

Fabrication of a porous anodic alumina membrane

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ABSTRACT

With the aim of developing a process for surface enlargement on an electrode for measuring brain activity attempts have been made to fabricate a porous anodic alumina membrane directly on the electrode. The porous membrane was intended to be used as scaffold for deposition of an electrically conducting polymer on the electrode surface.

A silicon wafer with gold electrodes was the base onto which the aluminum used in the anodization process was evaporated. The resulting device is a simplified model of an actual brain implant, and was anodized potentiostatically in oxalic acid solution while the current was recorded. The anodizing potential was set to 1 V to prevent damage to the electrodes. The experiments have been evaluated using light and scanning electron microscopy, SEM. Some electrodes expressed changes in color after anodization but the surface of aluminum seemed to be unaffected and no signs of pore formation were seen. SEM investigations showed that the initial aluminum layer had an inhomogeneous structure and it was observed that aluminum seemed to loosen from the electrode and drift away after long-term acid exposure. Electrodes where this had happened seemed to be affected by anodization and expressed changes in surface structure.

ABSTRACT

Målet med detta examensarbete har varit att utveckla och utvärdera en metod för att anodisera ett aluminiumlager till ett membran av porös aluminiumoxid. Porerna i membranet är sedan tänkta att användas för polymerisation av en ledande polymer på en elektrod som är utformad för att mäta elektriska potentialer inuti hjärnan. När membranet löses upp finns polymerpinnar kvar på elektroden, vilket ger en förstord elektrodyta.

Aluminium har evaporerats på testchip av kisel med guldelektroder som utgör en förenklad variant av det riktiga implantatet. Detta aluminium har sedan anodiserats i oxalsyra med en konstant spänning om 1 V samtidigt som strömmen registrerats. Experimenten har utvärderats med hjälp av ljus- och svepelektronmikroskopi. Vissa elektroder har ändrat färg under anodiseringen men inga förändringar relaterade till anodisering har konstaterats vid undersökning av aluminiumets ytstruktur. Däremot har det ursprungliga aluminiumlagret visat sig ha en skrovlig yta och det verkar som om aluminiumet lossnar då det utsätts för syraangrepp under en längre tid. Materialet under det lossnade aluminiumet har visat på förändringar i struktur relaterade till anodisering.

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1 INTRODUCTION

In the human body, communication and information is handled by nerve cells – neurons. They are present in the nerves, and in large quantities in the brain. Due to a change in the flux of ions through the cell membrane of a neuron, there is a change in the electric potential across the cell membrane when the neuron is active. This modified potential difference can travel long distances along the cell membrane and makes it possible to transmit signals from the brain to all parts of the body, and also to collect information for interpretation in the brain. The changing potential across the cell membrane causes a change in potential outside the cell, which can be measured and used as an indicator of neural activity.

The brain is constantly changing; new connections between neurons make it possible for us to learn and create new memories. It is not completely fixed to the skull, but floats in the cerebrospinal fluid, an efficient protection against mechanical shock. The movements of the brain means that any implant which is fixed and stiff would act as a knife, cutting the tissue as the brain moves. At Neuronano Research Center in Lund there is development of a new flexible electrode for measuring electric potentials inside the brain. The device needs to be small to fit among, and get close to the neurons, but at the same time a large surface area is required for a decent signal to noise ratio. The solution is to structure the electrode surface and make the area larger without letting it spread out, much like the mountains in Switzerland or the villi in our digestive system. The aim of this work has been to develop a process for fabrication of such a surface coating.

The surface for this particular application needs to meet certain requirements. First of all it needs to be made of a conductive material. It also has to be biocompatible and allow for the electrode to retain its flexibility. A simple fabrication process suitable for batch production is highly desirable. In the following section a process which meets all these requirements will be presented. Some alternative approaches will also be discussed before the mechanisms behind the chosen method are given in

the theoretical section. Experiments aiming to find suitable processing parameters will then be described and evaluated.

1.1 THE METHOD OF CHOICE

The surface enlargement method chosen for evaluation is polymerization of the conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) in a porous alumina membrane. A schematic drawing of the process is shown in Figure 1. The membrane is fabricated directly on the electrode by anodization of an aluminum layer evaporated onto the conducting surface of the electrode. Anodization turns the aluminum layer into a porous layer of aluminum oxide, alumina. The anodization process will be described further in section 2.1. With pores penetrating through the entire aluminum layer the electrode can be used for electropolymerization of PEDOT. Since alumina is an insulator the polymer will grow from the conducting surface of the electrode through the pores in the alumina and the polymerization can be stopped before the membrane is completely covered. The alumina is then readily dissolved in sodium hydroxide which leaves only the polymer nanowires on the surface. In comparison to many other chemicals used for nanofabrication the chemicals needed for anodization and dissolution of the oxide; oxalic acid, phosphoric acid and sodium hydroxide, are gentle and easy to handle. Because exposure of the electrode surface is essential for electropolymerization the experimental work has focused on producing a porous alumina membrane with pores penetrating the aluminum, and to find ways to monitor this process. Adjusting processing parameters to influence the pore diameters was of less importance during this initial stage of evaluation.

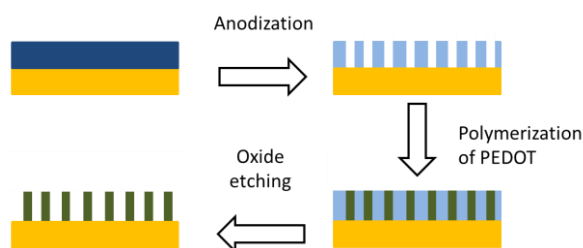


Figure 1. Fabrication of PEDOT nanowires using porous anodic alumina as scaffold. The process starts with anodization of aluminum to form porous alumina and the polymer is then electrodeposited in the pores. Finally the supporting oxide is removed.

1.2 ALTERNATIVE APPROACHES

The current method used to increase the surface area of the electrode is electroplating of platinum onto the surface. The resulting structure resembles cauliflower and increases the surface area sufficiently, but the adhesion is poor. Therefore there is a risk that the platinum coating will not withstand the stresses when implanted in the brain and there is a need for a new coating technique.

Porous membranes, to be used as scaffolds for nanowire growth, can be made by track-etching of polymers.[1] In this process the surface is bombarded with particles, either from radioactive specimens or a focused ion beam, and the damages will be the starting points of pores that are then etched through the material. If a radioactive specimen is used a collimator determining the angle and location of bombardment can be placed between the specimen and the substrate. This gives control over pore density. The biggest drawback with radioactive track-etching is of course the radioactivity itself, the risks related to it, and that membranes prepared in this way must be left for months before they can be used. Track-etching with ion beams do not suffer from this problem, but each pore must be addressed individually by the beam, and thus the process is very time consuming. Equipment for parallel bombardment (at more than one point and future pore at a time) is very costly. Addressing each pore individually is also done when using Electron Beam Lithography, EBL.[2] EBL can pattern electron-sensitive resists to produce pores for polymerization and offers fine control over the pore diameter and spacing, but is not suitable for batch production.

Porous polymer membranes can be formed with a technique using block copolymers, polymers with chains where two or more unique polymers can be distinguished. A di-block copolymer can be described as a polymer chain attached to chain of a different polymer, see Figure 2.



Figure 2. The structure of a di-block copolymer. The two monomer types form distinct polymer chains connected at the ends.

If these polymers are immiscible they will, under the right conditions, undergo a phase separation where one of the polymers organizes in vertical pillars stretching from the substrate to the surface, as shown in Figure 3.[3] The pillar polymer can then be selectively etched leaving a porous membrane of the other polymer. This is a very promising technique and the pore size can be adjusted between 5-50 nm depending on the relative concentrations of the polymers and chain lengths.[4] The difficulties lie in finding suitable concentration ratios between the polymers and getting the polymerization right. To get the correct organization of the phases the thickness of the polymer film is also important. If the circumstances are not correct, the phases might instead be separated into other more favorable shapes, like spheres or a bicontinuous gyroid shape.[5] Thus, there is a lot of optimization of numerous parameters required before the perfect process protocol is found.

