

REACTION-SPECIFIC PLATINUM ELECTRODES FOR IMPLANTABLE GLUCOSE FUEL CELLS: VERSATILE FABRICATION BY CYCLIC ELECTRODEPOSITION

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Abstract: We present a new versatile method for the generation of ultra porous noble metal electrodes based on cyclic Pt-Cu electrodeposition and anodic Cu dissolution. Performing this method, electrodes with tailored roughness factors (RF exceeding up to 2031) and thus reaction-specificity can be fabricated. Applied in implantable glucose fuel cells, the novel process enables a by 14 % increased power density compared to state of the art, at significantly reduced platinum consumption and substantially facilitated fabrication.

1 INTRODUCTION

Implantable glucose fuel cells (IGFCs) represent a promising approach for the self-sufficient power supply of low power implants by the electrochemical conversion of glucose and oxygen, available from tissue fluids [1;2] (see Fig. 1). Compared to mechanical generators, which harvest electrical energy depending on body movement, the advantage of IGFCs is the continuous generation of electricity. Their key components are the catalysts, which facilitate the electrochemical reaction of glucose and oxygen at two spatially separated electrodes. Here for instance microorganisms or enzymes can be employed. However, the use of microorganisms in implantable devices is problematic, because of the high risk of infection. Whereas enzymatically catalyzed IGFCs exhibit power densities of up to $430 \mu\text{W cm}^{-2}$ under physiological conditions [3], their operating time is limited to a few weeks at best due to the low enzyme stability.

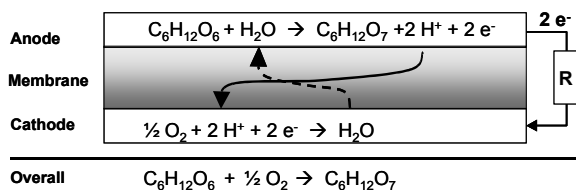


Fig. 1: General electrode reactions of an abiotically catalyzed IGFC [4].

Abiotic catalysts such as noble metals or carbon are another possibility to operate the IGFC. Here catalysts with high specific surface are desirable to achieve an efficient electrochemical reaction and high fuel cell power output. As catalyst material thus often porous platinum electrodes are used, which can be fabricated for instance by dealloying of thermally formed alloys [5;6], or from catalyst particles embedded in a polymer matrix [2;7].

Typically IGFC require two reaction-specific electrodes to achieve a reasonably high cell voltage.

This is because both electrodes are operated in the same media and a mixed electrode potential results from the two competing electrode reactions, namely the oxidation of glucose and the reduction of oxygen. This can be avoided by using an electrode with high specific surface as anode, which leads to domination of the kinetically controlled oxidation of glucose. To obtain reaction-specificity at the cathode a thin electrode with a low specific surface is used, which favors the diffusion controlled reduction of oxygen.

In state of the art IGFCs two different dealloying processes are needed to fabricate porous Pt-Zn-catalysts with roughness factors (RF) of (2668 ± 179) as anode, and thin-layer Pt-Al-catalysts (RF = 135 ± 13) as cathode [6;8]. Further disadvantages of this method are the high process temperatures and the long time demand for alloy formation. Also, these processes are not compatible with fabrication of the catalytic electrodes directly on the casing of medical implants, which would greatly facilitate integration of the concept together with e.g. cardiac pacemakers.

To circumvent the disadvantages of state of the art solutions we use a novel electrodeposition process for the fabrication of porous platinum electrodes. It consists of two steps: the co-deposition of a platinum-copper alloy and the dissolution of the copper. Cyclic repetition of these steps enables tailoring of the surface roughness of the catalyst [9]. Furthermore we show that this versatile process can be used to fabricate reactant specific anodes and cathodes for the use in implantable glucose fuel cells.

