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Kinetic Study of Homogeneously Mediated Electrode Reactions in Glucose-Based BioFuel Cells

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The use of biofuel cells (BFC) is a promising approach to generate electricity. BFC can be successfully applied to achieve long-term autonomous operation of miniaturized implantable Body-Area-Network (BAN) devices. BAN devices are important for the development of future healthcare technologies. Glucose-based enzymatic BFC are a good option to power BAN devices due to the high availability of the fuel (glucose) in body fluids. Moreover, it shows excellent catalytic selectivity and good chemical safety. In this paper, the design of a glucose-based enzymatic BFC demonstrator is described and the performance of both the individual electrodes and the complete cell is evaluated. The measured maximum power output of the designed BFC-demonstrator was 5.8 μW cm\textsuperscript{-2}. Additionally, the kinetics of the detailed energy conversion processes, occurring inside the BFC system, have been investigated from both an experimental and theoretical point of view. The proposed model describes the glucose oxidation at the anode of a BFC and includes the diffusion for all (electro-) chemically active species. The modeling results are qualitatively and quantitatively in good agreement with the experimental results.

Introduction

It is expected that advancements in technology will enable people in the near future to carry their own personal wireless Body-Area-Network (BAN) that monitors and even improves the health of the user. Such network comprises of a series of miniature wireless sensor/actuator nodes. These nodes can, for example, monitor vital functions of the wearer, and may control the health of the person by releasing medicines or stimulating body functions with electric pulses. Some of these nodes can be utilized externally, but for some functions implantable nodes are required. As these latter systems should operate wirelessly, each node should have its own on-board energy supply, consisting of both an electricity harvesting and storage system. Such a vision requires innovative solutions to remove the critical technological obstacles for the successful realization of wireless BAN sensor nodes (1).
These challenges have motivated the industry and research institutes to work on various advanced energy systems (ES) and low-power electronics. As a result, various types energy harvesting, electricity storage systems, and low-power electronics technologies are under investigation or penetrating the market (2). Among these, biofuel cells (BFC) are promising to generate electricity, enabling long-term autonomous operation and miniaturization of medical implants. In combination with energy storage and appropriate energy/power management as schematically indicated in Figure 1 (3, 17), BFC are an essential power source for future miniaturized BAN applications.

Figure 1. Block scheme of a fuel cell device integrating the Bio-Fuel Cell, power management, and energy storage.

Research efforts for implantable BFC have been focused on the investigation of different biocatalysts and fuels (4). Palmore et al. used three Nicotinamide Adenine Dinucleotide (NAD+) -based enzymes, comprising of Alcohol DeHydrogenase (ADH), Aldehyde DeHydrogenase (AldDH) and Formate DeHydrogenase (FDH), to form an enzyme-based anode that can completely oxidize methanol (5). Katz et al. reported a complete cell based on novel architectures for both electrodes (6). The anode was assembled by immobilizing apo-glucose oxidase onto a monolayer of PyrroloQuinoline Quinone (PQQ) and Flavin Adenine Dinucleotide (FAD). The cathode was assembled by attaching cytochrome oxidase onto a monolayer of cytochrome c. Because highly specific enzymes were immobilized on the electrodes a membrane separating the fuel from the oxidant was not necessary for this type of fuel cell.

Redox polymers were first employed for the immobilization and mediation of redox enzymes by Heller’s group (7, 8). Redox complexes based on osmium have been immobilized on water-soluble polymers. In such a structure, the mobility of the polymer backbone provides restricted translational mobility to the redox complex, allowing electron transport via exchange between neighboring centers while preventing their bulk diffusion. Furthermore, the electron-donor ligands can effectively tune the redox potential of the metal centre, allowing one to engineer the mediator at the molecular level to work in conjunction with the desired enzyme. A miniature BFC can be achieved if the redox polymer and enzyme are deposited on carbon fiber electrodes. As an alternative to the Os-based redox polymer, a polymer containing vitamin-K3 can be utilized to immobilize
Glucose DeHydrogenase (GDH) onto glassy carbon. Based on this process, Sony Corporation has produced a BFC prototype (9, 10).

