

Porous Gold Surfaces for Implantable Neural Electrodes

HELEN EDSTRÖM

Lund University

helen.karolin.edstrom@gmail.com

Abstract

Nanoporous gold electrodes have the advantage of a small geometric size combined with a large real surface area. When such an electrode is implanted into the brain, it is sufficiently small to cover only one brain cell, but with a real surface area sufficiently large to keep the noise at a low level. This is because the impedance scales inversely with the surface area, and increasing impedance decreases the signal-to-noise ratio. Attempts to increase the surface area of gold electrodes via anodization has been made. The impedance was measured before and after anodization. Cyclic voltammetry (CV) was used to calculate the real surface area of the electrodes. An optical microscope and a scanning electron microscope were used to investigate the colour and structure of the electrodes after anodization. The results of the CV show that the real surface area was enlarged up to seven times, which was confirmed by the impedance measurements, demonstrating a decreased impedance after anodization. However, more tests should be performed before anodizing real neural electrodes for implantation in order to obtain reliable results.

I. INTRODUCTION

Nanoporous gold is an attractive material for neural electrodes due to its large real surface area, stability, conductivity, biocompatibility [1] and durability (nanoporous gold can sustain macroscopic stresses up to 200MPa) [2]. One of the greatest advantages of nanoporous gold electrodes compared to conventional, planar gold electrodes is the decrease in impedance due to larger surface area, since impedance is inversely proportional to surface area. For comparison, at 1kHz the impedance for a planar gold electrode is $850\text{k}\Omega$ but only $30\text{k}\Omega$ for a nanoporous gold electrode of the same geometric size [3]. When the electrode is implanted into the brain in order to measure the electrical activity of the brain cells, the impedance should preferably be low to avoid noise [4].

For a neural electrode implanted into the brain, it is desirable that the electrode is small enough to cover only one cell. If many cells are covered by the electrode, it might be harder to distinguish the active cell, and there is also a risk of short-circuiting two cells. The problem

with just decreasing the size of the electrode is that the impedance increases. This leads to a decreased signal-to-noise ratio and only noise will be measured. A solution to this problem is to make the gold surface of the electrode nanoporous, increasing the real surface area without increasing the geometric size. A measure of the real surface area compared to the geometric size is the roughness factor, which is the former area divided by the latter area.

Nanoporous gold can be fabricated by anodizing pure gold substrates in an aqueous solution of oxalic acid. During this process, a thick layer of gold oxide is formed on the substrate surface. This layer appears red while nanoporous gold appears black, so a colour change might suggest formation of nanoporous gold [5].

In this project, circular test electrodes with a diameter of $100\mu\text{m}$ has been used. These are several times larger than real neural electrodes used for implantation, because their larger size makes them less sensitive and easier to handle. The aim of this project was to enlarge the surface area of the test electrodes using

anodization, to compare the impedance before and after anodization and to calculate the real surface area.

II. MATERIALS AND METHODS

i. FABRICATION OF ELECTRODES

Silicon wafers were wet oxidized (Thermco MB71) and cleaned by oxygen plasma (Diener FEMTO). A 45nm titanium layer and a 750nm gold layer was evaporated (Edwards Auto 306) by electron beam evaporation. Positive resist AZ1514H (Microchemicals) was spun (Sitek) onto the wafers and they were soft baked on a hot plate (Sitek), exposed to UV light (Karl Suss MA4) to structure the gold and developed in 351 Developer (Microchemicals), diluted with MilliQ water at 1 : 4. The wafers were then rinsed in MilliQ water and a gold etchant (4g KI (Merck), 1g I₂ (Sigma-Aldrich), 40ml MilliQ water, etching rate of 100nm/20s) was used to etch the exposed gold. Hydrofluoric acid (HF:MilliQ water at 1 : 5) was used to etch the exposed titanium and the wafers were rinsed in acetone, ethanol, MilliQ water and finally blown dry with N₂ gas. The wafers were then cleaned using oxygen plasma (Diener FEMTO) and negative resist SU8 2005 (Microchem) was spun (Sitek) onto them to isolate the gold conductors connecting the electrodes and the contact pads. The electrodes and contact pads were left unisolated. The wafers were soft baked in an oven (FN 300), exposed to UV light (Karl Suss MA4), post-baked in an oven (FN 300) and developed in MR DEV600 (Microchem). Finally, they were rinsed in isopropanol and MilliQ water and blown dry with N₂ gas. The wafers now contained a large number of chips with six circular electrodes with a diameter of 100μm each.

