



## Raney-platinum film electrodes for potentially implantable glucose fuel cells. Part 2: Glucose-tolerant oxygen reduction cathodes

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### ABSTRACT

We report the fabrication and characterization of glucose-tolerant Raney-platinum cathodes for oxygen reduction in potentially implantable glucose fuel. Fabricated by extraction of aluminum from 1  $\mu\text{m}$  thin platinum–aluminum bi-layers annealed at 300 °C, the novel cathodes show excellent resistance against hydrolytic and oxidative attack. This renders them superior over previous cathodes fabricated from hydrogel-bound catalyst particles. Annealing times of 60, 120, and 240 min result in approximately 400–550 nm thin porous films (roughness factors  $\sim$ 100–150), which contain platinum and aluminum in a ratio of  $\sim$ 9:1. Aluminum release during electrode operation can be expected to have no significant effect on physiological normal levels, which promises good biocompatibility. Annealing time has a distinct influence on the density of trenches formed in the cathode. Higher trench densities lead to lower electrode potentials in the presence of glucose. This suggests that glucose sensitivity is governed by mixed potential formation resulting from oxygen depletion within the trenches. During performance characterization the diffusion resistance to be expected from tissue capsule formation upon electrode implantation was taken into account by placing a membrane in front of the cathode. Despite the resulting limited oxygen supply, cathodes prepared by annealing for 60 min show more positive electrode potentials than previous cathodes fabricated from hydrogel-bound activated carbon. Compared to operation in phosphate buffered saline containing 3.0 mM glucose, a potential loss of approximately 120 mV occurs in artificial tissue fluid. This can be reduced to approximately 90 mV with a protective Nafion layer that is easily electro-coated onto the Raney-platinum film.

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### 1. Introduction

Raney-platinum film electrodes possess a number of advantages over conventional hydrogel-bound particle electrodes commonly used in abiotically catalyzed implantable glucose fuel cells [1]. These comprise [2,3] high catalytic activity for anodic glucose oxidation, excellent resistance against oxidative and hydrolytic attack, and the amenability to versatile surface modification with protective polymer layers [2].

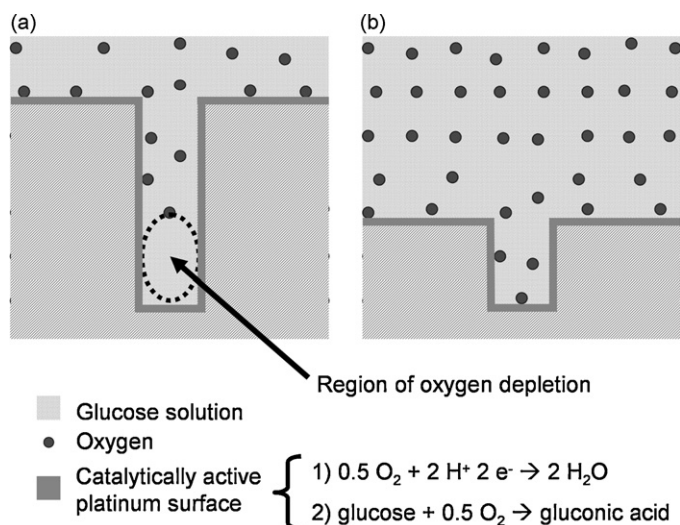
While platinum exhibits high catalytic activity also for oxygen reduction [4], corresponding Raney-type film cathodes have to date not been applied in implantable glucose fuel cells. This may be related to the simultaneous presence of glucose and oxygen in physiological environments. Under such conditions  $\sim$ 10–100  $\mu\text{m}$  thick porous platinum-based electrodes exhibit mixed potentials closer to the redox potential of glucose oxidation [5–7]. As illus-

trated schematically in Fig. 1, this can be explained by oxygen consumption on the catalytically active platinum surface in the outer region of the electrode [1], either by the direct chemical reaction of oxygen with glucose or the electro-reduction of oxygen to water in case the electrode is operated as fuel cell cathode. In the oxygen-depleted interior of the cathode the local potential is then dominated by the presence of glucose, which can drastically lower fuel cell voltage and thus power output.

Previous approaches to solve this problem employ for instance glucose insensitive oxygen reduction catalysts such as activated carbon [8,9] or silver [9,10]. Alternatively, hydrophobic membranes [6,11] have been placed in front of platinum cathodes to hinder glucose access. Both approaches come with several disadvantages [1]: while activated carbon and silver exhibit lower catalytic activity for oxygen reduction than platinum, the concept with hydrophobic membranes mandates reactant access to the fuel cell from two sides. This renders mounting of the fuel cell directly on the casing of a medical implant difficult.

We suggest to circumvent the interference of glucose oxidation with cathodic oxygen reduction by the construction of sufficiently

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**Fig. 1.** Schematic illustration of oxygen availability in porous platinum cathodes of different thicknesses. (a) Thick layer: oxygen is fully consumed in the outer region of the pore (either by (1) electro-reduction to water or by (2) direct chemical reaction with glucose). In the oxygen-depleted interior of the electrode the local potential is dominated by the redox potential of glucose oxidation. (b) Thin layer: sufficient oxygen to prevent the formation of anoxic regions can diffuse into the pore.

