A NOVEL FABRICATION ROUTE YIELDING SELF-SUPPORTING POROUS PLATINUM ANODES FOR IMPLANTABLE GLUCOSE MICRO FUEL CELLS

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Abstract: We present a novel fabrication route yielding highly active platinum anodes for body implantable glucose micro fuel cells. Such devices harvest electrical energy from glucose and oxygen in body fluids and are currently under development as sustainable power supply for medical implants. The novel anode fabrication process roots on the interdiffusion of an extractable non-noble metal with bulk platinum. Upon removal of the non-noble component a porous platinum structure is obtained, which is self-supporting and electrically conductive. This obviates the need for polymer binders and additional current collectors. Due to biocompatibility considerations we use zinc as extractable component, as opposed to the nickel suggested in the historic literature. In contrast to conventional activated carbon supported platinum-bismuth electrodes the novel self-supporting platinum anodes show excellent mechanical and chemical stability at a comparable glucose oxidation performance.

Key Words: glucose, fuel cell, implantable, electrode, platinum, zinc, surface modification

1. INTRODUCTION

1.1 Implantable glucose micro fuel cells

Implantable glucose micro 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]. These fuel cells directly generate electrical energy from the electrochemical reaction of glucose and oxygen available in body fluids. The general construction and operation principle of such a device is shown in Fig. 1.

Self supporting porous platinum structures, obtained from platinum-nickel alloys, have already been suggested in the 1970s for the use in implantable glucose fuel cells. These electrodes were overcoming the limited mechanical and chemical stability of conventional electrodes fabricated from catalyst particles with glucose permeable hydrogel as the binder [2]. However, due to its allergenic and carcinogenic properties [3], the use of nickel is likely to be problematic in the context of implantable electrodes. It can not be completely extracted from the alloy [2], and trace amounts of nickel might leach and cause immunogenic reactions in the body. As an alternative alloying partner we therefore chose zinc. Its considerable mean concentration in human blood is as high as 6.5 mg l^{-1} [4], rendering the possible leaching of trace amounts from electrodes insignificant.

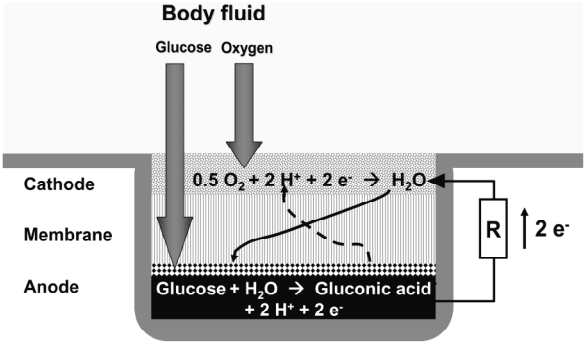

Fig. 1: Operational concept of an implantable glucose micro fuel cell: Oxygen reduction at the exterior cathode (activated carbon), glucose oxidation at the interior anode (platinum), according to [5].

2. EXPERIMENTAL

2.1 Fabrication process

The fabrication process is schematically shown in Fig. 2. Initially an approximately 30 µm thick layer of zinc is electrodeposited to one side of a

50 µm thick Platinum foil (1). Upon annealing at 200 °C in air atmosphere a platinum-zinc alloy is formed by interdiffusion of the components (2). Activation in sulfuric acid results in the removal of zinc from the alloy (3), leaving a self-supporting porous platinum structure (4).

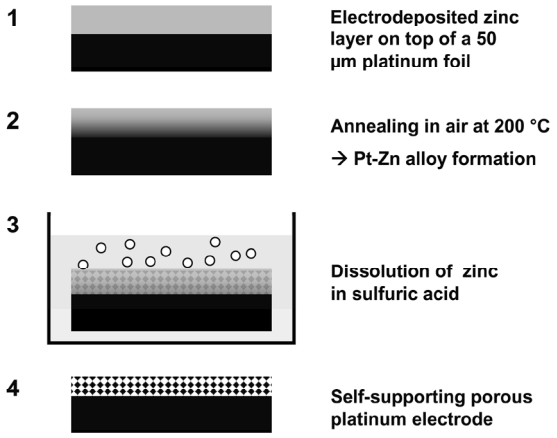

Figure 2: Schematic of the novel fabrication process. See text for explanations.

