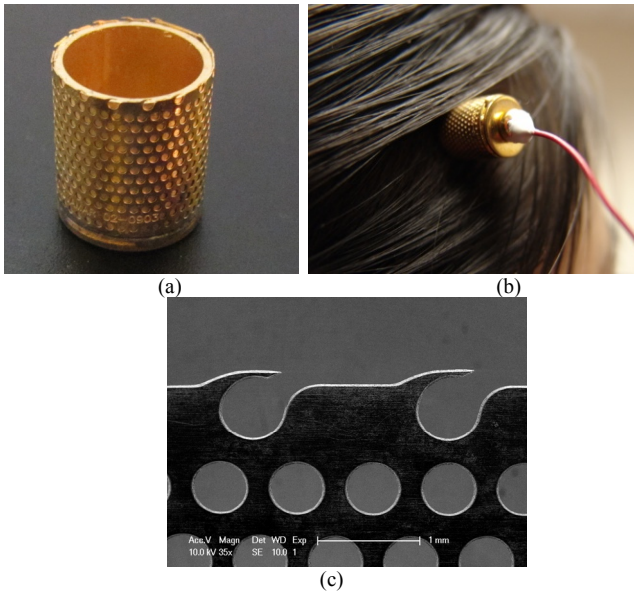


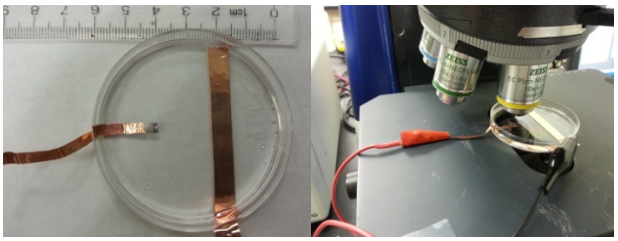
Figure 2. (a) Prototype of the electrode; (b) Installed electrode on scalp; (c)Scanning electron microscope picture of the microteeth.

B. Fluorescent Coating

Several strips (each with one or two teeth on its tip) were cut from two electrodes with different tooth sizes and used in our experiment. Each electrode strip was first degreased by sonication for 20 minutes in 2M KOH containing 200 mg/L of sodium dodecyl sulfate. After rinsing thoroughly with distilled water, the electrode was cleaned by acetone/ethanol sonication/ultra-violet ozone. Pyrrole was distilled under vacuum prior to use. Fluorescein sodium salt was used as the fluorescent probe. The deposition solution contained 0.2 M pyrrole and 0.01 M fluorescein sodium salt. Polypyrrole (PPy) films doped with fluorescein sodium were electrodeposited onto the electrode surface at a constant potential of 0.9 V for 300 seconds. The platinum wire mesh was used as the counter electrode and Ag/AgCl as the reference electrode. The electrode was rinsed with de-ionized water and stored in 1X Phosphate Buffered Saline (PBS) at 4°C. Before the experiment, the electrode strip was rinsed thoroughly with distilled water.

C. Experiment Procedure

The electrode strip was fixed in a cell culture dish with a diameter of 60mm. 1X PBS buffer was used as the electrolyte. A long copper strip was used as the ground electrode. The layout of the electrode strip and ground is shown in Fig. 3 (a). A constant-voltage power supply of -1.5 V was applied across the electrode strip and the ground at room temperature as the trigger to release the florescent film. The trigger at this voltage was found to be efficient in releasing the fluorescein. The release of fluorescein was monitored using a Carl Zeiss Axio Imager A1 fluorescent microscopy (Fig. 3(b)). The exposure time was set to 50ms. A total of 15 images were acquired at a speed of one image per second.



(a) (b)

Figure 3. (a) Layout of the tested electrode and the ground; (b) Microscopic imaging in which the red and black clips represent the positive and ground electrodes, respectively.

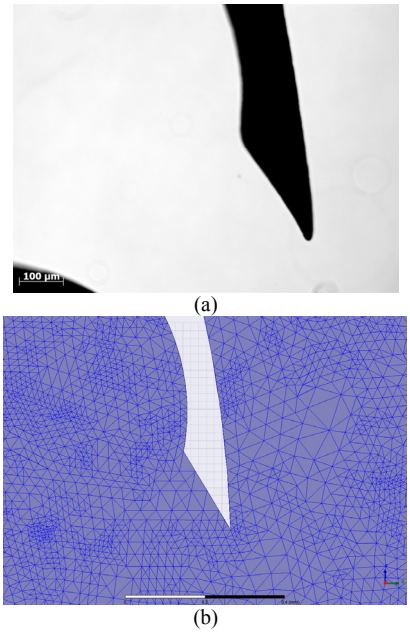
V. Simulation

The electric distribution at the interface was simulated with the help of Maxwell v16.0 (Ansys Inc, Pittsburgh, PA). Since the thickness of our electrode was very small, around 0.1mm, the simulation was conducted based on a 2D design. Because the length of the tooth was only several hundred micrometers, much smaller compared to the culture dish, only a small part of the tooth was modelled to balance the spatial resolution of the simulation and the computational complexity. This part is the tip of the tooth that contacts the tissue/electrolyte (i.e., penetrates into the skin). The finite element model was created by assuming a circular area with 2mm diameter filled with PBS. The modelled electrode tip was placed in this buffer. The material of the electrode was assumed to be stainless steel. The actual structure of the electrode and the modeled structure with mesh pattern are plotted in Fig. 4. A voltage excitation of -1.5V was applied at the electrode and 0V at the boundary.

