A ONE-COMPARTMENT, DIRECT GLUCOSE FUEL CELL FOR POWERING LONG-TERM MEDICAL IMPLANTS

F. von Stetten[1], S. Kerzenmacher[1], A. Lorenz[1], V. Chokkalingam[1], N. Miyakawa[1] R. Zengerle[1,2], and J. Ducrée[2]

[1]University of Freiburg - IMTEK, Laboratory for MEMS Applications,
Georges-Koehler-Allee 106, D-79110 Freiburg, Germany
e-mail: vstetten@imtek.de
[2] HSG-IMIT, Wilhelm-Schickard-Str. 10, D-78052 Villingen-Schwenningen, Germany

ABSTRACT

We present the operational concept, microfabrication, and electrical performance of an enzyme-less direct glucose fuel cell for harvesting the chemical energy of glucose from body fluids. The spatial concentrations of glucose and oxygen at the electrodes of the one-compartment setup are established by self-organization, governed by the balance of electro-chemical depletion and membrane diffusion. Compared to less stable enzymatic and immunogenic microbial fuel cells, this robust approach excels with an extended life time, the amenability to sterilization and biocompatibility, showing up a clear route towards an autonomous power supply for long-term medical implants without the need of surgical replacement and external refueling. Operating in physiological phosphate buffer solution containing 0.1 wt% glucose and having a geometrical cathode area of 10 cm², our prototype already delivers 20 µW peak power over a period of 7 days.

1. INTRODUCTION

With an increasing number of low power medical MEMS implants, often intended for the treatment of life-long disabilities, the lack of a sustainable power-source becomes increasingly evident. This need pushes the development of devices making use of ambient body energy. Biofuel cells are considered to be superior to other energy harvesting technologies, especially with respect to continuous power output, longevity, biocompatibility, and integrability into medical devices. Using the naturally occurring glucose of the body as energy source, the biofuel concept obviates surgical replacements, leading to an improved quality of life for the patient relying on long-term implants.

Types of biofuel cells

Enzymatic fuel cells [1] exhibit a high reactant specificity, allowing a simple, one-compartment design. However, they lack longevity and amenability to steam sterilization, which is a prerequisite for the use as long-term medical implant. Due to their self regenerating capability, *microbial fuel cells* [2] have shown superior longevity, but they have not been considered implantable because of the infective or immunogenic nature of most known microorganisms. The only known biofuel cell concept which does not interfere with the strict demands of long-term medical implants is the *direct glucose fuel cell* [3,4]. Its key advantages are longevity, amenability to sterilization, and biocompatibility.

A historical interlude

Research in the field of implantable direct glucose fuel cells dates back to the early seventies [3,4]. These early efforts were motivated by the short life-time of the zinc/mercury oxide batteries at that time. These batteries were used to power cardiac pace makers, but they required frequent replacement. The power output of these first implantable fuel cells in the 1970s was in the range of 50 µW, sufficient to supply a cardiac pace maker. Their durability in animal trials amounted to more than 150 days, but their biocompatibility was not fully proven. In spite of these promising results, no further development of implantable direct glucose fuel cells has been reported since the introduction of Li-Iodine batteries for cardiac pace makers in 1970, possessing a minimum life time of five years.

New perspectives

The aim of our research is to further develop the direct glucose fuel cell technology, making use of novel, biocompatible materials. Intended applications are medical low power MEMS implants for long-term applications. This study focuses on operational design aspects, the development of a microfabrication process for a direct glucose fuel cell, and on the characterization of our first prototype.

2. DESIGN

Operational principle

Our direct glucose fuel cell exhibits an anode for the oxidation of the fuel (glucose), and a cathode for the reduction of the terminal electron acceptor (oxygen). The main electro-chemical reactions involved are illustrated in Fig. 1. Theoretically, the oxidation of one glucose molecule yields as much as 24 electrons. However, on the surface of a platinum anode, glucose is primarily oxidized to gluconic

acid, yielding two electrons, only. The succeeding oxidation steps are much slower and do not significantly contribute to the overall electron yield [5].

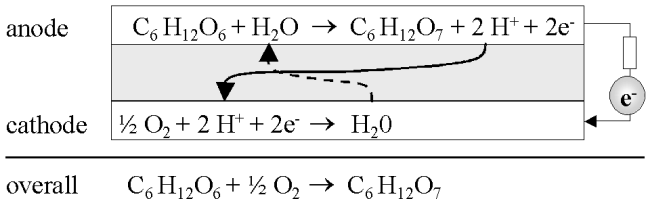

Figure 1: Schematic representation of the reactions of a direct glucose fuel cell. In an acidic environment, charge exchange takes place by the diffusion of protons, in an alkaline environment by hydroxyl ions (not shown).