The chips on one wafer were diced out (Micro Automation Model 602M) and glued onto circuit boards. Contact between the contact pad and the circuit board was established by wirebonding (Bausch & Lomb S-823) a thin aluminum wire. For protection and isolation

of the aluminum wires, part of the sample was covered with silicone (Elastosil A07).

ii. ANODIZATION

In order to make the surface area on the electrodes porous, the electrodes were anodized using an apparatus containing a potentiostat (Ivium CompactStat) with its own multiplexer system (Ivium MultiWE 32), controlled from the manufacturer's software (IviumSoft). The electrode worked as the anode and a platinum helical wire worked as the cathode. A reference electrode (silver/silver chloride) was used to control the applied potential. 0.5M oxalic acid (oxalic acid dihydrate, 99% purity, Sigma-Aldrich, MilliQ water) constituted the electrolyte. Both potentiostatic anodization (constant potential, varied current) and galvanostatic anodization (constant current, varied potential) were performed. In the former mode, the potential was set to 1V and in the latter mode, the current was set to 1.5μA. Different anodization times were tested, from a few seconds up to several hours.

iii. IMPEDANCE MEASUREMENTS

For the impedance measurements, the same apparatus as for the anodization was used. The electrolyte consisted of 0.01M PBS (phosphate buffered saline, sodium perborate, Sigma-Aldrich, MilliQ water). The impedance was measured both potentiostatically and galvanostatically, before and after anodization. Potentiostatic impedance measurement seemed like the most stable mode.

iv. CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) was used to measure the surface charge on the electrodes. The aforementioned apparatus was used and the electrolyte consisted of 0.5M sulfuric acid (GPR Rectapur, 95% purity, MilliQ water). The start potential was -0.2V and the end potentials were 1.3V, 1.4V, 1.5V and 1.6V, respectively. The scan rate was 100mV/s. The area under the curve (AUC) of the reduction peak in the

CV graph was calculated and divided by the scan rate to obtain the surface charge, which in turn was divided by the experimentally calculated surface charge density of $138\mu\text{C}/\text{cm}^2$. The *AUC* was calculated using an integration function in the calculation and simulation program MATLAB® R2104a (The MathWorks Inc., Natick, MA, 2014).

V. INVESTIGATION

The electrodes were investigated using both an optical microscope (Olympus BX40), equipped with a camera (Edmund SO-5012C), and a scanning electron microscope (SEM, Hitachi SU8010). Before SEM investigation, the samples were partly covered with copper tape, to avoid charging effects, and sputtered (Polaron E5100 DC) with approximately 10nm platinum, to make the gold visible in the SEM.

III. RESULTS

i. ANODIZATION

The first anodization tests showed that the best combination of anodization mode and time seemed to be galvanostatic anodization at $1.5\mu\text{A}$ for 1h , see Figure 1. After 1h , the gold surface on the electrode appeared porous and continuous, but after 2h , some of the gold was extricated. So 2h seemed too long to anodize the electrodes in this mode. Later on, this provided a starting point for further investigation, were a test series of potentiostatic impedance measurement before and after galvanostatic anodization at $1\mu\text{A}$ for 60min , 75min and 90min , respectively, and CV measurement to end with.

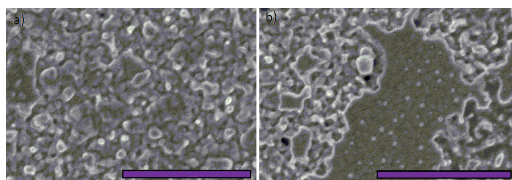


Figure 1: SEM image of an electrode anodized galvanostatically at $1.5\mu\text{A}$ for a) 1h and b) 2h (scalebar = $1\mu\text{m}$).

ii. IMPEDANCE MEASUREMENTS

Figure 2 shows the results of the impedance measurements (mean impedance and standard deviation). All of these graphs show a decrease in impedance after anodization, which suggests an enlarged surface area.