Instead of small organic molecules like methanol, ethanol and glucose, H$_2$ has also been used as fuel in BFC. Armstrong et al. used O$_2$-tolerant hydrogenase as anodic biocatalyst to construct a H$_2$/O$_2$ BFC (11). A membraneless fructose/O$_2$ BFC was described by Kano and co-workers (12). Heme-containing fructose dehydrogenase and laccase were immobilized on carbon with powdered or mesoporous morphologies. Another example of such BFC was reported by Gorton et al. In this case, cellobiose dehydrogenase and laccase were used as anodic and cathodic biocatalysts, respectively (13). These fuel cells may present advantages for implantable applications because they avoid toxic mediators or by-products. However, their power output is lower when compared with the fuel cells using mediators.

Regarding kinetic studies and mathematic modeling of enzymatic biofuel cells only a few reports can be found in the literature. For instance, in the theoretical work by Kjeang et al. a conceptual model for an enzymatic fuel cell was shown, without presenting experimental details (14). They tried to optimize the structure of a microfluidic enzymatic fuel cell, involving three-step-catalyzed methanol oxidation. Delle Noci et al. used a one-dimensional numeric model to obtain kinetic information from cyclic voltammetry experiments (15). Ohgaru et al. adopted some empirical relationships to estimate the kinetic parameters of the enzymatic driven reactions (16).

The glucose-based enzymatic fuel cell seems, however, to be the most promising candidate for the applications in BAN due to the highly specific and active enzymes and the fuel abundance in body fluids (17). The working principle of such BFC is schematically shown in Figure 2. Glucose oxidase (Gox) and Laccase (Lac) are examples of biocatalysts for the anode and cathode, respectively. FAD is the active centre of Gox. Glucose and oxygen are used as fuel and oxidant, respectively. The cell voltage (ΔE) is determined by the formal potential of the two redox mediator molecules (M and M'), reacting at the surface of the anode and cathode separately.

Figure 2. Working principle of glucose-based enzymatic fuel cells. The voltage is defined vs. the Ag/AgCl reference.
The electronic coupling between the enzyme active centers and electrodes is the key factor influencing the performance of a BFC (18). As the active centers of most redox enzymes are buried deep inside the isolated protein matrices it is, however, very hard to achieve direct electron transfer between the enzymes and electrodes. A way to overcome this problem is to employ a mediator, a small organic molecule or metal complex, to assist electron transfer. Ferrocene-carboxylic acid (Fc) is a stable one-electron exchanging mediator for Gox (19). The detailed anode reactions involving Fc as mediator are shown in Eqs. 1-3. Glucose is homogeneously oxidized in the electrolyte by glucose oxidase (Gox(FAD)) to become gluconolactone. FAD will obtain two protons and two electrons to become FADH$_2$ during the catalytic reaction (Eq. 1). The reduced form of glucose oxidase (Gox(FADH$_2$)) will chemically transfer two electrons to two oxidized ferrocene-carboxylic acid molecules (Fc$^+$) and release two protons (Eq. 2) that will be transferred through a membrane to the cathode. The reduced form of ferrocene-carboxylic acid (Fc) finally reacts at the electrode surface to form its oxidized state again, releasing electrons through which the current is generated (Eq. 3).

\[
\text{Glucose + Gox(FAD) \rightarrow Gluconolactone + Gox(FADH}_2) \quad [1]
\]
\[
\text{Gox(FADH}_2) + 2 \text{Fc}^+ \rightarrow \text{Gox(FAD) + 2 Fc + 2 H}^+ \quad [2]
\]
\[
2 \text{Fc} \Leftrightarrow 2\text{Fc}^+ + 2 \text{e}^- \text{ (at electrode surface)} \quad [3]
\]

In this paper, a BFC based on Gox and Lac (20) as biocatalysts for the anode and cathode, respectively, is studied and demonstrated. Optimization of the BFC performance requires a deeper understanding of the energy conversion processes. This can be achieved by developing models describing the BFC thermodynamics and kinetics. For this purpose a detailed kinetic study and a systematic model description of the homogeneously mediated electrode reactions has been set up.