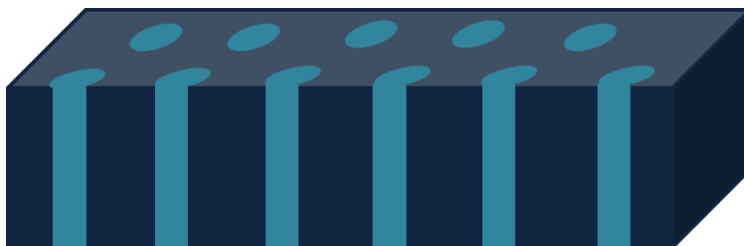


Figure 3. A block copolymer where one of the polymer components has formed vertical pillars.

Electropolymerization of PEDOT into nanowires is possible without a supporting scaffold.[6] This is done by polymerization of the monomer between two electrodes. A process like this would be difficult to use for this application since the counter electrode needs to be close to the electrode to be coated, about 5 μm . The counter electrodes could be incorporated in the device design and then be removed after polymerization of PEDOT. Fabrication of the devices would then be very

complex and it is uncertain whether all the requirements for successful nanowire polymerization, such as proper diffusion of monomer, could be met.

2 THEORY

2.1 ALUMINUM ANODIZATION

Anodization is a process where the native oxide layer on aluminum is thickened and modified. During anodizing the aluminum object is immersed in an electrolyte solution and made the anode of an electric circuit. Depending on the electrolyte the oxide layer will either be a uniform barrier type layer or express a porous structure.[7] Anodization is commonly used to increase the corrosion resistance for aluminum and aluminum alloy objects. In addition, the new surface is easier to dye than native aluminum oxide and thus anodization can provide a surface coating which is functional as well as decorative. During the nineties the parameters determining pore size and regularity were described and since then porous aluminum oxide made by anodization has become a popular scaffold for nanowire fabrication for various applications.[8]

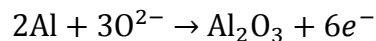
2.1.1 THE CHEMICAL REACTIONS INVOLVED IN ANODIZATION OF ALUMINUM

When aluminum is placed in an aqueous solution and a current is passed through the material and the electrolyte several chemical reactions take place at the interfaces between the metal and the oxide (m/o interface) and the oxide and the electrolyte (o/e interface), illustrated in Figure 4.[9]

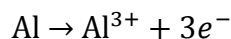
These reactions are important for formation and structuring of the oxide. In the electrolyte there is splitting of water into hydrogen and oxygen ions



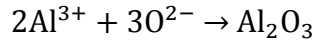
The oxygen ions then migrate through the oxide along their electrical gradient to react with aluminum at the m/o interface and form aluminum oxide



In the metal there is also formation of aluminum ions



These aluminum ions can either react with the oxygen ions at the m/o interface or continue to the o/e interface and form oxide there



These reactions and movements of ions suggest that oxide forms at both interfaces simultaneously, which has been confirmed by experiments where impurity ions are added to the metal or the electrolyte before anodization.[10] Another important reaction is the dissolution of oxide into the electrolyte



The dissolution of oxide is crucial for the formation of porous alumina. If no dissolution occurs the oxide layer will be of barrier type.

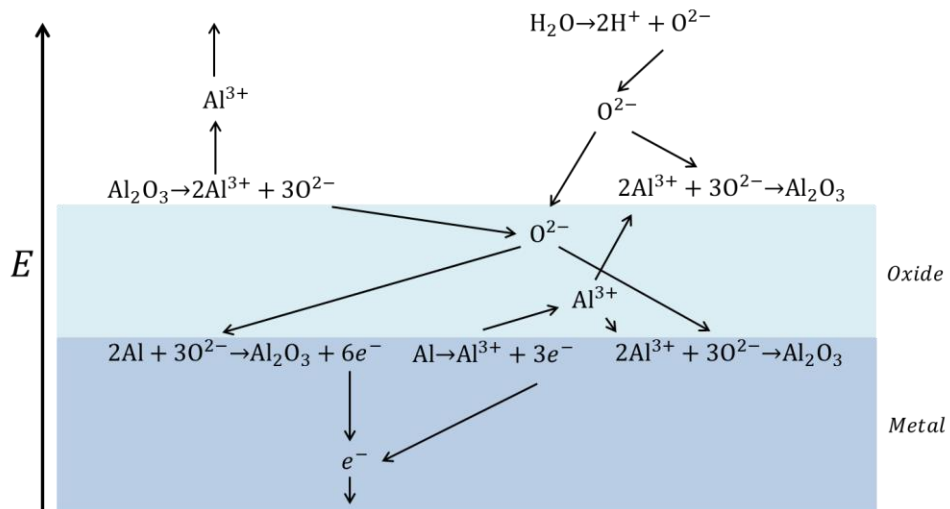


Figure 4. Chemical reactions at the m/o and o/e interfaces during aluminum anodization. Oxygen and aluminum ions migrate along their electrical gradients, created by the electric field (E), to form oxide at both interfaces. Dissolution of oxide into the electrolyte is essential for pore formation.

2.1.2 BARRIER TYPE OXIDE LAYERS

Alumina layers of barrier type are oxide layers lacking pores. They are formed during anodization when the pH of the electrolyte is neutral or nearly neutral. Under these conditions no material is dissolved into the electrolyte and the oxide layer grows homogeneously. The anodizing voltage determines the thickness of the oxide layer. In order to move ions through the oxide a certain strength of the electric field across the oxide is required. As the oxide grows thicker the strength of the field across it decreases, and eventually the field is so weak that ion movement ceases. At this point there will be no further thickening of the oxide. Typically the oxide film thickness is about 1.4 nm/V.[11] Aluminum oxide is an electric insulator and the resistance will increase as the oxide layer grows, leading to a decreased current if the anodizing potential is kept at a constant level.

2.1.3 POROUS ALUMINUM OXIDE

Films of porous aluminum oxide are obtained when anodization is performed in acidic conditions with pH about 1-4. The pores form because some of the aluminum is dissolved into the electrolyte. If more aluminum is dissolved the process will instead be termed electropolishing, a way of cleaning aluminum surfaces. The mechanisms for pore initiation and dissolution of oxide in the pores are still in debate and the suggested models will not be described here. But, worth to notice is that dissolution of oxide seems to be field-dependent.[8] Once pores have formed in the barrier layer the electric field will, due to the thinner oxide layer, be stronger at the bottom of the pores and the oxidation and dissolution rates will be increased here. Due to the dissolution, the barrier layer at the bottom of the pores will not build up and reach a critical size where the oxidation stops. Instead, the thickness of the bottom layer will be kept at a constant level and the pores will penetrate deeper into the metal. What determines the thickness of the porous layer is thus not the applied potential but the total amount of transferred charge.

