

A Binder-less Glucose Fuel Cell with Improved Chemical Stability Intended as Power Supply for Medical Implants

S. Kerzenmacher¹, U. Kräling¹, J. Ducrée², R. Zengerle^{1,2} and F. von Stetten¹

¹Laboratory for MEMS Applications, Department of Microsystems Engineering - IMTEK, University of Freiburg, Georges-Koehler-Allee 106, D-79110, Freiburg, Germany

²HSG-IMIT, Wilhelm-Schickard-Strasse 10, D-78052, Villingen-Schwenningen, Germany

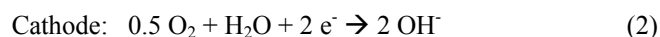
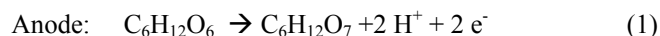
Abstract — We present an improved abiotically catalyzed glucose fuel cell, intended as tissue implantable power supply for medical implants. A novelty is the application of binder-less platinum electrodes for both, anode and cathode. This overcomes the limited chemical stability of glucose fuel cells fabricated from activated carbon particles dispersed in a hydrogel matrix. For the first time the diffusion resistance to be expected from tissue capsule formation has been taken into account during performance characterization under physiological concentrations of glucose and oxygen. Despite the resulting limited oxygen supply, the binder-less fuel cells exhibit a power density of $(2.3 \pm 0.2) \mu\text{W cm}^{-2}$, which is comparable to our previous prototypes. We show that this is due to the increased performance of the novel electrodes.

Keywords — glucose, fuel cell, implantable, energy harvesting, platinum

I. INTRODUCTION

A. Sustainable power supply for medical implants

Implantable glucose fuel cells employing abiotic catalyst (e.g. noble metals, activated carbon) are a newly rediscovered approach to realize a battery-independent power supply for medical implants [1]. With this concept electricity is directly generated from glucose and oxygen available in body fluids. The predominant electrode reactions are given as [2]:



A favorable embodiment of such an abiotically catalyzed glucose fuel cell is a stacked electrode arrangement, where a permeable activated carbon cathode that selectively catalyzes oxygen reduction is situated in front of the anode [2]. This way a predominantly anoxic environment is created inside the fuel cell. At the anode, glucose can thus be electro-oxidized without oxygen interference, using a non-selective platinum catalyst. The prime advantage of this concept is that reactant access from one side is sufficient,

enabling easy integration of the fuel cell directly onto the surface of medical implants.

B. Limitations of state-of-the-art electrodes

A drawback of previous designs is the limited hydrolytic stability of fuel cell electrodes fabricated from catalyst particles embedded in a poly(vinyl alcohol)-poly(acrylic acid) hydrogel [3]. Furthermore, the low electrical conductivity of hydrogel-catalyst compounds mandates the use of mesh-like current collectors embedded within the electrodes, leading to relatively thick structures in the range of several hundred μm [3].

To overcome these limitations, already in the 1970s self-supporting Raney-type anodes, obtained from approx. 50 μm thin platinum-nickel alloy foils, have been implemented as anode. Since the biocompatibility of nickel is questionable, we recently presented an alternative fabrication route for anodes employing zinc as less problematic alloying partner [4].

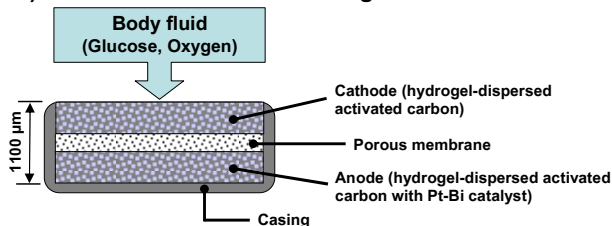
However, the development of correspondingly fabricated cathodes for oxygen reduction has not yet been reported. This is related to the operation of implantable glucose fuel cells in a mixture of both, glucose and oxygen. Since platinum is catalytically active toward glucose oxidation as well as oxygen reduction, the simultaneous presence of both reactants at a platinum electrode can thus lead to the formation of a more negative, mixed cathode potential. Especially for relatively thick (several 100 μm) platinum electrodes this effect and the associated decrease in fuel cell performance is well documented in literature [5-7].

C. Towards a binder-less glucose fuel cell

Experiments in our lab have shown that the detrimental interference of glucose is effectively circumvented by the construction of very thin, porous platinum cathodes. Such structures can be fabricated by annealing a several hundred nanometer thin bi-layer of platinum and aluminum and subsequent leaching of the non-noble component in caustic [8]. In the present work we report on the application of this

process to deposit thin porous platinum cathodes on top of a permeable silicon substrate as mechanical support. In combination with our recently presented self-supporting glucose oxidation anode fabricated from platinum-zinc alloys [4] we are thus able to assemble a fuel cell that completely obviates the need for polymer binders.