2 EXPERIMENTAL

2.1 Fabrication process

The electrode fabrication process is based on cyclic voltammetry (50 mV s^{-1} , between -0.6 and 1.4 V vs. a saturated calomel electrode (SCE)) in an acidic solution of H_2PtCl_6 (0.02 mol l^{-1} , Pt-%: 40.02, Chempur, Germany) and CuSO_4 (0.02 mol l^{-1} , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Merck, Germany). As substrate for the

anode a silicon chip with an evaporated layer of platinum (250 nm) was used. The cathode is fabricated on a permeable gold-coated polycarbonate track-etch membrane (TEM, 800 nm pores, Nuclepore, Whatman, England). This enables the diffusion of glucose through the permeable substrate, and consequently the cathode can be mounted in front of the anode (see Fig. 2) in a place-saving assembly.

2.2 Electrode characterization

The electrode surface was determined by cyclic voltammetry (CV) in H_2SO_4 (0.5 mol l^{-1} , Merck, Germany) by measuring the charge associated with the desorption of a hydrogen monolayer at the platinum surface [10]. The surface roughness per cm^2 (expressed as roughness factor (RF) or true surface area) was calculated according to

$$RF = \frac{Q_{\text{HDes}}}{Q_{\text{ideal}} \cdot A_g}$$

wherein Q_{HDes} is the measured desorption charge, and A_g is the geometric electrode area. The value of an ideally polished polycrystalline platinum surface Q_{ideal} was assumed to be $210 \mu\text{C cm}^{-2}$ [11].

2.3 Fuel cell assembly and testing unit

The assembly of the fuel cell is shown in Fig. 2. The cathode, fabricated on a permeable TEM, is placed in front of the anode. To simulate the diffusion barrier resulting from typical tissue capsules forming around implanted devices a $136 \mu\text{m}$ thick porous membrane (Supor-450, Pall, New York, USA) is mounted in front of the fuel cell [8]. The same membrane is placed between anode and cathode for electrical insulation.

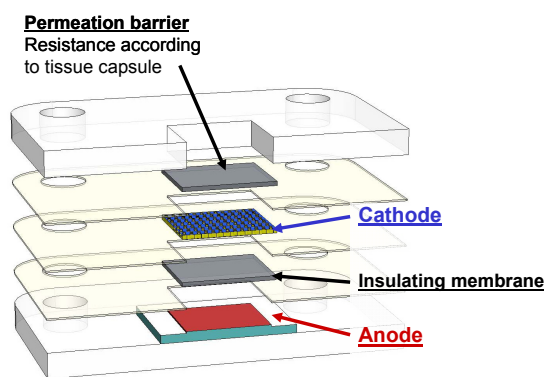


Fig. 2: Schematic illustration of the fuel cell assembly used for *in vitro* tests. All functional layers are fixed between thin layers of silicone and two solid frames of polycarbonate. The cathode is fabricated on a permeable membrane. The anode is deposited on a Pt-coated silicon substrate. The expected tissue encapsulation is experimentally simulated by a filter membrane of similar permeation resistance for glucose [8].

For load curve experiments the fuel cells were mounted in a reactor, sterilized at 121°C for 15 min, and connected to a biofuel cell testing unit, as described elsewhere [12]. The media was a phosphate buffered saline (PBS) at 7 % oxygen saturation with physiological glucose concentration (3 mmol l^{-1}). The galvanostatic load was increased from 0 to $20 \mu\text{A cm}^{-2}$ in steps of $2 \mu\text{A cm}^{-2}$ every 6 hours.

3 RESULTS AND DISCUSSION

3.1 Fabrication results

As shown in Fig. 3 the fabrication process by CV consists of two steps: (1) at potentials lower than approx. 0 V vs. SCE the Pt-Cu alloy deposition takes place, and (2) at potentials higher than approx. 0.3 V vs. SCE the copper is dissolved from the Pt-Cu alloy. These steps are cyclically repeated during the fabrication and leave behind a porous platinum layer. Its thickness and surface roughness increases with each deposition cycle ([9], see Fig. 3).