The progress of potentiostatic anodization, where the applied potential is controlled and fixed, can be monitored measuring the current.[12] Initially the current will drop while a barrier type oxide layer is formed at the surface, as shown in Figure 5. Because of the growing surface area during the formation of pores the current will then increase before it reaches a

stable level. In this stable phase the porous oxide layer will increase in thickness and there is a balance between the oxidation and the dissolution of aluminum. This balance keeps the thickness and geometry of the barrier layer at the bottom of the pores constant.[9] Fluctuations in the current will be seen when the aluminum is completely consumed and the pores reach the underlying material.[13]

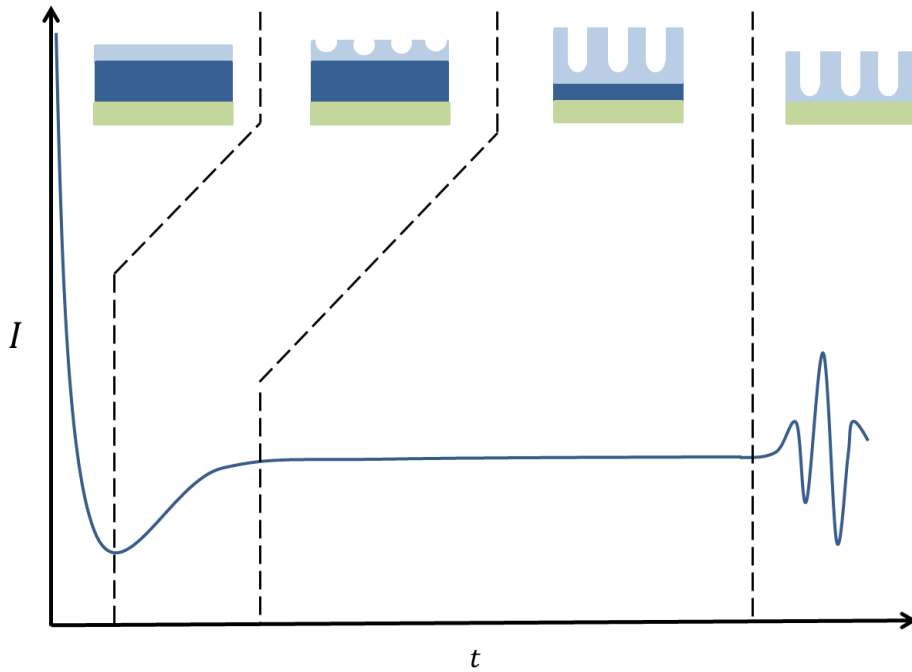


Figure 5. Behavior of the current during potentiostatic anodization. The illustration shows the different stages of oxidation and pore growth. During the first phase a barrier type oxide layer, with higher resistance than pure aluminum, is formed and the current drops. The current then increases again as the pores are initiated before it finds a stable level while the pores grow deeper. This stable level is maintained until the aluminum is consumed and the pores reach the underlying material. The time for this depends on the initial thickness of the aluminum and the current during the stable phase.

Anodization can also be performed galvanostatically, with a fixed current and the required potential as a process indicator. The process shows the same steps as the potentiostatic with initial growth of a barrier type layer, followed by stabilization of the potential while the pores are growing, see Figure 6. For galvanostatic anodization current densities of 0.1-100 mA/cm² are used, calculated from the initial aluminum surface area.[8]

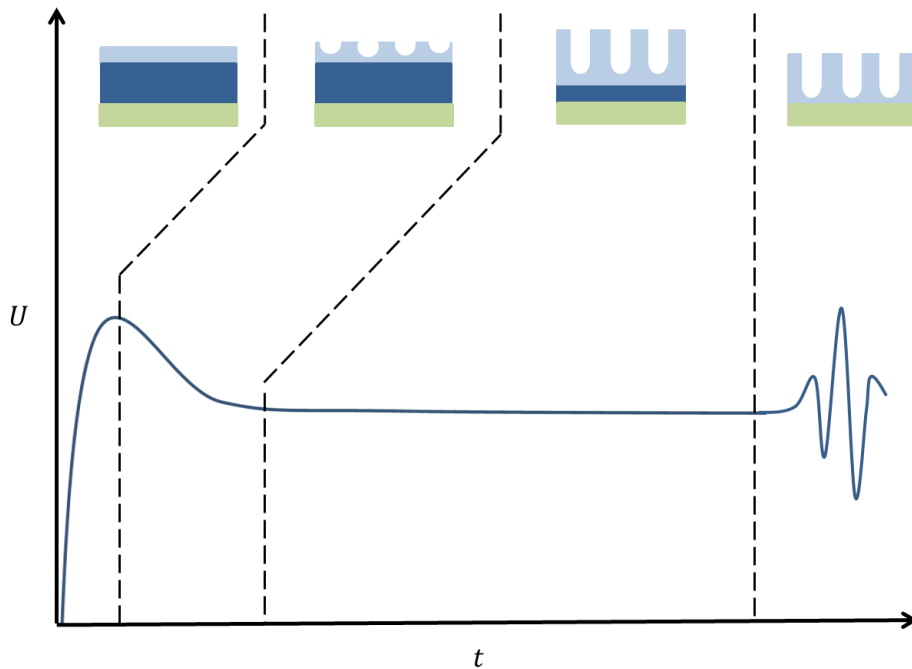


Figure 6. Voltage-time curve for galvanostatic anodization. The material undergoes the same phases as in potentiostatic anodization with formation of barrier layer and pore initiation and propagation.

When describing the characteristics of a porous alumina membrane the terms interpore spacing, or interpore distance, and pore width are of interest. Interpore spacing is the length from center to center of adjacent pores and pore width the pore diameter. These values are connected, it is obvious that the pore width cannot exceed the interpore spacing, but membranes with a larger interpore spacing also tend to have wider pores. Several studies have shown that, for different anodizing acids, the interpore spacing is linearly proportional to the anodizing potential.[14] The acids

most frequently used for aluminum anodization are oxalic acid, sulphuric acid and phosphoric acid, the anodizing potential differ between 10-200 V.[8] The pore width can be adjusted after the anodization has been completed by etching of the oxide, this is normally referred to as pore widening, resulting in thinner pore walls. This procedure does not affect the interpore distance but removes some of the oxide at the pore walls and the thin barrier layer at the bottom of the pores, exposing the underlying metal.

2.1.3.1 Applications and recent research

Porous anodic alumina is industrially used for surface coating and passivation. The oxide layer provides resistance against corrosion and is harder than the native surface. But since the oxide is very thin at the pore bottom the pores are sealed to ensure the corrosion resistance is sufficient. Before the sealing procedure dyes can be added to the surface and fill the pores. This kind of coating technique has been used in large scale production since the 1960's, and the pore structure was first visualized with a transmission electron microscope in 1953.[8] These surface coatings are usually made fast (50-100 $\mu\text{m}/\text{h}$) at high potentials and show an irregular pore pattern.[15]

Anodization at more controlled conditions can produce regular patterns of pores. One of the techniques to improve the regularity is to use a two-step anodization process.[16] Here the oxide is removed by etching after the pore formation, see Figure 7. The exposed aluminum surface has then been structured by the penetrating pores and these cavities will determine the locations for the pores when the sample is again anodized. This access to a simple method for producing a porous membrane with high regularity has opened up a wide range of possibilities for nanofabrication.

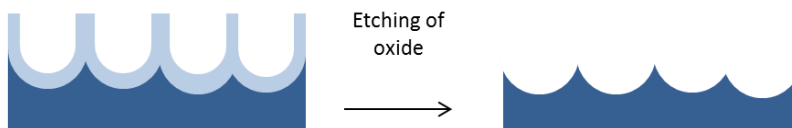


Figure 7. By removal of the oxide after an initial anodization the aluminum surface is structured.

