BIO-INSPIRED FUEL CELLS FOR MINIATURIZED BODY-AREA-NETWORKS APPLICATIONS

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Abstract: The improvement in quality of modern health-care is closely related to the need for medical autonomous systems that enable people to 'carry' their personal wireless Body-Area-Network (BAN). Bio-inspired fuel cells (BFC) are a promising approach of energy harvesting to achieve autonomy and miniaturization in implantable BAN. This paper deals with BFC design and modelling. A glucose-based enzymatic BFC system is designed and tested by an in-house developed electrochemical testing set-up. The demonstrator shows the power output can be up to 5μW/cm^2. Subsequently, a systematic BFC model has been set-up primarily based on the (electro)chemical reaction kinetics and mass transport of species involved in the complex electricity generation process.

Keywords: Body-Area-Network, Bio-inspired fuel cells, enzymes, glucose, modelling

1. INTRODUCTION

The increase of functionalities in health-care is directly connected with the increasing need of medical autonomous sensors. It is expected that technology will enable people to 'carry' their personal wireless body area network (BAN) that provides medical functions for the user. Such network comprises a series of miniature sensor/actuator wireless nodes each of which has its own energy supply, consisting of energy harvesting and storage systems. Successful realization of such a vision requires innovative solutions to remove the critical technological obstacles for realizing the wireless BAN sensor nodes [1].

These challenges have motivated the industry and the research institutions to work on various advanced energy systems (ES) and low-power electronics. As a result, various types of energy systems, *e.g.* energy harvesting and storage, and low-power electronics technologies are under investigation or exist on the market. Among them bio-inspired fuel cells are a promising approach of energy harvesting, enabling autonomy and miniaturization of medical implants.

This paper discusses one example of glucose-based enzymatic fuel cells which seems to be most promising due to the high catalytic-specificity and activity and fuel abundance in body fluids.

2. STATE-OF-THE-ART OF ENZYMATIC BIO-FUEL CELL

Enzymes are well-known as active and specific catalysts at low temperature and near-neutral pH environment, which makes enzymatic bio-fuel cells more suitable for miniature power sources in, for example, implantable devices. The key-challenge of enzymatic bio-fuel cell is the electron coupling between enzyme electro-active centre and the electrode [2].

Direct electron transfer (DET) is possible if the active centre itself, or electron relay centre, lies close to the protein surface (see Fig. 1a). The alternative way of overcoming the electron coupling problem is to employ mediators, a small organic molecules or metal complex, to assist electron shuttling between the electrode and enzyme. The process is denoted as mediated electron transfer (MET) (see Fig. 1b). Particular for medical implant applications the mediators should be biocompatible. Mediators can exist free in solution, referred to as diffusible mediators, or immobilized on the surface of electrode, referred to as non-diffusible mediators. There are both advantages and disadvantages for using mediators. As an example, they are essential if the active site of the enzyme is deeply buried in the insulating protein matrix or if the enzyme preferentially attaches in a non-electroactive orientation on the electrode surface. Moreover, the mediators can also help the electron coupling between the outer layers of enzyme and the electrode surface, resulting in enhanced current densities. However, an important drawback is that a mediator adds an extra step to the electron transfer chain. So, the generated fuel cell voltage and power will be lower.

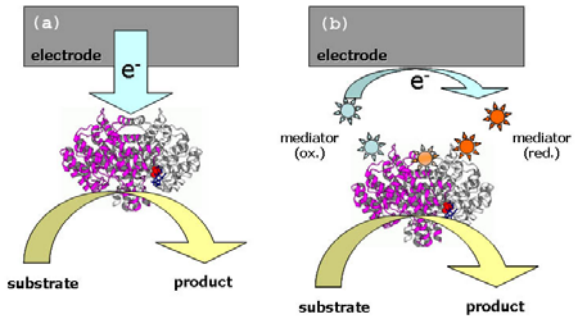

Fig.1. Types of electron transfer pathway. (a) Direct electron transfer (DET). (b) Mediated electron transfer (MET).