Requirements of fuel cells operated in body fluids

In conventional direct fuel cells, fuel and oxygen are supplied separately to anode and cathode, respectively. The challenge of an implantable direct fuel cell is that it must run on physiological fluid containing both reactants (oxygen and glucose) simultaneously. While catalysts for the selective reduction of oxygen in the presence of glucose are available, no non-enzymatic catalyst is presently known for the selective oxidation of glucose in the presence of oxygen. With a non-selective catalyst, glucose would directly transfer its electrons to available oxygen, and no power could be supplied to an external circuit.

One-compartment design and self-organization

In order to circumvent this chemical short-circuit, we chose a special electrode arrangement, originally proposed by Weidlich *et al.* [4] (Fig. 2). Instead of an active separation of oxygen and glucose, the power-efficient self-organization establishes an anaerobic region in the vicinity of the central anode. This self-organization roots on the selective reduction of oxygen at the outer electrodes, and the resulting depletion of oxygen at the central glucose electrode. The entire cell consists of one compartment which is permeable to both, oxygen and glucose.

Construction

The construction of the direct glucose fuel cell is illustrated in Fig. 3. The electrodes consist of activated carbon coating a noble metal screen that collects the electrons. The activated carbon at the glucose electrode contains an additional 10 % of platinum. An epoxy resin frame is used to electrically insulate the wire connections, and to protect the anaerobic glucose electrode against oxygen breakthrough. A poly(vinyl alcohol)-poly(acrylic acid) hydrogel (PVA-PAA) matrix occupies the inter-electrode space of the fuel cell, and is also used as binder for the activated carbon particles. The geometrical surface area of the electrode amounts to 2.2 x 2.2 cm².

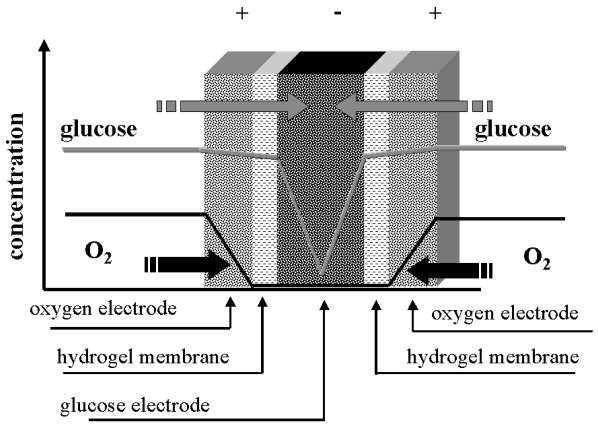

Figure 2: One-compartment design of direct glucose fuel cell. Porous electrodes are arranged in a sandwich structure in the order cathode – anode – cathode to establish a self-organization of the spatial glucose and oxygen concentrations (concentration profiles shown schematically). The activated carbon catalyst on the cathode selectively reduces the oxygen, whereas glucose is anaerobically oxidized at the platinum catalyst. A hydrogel membrane serves as spacer between the electrodes.

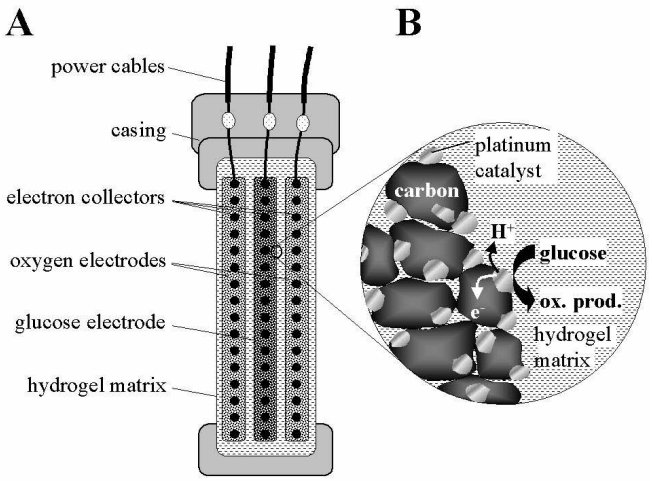

Figure 3: A) Schematic cross-section of the fuel cell. B) Detail of the interface between the oxygen electrode and the hydrogel matrix.