There are many examples of porous anodic alumina membranes used as scaffolds for nanowire fabrication. The wires can be grown directly on an underlying substrate, as intended in this project, and for example become an important feature in optoelectronic or bio sensing devices.[17][18] By altering the anodization potential during anodization the pores will have a non-uniform diameter. If anodization starts at a low potential which is later increased the pores will be wider at the bottom than near the surface.[15] It is also possible to widen the pores between deposition steps to create wires with different radial compositions, meaning the pores are filled with one material before the pores are widened and then a second material is added around the first one. Selective etching of the core then results in nanotubes.[19] Both polymers and metals can be deposited in the pores. It is also possible to use free standing membranes as evaporation mask for gold to pattern a substrate with gold particles for subsequent growth of semiconductor nanowires.[20]

2.2 PEDOT

Poly(3,4-ethylenedioxythiophene), PEDOT, is a conducting polymer developed in the 1980's.[21] The key to the conductive properties lies in the conjugated π -bonds along the carbon backbone, see Figure 8. These bonds can be destabilized by adding dopant molecules, such as poly(styrenesulfonate), PSS. Doping increases the conductivity of the polymer which in the undoped state is in the range of a semiconductor's.[22] PEDOT and other conducting polymers have gained much interest during the past decades. Polymer chain length and side chains can be selected to obtain the desired electrical and chemical properties, and in their thin film state they are often transparent, opening up for optoelectronic applications. The combination PEDOT:PSS has shown to be as good for cell culturing as conventional glass slides.[23]

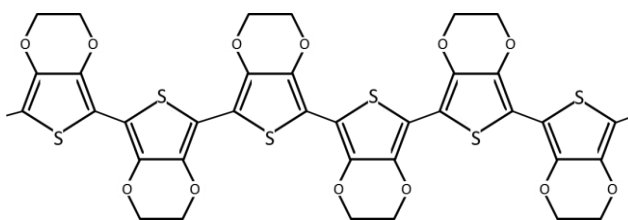


Figure 8. The conducting polymer PEDOT with alternating single and double bonds along the backbone.

Electropolymerization, also termed electrodeposition, of PEDOT can be performed by applying a voltage between two electrodes in a solution of the monomer EDOT. A polymer film will then form at the anode by an oxidative polymerization induced by the potential.[24] When electrodepositing PEDOT in an alumina scaffold the resulting structure can be wires or tubes depending on the polymerization parameters.[17] A larger potential leads to faster consumption of the monomer and less time for the monomer to diffuse. This will cause the polymer to grow close to the pore walls and produce tubes. If the potential is lowered or the concentration of monomer is increased there will be enough monomer to produce solid wires as the polymerization proceeds.

3 MATERIALS AND METHODS

3.1 CHIP DESIGN AND FABRICATION

The actual electrodes intended for measurements in the brain are made in a rather complicated process. They are also quite sensitive and difficult to handle, which is why a test environment with larger electrodes has been developed. Since there were already lithography masks for fabrication of the test chips and electronic equipment needed to contact these chips available it was decided that no changes would be made to the design.

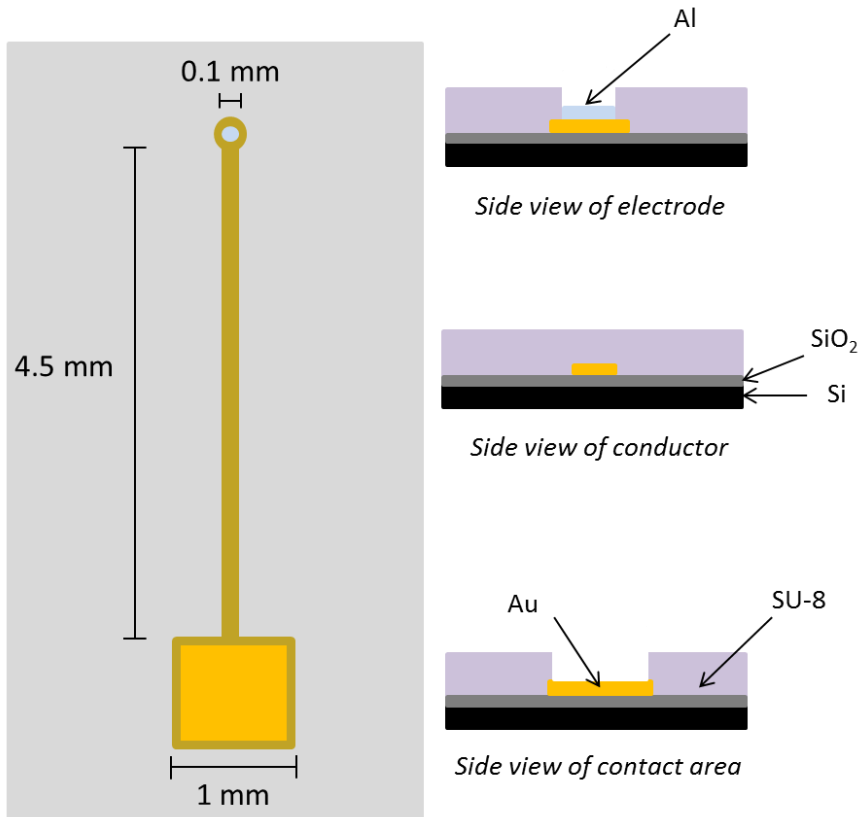


Figure 9. Top and side views of the chip units used to test the anodization technique. Each chip has six of these units.

Each chip has six units; each unit consisting of a rectangular contact surface and a conductor that runs in a straight line to the circular electrode, see Figure 9. The chip is made of gold on a silicon wafer and is insulated

with SU-8. For insulation towards the silicon the wafer is oxidized before patterning. There are openings in the polymer for the contact and electrode surfaces. To reduce the need for high precision mask alignment the aluminum layer on the electrode has a larger diameter than the opening in the SU-8. This ensures that the entire electrode surface is covered with aluminum. In most cases the aluminum did not adhere very well to the SU-8, meaning that the only aluminum remaining was on top of the gold, in the SU-8 opening. The diameter of the part of the electrode that is not covered with SU-8 is 100 μm . All metal patterning is done using UV-lithography with negative lift-off resists and evaporation of metal. A schematic patterning process is shown in Figure 10.

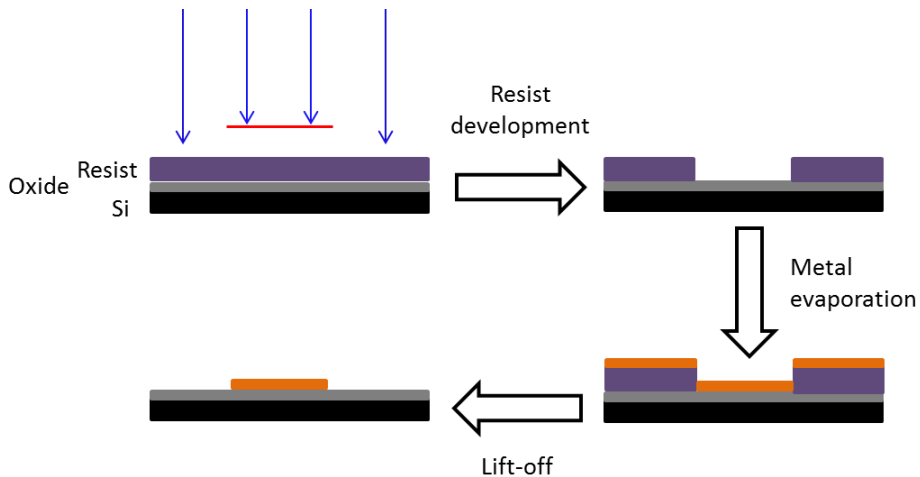


Figure 10. Metal patterning using lift-off with a negative resist. The resist is exposed to UV-light and the pattern is set by a mask shielding parts of the substrate. The unexposed resist will be washed away during development and it becomes possible to place a metal on the oxide surface. The remaining resist is then removed and the metal on top of it follows.