**Experimental**

For the anode, Gox (160 kDa) was selected as catalyst. Two different mediators were used, *i.e.* Ferrocene-carboxylic acid and Phenazine methosulfate (Pm). The solution was bubbled with argon or nitrogen to eliminate dissolved oxygen. For the cathode, Lac (65 kDa) was used as biocatalyst and 1 mM 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) as mediator. All chemicals were obtained from Sigma-Aldrich.

Both enzymes and mediators were dissolved in 20 mL electrolyte, consisting of a 0.067 M Phosphate Buffer Solution (PBS) of pH=7.2. During this experiment, a glassy carbon disk electrode was used as working electrode, Ag/AgCl as reference electrode and a porous, high surface area, Pt electrode as counter electrode. Before the electrochemical measurements, the glassy carbon disk electrode was polished to a mirror-like surface using 0.3 µm Al$_2$O$_3$ powder followed by a 0.05 µm Al$_2$O$_3$ polishing step. Then the polished electrode was ultrasonically cleaned in distilled water and ethanol, successively, to remove the adsorbed alumina particles. Finally, the electrode was dried in air. The geometric surface area of the glassy carbon electrode is 0.18 cm$^2$. 


The experimental set-up consisted of a potentiostat (PGSTAT30 from Metrohm-Autolab, the Netherlands), an in-house developed glass electrochemical 3-electrode cell with a gas supplying system and a personal computer (PC).

Different electrochemical methods, i.e. Cyclic Voltammetry (CV), Chronopotentiometry, and Chronoamperometry, were employed to measure both the anode and cathode performance in a half-cell configuration and the complete BFC system under a wide range of experimental conditions. All electrochemical measurements were performed at room temperature and all potentials in the half cell experiments are given with respect to the Ag/AgCl reference electrode (0.198 V vs. NHE).

Results and Discussion

The cyclovoltammograms of the (half-cell) anode are shown in Fig. 3. In this experiment, a 1 mM solution of Fc mediator and 3µM Gox was used in the buffered PBS electrolyte (pH=7.2) and the glucose concentration was varied. A pair of well defined and symmetric redox peaks was observed at 0.34 and 0.28 V at 20 mV/s without glucose in the electrolyte (curve (a) in Fig. 3). The peak-to-peak separation (∆Ep) is about 60 mV and the ratio between the anodic (Ipa) and cathodic (Ipc) peak currents is close to unity (0.978), indicating that electron transfer between Fc and the glassy carbon electrode is reversible and fast. When the glucose concentration is stepwise increased in curves (b)-(e) in Fig. 3, it is clear that larger oxidation currents and smaller reduction currents are obtained. The lower reduction currents are caused by the lower concentration of oxidized mediator (Fc+ in Eq. 2). From these results it can be concluded that glucose is oxidized and that electrons are transferred to the electrode.

![Figure 3. Cyclovoltammograms of a glassy carbon electrode in a buffered electrolyte (PBS of pH=7.2), containing 1 mM Fc as mediator and 3µM Gox enzyme. The glucose concentration was varied between 0 (a), 10 (b), 20 (c), 30 (d) and 40 mM (e).](image-url)
The electrochemistry of oxygen reduction at the cathode was examined under constant current conditions by chronopotentiometry. The measurements have been performed in the range of 0 to 4.8 μA in steps of 0.6 μA. Each constant current period had a duration of 1000 s to allow the electrode to reach steady-state. The investigated system consisted of the enzyme Lac and mediator ABTS, dissolved in the PBS buffer. Two parameters were varied (Fig. 4): with (curves (a) and (d)) and without (curves (b) and (c)) the presence of oxygen (air) and with (curves (c) and (d)) and without (curves (a) and (b)) the presence of the enzyme. It can be concluded that high reduction currents are obtained in the oxygen-containing electrolytes (compare curves (a) and (d) with curves (b) and (c)) and that the reduction is further enhanced when Lac is added to the electrolyte (compare curve (d) with curve (a)). Conclusively, enzymatic reduction of O$_2$ obviously takes place and the equilibrium voltage of this reaction is +0.48 V vs. Ag/AgCl.