A) State-of-the-art fuel cell design



B) Novel concept with binder-less electrodes

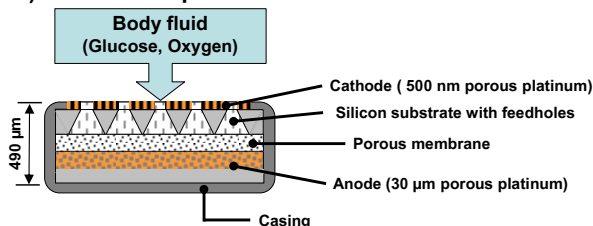


Fig. 1 Comparison of two fuel cell construction concepts: A) State-of-the-art approach with hydrogel-dispersed activated carbon electrodes. B) Binder-less concept with a thin layer platinum cathode deposited on a slitted silicon substrate, and a self-supporting thick-layer platinum anode.

II. DESIGN CONSIDERATIONS

A. Permeable cathode substrate

In a stacked fuel cell setup a permeable cathode is necessary to allow for glucose diffusion from the surrounding environment to the interior anode. We therefore chose to fabricate a regular array of feedholes into a silicon substrate, using the standard anisotropic wet-etching process with KOH [9]. Onto this structure platinum can be deposited and subsequently annealed with aluminum. A desirable characteristic of KOH-etching is the resulting trapezoid feedhole geometry. This way both, maximum surface for cathode deposition as well as homogenous distribution of glucose at the anode can be achieved.

To form a complete binder-less fuel cell the cathode is arranged together with the binder-less anode, electrically insulated by porous membrane. Both, the state-of-the-art construction concepts with hydrogel-embedded activated carbon particles and the novel concept employing binder-less electrodes are compared in Fig. 1.

B. Consideration of tissue capsule formation

For realistic fuel cell characterization the formation of a tissue capsule around the implanted device has to be considered. Based on the results of Sharkawy et al. [10] the diffusion resistance of fluorescein through a tissue capsule at 25 °C can be estimated to be in the range of $1.3 \times 10^4 \text{ s cm}^{-1}$ (200 μm tissue capsule around stainless steel implant, rat model). To account for this additional diffusion resistance during *in-vitro* characterization of the fuel cell we chose a 140 μm thick porous filter membrane (Supor-450, Pall, East Hills, New York/USA), situated in front of the cathode. Its diffusion resistance toward glucose amounts to $5.0 \times 10^3 \text{ s cm}^{-1}$ (in phosphate buffered saline at 37°C, unpublished data). Taking into account the larger molecular weight of fluorescein ($M_w = 376 \text{ g/mol}$) as compared to glucose ($M_w = 198 \text{ g/mol}$) as well as increased diffusion at higher temperatures, this porous membrane is thus a reasonable approximation to tissue capsule formation.

III. MATERIALS AND METHODS

A. Anode fabrication

Self-supporting platinum anodes of the Raney-type were prepared following the procedure reported elsewhere [4]. In short, an approximately 30 μm thick zinc layer was electro-deposited on a 50 μm thick platinum foil (Chempur GmbH, Karlsruhe/Germany) and annealed for 48 h at 200 °C in air atmosphere. After alloy formation, the remaining zinc was removed in 0.5 M H_2SO_4 , leaving a self-supporting porous platinum structure. Further cleaning was achieved by cyclic voltammetry sweeps in de-aerated 0.5 M H_2SO_4 (10 cycles at 10 mV s^{-1} , between 1.3 V and -0.3 V versus SCE).

B. Cathode fabrication

As substrate for fabrication of the cathodes double-side polished silicon wafers (n+, P-doped, Okmetic, Vantaa/Finland) in <100> orientation were used. Standard photolithography and anisotropic KOH-etching techniques [9] have been used to micro-fabricate a regular feedhole array into the silicon substrate. To investigate the influence of cathode permeability on fuel cell performance, two different versions with slit sizes of 50 μm and 200 μm have been fabricated. The remaining area for cathode deposition thus amounted to 92.5 % and 77.1 % of the overall area, respectively. The resulting feedhole geometry is illustrated in Fig. 2.