Extensive studies on enzymatic bio-fuel cells

started from 1990's. In 1998, Palmore *et. al.* used three NAD^+-dependent enzymes, comprising of alcohol dehydrogenase (ADH), aldehyde dehydrogenase (AldDH) and formate dehydrogenase (FDH), to create a bio-anode that can completely oxidize methanol [3]. Katz *et. al.* reported a complete cell based on novel architectures at both electrodes. The anode was assembled by reconstitution of apo-GOx onto a monolayer of PQQ and FAD. The cathode was assembled by attaching Cytochrome Oxidase onto a monolayer of Cytochrome c [4]. The membrane separating the fuel from oxidant was not necessary for this type of fuel cell. Redox polymers were first employed for immobilization and mediation of redox enzymes by Heller's group [5, 6]. Redox complexes based on Osmium are 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 neighbouring centre 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 a desired enzyme. Miniature bio-fuel cell can be achieved if the redox polymer and enzyme were deposited on carbon fiber electrodes. The high electron transfer efficiency also makes the membrane unnecessary. As an alternative to the Os-based redox polymer, a polymer containing Vitamin-K3 was utilized to immobilize GDH onto glassy carbon. Based on this process, Sony corporation has produced an bio-fuel cell prototype, which can generate at 0.3V, 1.5mWcm-2 [7, 8]. Instead of small organic molecules like methanol, ethanol and glucose, H_2 has also been used as fuel to biofuel cell. Armstrong *et al*. employed O_2-tolerance hydrogenase as anodic biocatalysts to construct a H_2/O_2 bio-fuel cell [9]. Membrane-less fructose/O_2 bio-fuel cell based on DET was described by Kano and co-workers [10]. Heme-containing fructose dehydrogenase and laccase were immobilized on powdered or mesoporous carbon morphologies. Fuel cells based on DET may present advantages for implantable applications because they avoid toxic mediators or by-products of their breakdown. However, their power output is lower when compared with the fuel cells based on MET. Another example of bio-fuel cells based on DET was reported by Gorton *et al*. In this case, cellobiose dehydrogenase and laccase were used as anodic and cathodic biocatalysts, respectively [11].

3. EXPERIMENTAL

The in-house developed BFC characterization system and materials will be described in this section.

3.1 In-house developed BFC characterization system

A performance analysis is necessary in order to measure the anode, cathode and/or the complete BFC system characteristics under an extended range of conditions. An experimental set-up has been designed (see Fig. 2), consisting of an Autolab [12] electrochemical system with control software, in-house developed electrochemical 3-electrode cell with gas a supplying system and a personal computer (PC).

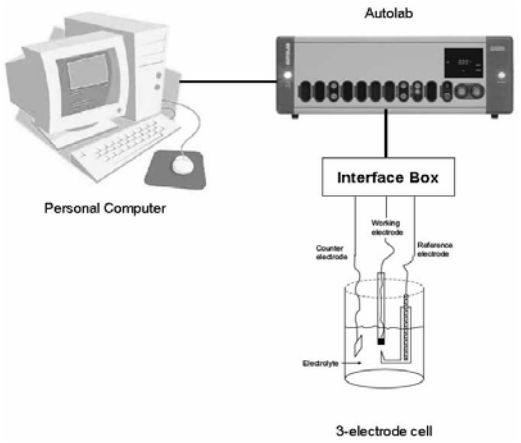

Fig. 2. Schematic representation of the bio-fuel cell testing system.

3.2 Experimental materials

Both enzymes and mediators were dissolved in the electrolyte. During this experiment, a glassy carbon electrode was used as the working electrode, Ag/AgCl as reference electrode and Pt as the counter electrode. All electrochemical measurements were performed in phosphate buffer solution (PBS), pH 7.2, at room temperature. Most of the chemicals were obtained from Aldrich Chemical Company.

For the anode, glucose oxidase (Gox) was selected as catalyst. Two different mediators were used, *i.e.* Ferrocene(Fc) and Phenazine. The solution was bubbled with Argon or Nitrogen to eliminate dissolved Oxygen.

For the cathode, laccase was used as biocatalyst and 1mM 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) as mediator.

4. RESULTS AND DISCUSSIONS

The electrochemical results of the anode are shown in Fig. 3, where the anode immersed in an electrolyte containing dissolved Fc and Gox, generates larger glucose oxidation currents and smaller reduction currents at the redox peak of 0.33V in the presence of higher glucose concentration. So, the glucose is oxidized to release electrons. The influence of various glucose concentrations, *i.e.* 0, 10, 20, 30 and 40 mM, on the glucose oxidation current has been further investigated by amperometry. The results are plotted against the overpotential in Fig. 4. The kinetic- and

diffusion- controlled regions can clearly be distinguished.