Figure 4. Chronopotentiometry curves of ABTS as mediator in electrolyte (PBS pH=7.2) of 1 mM ABTS+air (a), 1 mM ABTS+Ar (b), 1 mM ABTS+7.4μM Lac+Ar (c) and 1 mM ABTS+7.4μM Lac+air (d).

In order to investigate the power generation capability of an entire BFC system, a demonstrator has been designed which is shown in Fig. 5a. The BFC has two compartments, one for the anode and one for the cathode, separated by a Nafion 112 membrane, which acts as a proton-exchange membrane. The geometric surface area of each electrode is approximately 0.18 cm$^2$. This set-up was tested with two different mediators in the anode compartment, Pm and Fc.
Figure 5. (a) BFC demonstrator. (b) BFC performance using different mediators: (a) Anode: 1 mM Pm as mediator, 3µM Gox and 10 mM Glucose; Cathode: 1 mM ABTS, 7.4µM Lac and air. (b) Anode: 1 mM Fc as mediator, 3µM Gox and 10 mM Glucose; Cathode: 1 mM ABTS, 7.4µM Lac and air.

The steady-state power density obtained under constant current loads is displayed in Fig. 5b. The maximum power density of 5.8 µWcm\(^{-2}\) is obtained for the Pm-based system (curve (a)). For the Fc-based system (curve (b)) this is substantially lower (1.8 µWcm\(^{-2}\)) at an open-circuit voltage of 0.35 V. The power output of the Fc-based system has also been investigated at different loads, i.e. by making use of different load resistances (R) in combination with a high accuracy multi-meter. In these loading tests, the maximum power density is 1.2 µWcm\(^{-2}\) when R=100 Ω. This is somewhat lower than the result obtained by constant current measurements (1.8 µWcm\(^{-2}\)) due to the power consumption of the loads.

**Theoretical considerations**

The kinetics of enzymatic-driven reactions has, in general terms, been studied by Bisswanger et al. (21). To improve the performance of BFC further, the reaction kinetics of the glucose oxidation reaction have been investigated in more detail. The mathematic description of the complex reaction sequence, given by Eqs. 1-3, has been set up and will, in general terms, be presented in this section. More details about the mathematical derivations can be found in our previous report (22).

The glucose oxidation reaction is based on a shuttle mechanism for homogeneously mediated reactions, which is appropriate for the current BFC system with Fc as mediator and Gox as enzyme. Our mathematical model includes Nernst-Planck diffusion and migration for all (electro)chemically active species involved and allows us to mathematically derive the as-denoted Michaelis-Menten equation. The most relevant simulations performed with this model will be described in this section. The simulations will be validated with experimental results.
The simplest description of the enzyme-driven reaction kinetics under steady-state conditions is based on the work of Michaelis and Menten (23) and considers just one catalyzed reaction. For the presently described BFC system, a mediator is used to couple the homogeneous reaction, occurring at the active sites of the enzyme, to the charge transfer reaction at the electrode, making this reaction sequence much more complex. The mathematical description of Michaelis-Menten has therefore to be expanded significantly. Eqs. 4-6 show the (electro)chemistry of the enzyme- and mediated-catalyzed glucose oxidation reaction (see also Eqs. 1-3) in which glucose as fuel is denoted by G, the reaction product gluconolactone by P, the oxidized and reduced form of the enzyme (E) by $E^{\text{ox}}$ and $E^{\text{red}}$, respectively and the oxidized and reduced form of the mediator (M) by $M^{\text{ox}}$ and $M^{\text{red}}$, respectively.