The RF of the fabricated platinum electrodes (Pt-Cu) increases from $RF = 20$ after 1 deposition cycle, up to $RF = 2031$ after 500 deposition cycles. The analysis of deposited weight shows that the electrode with 500 cycles needs only $11 \mu\text{g}$ platinum per cm^2 true surface area. This is significantly less platinum than state of the art Raney platinum film electrodes fabricated from $50 \mu\text{m}$ thick platinum foils (about $39 \mu\text{g}$ per cm^2 true surface area).

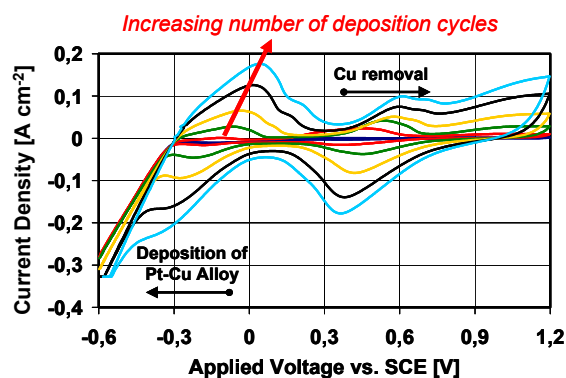


Fig. 3: Evolution of cyclic voltammograms during deposition from H_2PtCl_6 and CuSO_4 (0.02 mol l^{-1} each) in H_2SO_4 (0.5 mol l^{-1}) shown for cycles 1, 5, 20, 50, 100, 150.

Electron micrographs of the Pt-Cu anodes (500 deposition cycles) show a porous structure with a nano-scaled substructure (Fig. 4).

The images of the Pt-Cu cathode (12 deposition cycles) show a coating of porous platinum situated on top of the gold-coated track-etch membrane (Fig. 5). The holes of the membrane are still accessible (see arrows), so that the glucose molecules can diffuse easily towards the anode.

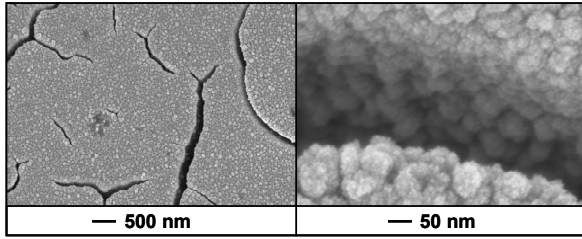


Fig.4: Electron micrographs of the anode surface fabricated with 500 deposition cycles.

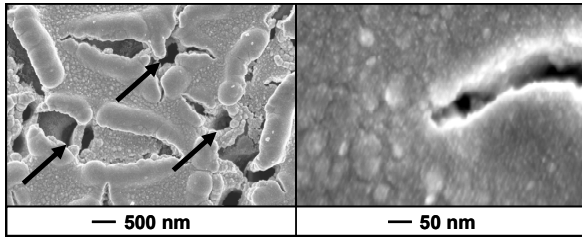


Fig. 5: Electron micrographs of the cathode surface fabricated with 12 deposition cycles.

The platinum-coating of the cathodes shows a substructure comparable to the anode. The difference in the RF between anode and cathode can be attributed to the thicker layer of porous platinum deposited at the anode [9].

3.2 Open circuit potential of the electrodes

Fig.6 shows open circuit potentials (OCP) recorded at 7% oxygen saturation for Pt-Cu electrodes fabricated with differing numbers of deposition cycles, as indicated.

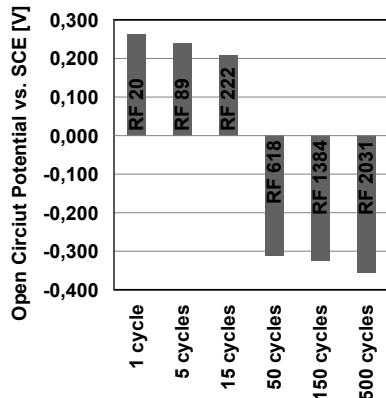


Fig. 6: OCPs recorded in PBS + glucose (3 mmol l⁻¹) at 37 °C and 7% O₂-saturation. Surface area is indicated by RF (ratio between true surface and geometric area).