VI. Results

Three fluorescent microscopic images, taken at roughly the first, third, and fifth seconds after the activation electrical potential was applied, are shown in Fig. 5a, 5b and 5c respectively. The change of the electrical current distribution around the electrode tooth can be clearly observed. It can also be seen that the current distribution highly depends on the local geometric shape of the electrode.

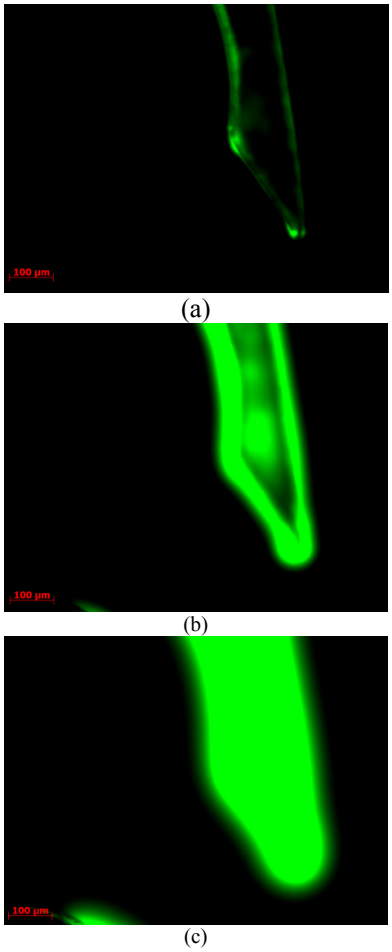
In comparison, the simulated electrical current distribution is shown in Fig. 6. It can be observed that this current distribution is consistent with the first fluorescent image, which is geometrically non-uniform and concentrated at electrode locations with large curvatures.



(a)

(b)

Figure 4. (a) Microscopic image of a single bioelectrode tooth (partial view); (b) finite element mesh of (a). The length of the scale bar is 0.4mm.



(a)

(b)

(c)

Figure 5. Images of electrical current distribution around the tooth: (a) the first image taken approximately one second after the fluorescent release; (b) the second image; (c) the fifth image. Note that the fluorescent pattern in the lower left corner of the images comes from another part of the electrode.

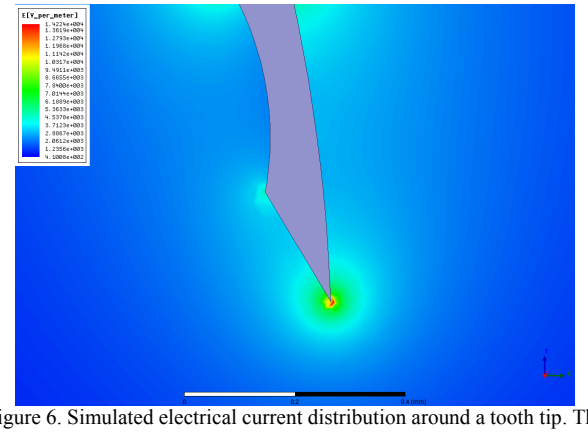


Figure 6. Simulated electrical current distribution around a tooth tip. The length of the scale bar is 0.4mm.

VII. Discussion

Although we have demonstrated the feasibility of the proposed approach, there are several questions and practical problems to be addressed. For example, the uniformity of the coated florescent material on the surface of the bioelectrode likely affects the current distribution. How to control the thickness and uniformity of the coating is still an unanswered question. In our experiment, the coating time was 300 seconds to guarantee that the coated film was sufficiently thick. But we still encountered the problem of non-uniformity (see Fig. 7). The variation of the coating time with respect to performance also needs to be studied further.

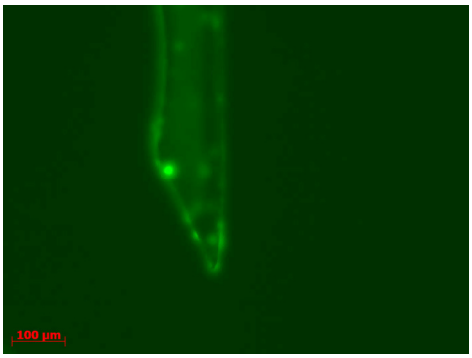


Figure 7. Image of electrical current distribution for a non-uniformly coated tooth.

In our experiment, a -1.5V potential was used to trigger the release of the fluorescent tracer. A trigger of larger amplitude may make the system more responsive. However, a higher voltage may distort the current distribution. The optimal trigger balancing these two effects is desirable.

Furthermore, it is highly desirable to measure the current distribution based on the fluorescent intensity quantitatively. Unfortunately, at this initial state, we have not been able to do this because the release of the fluorescent tracer depends on not only the current density, but also the diffusion of the tracer in the electrolyte. These two effects should be separated and studied further. We will continue working on this problem.

Finally, for better visualization of the fluorescent release, it is necessary to use a high-speed camera in the microscope to acquire images in a higher quality. Due primary to the low speed of our imaging system, the release of the florescent tracer could not be observed completely in all tested strips.

VIII. Conclusion

In this paper, we have presented a new approach to the imaging of the electrical current distribution at the electrode-electrolyte interface microscopically in local regions. This imaging technique provides a new tool for the optimization of bioelectrode design.

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