$$
E^{\text{ox}} + G \xrightleftharpoons[k_{-1}]{k_1} EG \xrightarrow[k_2]{k_3} E^{\text{red}} + P
$$

$$
E^{\text{red}} + 2M^{\text{ox}} \xrightleftharpoons[k_{-3}]{k_3} EM_2 \xrightarrow[k_4]{k_5} E^{\text{ox}} + 2M^{\text{red}} + 2H^+
$$

$$
M^{\text{red}} \xrightarrow[k_{-5}]{k_5} M^{\text{ox}} + e^-
$$

The intermediate reaction products $EG$ and $EM_2$ are also indicated together with the various reaction rate constants. The concentrations of the various species involved are given by $C_G$, $C_P$, $C_{E^{\text{ox}}}$, $C_{E^{\text{red}}}$, $C_{H^+}$, $C_{EG}$, $C_{EM_2}$, $C_{M^{\text{ox}}}$, $C_{M^{\text{red}}}$. The reaction rate ($r$) of the overall process can be expressed by

$$
r = \frac{K_{\text{cat}}C_E}{1 + \frac{K_M}{\left(C_{M^{\text{ox}}}\right)^2} + \frac{K_G}{C_G}}
$$

in which the combined rate constants are defined as $K_{\text{cat}} = \frac{k_2k_4}{k_2 + k_4}$, $K_M = \frac{k_3(k_2 + k_4)}{k_1(k_2 + k_4)}$ and $K_G = \frac{k_4(k_{-3} + k_3)}{k_1(k_2 + k_4)}$. A more detailed derivation of this expression can be found in literature (22). Eq. 7 is very similar to the Michaelis–Menten equation for BFC where $K_{\text{cat}}$, $K_M$, $K_G$ have been denoted as the enzyme catalytic constant and the Michaelis constants for $M^{\text{ox}}$ and Glucose, respectively. However, in line with Eq. 5 the derived Eq. 7 takes into account the 2\textsuperscript{nd} order reaction kinetics for enzyme oxidation. This therefore differs from the classical Michaelis–Menten equation which is based on a first order reaction (23).

In order to model the current generated at the anode, the charge transfer reaction of the mediator (Eq. 6) should be considered together with the derived enzyme kinetics. In Eq. 6, $k_5$ and $k_{-5}$ are denoted as forward (oxidation) and backward (reduction) reaction rate.
constants. As \( k_5 \) and \( k_{-5} \) are functions of the electrode voltage, the partial anodic and cathodic currents can be described by

\[
I_a = F \alpha_j^0 \kappa_5^0 e^{\alpha_j \frac{E - E^0}{RT}} \quad \text{and} \quad I_c = F \alpha_j^0 \kappa_{-5}^0 e^{-(1-\alpha_j) \frac{E - E^0}{RT}},
\]

where \( \alpha_j^0 \) is the (surface) activity of species \( j \) [mol‧m\(^{-3}\)], \( A \) the electrode surface area [m\(^2\)], \( F \) the Faraday constant (96485 [C‧mol\(^{-1}\)]), \( R \) the gas constant (8.314 [J‧mol\(^{-1}‧K^{-1}\)]), \( T \) the absolute temperature [K] and \( \alpha \) is the charge transfer coefficient for the charge transfer reaction of the mediator at electrode surface (Eq. 6).

In the equilibrium state, obviously, no concentration profiles are established, implying that the surface activities are equal to their corresponding bulk activities, \( i.e. \alpha_j^s = \tilde{\alpha}_j \). Moreover, in equilibrium \( I_c = I_a = I^0 \) where \( I^0 \) represents the exchange current. From Eqs. 8, it follows that under these conditions the equilibrium potential \( E^{eq} \) can be represented by

\[
E^{eq} = \frac{RT}{F} \ln \frac{\kappa_5^0 \tilde{\alpha}_{\text{Max}}}{\kappa_{-5}^0 \bar{\alpha}_{\text{Med}}} = \frac{RT}{F} \ln \frac{\kappa_5^0}{\kappa_{-5}^0} + \frac{RT}{F} \ln \frac{\tilde{\alpha}_{\text{Max}}}{\bar{\alpha}_{\text{Med}}}
\]

which can be recognized as the Nernst equation for the electrode potential. The first term on the right-hand side represents the standard redox potential and the second term takes into account the concentration dependence.