3.1.1 DETAILED DESCRIPTION OF CHIP FABRICATION PROCESS

A silicon wafer was wet oxidized in an oven at 1100 $^{\circ}\text{C}$ for 6 hours. The oven was then set to 400 $^{\circ}\text{C}$ and the wafers were left in the oven to cool down during the night. To ensure proper adhesion of the resist to the oxide the wafers were cleaned using oxygen plasma (Diener FEMTO). The negative lift-off resist AZ 2070 (AZ Electronic Materials) was spun onto the wafers at 4000 rpm for 30 s followed by soft baking in an oven at 85 $^{\circ}\text{C}$ for 35 min. UV-lithography was performed using an 8 s exposure

(Karl Suss MA4) and the wafers were then hard baked on a hot plate for 60 s, 110 °C. The resist was developed in AZ 326 MIF (AZ Electronic Materials) for 90 s. Since the lattices of silicon oxide and gold do not match, a 30 nm thick chrome layer was evaporated before evaporation of a 500 nm thick gold layer (Edwards Auto 306). The growth rate was 0.1 nm/s. For lift off DMSO was used, heated to 70 °C. The process was aided by use of an ultrasonic bath.

Before being covered with SU-8 2005 (MicroChem) the wafers were again cleaned with oxygen plasma. SU-8 2005 was spun at 400 rpm for 30 s and then baked in an oven heated to 90 °C. After 20 min the oven was turned off and the wafers were taken out at 50 °C. Exposure time for the UV-lithography was 6 s and the resulting thickness of SU-8 was about 3 µm. The patterns were developed in MR DEV 600 (Micro Resist Technologies) for 1 min and then baked at 200 °C for 1 h, after which the wafers were left inside the oven to slowly cool to room temperature.

The procedure with which aluminum was structured is similar to that of chrome and gold in terms of resist choice and handling. 0.8 µm of aluminum was evaporated (Pfeiffer Classic 500) onto the wafer. Lift-off was again performed using AZ 326 MIF, but before that most of the excess aluminum was removed using tape. After this processing step the chips were cut apart, glued onto simple circuit boards and connected to them with aluminum wires, attached using a wire bonder. Before anodization the unshielded gold contacts and copper conductors on the circuit boards that would otherwise be exposed to the anodizing electrolyte were covered with silicone glue.

3.2 GENERAL DESCRIPTION OF EXPERIMENTS

The experiments performed had a clear focus on producing a porous aluminum membrane with through-holes to the underlying gold surface since contact with the gold is essential for electropolymerization of PEDOT inside the porous membrane.

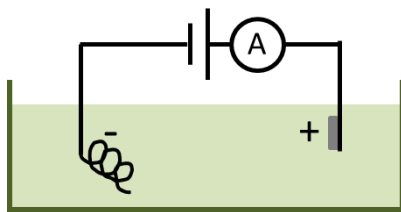


Figure 11. Two-electrode experimental setup. The working electrode is the chip to be anodized and the counter electrode is a platinum wire.

Anodization was performed in a two-electrode configuration with the aluminum acting as the anode and platinum wire as a cathode counter electrode. Figure 11 shows a schematic drawing of the setup. In the standard procedure the electrodes were anodized potentiostatically and the current was recorded. After anodization the electrodes were examined using a light microscope and a scanning electron microscope (SEM). Additional measurements were done under galvanostatic conditions and there were also a few attempts made at anodizing aluminum foil.

3.3 POTENTIOSTATIC ANODIZATION

Most of the electrodes were anodized potentiostatically using two different setups. The first set of experiments is described in Figure 11. It includes a power supply (Agilent 6654A), a system switch/multimeter (Keithley 3706) used as amperemeter and a container with 0.5 M oxalic acid, prepared from oxalic acid dehydrate (Sigma-Aldrich, 99% purity). The pH of the acid was measured to be 1.1. The instruments were connected to a computer and controlled from a LabView program where the desired voltage was set and then the current and time were both logged to a data file and plotted on the screen for live evaluation of the experiment. After anodization of each electrode the cables had to be connected manually to the next electrode. The first anodizing potential tried was 20 V, but it soon became clear that this was too high and the voltage was gradually lowered until the electrodes could withstand the anodization. This was achieved when the potential was 1 V. The lower voltage made it possible to connect a multiplexer to the setup to have an automatic change of electrode between anodizations, meaning all six electrodes on a chip could be anodized before any manual changes had to be done. This setup was also controlled via a LabView program.

The low anodizing potential also enabled use of a potentiostat (Ivium CompactStat), a device replacing the power supply and the amperemeter. It also has its own multiplexer system (Ivium MultiWE 32). The Ivium potentiostat was controlled from the manufacturer's software IviumSoft. The transition from the LabView-controlled setup to the Ivium setup was mainly driven by software issues; otherwise the two techniques are interchangeable.

A wide range of anodizing times was tried on different chips. The shortest was 3 s and the longest 24 h. On some chips all the electrodes were anodized and on others there were electrodes left that were only exposed to the oxalic acid.

3.4 GALVANOSTATIC ANODIZATION

The Ivium potentiostat can also be operated in a galvanostatic mode, meaning it is set to force a constant current between the electrodes instead of applying a constant voltage. The electrodes on one chip were anodized in this way, with the current set to 0.3 μA , corresponding to a current density of 4 mA/cm^2 . The possibility of setting the current to a desired level would provide more control over the time needed for anodization of the entire aluminum layer than setting the voltage. Electrodes were anodized in 0.5 M oxalic acid.

3.5 ANODIZATION OF ALUMINUM FOIL

To test anodization on something else than the electrodes on the test chips a setup with a 30 μm thick aluminum foil (Universal) was prepared as shown in Figure 12. The foil is placed as a separator between two containers of 0.5 M oxalic acid. The two compartments each hold a platinum wire, one acting as the anode and the other as cathode. This setup includes the Agilent power supply and the Keithley multimeter.

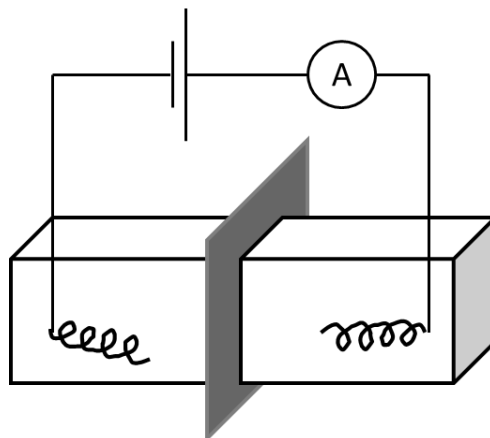


Figure 12. Experimental setup for anodization of aluminum foil. The foil is placed as a separator between two oxalic acid containers, each holding a platinum wire electrode.

3.6 ANODIZATION IN NEAR-NEUTRAL ELECTROLYTE

To try to make a barrier type oxide layer the electrodes on one of the chips were anodized in a near-neutral electrolyte. The electrolyte used was 0.5 M sodium sulfate, prepared from anhydrous sodium sulfate (Fluka, >99% purity). The pH of the solution was 5.8. Anodization was performed with the Ivium potentiostat at 2 V and 1 V.

3.7 SEM PREPARATION AND IMAGING

Before SEM-investigation the chips were placed in 0.5 M phosphoric acid (prepared from 85% w/w phosphoric acid, Sigma-Aldrich) for 30 min for pore widening. The pH of the acid was 1.3. All chips were also sputtered with 5 nm of platinum (Polaron E5100 DC) to avoid charging of the surrounding SU-8 layer. For SEM imaging a Hitachi SU1510, operated at 5 kV, and a LEO 1560, operated at 5-10 kV, were used. Reference images were taken of a completely untreated chip and a chip only subjected to pore widening, not anodization. The light microscope used for imaging was Olympus BX40 equipped with an Edmund EO-5012C camera.

4 RESULTS

4.1 THE PHASES OF ANODIZATION

In total 57 individual electrodes on 22 chips were anodized potentiostatically in oxalic acid, six were anodized galvanostatically and six were anodized in the nearly neutral solution. Thus, the majority of the gathered data concerns potentiostatic anodization in oxalic acid. In this collection some common traits can be seen in the current-time curves. During the first seconds of anodization the current drops from a few μA to about $0.5\text{-}0.8\ \mu\text{A}$ where it stabilizes. About 30 s into the experiment the current drops to $0.1\text{-}0.3\ \mu\text{A}$. After the smaller drop the current is more or less stable until the experiment is terminated. Some of these curves are shown together in Figure 13a. About 42% of the examined electrodes showed this behavior, while 23% did not show the second drop but went directly for the stable level, see Figure 13b. The remaining electrodes behaved in somewhat different ways; some made a slight increase in current after the initial drop, while others did not show the initial drop at all. Two examples are shown in Figure 14.