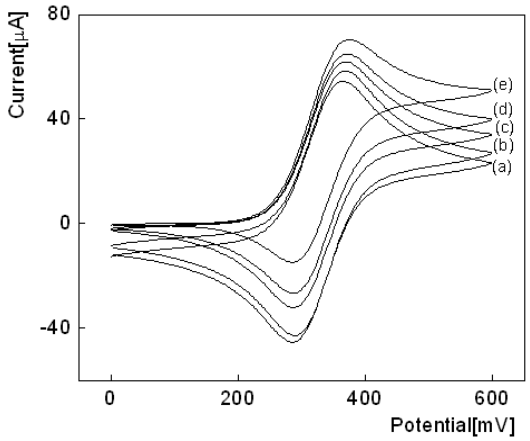

Fig. 3. Cycl.ovoltammograms at a glassy carbon electrode in a buffered electrolyte (PBS pH 7.2) containing 1 mM Ferrocene as mediator; (a) Ferrocene+Gox; (b) Ferrocene+Gox +10 mM Glucose; (c) Ferrocene+Gox +20 mM Glucose; (d) Ferrocene+Gox +30 mM Glucose; (e) Ferrocene+Gox +40 mM Glucose.

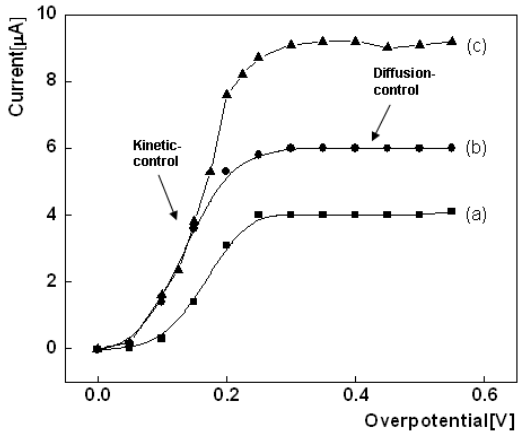

Fig. 4. Potential-step curves at a glassy carbon electrode in a buffered electrolyte (PBS pH 7.2) containing 1 mM Ferrocene as mediator. (a) Ferrocene+Gox; (b) Ferrocene+Gox +10 mM Glucose; (c) Ferrocene+Gox+20 mM Glucose.

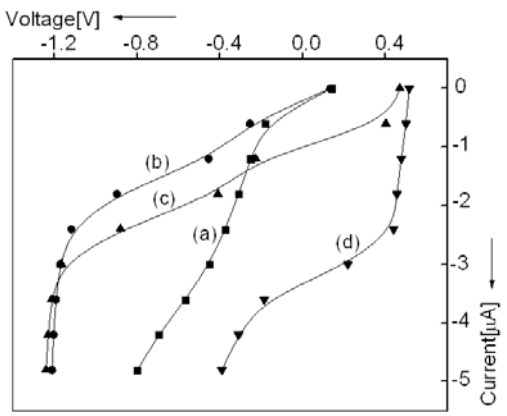

Fig.5. Polarization curve of ABTS as mediator in electrolyte (PBS pH 7.2) (a) 1 mM ABTS+air (b) 1 mM ABTS+Ar (c) 1 mM ABTS+lac+Ar (d) 1mM ABTS+lac+air.

Fig. 5 shows the polarization results for the cathode when laccase and ABTS are used as biocatalyst and mediator separately in electrolyte. It follows from Fig. 5 that at the same current the voltage change of the sample with air in electrolyte is smaller than that of the electrolyte containing Ar. So, reduction of O_2 obviously takes place at the surface of electrode and the Equilibrium Voltage equals 0.48 V *vs* Ag/AgCl.

In order to investigate the power generation capability, a BFC demonstrator has been designed (Fig. 6). The demonstrator has two chambers for the anode and cathode, separated by a Nafion 112 membrane, acting as proton-exchange membrane. The volume of each chamber is 20 ml.

The measured galvanostatic power density b can be as high as 1.2 μWcm^{-2} for the Fc-based system and 5.5 μWcm^{-2} for the Phenazine-based system (Fig. 7). The surface area of each electrode is 0.18 cm^2. For the Fc-based system, the Open-circuit Voltage is 0.35 V, the short-circuit current is 2.5 μA. The power output of the Fc-based system is also confirmed at different loads, *i.e.* as a function of different load resistances by using a high accuracy multi-meter (Fig. 8).