For fabrication of the catalyst layer, 20 nm titanium as adhesion interlayer, followed by 500 nm platinum and 500 nm aluminum were consecutively deposited by

evaporation. Subsequently the wafer was diced in pieces of 20 mm by 20 mm. Similarly to the anodes, the samples were then annealed for 1 h at 300 °C to form a Raney-type catalytic structure. Un-alloyed aluminum was afterwards removed in 1 M NaOH, while further cleaning was achieved by cyclic voltammetry in 0.5 M H₂SO₄ (20 cycles at 50 mV s⁻¹ between 1.3 V and -0.3 V vs. SCE).

C. Fuel cell construction

In Fig. 3 the to-scale cross-sectional view of the complete fuel cell is shown. To reduce mechanical stress upon assembly, each electrode was placed in the center of a 300 μm thick polycarbonate interlayer frame. For electrical insulation a 140 μm thick porous membrane (Supor-450, Pall, East Hills, New York/USA) is situated between anode and cathode. The same membrane was placed on top of the cathode to experimentally simulate the diffusion resistance expected from tissue capsule formation. Together with a 500 μm thick silicone rubber foil on top the whole assembly has been clamped between 5 mm polycarbonate fixtures. To eliminate contact resistances from the measurement separate platinum wires for voltage and current have been attached to each electrode, using small amounts of conductive carbon cement (Leit-C, Plano, Wetzlar/Germany).

D. Performance characterization

Prior to testing, the fuel cells were autoclaved for 15 min at 121°C in phosphate buffered saline (PBS). For electrochemical cleaning of the electrodes the cathodes were then operated for 60 min at an oxidative current density of 44.44 μA cm⁻². After the glucose concentration had been adjusted to 3.0 mM the anodes were then subject to 5 cyclic voltammetry cycles (at 10 mV s⁻¹ between 1.3 V and -0.9 V vs. SCE, the final cycle ended at -0.5 V).

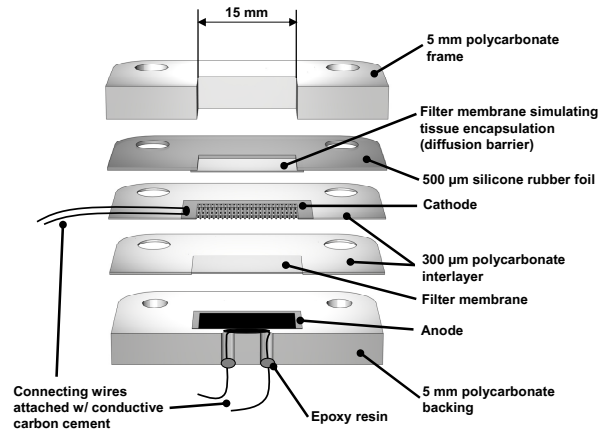


Fig. 3 To-scale cross-sectional view of the binder-less glucose fuel cell. See text for explanations.

Electrical characterization was carried out under sterile conditions in fresh PBS at 37°C. The oxygen concentration was set to 3.5 % oxygen saturation, whereas the glucose concentration amounted to 3.0 mM. Both values correspond to the lower value of the estimated physiological range in body tissue [1]. The load current density was increased in steps of 4.4 μA cm⁻² every 12 h, starting from open circuit to a maximum of 17.8 μA cm⁻². Polarization curves were constructed from the stable electrode potentials, recorded vs. the SCE reference electrode after 12 h of operation at given load current density.

IV. RESULTS AND DISCUSSION

In Fig. 4 the fuel cell’s polarization curves, individually resolved for cathode and anode, are shown. Apparent is the

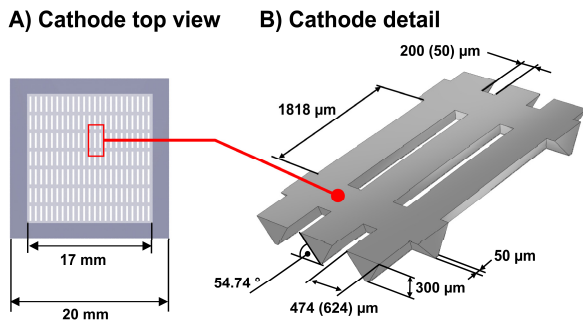


Fig. 2 A) Top view of the permeable cathode. The light-colored area represents the slit-array onto which the catalyst is deposited. B) To-scale cross-section of the slit-array. Dimensions for the feedhole geometry with 50 μm slit size are given in parentheses.