2.2 Electrode preparation

Initially, the 50 µm platinum foil substrates (Chempur GmbH, Karlsruhe/Germany) were thoroughly cleaned in acetone, isopropanol, and de-mineralized water. The substrates where then mounted between silicone rubber gaskets in a polycarbonate frame, exposing a 15 mm x 15 mm section of one side of the platinum foil. To each foil substrate two platinum wires were attached for electrical connection. Further cleaning of the platinum surface was achieved by 10 cyclic voltammetry sweeps in de-aerated 0.5 M H_2SO_4. The scan rate was 10 mV s^{-1}, between 1.3 V and -0.3 V versus a saturated calomel reference electrode (SCE).

Subsequently zinc was deposited on the foils at room temperature from a commercially available electroplating bath (Enthobrite CLZ SBR, Enthone GmbH, Langenfeld/Germany) in a standard three-electrode electrochemical cell. A solid piece of zinc served as the counter electrode. The deposition current density was fixed at 25 mA cm^{-2}. With 40 min the deposition time was chosen to yield a zinc layer of approximately 30 µm thickness.

Annealing was performed in air atmosphere at a temperature of 200 °C for periods of 24 h, 48 h, and 97 h. The heating and cooling rate was 170 K per hour in each case. Thereto the platinum-zinc bi-layers were removed from the polycarbonate frame and for each annealing time two samples were prepared:

- An 8 mm x 8 mm sample that later was cut in half to prepare micrographs of *as annealed* and *acid-treated* samples.
- A 15 mm x 15 mm sample, that later was split into three parallels of 5 mm x 5 mm active surface area for performance characterization.

The samples were then clamped between two polished aluminum plates to prevent buckling during annealing. Aluminum foil served as interlayer between the samples and the aluminum holder plates to avert sticking. After annealing, the extractable zinc was removed by immersing the samples for 2 h in 0.5 M H_2SO_4.

2.2 Sample characterization

The samples for micro-structural characterization were mounted in epoxy resin and polished as cross-section. The cross-sections were further coated with carbon to allow for elemental composition analysis with an Oxford Scientific INCA300 energy dispersive X-ray (EDX) system.

Prior to testing, the electrodes for electrochemical characterization were further treated by cyclic voltammetry as described above. The roughness factor was estimated from the charge under the hydrogen desorption peaks in the cyclic voltammogram. For ideally polished polycrystalline platinum with a roughness factor of 1 this value amounts to 210 µC cm^{-2} [6]. Glucose oxidation performance of the novel electrodes was characterized in de-aerated phosphate buffered saline (PBS tabs ph 7.4, Invitrogen GmbH, Karlsruhe/Germany) at 37 °C, containing 3.0 x 10^{-3} mol L^{-1} glucose (physiological concentration).

Starting from open circuit (0 µA cm^{-2}), the load current density was stepwise increased to values of 7.7 µA cm^{-2}, 15.9 µA cm^{-2}, and 24.0 µA cm^{-2} in intervals of 12 h. Throughout the experiment the electrode potentials were recorded against a saturated calomel electrode in the same solution. Current density - potential plots were constructed

from the final electrode potentials measured after 12 h of operation at a given current density.

3. RESULTS AND DISCUSSION

3.1 Microstructure evaluation

Fig. 3 shows cross-sections and the top view of samples annealed for 24 h and 48 h at 200 °C. The corresponding sample annealed for 97 h suffered from severe delamination of the porous layer and was thus not further characterized.