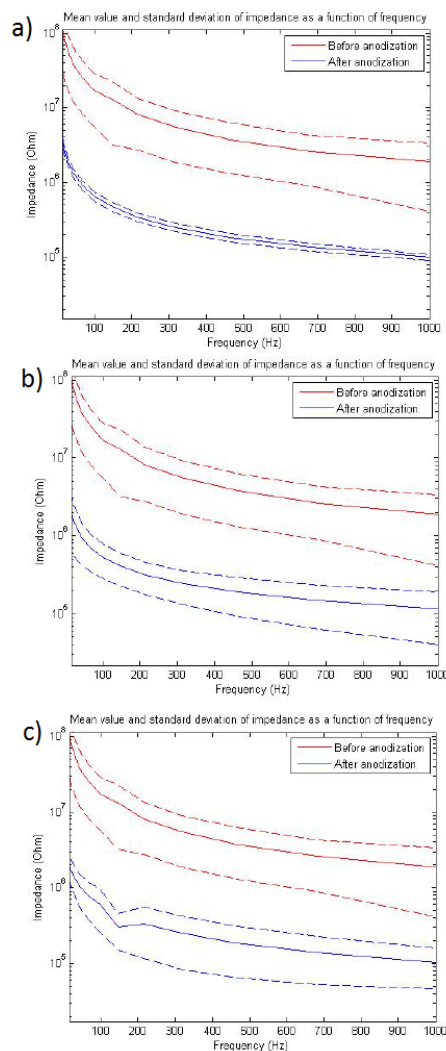


Figure 2: Impedance as a function of frequency for the electrodes anodized for a) 60min ($n = 4$), b) 75min ($n = 9$) and c) 90min ($n = 7$). The red curves show the impedance before anodization and the blue curves show the impedance after anodization. The solid lines show the mean impedance at each frequency and the dashed lines show the standard deviation.

iii. CYCLIC VOLTAMMETRY

Figure 3 shows the CV graphs for three electrodes anodized for different times. The marked out coordinates in the graphs forms the border of the reduction peak, for which the AUC was calculated, leading to the real surface area of the electrodes.

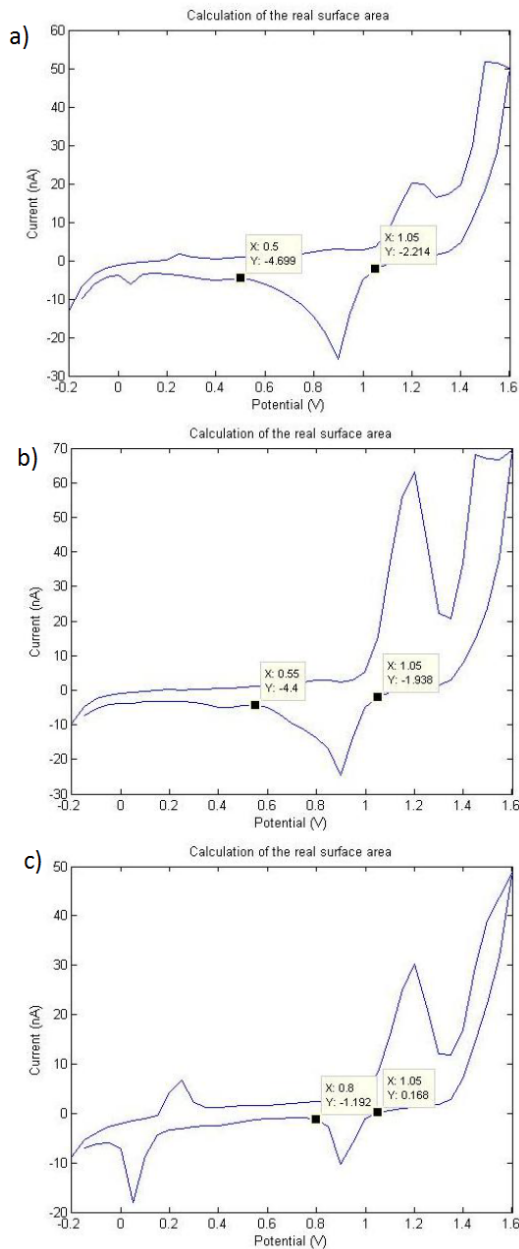


Figure 3: CV graph of an electrode anodized for a) 60min, b) 75min and c) 90min.

Below, the mean real surface areas and mean roughness factors with their standard deviations for the three different anodization times are given.

- 60min: 22500 ± 12200 (μm^2), 2.87 ± 1.55
- 75min: 59500 ± 36800 (μm^2), 7.58 ± 4.69
- 90min: 51500 ± 30200 (μm^2), 6.56 ± 3.85

iv. INVESTIGATION

Figure 4 shows some SEM images for three electrodes anodized three different times.