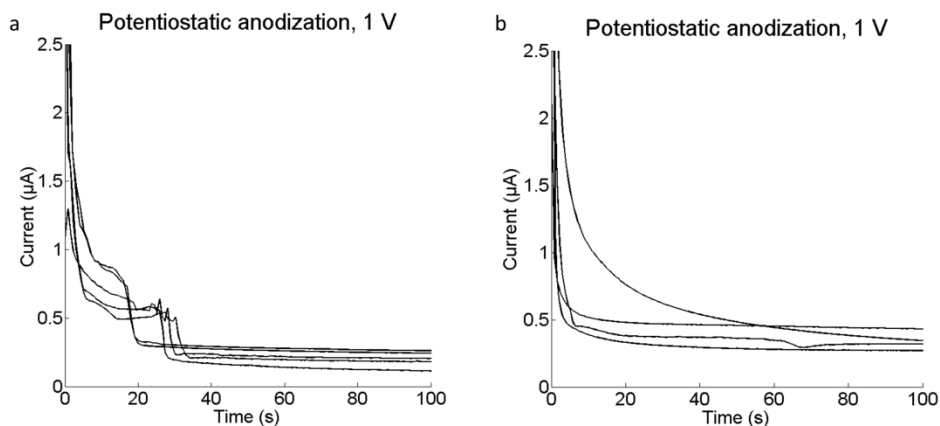


Figure 13. Examples of current-time curves obtained during anodization in $0.5\ \text{M}$ oxalic acid. For the first main curve type, the current stabilizes a while around before it continues to fall at about 20-4 s (a). For the other main type of behaviors the current drops to the final level without any initial stabilization (b).

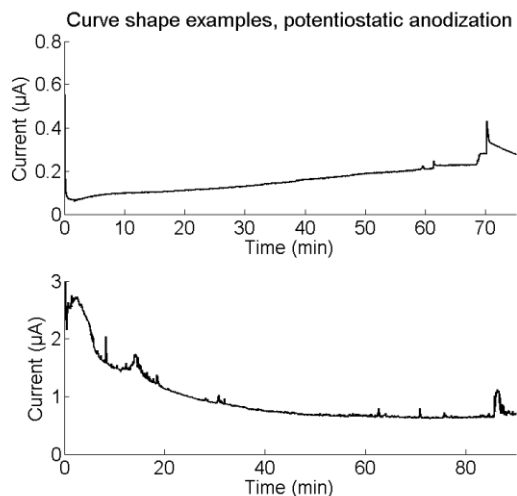


Figure 14. Current-time behavior not possible to categorize as one of the shown in Figure 13.

The galvanostatic anodization showed results corresponding to the potentiostatic. This means that the potential rises quickly and then finds a stable level. The curves for the six electrodes anodized galvanostatically are shown in Figure 15. They were all from the same chip and anodized directly after one another.

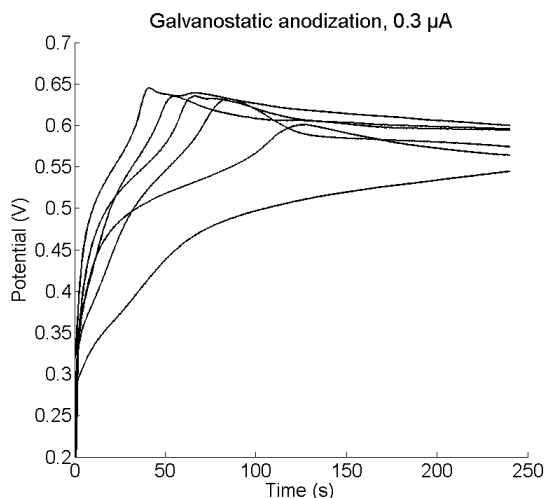


Figure 15. Voltage-time behavior for electrode anodized galvanostatically in 0.5 M oxalic acid.

Anodization performed at near-neutral conditions gave a current-time curve similar to the ones obtained in oxalic acid, but with a lower final current. Two of the curves are shown in Figure 16.

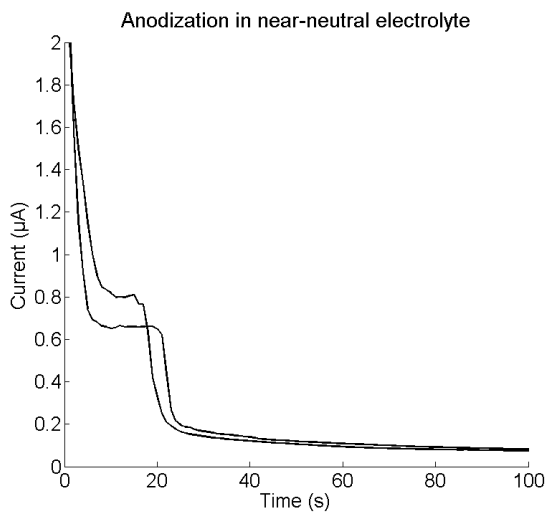


Figure 16. Anodization in near-neutral sodium sulfate solution. The anodizing potential is 1 V.

4.2 SURFACE STRUCTURES

The reference images of an untreated electrode and an electrode only subjected to pore widening are shown in Figure 17 and Figure 18, respectively. Figure 19 shows the surface of anodized aluminum foil, but no difference in surface structure was seen between the anodized and unanodized areas in this sample. The aluminum foil has been pore widened, but comparisons made with images of completely untreated foil show there are no differences between the two. Anodization of the foil was performed in 0.5 M oxalic acid at 5 V.

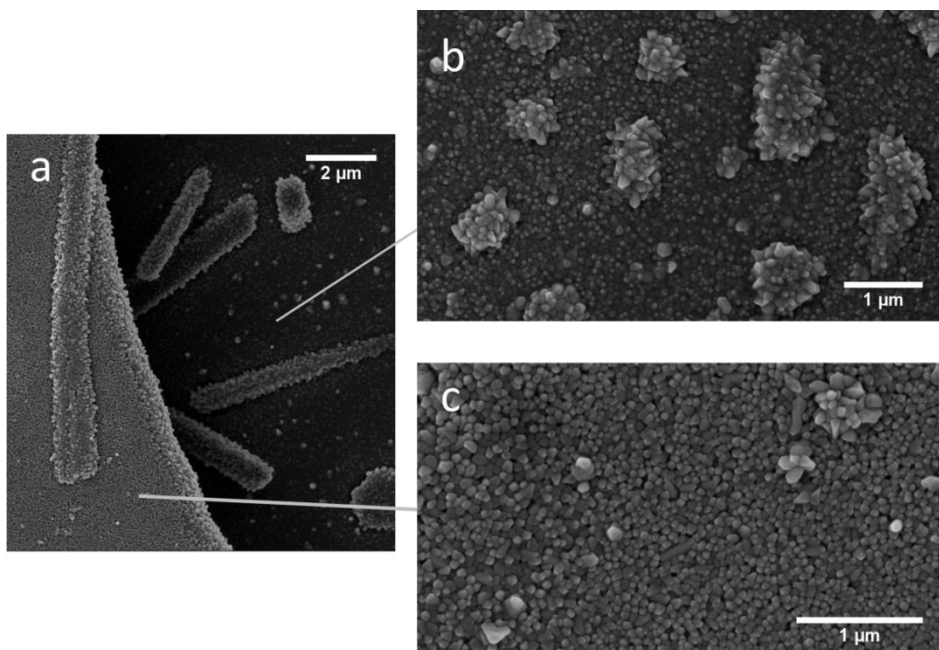


Figure 17. *Electrode that has not been anodized or pore widened. This electrode has still got the aluminum on top of the SU-8 (a). The grainy surface is seen on both the outer ring (c) and on the actual electrode surface (b). The collections of grains on the surface of the electrode are visible as black spots in a light microscope.*