At the interface of the two metals a clearly distinguishable zone of platinum-zinc alloy is formed during heat treatment, which is transformed into a porous layer upon zinc extraction with sulfuric acid. With the sample annealed for 24 h this results in a crack-free, porous structure of approximately 14 µm thickness, that is well adhering to the bulk platinum foil. In contrast, the sample annealed for 48 h shows vertical cracks that form approximately 2 µm wide trenches upon removal of the top zinc layer. These trenches appear as mud-crack pattern in the top view. Despite the formation of horizontal cracks in some parts of this sample, the 28 µm thick porous layer is still well adhering and mechanically stable. EDX analysis revealed that both, for annealing times of 24 h and 48 h (58 ± 3) atom % zinc remain throughout the porous layer after acid treatment (mean ± sample standard deviation of 15 point probes at different locations in the porous layer).

3.1 Electrochemical characterization

In Fig. 4 the cyclic voltammograms of platinum foils before and after annealing with zinc are compared. The measured hydrogen desorption charge of the sample annealed for 24 h corresponds to a roughness factor of 2.0 x 10^3. With the increased annealing time of 48 h a roughness factor of 3.0 x 10^3 can be obtained. For comparison, the roughness factor of the untreated platinum foils amounted to 31 ± 4.

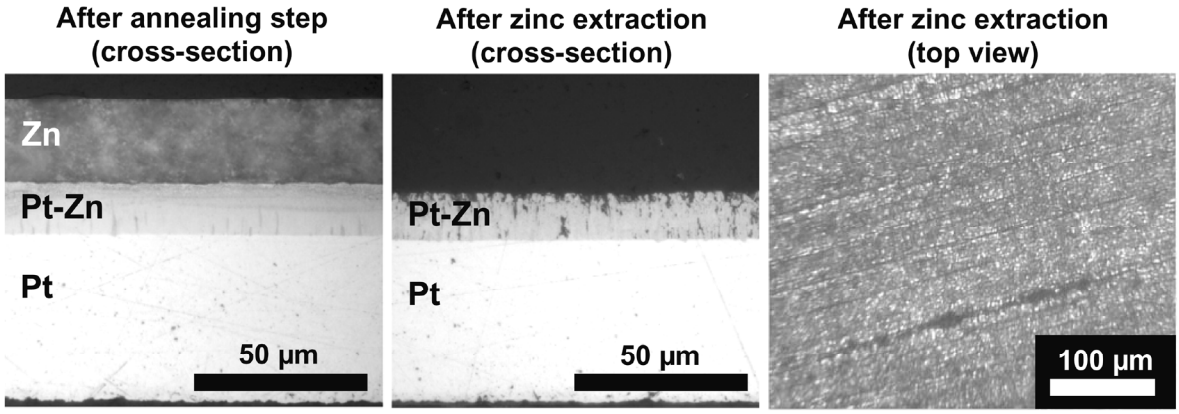

Figure 3: Microstructure of samples annealed for 24 h at 200 °C (optical micrograph).

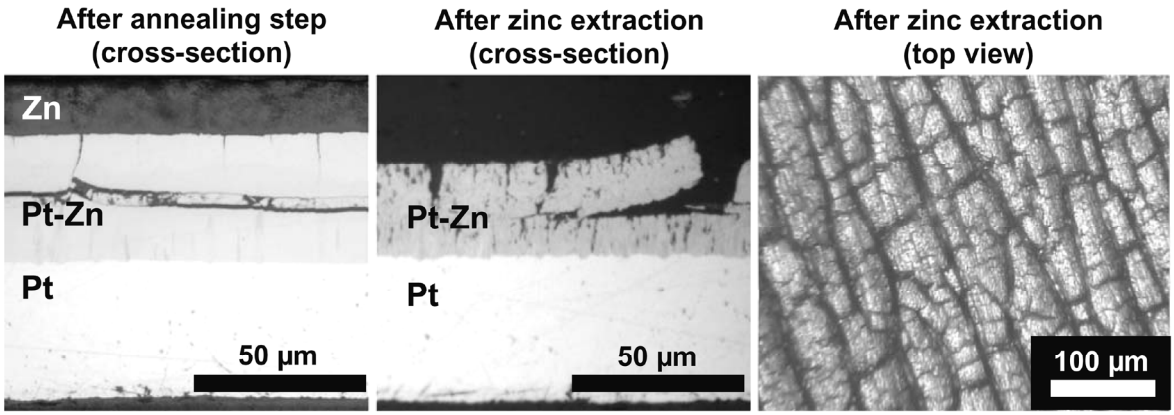

Figure 4: Microstructure of samples annealed for 48 h at 200 °C (optical micrograph).