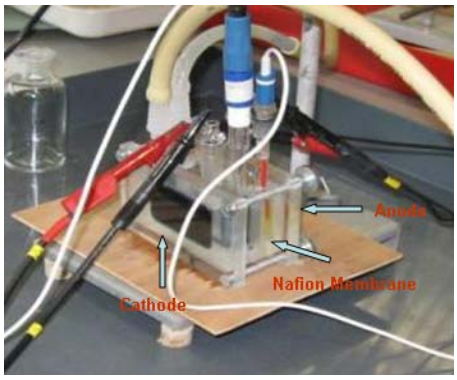

Fig.6. BFC demonstrator.

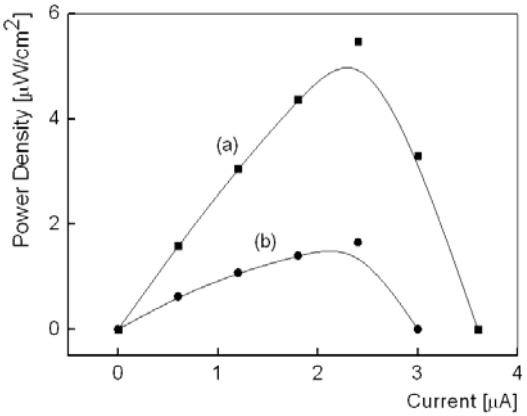

Fig.7. Comparative performance of cells with different mediators(a) Anode:1mM Phenazine as mediator and 10mM Glucose; Cathode:1mM ABTS (b) Anode:1mM Ferrocene as mediator and 10mM Glucose; Cathode:1mM ABTS.

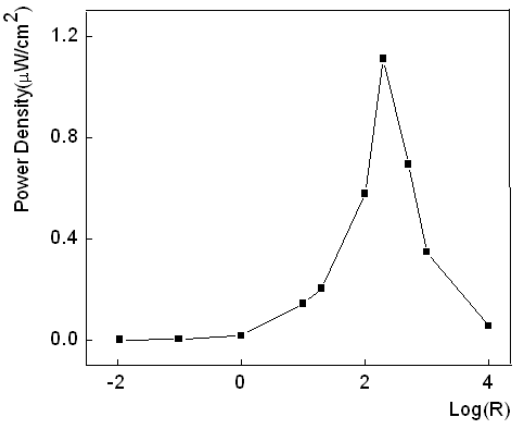

Fig.8. The power density of Fc-ABTS system tested by multimeter.

Optimization of the BFC performance requires a more deep understanding of the electrochemistry of the energy conversion processes. This can be achieved by developing a model describing the BFC thermodynamics and kinetics. For this purpose a systematic model description has been set up based on Butler-Vollmer and Nernst principles. Fig. 9 illustrates the simulated oxidation current as a function of overpotential. These simulations are in good quantitative agreement with the experimental results (Fig. 4).

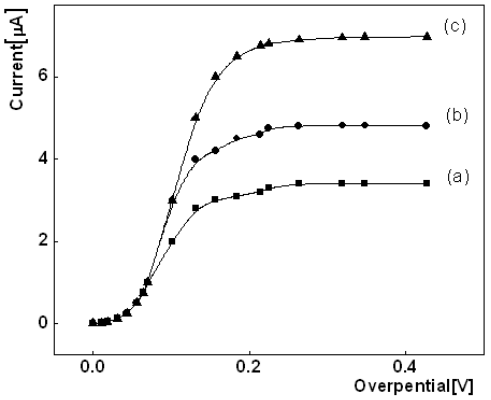

Fig.9. Simulation of current-voltage curves of a BFC system in a buffered electrolyte (PBS pH 7.2) containing 1 mM Ferrocene as mediator. (a) Ferrocene+Gox +1 mM Glucose; (b) Ferrocene+Gox +10 mM Glucose; (c) Ferrocene+Gox +20 mM Glucose.

5. CONCLUSIONS

The focus of this paper has been on the development of a specific example of bio-inspired fuel cells, *i.e.* the glucose-based enzymatic fuel cell. Firstly, the state-of-the-art of various bio-fuel cells has been discussed.

Using glucose oxidase and laccase as biocatalysts and different mediators for the anode and cathode, a single module of bio-fuel cells is described. The performance has been tested by an in-house developed BFC characterization system. In addition, a demonstrator has been constructed, which achieves up to 5 μW/cm^2 at an open-circuit voltage (OCV) of 0.35 V. For this system, a preliminary model has been set up, which will be finalized in the near future. The simulations show good agreement with the measurements.

The formation of a diffusion layer at the electrode surface and the dependence of the current on different experimental parameters, such as temperature, time, *etc.* will be included into the BFC model in the near future. Furthermore, advanced immobilization methods of enzymes/mediators will be studied to improve the BFC output power.

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