3. EXPERIMENTAL

Fabrication

Membranes with a thickness of 30 µm are cast from a 3 wt% PVA-PAA solution. The electrodes are manufactured by a doctor blade technique (Fig. 4). The catalyst ink consists of activated carbon saturated with 7 wt% PVA-PAA solution.

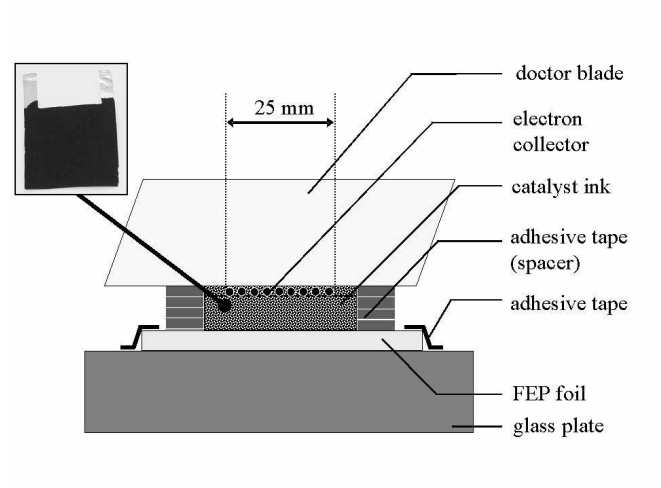

Figure 4: Fabrication of a fuel cell electrode. The catalyst ink is spread with a doctor blade, thereby embedding the electron collector.

After drying, membranes and electrodes are assembled by wet gluing (Fig. 5). Subsequently, the assembly is crosslinked at 145°C for 40 minutes. Finally, the wires are connected to the contact flags of the electrodes, and the fuel cell is protected with an epoxy resin frame. Alternatively, electrodes and membranes can be crosslinked individually and arranged in a holder setup for electrochemical characterization (Fig. 6 A, C).

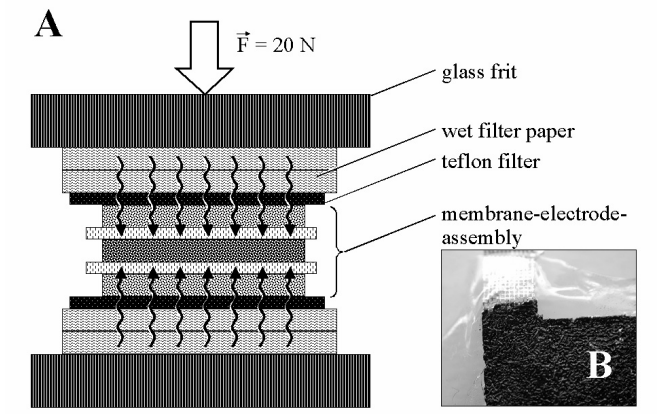

Figure 5: Membrane-electrode-assembly. A) Membranes and electrodes are stacked, pressed and connected by wet gluing. B) Membrane-electrode-assembly after wet gluing.

Characterization

The electrical characterization of our direct glucose fuel cell is carried out at 37°C in physiological phosphate buffer (pH = 7.4) as a model solution, containing 0.1 wt% glucose. Throughout the experiment, the solution is kept at equilibrium with air. For extended testing, an electrochemical cell is constructed that allows the flexible assembly of individually crosslinked electrodes and membranes, without the need of an epoxy frame (Fig. 6 A, B). Current-potential and power characteristics are characterized by a self made variable resistor unit (Fig. 6 C).

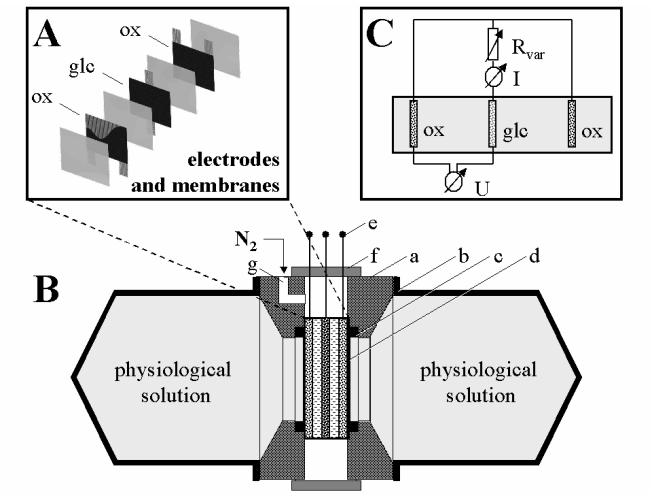

Figure 6: Setup for electrochemical characterization of the fuel cell and its individual components. Fuel cell components (A) can be clamped together with the holder part of the electrochemical cell (B). a) Teflon holder, b) glass bulb, c) silicone o-ring, d) fuel cell (or components), e) contact flags of the electrodes, f) sealing tape, g) nitrogen inlet. The two half cells harbour additional reference and counter electrodes, as well as oxygen and pH sensors (not shown). C) Principle of the variable resistor unit.

