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Nanofiber-deposited porous platinum enables glucose fuel cell anodes with high current density in body fluids

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HIGHLIGHTS

- Novel 3-D anode material for implantable glucose fuel cells.
- Continuous operation in horse serum for at least 30 days.
- About six times higher stable current density compared to the state-of-the-art.
- Improved catalytic activity and/or poisoning resistance.

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ABSTRACT

The poisoning of platinum anodes by body-fluid constituents such as amino acids is currently the main hurdle preventing the application of abiotic glucose fuel cells as battery-independent power supply for medical implants. We present a novel anode material that enables continuous operation of glucose oxidation anodes in horse serum for at least 30 days at a current density of (7.2 ± 1.9) μA cm^{-2}. The fabrication process is based on the electro-deposition of highly porous platinum onto a 3-dimensional carbon nanofiber support, leading to approximately 2-fold increased electrode roughness factors (up to 16500 ± 2300). The material's superior performance is not only related to its high specific surface area, but also to an improved catalytic activity and/or poisoning resistance. Presumably, this results from the micro- and nanostructure of the platinum deposits. This represents a major step forward in the development of implantable glucose fuel cells based on long-term stable platinum electrodes.

1. Introduction

Implantable glucose fuel cells are a promising technology to realize a battery-independent power supply for medical implants. They enable the continuous generation of electricity from body fluids based on the oxidation of glucose at the fuel cell's anode, coupled to the reduction of oxygen at the cathode [1,2]. In the context of implantable devices, noble metal electro catalysts are considered to be favorable since they are biocompatible, amenable to heat sterilization, and in contrast to enzymes are not subject to denaturation and loss of catalytic activity. Detailed reviews of the field can be found in Refs. [1,3]. Whereas already in the 1970s such fuel cells have been successfully tested in the subcutaneous tissue of dogs (delivering ~2 μW cm^{-2} for up to 5 months) [4,5] their construction and the experimental procedures were not fully disclosed at that time, presumably due to the strong involvement of industry. While the technology lost momentum after the introduction of powerful lithium-iodine batteries in the mid-1970s, it has again attracted significant research interest over the last decade. Since then, a number of different fuel cell designs have been reported. The employed anodes are predominantly based on porous platinum or gold, fabricated for instance by electrodeposition or from carbon-supported nanoparticles [6]. At the cathode

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usually platinum and in some cases also carbon-based electrodes are used [6].

When operated in stagnant neutral saline containing glucose and oxygen, sustainable power densities of up to 16.2 μW cm^{-2} are reported [7]. Under more realistic operation conditions resembling the situation in body tissue (3 mM glucose, 7% oxygen saturation) [8] and considering the diminished reactant supply due to tissue capsule formation [9] significantly lower power densities of up to 6 μW cm^{-2} have been reached [10]. Nevertheless, this power density would already be sufficient to power e. g. a cardiac pacemaker consuming about 5–10 μW [11,12].

In practice, small organic molecules present in body fluids, in particular amino acids, adsorb on the surface of platinum electrodes and drastically reduce their electro-catalytic activity for glucose oxidation. The resulting poor long-term stability of a few days at best [10] is currently the main hurdle preventing the application of this technology as reliable implant power supply. The underlying poisoning effect is well described in the literature [13–19], and with respect to simulated tissue and cerebrospinal fluids most drastically affects glucose oxidation at the anode [10]. Using highly porous platinum anodes under conditions relevant for glucose fuel cell application, we could show that alkaline amino acids, some neutral amino acids as well as uric acid and creatinine exhibit the strongest poisoning effect [20]. Nevertheless, even in the presence of poisoning amino acids a residual glucose oxidation current remains. In their pioneering works Rao et al. assumed, that a dynamic equilibrium between the adsorbed and desorbed amino acids exists so that, to some degree, there are always free catalytic sites available [19]. Their conclusion, that the blockage by amino acids is reversible, is supported by the recent findings of Köhler et al. They showed that in case of the most drastically poisoning tissue fluid constituents the catalytic activity of the platinum electrode was restored once the poisoning substance was no longer present in the media [20]. In summary, these experimental findings suggest that increasing the electrode's specific surface area would lead to an increase in the residual glucose oxidation current in the presence of endogenous amino acids.

Here, we present a new way of preparing platinum anodes with very high surface area and demonstrate their continuous operation in blood serum over a period of 30 days. The fabrication process is based on the electro-depositing of highly porous platinum [21] onto a three-dimensional carbon nanofiber support prepared by electrospinning.