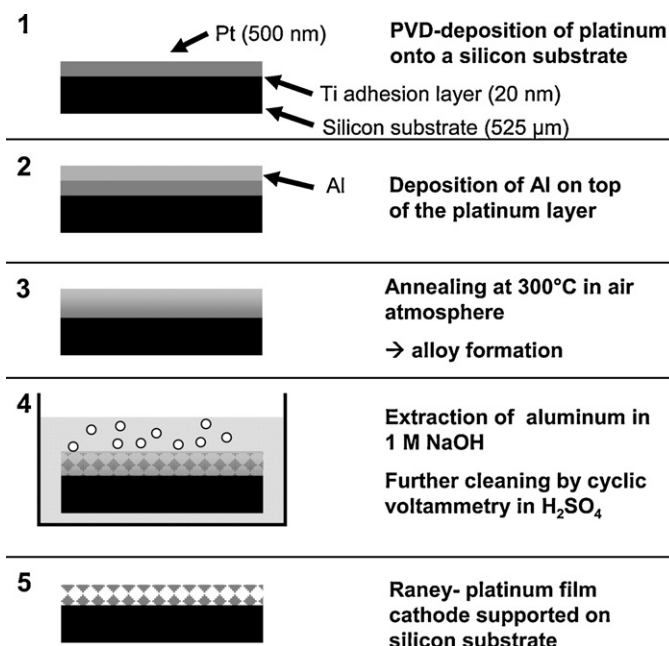
thin, porous platinum electrodes. As illustrated in Fig. 1, a sufficiently thin enough electrode would prevent the formation of oxygen-depleted regions within the cathode and thus decrease the extent of mixed potential formation. According to this concept we here investigate the fabrication and applicability of Raney-platinum electrodes as chemically resistant and glucose-tolerant oxygen reduction cathodes for implantable glucose fuel cells. An attractive possibility to fabricate sub-micrometer thin Raney-type platinum electrodes is the annealing of PVD-deposited bi-layers of platinum and an extractable metal [12–14]. As extractable metal forming alloys with platinum we chose aluminum [15], due to its established use and thus ready availability as sputtering target for the PVD (physical vapor deposition) process. The electrode materials formed upon different annealing times are characterized by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDX). Their oxygen reduction performance under physiological concentrations of glucose and oxygen is characterized by recording current density–potential curves in both, phosphate buffered saline and artificial tissue fluid. To account for the limited oxygen supply to be expected from tissue encapsulation upon implantation an appropriate diffusion barrier is placed in front of the cathode. Included into the study is the analysis of aluminum leaching upon prolonged operation, and a first step towards improving cathode performance in terms of glucose sensitivity and tolerance towards artificial tissue fluid by application of a protective Nafion coating [16–18].

## 2. Experimental

### 2.1. Fabrication of Raney-platinum cathodes

The individual fabrication steps are schematically illustrated in Fig. 2, and described in the following. As substrate for metal deposition 525  $\mu\text{m}$  thick silicon wafers (native oxide removed in 1% HF, orientation (100), n+ doped with phosphorus, 100 mm diameter, Siltronix, Archamps, France) were used.

Electrodes were prepared by firstly evaporating a 20 nm thin titanium adhesion layer on the silicon substrate, followed by 500 nm platinum and a final 500 nm aluminum layer. During subsequent dicing of the wafer into 17 mm  $\times$  17 mm chips the thin metal



**Fig. 2.** Schematic of the cathode fabrication processes. See text for explanations.

surface was protected with approximately 2  $\mu\text{m}$  photoresist that was afterwards removed. Following this, the chips were annealed at 300 °C in air atmosphere for 60, 120, or 240 min. In accordance with annealing time these samples are designated as *Pt–Al<sub>60</sub>*, *Pt–Al<sub>120</sub>*, and *Pt–Al<sub>240</sub>*, respectively. Subsequently the samples were immersed in 1 M NaOH (Merck KGaA, Darmstadt, Germany) for approximately 15 min to extract aluminum from the alloy. Further cleaning was achieved by 20 cyclic voltammetry sweeps in de-aerated 0.5 M  $\text{H}_2\text{SO}_4$  (Merck KGaA, Darmstadt, Germany). The scan rate was 50  $\text{mV s}^{-1}$  between 1.3 and  $-0.3 \text{ V}$  vs. a saturated calomel reference electrode (SCE).

### 2.2. Nafion modification

*Pt–Al<sub>60</sub>* cathodes were modified by an approximately 300 nm thin electro-coated Nafion layer on top of the porosified platinum layer according to the procedure reported elsewhere [2]. In short, the sample was immersed in 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 ( $\varnothing$  1 mm, 40 mm long, Chempur, Karlsruhe, Germany). After 120 s the sample was pulled out of the solution at 40  $\text{mm min}^{-1}$  while maintaining the potential at +1.5 V. Subsequently, the Nafion layer was cured at 70 °C for 30 min.

### 2.3. Microstructural evaluation

Roughness factors were estimated from the charge under the hydrogen desorption peaks in the cyclic voltammograms as described in Ref. [2]. Also the determination of platinum to aluminum ratios of the Raney-platinum electrodes (after operation) by means of energy-dispersive X-ray (EDX) analysis was performed as previously described [2]. The results are presented together with the sample standard variation, given in parentheses.

Cross-sections were prepared using an Ar-ion beam cross-section polisher (SM-09010, Jeol GmbH, Eching, Germany) and observed with a Zeiss Supra 60 VP scanning electron microscope operating at 5 kV.

The intermetallic phases present in the porosified platinum layers were identified by X-ray powder diffraction, using a PSD

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