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Raney-platinum film electrodes for potentially implantable glucose fuel cells. Part 1: Nickel-free glucose oxidation anodes

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ABSTRACT

We present a novel fabrication route yielding Raney-platinum film electrodes intended as glucose oxidation anodes for potentially implantable fuel cells. Fabrication roots on thermal alloying of an extractable metal with bulk platinum at 200 °C for 48 h. In contrast to earlier works using carcinogenic nickel, we employ zinc as potentially biocompatible alloying partner. Microstructure analysis indicates that after removal of extractable zinc the porous Raney-platinum film (roughness factor ~2700) consists predominantly of the Pt_3Zn phase. Release of zinc during electrode operation can be expected to have no significant effect on physiological normal levels in blood and serum, which promises good biocompatibility. In contrast to previous anodes based on hydrogel-bound catalyst particles the novel anodes exhibit excellent resistance against hydrolytic and oxidative attack. Furthermore, they exhibit significantly lower polarization with up to approximately 100 mV more negative electrode potentials in the current density range relevant for fuel cell operation. The anodes' amenability to surface modification with protective polymers is demonstrated by the exemplary application of an approximately 300 nm thin Nafion coating. This had only a marginal effect on the anode long-term stability and amino acid tolerance. While in physiological glucose solution after approximately 100 h of operation gradually increasing performance degradation occurs, rapid electrode polarization within 24 h is observed in artificial tissue fluid. Optimization approaches may include catalyst enhancement by adatom surface modification and the application of specifically designed protective polymers with controlled charge and mesh size.

1. Introduction

Implantable glucose fuel cells employing abiotic catalysts (e.g. noble metals, activated carbon) are currently under consideration to realize a battery-independent power supply for medical implants [1,2]. These fuel cells directly generate electrical energy from the electrochemical reaction of glucose and oxygen available in body fluids. In previous prototypes both, cathode and anode have been fabricated mainly from hydrogel-embedded catalyst particles [2–8]. However, the application of hydrogel-polymers as structural component results in a complex system. On the one hand the hydrogel has to be mechanically and chemically stable to maintain structural integrity of the electrode. Here in particular poly(vinyl alcohol)–poly(acrylic acid) hydrogels used in previous works are susceptible to hydrolytic and oxidative attack upon prolonged electrode operation [8]. On the other hand the hydrogel must be sufficiently permeable to allow for the reactants to reach the catalyst surface. Furthermore, the presence of a hydrogel matrix for structural support of the catalyst particles renders the additional application of specific polymers to favorably influence catalytic behavior [9,10] and to reduce electrode poisoning [10–12] difficult.

An attractive alternative electrode fabrication concept that obviates the need for hydrogel binders has been reported by Gebhardt et al. [13]. They fabricated Raney-platinum film anodes by extraction of the non-noble component from annealed platinum–nickel bi-layers or homogenous alloy foils fabricated from a fusible regulus. Compared to conventional anodes, these anodes exhibited improved glucose oxidation performance as well as excellent resistance against oxidative and hydrolytic attack. However, the use of nickel as non-noble, extractable component is likely to be problematic in the context of implantable electrodes due to its allergenic and carcinogenic properties [14]. Nickel cannot be completely extracted from the alloy [13], and thus trace amounts might leach upon operation of the electrode and provoke immunogenic reactions of the body tissue. To solve this problem, a more suitable, biocompatible alloying partner would be required. A promising alternative can-

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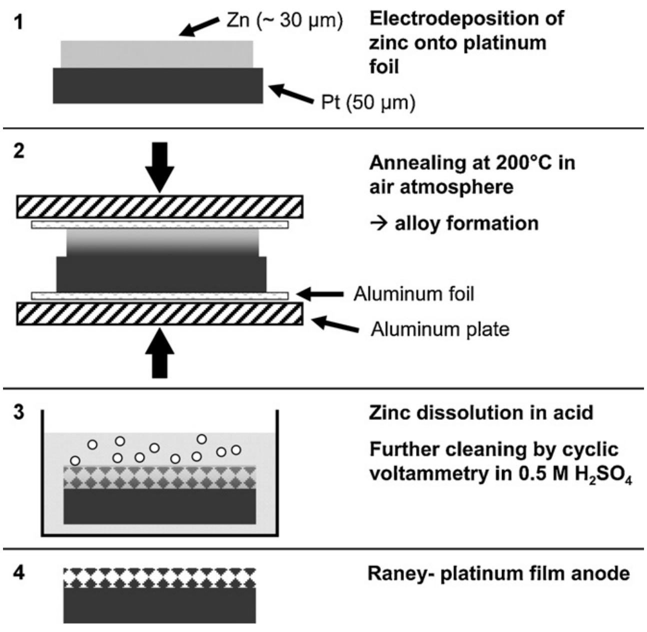

Fig. 1. Schematic of the anode fabrication processes. See text for explanations.

didate forming alloys with platinum [15] is zinc, which in terms of potential biocompatibility can be regarded as less problematic compared to nickel. Zinc's considerable mean concentration in the human body is as high as 6.5 mg l^{-1} in blood and 1 mg l^{-1} in serum [16], which renders the possible leaching of trace amounts from electrodes insignificant.