With increasing number of deposition cycles and thus increasing surface roughness the electrodes show an increasingly more negative OCP. For electrodes fabricated with only a few deposition cycles an OCP typically observed for cathodes used in IGFCs is obtained. In contrast, the application of 50, 150, 500 deposition cycles leads to OCPs typical for anodes.

This can be explained by the kinetic control of the anodic electrooxidation under physiological conditions [13]. With increasing surface roughness thus the anodic reaction is favored compared to the diffusion controlled cathodic oxygen reduction. This results in a more negative mixed electrode potential. Accordingly a difference in OCP of 0.73 V is observed between electrodes fabricated with 1 and 500 deposition cycles, which is more than sufficient for fuel cell application.

3.3 Fuel cell performance

The dependence of fuel cell electrode potential on load current density (per geometric electrode area) is shown in Fig. 7. Compared to state of the art anodes (Pt-Zn) the novel Pt-Cu anodes (500 cycles) exhibit a less negative OCP, but the potential increase with increasing current density is less pronounced. Together with Pt-Cu cathodes (12 cycles), whose potential decrease is significantly lower than that of state of art cathodes (Pt-Al), a higher operating potential is observed. The resulting cell voltage at maximum power density (see Fig. 8) is approx. 440 mV compared to only approx. 420 mV with state of the art electrodes.

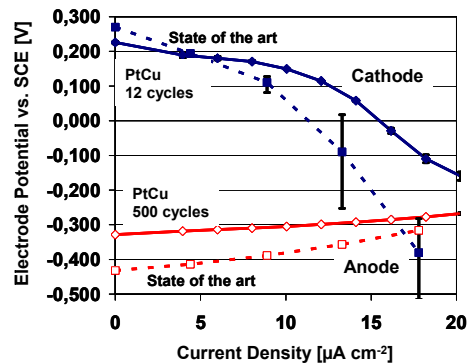


Fig. 7: Current density - potential plot of Pt-Cu anode and cathode compared to state of the art (Pt-Zn) [14]. The experiments were performed in PBS + glucose (3 mmol l⁻¹) at 37 °C and 7% O₂-saturation.

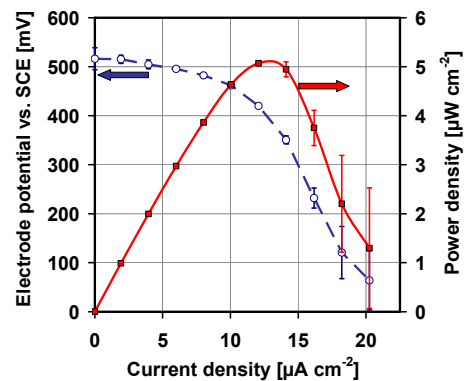


Fig. 8: Cell voltage and power density of fuel cells recorded in PBS + glucose (3 mmol l⁻¹) at 37 °C and 7% O₂-saturation.

CONCLUSION

We demonstrated a facile and versatile process for the deposition of platinum electrodes, which enables the control of electrode porosity by simply adjusting the number of deposition cycles. This way, reaction-specific electrodes for implantable glucose fuel cells can be fabricated by means of a single process. Compared to state of the art both, shorter process time and lower process temperature lead to a significantly facilitated fabrication of the electrodes. Also, the novel process uses platinum more efficiently and thus requires about 70 % less platinum to achieve the same electrode roughness factor.

Correspondingly fabricated fuel cells show power densities of $5.1 \pm 0.1 \mu\text{W cm}^{-2}$, which is 14 % better than state of the art. Furthermore, the novel deposition process can in principle be applied to any electrically conductive substrate. In future this would allow for deposition of the fuel cell electrodes as energy harvesting coating directly on the titanium casing of medical implants such as cardiac pacemakers.

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