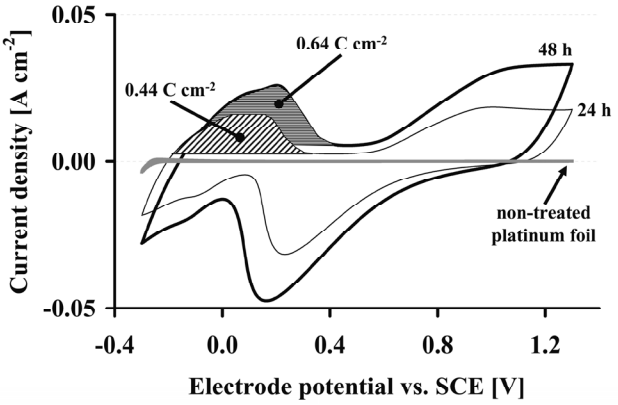

Figure 4: Cyclic voltammetry in H_2SO_4: Non-treated platinum foil compared to samples annealed at 200 °C for 24 h and 48 h, as indicated. The patterned area corresponds to the hydrogen desorption charge of the samples, respectively.

In Fig. 5 the glucose oxidation performance of the novel electrodes is compared to our standard activated-carbon supported Pt-Bi anode, whose fabrication is described elsewhere [7].

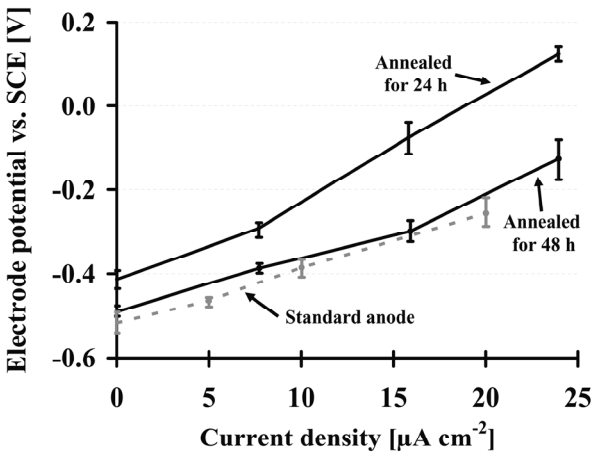

Figure 5: Glucose oxidation performance of the self-supporting porous platinum anodes compared to our conventional activated carbon supported Pt-Bi anode. Given is the average of three parallels, error bars represent maximum and minimum.

It is obvious that the annealing time of the platinum-zinc compound has a distinct effect not only on roughness factor, but also on glucose oxidation performance. Whereas the electrode fabricated with a 48 h annealing step is comparable to our standard anode, the sample annealed for 24 h exhibits a lower performance, with a by ca. 78 mV more positive open circuit potential and noticeably increased polarization at current densities above 7.7 µA cm^{-2}.

4. CONCLUSION

We successfully developed a novel fabrication route for self-supporting porous platinum anodes that obviates the use of nickel as alloying partner. Intended for the use in implantable glucose micro fuel cells the novel anodes, fabricated from a platinum zinc bi-layer annealed for 48 h at 200 °C, pose a significant improvement over our conventional anodes in terms of mechanical and chemical stability at comparable glucose oxidation performance.

Although developed in the context of glucose fuel cells, the presented process may also be suitable to fabricate highly active thin layer electrodes for other micro fuel cell types and electrochemical sensors.

In our current work we are exploring the possibilities to modify the surface of the porous platinum structure with bismuth, to further improve glucose oxidation performance.

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