The aim of the present work is to develop a nickel-free fabrication route for Raney-platinum film anodes using zinc as alloying partner, and evaluate their applicability as anodes in potentially implantable glucose fuel cells. Thereto their current density–potential behavior upon glucose electro-oxidation is investigated under physiologically relevant conditions, including the presence of endogenous amino acids in artificial tissue fluid. Special care is given to obtain significant performance data by carrying out triplicate experiments and by recording polarization curves with a stepwise galvanostatic technique (multi-step chronopotentiometry), which prevents performance overestimation resulting from too fast current sweep rates [17].

Furthermore included into the study is the characterization of the electrode material by means of X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX), the analysis of metal-leaching upon prolonged electrode operation, and the exemplary application of a thin Nafion layer as easy to implement polymer modification. Considered to be biocompatible [18,19], Nafion has successfully been applied in the field of biosensors to reject anionic interferents such as ascorbic and uric acid [20] and acetaminophen (paracetamol) [19], and to improve the response of non-enzymatic glucose sensors in human plasma [21].

The fabrication of Raney-platinum film electrodes for cathodic oxygen reduction using aluminum as alloying partner will be reported in part two of this paper series [22].

2. Experimental

2.1. Fabrication of Raney-platinum anodes

The general fabrication process is shown schematically in Fig. 1 and described in the following. As substrates 17 mm × 17 mm pieces of 50 μm platinum foil (Chempur GmbH, Karlsruhe/Germany) were mounted together with two platinum wires for electrical connection between silicone rubber gaskets in the polycarbonate frame described elsewhere [17], exposing only a 15 mm × 15 mm section of one side of the foil. The exposed surface was cleaned by 10 cyclic voltammetry sweeps at 10 mV s^{-1} between 1.3 and −0.3 V vs. a saturated calomel reference electrode (SCE) in de-aerated (nitrogen-purged) 0.5 M H_2SO_4 (Merck KGaA, Darmstadt/Germany).

Pt–Zn anodes were prepared by depositing zinc onto the cleaned side of the platinum foil, using a standard three-electrode electrochemical cell and a commercially available electroplating solution (Enthobrite CLZ SBR, Enthone GmbH, Langenfeld/Germany) at room temperature. To prevent gas evolution and to maintain the zinc concentration in the plating solution a solid piece of zinc served as counter electrode. With a deposition time of 40 min at 25 mA cm^{-2} the deposition parameters were chosen to yield an approximately 29 μm thick zinc layer (deposition efficiency ~100%, determined by measuring weight before and after deposition).

For thermal alloying the platinum–zinc bi-layers were removed from the polycarbonate frame and clamped between two polished aluminum plates to prevent buckling during alloy formation. Pieces of 25 μm thin aluminum foil (Carl Roth, Karlsruhe/Germany) served as interlayer between the samples and the aluminum holder plates to avert sticking. Annealing was performed in air atmosphere at a temperature of 200 °C for periods of 24, 48, and 96 h. The heating and cooling rate was 170 K per hour in each case. After annealing, extractable zinc was removed by immersing the samples for 2 h in 0.5 M H_2SO_4. Subsequently all samples were re-mounted in the polycarbonate holder and subjected to 10 cyclic voltammetry cycles as described above. Corresponding to their annealing time, the samples are in the following designated as $Pt–Zn_{24}$, $Pt–Zn_{48}$, and $Pt–Zn_{96}$, respectively.

2.2. Nafion modification

In addition, $Pt–Zn_{48}$ was also modified by an electro-coated Nafion layer on top of porous Raney-structure, similar to the procedure reported by Rice and Nicholson [23]. Electro-coating is the preferred method to reach uniform Nafion films, involving the electrostatic attraction of negatively charged sulfonate groups in the polymer to the positively charged electrode [20]. Thereto, the electrode was electrically connected with a crocodile clip, which itself was fixed to the extension arm of a dip coater (RDC 15, Bungard Elektronik GmbH, Windeck/Germany). Each sample was then completely immersed in the Nafion solution (5% Nafion 521, Quintech, Göppingen/Germany) and a potential of +1.5 V was applied between the cathode and a platinum wire counter electrode (Ø1 mm, 40 mm long, Chempur, Karlsruhe/Germany). After 120 s the sample was pulled out of the solution at 40 mm min^{-1} while maintaining the potential at +1.5 V. Subsequently, the Nafion layer was cured at 70 °C for 30 min. These samples are designated as $Pt–Zn_{48}$(Nafion). Due to the irregular sample surface the thickness of the Nafion layer could not be determined directly. Therefore a platinum layer sputtered onto silicon was used as substrate in a separate experiment with the deposition process as described above. Here thickness analysis with a surface profiler (Dektak 3030, Veeco Instruments Inc., Plainview/NY) yielded a Nafion layer thickness of approximately (300 ± 20) nm.

2.3. Microstructural evaluation

Roughness factors were estimated from the charge under the hydrogen desorption peaks in the cyclic voltammograms recorded during cleaning of the samples (see Section 2.1), assuming a hydrogen desorption charge of 210 μC cm^{-2} [24] for ideally polished polycrystalline platinum with a roughness factor of 1.