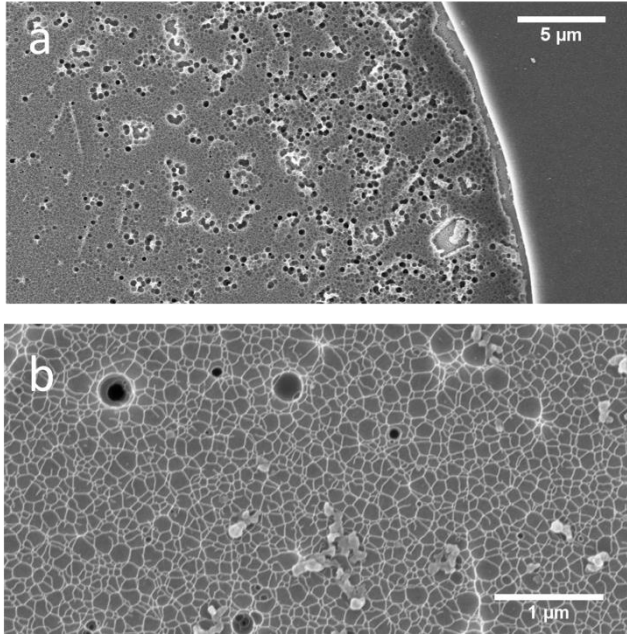


Figure 18. *Electrode that has only been pore widened. Structure near the edge (a) and in the middle (b).*

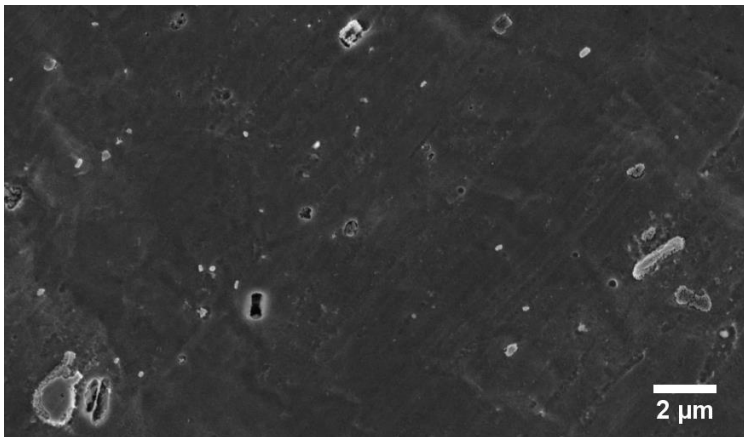


Figure 19. *Aluminum foil that has been anodized and pore widened. No difference was seen compared to the unanodized area, or completely untreated foil. The image shows the matte side of the foil.*

The surface structure of an electrode which has been anodized but not pore widened is similar to the surface of the completely untreated electrode. Figure 20 shows the surfaces of two electrodes on a chip which has been anodized but not pore widened. The anodization curves of the electrodes are also shown.

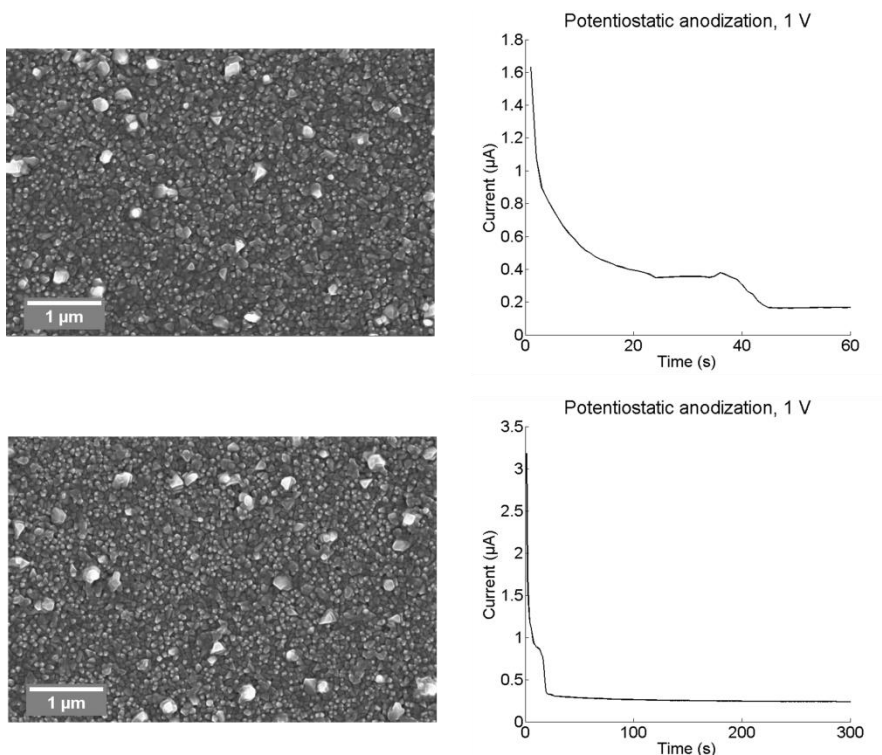


Figure 20. Surface structures and anodization curves for two electrodes that have been anodized potentiostatically but not pore widened.

The surface of the anodized electrodes looks rather different when they have gone through the pore widening process. The surfaces of anodized and pore widened electrodes are similar to the surfaces of electrodes which have only been pore widened. Figure 21 shows anodization curves for three electrodes anodized for different times and the resulting surfaces after pore widening. There seems to be no difference in structure between an electrode where anodization had merely started and one where anodization was terminated just after the second current drop. The same surface structure is also seen in an electrode where anodization continued for

30 minutes. Electrodes that were anodized in near-neutral electrolyte and pore widened expressed the same surface characteristics as the ones anodized in oxalic acid with subsequent pore widening step.