An expression for the overall current (\( I = I_a - I_c \)) can be derived directly using the previous equations. This will finally result in complete voltage-current relationship.

\[
I = I^0 \left[ \frac{\alpha_j^s}{\bar{\alpha}_{\text{Med}}} e^{\alpha_j \frac{E - E^{eq}}{RT} \eta} - \frac{\alpha_j^0}{\tilde{\alpha}_{\text{Max}}} e^{-(1-\alpha_j) \frac{E - E^{eq}}{RT} \eta} \right], \quad [10]
\]

in which \( \eta = E - E^{eq} \) is the overpotential. Note that Eq. 10 can be further simplified to the Butler-Volmer equation when \( \frac{\alpha_j^s}{\bar{\alpha}_{\text{Max}}} \approx 1 \) and \( \frac{\alpha_j^0}{\tilde{\alpha}_{\text{Max}}} \approx 1 \).

\[
I = I^0 \left[ e^{\alpha_j \frac{E - E^{eq}}{RT} \eta} - e^{-(1-\alpha_j) \frac{E - E^{eq}}{RT} \eta} \right]. \quad [11]
\]

The voltage-current relationship, the Nernst equation and the bulk concentration equations (22) have been solved in Matlab. The kinetic data of Fc and Gox have been taken from literature (24, 25) and the parameter values used in the present simulations are...
$D_M=8\cdot10^{-6}$ cm$^2$ s$^{-1}$, $D_E=5\cdot10^{-6}$ cm$^2$ s$^{-1}$, $D_G=D_P=6\cdot10^{-6}$ cm$^2$ s$^{-1}$, $D_{H^+}=9.31\cdot10^{-5}$ cm$^2$ s$^{-1}$. $K_M=0.13$ (mM)$^2$, $K_{cat}=750$ s$^{-1}$, $K_G=4.16$ mM. Fig. 6 illustrates, as an example, the simulated steady-state oxidation current as a function of the overpotential. The simulations (lines) are in good agreement with the experimental results (symbols) and clearly reveal the kinetic- and diffusion-controlled regions.

![Graph of current-overpotential curves](image)

Figure 6. Measured (symbols) and simulated (lines) current-overpotential curves (vs. Ag/AgCl) of a BFC anode in a buffered electrolyte (PBS pH=7.2), containing 1 mM Fc as mediator, 3µM Gox and 1 mM Glucose (a), 10 mM Glucose (b) and 20 mM Glucose (c).

The development of the concentration profiles for $M_{ox}$ and $P$ as a function of time are shown in Fig. 7a and b, respectively. It clearly shows that the concentration of $M_{ox}$ at the electrode surface is increasing quickly and that the concentration gradient is very strong at the electrode surface (close to distance 0). The same holds for the reaction product gluconolactone although it should be noted that the concentrations are much lower in this case and that the built-up of the P-gradient seems to be delayed with respect to that of $M_{ox}$. 

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Conclusions

A BioFuel Cell device is described using glucose oxidase and laccase as biocatalysts and different mediators for both the anode and cathode. A working demonstrator has been
constructed, which delivered a power density of up to 5.8 µW·cm⁻² at an open-circuit voltage of 0.35 V. To further optimize the power output of the mediated BFC in a homogenously diffusive system, the kinetics, including the homogeneous chemical reactions in the bulk of the electrolyte and the electrochemical charge transfer reaction at the electrode surface are discussed in detail.

Based on the experimental kinetic studies, a systematic mathematic model describing the homogeneously mediated electrodes has been designed. From the mathematic description, a second order Michaelis–Menten equation has been derived. The simulations are both qualitatively and quantitatively in good agreement with the experimental results. The concentration profiles of reactive species have been calculated as a function of time and distance from the electrode surface.

In the near future, this study will be expanded, focusing on three main areas: Firstly, a model will be composed describing the three-dimensional cell, including anode, cathode, and proton-exchange membrane, which will be used to simulate the operation of a practical BFC. This model will demonstrate the influence of the size of the cell and the position of the electrodes on the performance of the BFC. Variation in the membrane properties can even model the membrane aging. This model will be closer to practical fuel-cells and will help to improve the development of BFC for miniaturized BAN applications. Secondly, miniaturization of BFC is essential. Micro-fabrication of BFC will be studied in connection to relevant modeling. Finally, the kinetic studies and mathematic modeling will be extended to the immobilization of the reactive species (enzyme and/or mediator), which is crucial for the development of more stable and miniaturized BFC.

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