4. RESULTS

An image of our direct glucose fuel cell prototype is shown in Fig. 7. The fabrication procedure has been described above. Electrochemical tests of our direct glucose fuel cell are performed with a setup as described in Fig. 6. A current-potential plot is shown in Fig. 8.

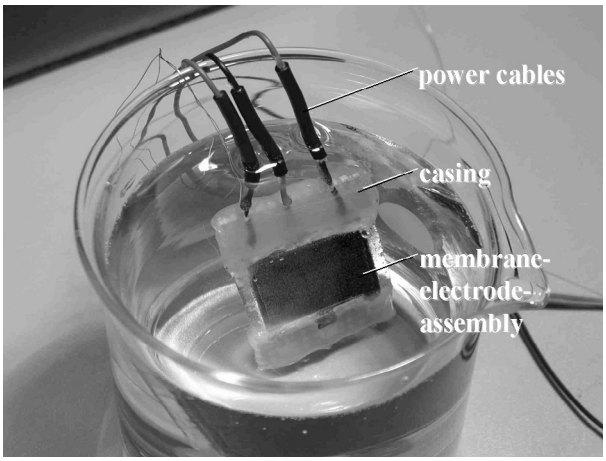

Figure 7: Prototype of our direct glucose fuel cell.

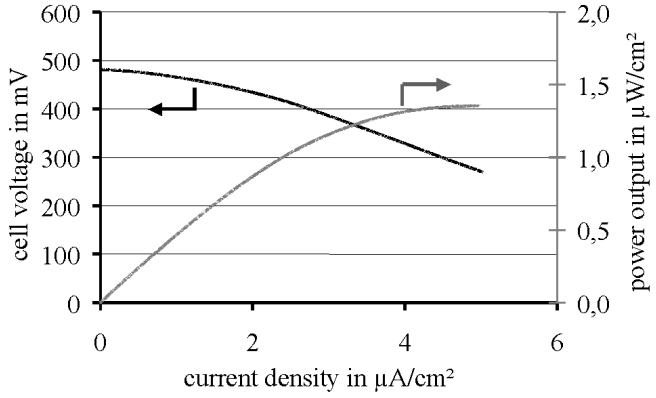

Figure 8: Current density potential plot of direct glucose fuel cell after 11 days of operation.

As shown in Fig. 9, power densities of ~2 µW/cm² could be reached over a period of seven days, corresponding to 20 µW peak power output of our prototype with a geometrical cathode area of 10 cm² (electrode dimensions 2.2 x 2.2 cm²). Two of our prototype fuel cells thus already deliver enough electrical power to operate a cardiac pace maker. Over the time the power output slightly decreased, presumably due to the poisoning of the platinum catalyst by oxidation products.

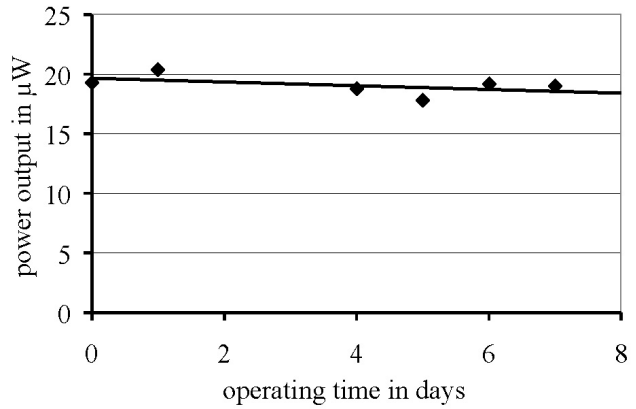

Figure 9: Peak power output of our prototype direct glucose fuel cell during one week of operation (surface area 10 cm²).

5. CONCLUSIONS AND OUTLOOK

The presented concept of a direct glucose fuel cell is well compatible with the technical and important legislative demands regarding implantable power sources for long-term medical implants. By rearranging the presented 3-electrode sandwich setup with a 2-electrode blind-end concept this microfluidic cell can even be implemented as an external coating of implants, which is part of our current research. Our future work will also focus on biocompatibility issues, methods for catalysts regeneration, and further enhancement of the power density.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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