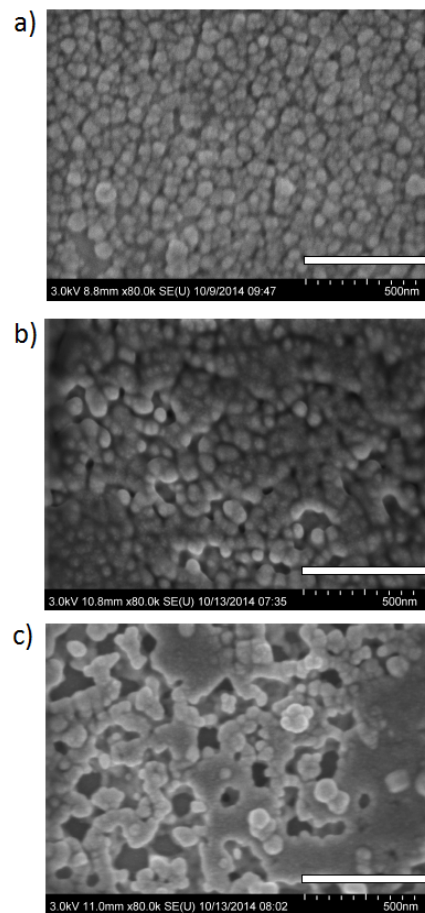


Figure 4: SEM image of an electrode anodized for a) 60min, b) 75min and c) 90min (scalebar = 500nm).

Figure 5 shows some optical microscope images for three electrodes anodized at three

different times. Three electrodes underwent a colour change to a darker colour (all of them anodized for 90min), ten electrodes had no visible colour change (four of them anodized for 60min and the other six anodized for 75min) and seven electrodes obtained a heterogeneous colour scale (three of them anodized for 75min and the other four anodized for 90min).

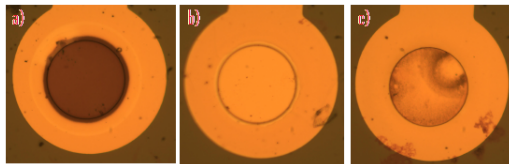


Figure 5: Optical microscope image for an electrode anodized for a) 90min, b) 60min and c) 75min. The inner circle is the electrode with a diameter of 100 μ m.

IV. DISCUSSION

Since the aim of this project was to enlarge the surface area of gold electrodes, the obtained results are satisfying. The real surface area was increased for both 60min, 75min and 90min of anodization, up to seven times, and impedance measurements confirmed this conclusion. The real surface area was smallest for 60min and largest for 75min. Perhaps one would expect the real surface area to be larger for 90min than for 75min, but this result might be due to extrication of the gold after 90min of anodization. In other words, 90min might be too long to anodize the electrodes galvanostatically at 1 μ A.

According to Figure 4, the surface structure of the electrodes resembles the surface structure seen in Figure 1. However, the electrodes in the former figure were the best ones for each anodization time, most of the electrodes did not exhibit any structure like this. The darker colour revealed by the optical microscope could indicate either nanoporous gold or extricated gold.

V. FUTURE WORK

The method for increasing the surface area of gold electrodes tested in this project seems viable. However, since real neural electrodes are smaller than test electrodes, the processing parameters ought to be calibrated. The times for e.g. anodization should be shorter for smaller electrodes. Furthermore, more test electrodes should undergo the treatment carried out in this project in order to have more replicas and more reliable results before anodizing real neural electrodes and implant them in the brain of animals and humans.

REFERENCES

- [1] Yang, Y. et al, "Fabrication of nano-network gold films via anodization of gold electrode and their application in SERS", *Journal of Solid State Electrochemistry*, vol. 16, pp 1733 – 1739, Nov. 2011
- [2] Zhong, G. et al, "Electrochemical biosensor based on nanoporous gold electrode for detection of PML/RAR α fusion gene", *Biosensors and Bioelectronics*, vol. 26, pp 3812 – 3817, Mar. 2011
- [3] Seker, E. et al, "The fabrication of low-impedance nanoporous gold multiple-electrode arrays for neural electrophysiology studies", *Nanotechnology*, vol. 21, no. 2010, pp 1 – 7, Mar. 2010
- [4] Quan, X. et al, "Development of nanoporous gold electrodes for electrochemical applications", *Microelectronic Engineering*, vol. 88, pp 2379 – 2382, Jan. 2011
- [5] Xu, S. et al, "Anodic Fabrication of Nanoporous Gold Films from Pure Gold in Oxalic Acid Solution and Their Applications in Electrocatalysis and SERS", *International Journal of Electrochemical Science*, vol. 8, pp 1863 – 1870, Feb. 2013