2. Experimental section

2.1. Fabrication of electrospun carbon fiber mats

For electrospinning, a 6 wt% solution of polyacrylonitrile powder (PAN, Sigma-Aldrich, Taufkirchen, Germany) in *N,N*-Dimethylformamide (DMF, Sigma-Aldrich, Taufkirchen, Germany) was prepared by stirring at 70 °C overnight. The PAN solution was then spun using a modified KatoTech (Kyoto, Japan) NEU electrospinning device operating at 20 kV. To achieve a uniform fiber deposition on the collector the device was equipped with a square shaped shield connected to the same high voltage source as the needle. A schematic of the modified electrospinning setup is given in the supporting information (Fig. S1). The resulting electrospun PAN fiber mats were carbonized by heating first to 230 °C at 30 °C h^{-1} in air, and subsequently to 1100 °C at 120 °C h^{-1} in N_2 atmosphere using a tube furnace (Gero, Neuhausen Germany).

These carbon nanofiber mats have a mean fiber diameter of d = (107 ± 35) nm and an area density of ρ_A = (4.63 ± 0.07) mg cm^{-2}. The initial roughness factor (RF_{CF}) of the plain carbon nanofiber electrode defined by the fiber surface area A_{fibers} divided by the geometrical area $A_{geometrical}$ of the electrode can be estimated according to

$$RF_{CF} = \frac{A_{specific}}{A_{geometrical}} = \frac{A_{fiber}}{A_{geometrical}} = \frac{2\pi r \cdot l_{fiber}}{\frac{1}{\rho_A}\cdot m_{fiber}} = \frac{2\pi r \cdot V_{fiber}}{\left(\frac{1}{\rho_A}\cdot m_{fiber}\right)\cdot \pi r^2}$$

$$= \frac{2\pi r \cdot m_{fiber}}{\left(\frac{1}{\rho_A}\cdot m_{fiber}\cdot \pi r^2\right)\cdot \rho} = \frac{4\rho_A}{\rho d}$$

In this calculation it is assumed that the fiber mat can be described as a single fiber of the length corresponding to the total lengths of the fibers per area in the fiber mat. Considering a carbon fiber mat with an area density of ρ_A = (4.63 ± 0.07) mg cm^{-2}, a fiber diameter of d = (107 ± 35) nm, and a carbon density of ρ = 1.77 g cm^{-3} [22], one obtains an initial roughness factor of the plain electrospun carbon fiber mats of RF_{CF} = 978.

2.2. Deposition of porous platinum

The electrospun carbon fiber mats were cut into pieces of 1.4 cm × 1.4 cm, contacted with a titanium wire (0.2 mm diameter, grade 2, SELFAN Fine + Metal GmbH, Köln, Germany), and assembled in a polycarbonate frame with silicone rubber gaskets as holder similar to the one described in Ref. [23]. The frame was open on both sides, exposing an anode area of 1 cm^2 on each side to the electrolyte solution. SEM pictures of outer and inner layers of the fiber mats confirmed that platinum was deposited only within this defined area of 1 cm^2.

Prior to deposition, the carbon fiber mat was first wetted with Isopropanol (99.5%, Carl Roth, Karlsruhe, Germany), followed by washing with deionized water to fill the pores with water and wash out traces of Isopropanol. Afterwards, the carbon fiber mat was placed as working electrode into a standard three-electrode electrochemical cell. As counter electrode a platinum mesh (0.06 mm wire diameter, 99.9%, Chempur, Karlsruhe, Germany) on a platinum wire (0.1 mm diameter, Chempur, Karlsruhe, Germany) was used, a saturated calomel electrode (SCE, KE 11, Sensortechnik Meinsberg, Ziegra-Knobelsdorf, Germany) served as reference electrode as principally shown in e.g. Refs. [8,23].

To deposit the porous platinum structure, the pulsed deposition process described by Köhler et al. has been adopted to our needs [21]. In principle, this process involves the repeated electrodeposition of a PtCu alloy, followed by the selective removal of the copper content at an oxidizing potential. As deposition electrolyte sulfuric acid (50 ml, 0.5 M, TitriPUR, Merck, Darmstadt, Germany) containing H_2PtCl_6 (0.02 M, Pt-%: 40.04, Chempur, Karlsruhe, Germany) and Cu_2SO_4 (0.02 M, Merck, Darmstadt, Germany) were used. To remove oxygen the solution was purged with nitrogen prior to deposition and kept under nitrogen during the process. Deposition and dissolution potentials (−0.5 V vs SCE; 0.7 V vs SCE) as well as deposition and dissolution times (9 s; 4.5 s) were chosen as in the original process [21]. This alternation between the deposition and the dissolution potential was performed several times (20, 40, 80, 120, 240, 480 pulses) to yield anodes with different roughness factors, using a 1470E potentiostat from Solartron Analytical (Farnborough, United Kingdom). In contrast to the original protocol, we introduced a waiting time of 1000 s after each dissolution pulse to ensure diffusion of fresh electrolyte into the porous structure before the next deposition pulse. This waiting time was chosen based on a calculated diffusion coefficient of the metal ions in H_2SO_4 (0.5 M) and an assumed diffusion length of the full thickness of the carbon fiber mat. For comparison, state-of-the-art anodes were fabricated with 1200 pulses and no waiting time