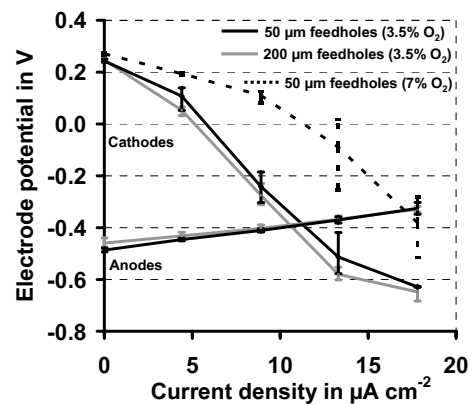


Fig. 4 Individual polarization curves of anode and cathode recorded at 3.5 % oxygen saturation. The cathode polarization curve at 7.5 % oxygen saturation is shown for comparison, as indicated in the figure. Average of three simultaneous experiments, bars represent maximum and minimum.

lack of a significant difference between the two investigated feedhole geometries with 50 μm and 200 μm feedhole width. Independent of cathode feedhole size, the anodes show no indication of increased polarization due to insufficient glucose supply. In contrast, the cathodes exhibit in general a larger polarization that is more pronounced at current densities beyond 4.4 $\mu\text{A cm}^{-2}$. The improved cathode performance at the higher oxygen saturation of 7 % (Fig. 4) confirms that this can be attributed to an increasing dominance of oxygen mass-transport limitation at higher current densities.

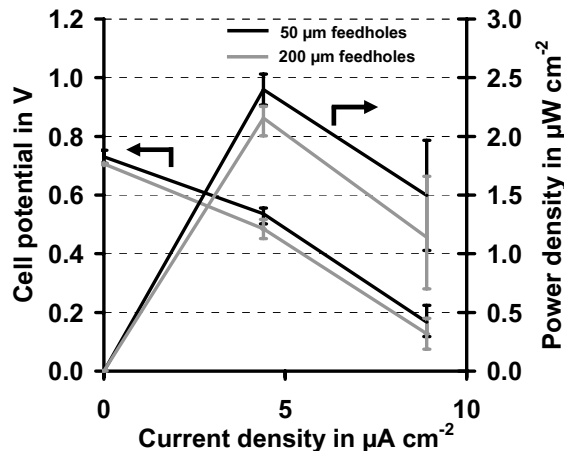


Fig. 5 Polarization curves of complete fuel cells, recorded at 3.5 % oxygen saturation. Average of three simultaneous experiments, bars represent maximum and minimum.

In Fig. 5 the dependency of cell voltage and power density on current density is shown for the complete fuel cells. For both feedhole geometries, the average open circuit voltage amounts to (716 ± 21) mV, which is by approx. 260 mV higher compared to our previously reported activated carbon prototypes under the same oxygen partial pressure [11]. On one hand this tremendous increase in open circuit voltage can be attributed to the higher catalytic activity of platinum for oxygen reduction, since the binder-less cathodes exhibit a by approx. 90 mV more positive open circuit potential than activated carbon cathodes. In addition, the open circuit potential of the binder-less anodes is by approx. 170 mV more negative compared to the activated carbon based Pt-Bi anodes, suggesting increased oxygen tolerance. The peak performance of the fuel cells with 50 μm wide feedholes amounts to (2.3 ± 0.2) $\mu\text{W cm}^{-2}$. This is in the range of the state-of-the-art fuel cells, although a direct comparison is difficult since the latter have been operated at higher glucose concentration and without a diffusion barrier in front of the fuel cell.

V. CONCLUSIONS

We successfully fabricated a potentially implantable glucose fuel cell that completely obviates the use of polymer binders and current collectors embedded within the electrodes. This way both, improved chemical stability as well as a by more than 50 % reduced overall thickness of the fuel cell has been achieved.

Compared to our previous prototypes based on activated carbon, the binder-less fuel cells show higher open circuit potential, which can be directly attributed to the high catalytic activity of platinum cathodes as well as increased oxygen tolerance of our platinum-zinc anodes. The binder-less fuel cells therefore exhibit comparable performance, although we included a diffusion barrier simulating tissue encapsulation in our experiments. Under these conditions oxygen mass transfer to the cathode has been identified to limit the overall power density of the fuel cell.

The investigated cathode feedhole sizes had no significant effect on anode performance, suggesting that sufficient glucose supply to the anode can be sustained even with smaller feedholes. The consequent increase in geometrical cathode area may thus help to reduce cathode polarization. In addition, the binder-less design opens up the possibility to specifically modify the electrode surface toward poisoning resistance. Promising strategies are the enhancement of the catalytic platinum structures with surface alloys, and the application of thin polymer layers to hinder endogenous substances from blocking the electrodes.

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Author: Sven Kerzenmacher
Institute: Laboratory for MEMS Applications, Department of Micro systems Engineering - IMTEK, University of Freiburg
Street: Georges-Koehler-Allee 106
City: Freiburg
Country: Germany
Email: sven.kerzenmacher@imtek.uni-freiburg.de