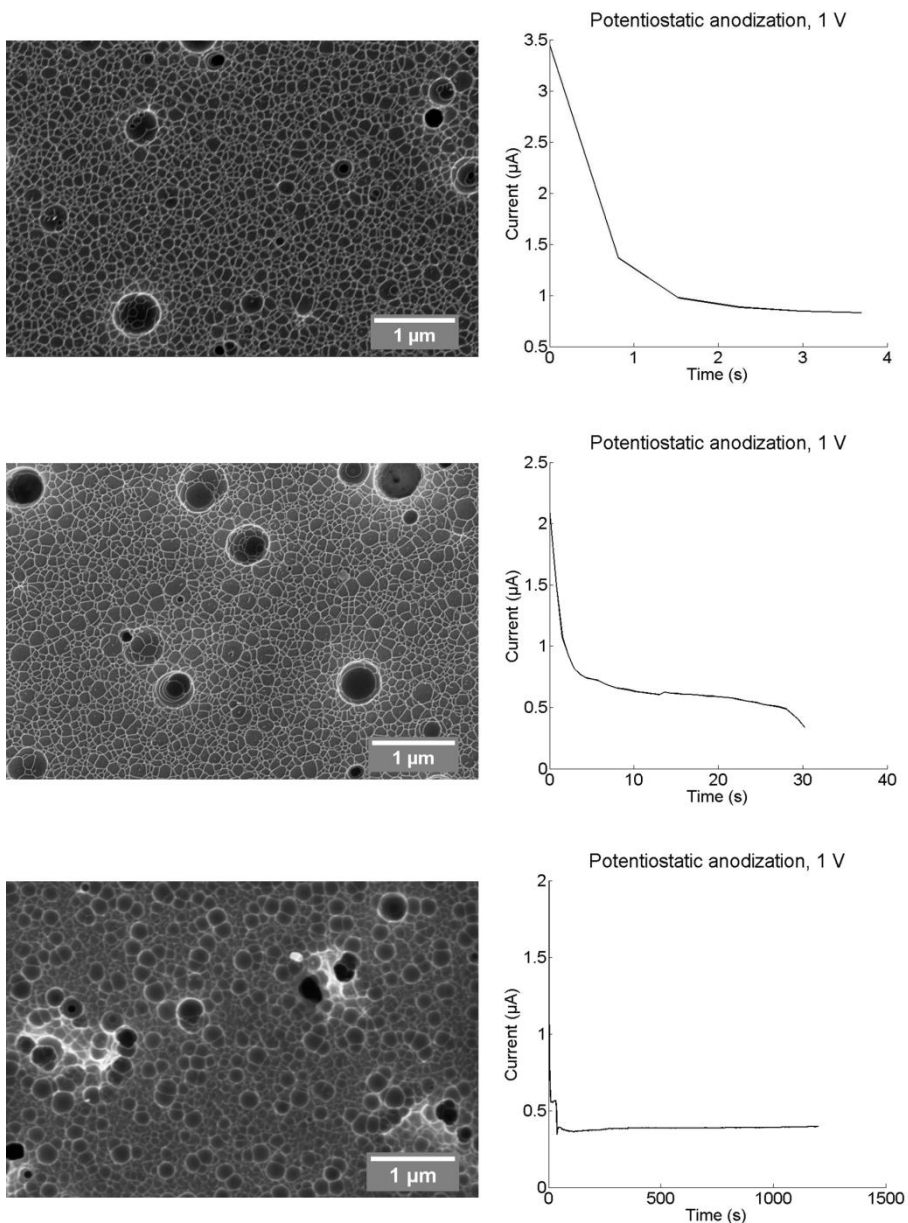


Figure 21. Surfaces and anodization curves for three electrodes anodized for 3.5, 30 and 1200 s respectively. The electrodes have been pore widened.

4.3 CHANGES IN COLOR

Some of the electrodes anodized for a little longer period, more than 30 minutes, demonstrated a change in color of the aluminum. The new colors ranged from light pink/red and pale purple to green and red ring patterns. Two examples of the colors and the corresponding current-time curves are shown in Figure 22 and Figure 23. Color changes were persistent over time. The electrode in Figure 22 has been pore widened.

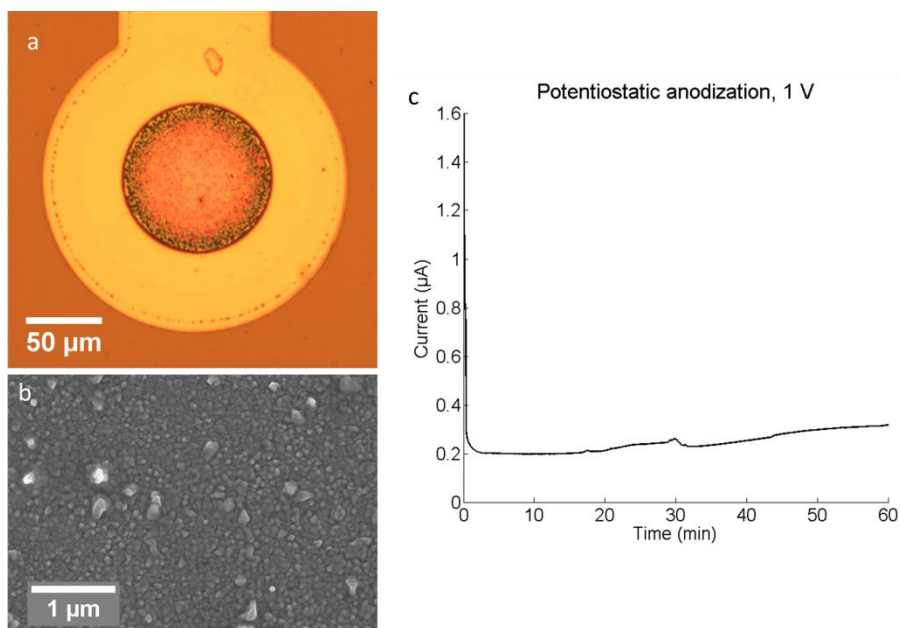


Figure 22. *Electrode turning pink during anodization (a). The electrode has been pore widened before SEM imaging. The image shows the surface in the middle of the electrode (b). Though not clearly visible in this figure, the current makes the characteristic drop after about 30 s (c).*

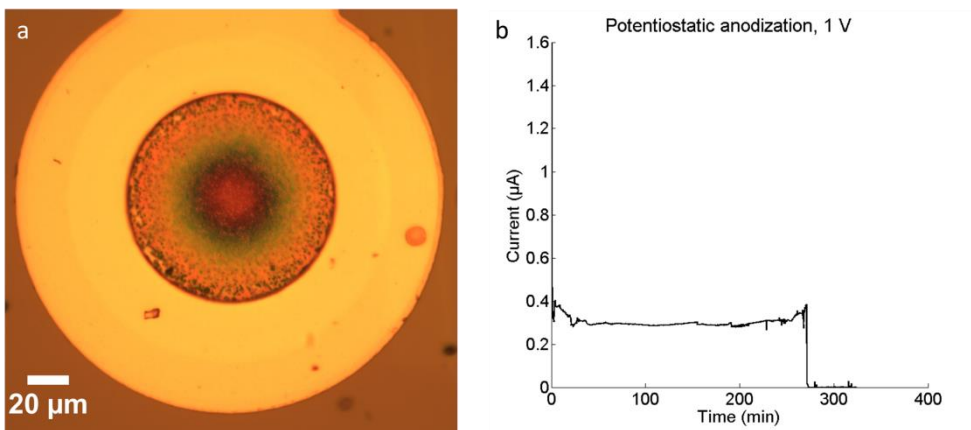


Figure 23. *Electrode turning red and green upon anodization (a). The acid dried out during the experiment and this caused the sudden drop in current (b). Unfortunately this particular electrode was damaged during the pore widening process.*

4.4 ELECTRODE DEGRADATION DUE TO PROLONGED EXPERIMENT TIME

While searching for indications that possible pores had penetrated the aluminum layer and moving to longer and longer anodization times it became obvious that the aluminum on the electrodes was in some way affected by the acid. Anodized electrodes and electrodes that had only been placed in the acid but not anodized showed changes when examined in a light microscope. The aluminum of untreated electrodes appeared white in the microscope while the electrodes subjected to acid had a more golden color. The color was not identical to the one of the rest of the gold visible from underneath the SU-8, but had a greyish dustiness to it. These changes have not been seen to happen gradually, either the aluminum is white or the surface color looks like grey and dusty gold. Some of the aluminum layers have also been affected during rinsing or pore widening, meaning the change happened in only a few minutes (in the rinsing case) and not always in oxalic acid. These circumstances indicate that the entire aluminum layer or parts of it has loosened from the gold and drifted off, rather than that the aluminum has been gradually dissolved into the acid. Some electrodes showed these changes after six hours, while others could last longer.

4.5 EFFECTS OF ANODIZATION COMBINED WITH LONG-TERM ACID EXPOSURE

On chips where the white luster of aluminum has been lost there are differences in the surface structures of anodized and unanodized electrodes. Figure 24 shows gold from the contact area of two chips, one that was completely untreated and one that has gone through the pore widening procedure. Neither one of them has been anodized. Figure 25 shows an electrode that has been anodized for 24 h. The electrode in Figure 26 has not been anodized, but has been submerged into the oxalic acid for 3 days. These two electrodes have been pore widened.

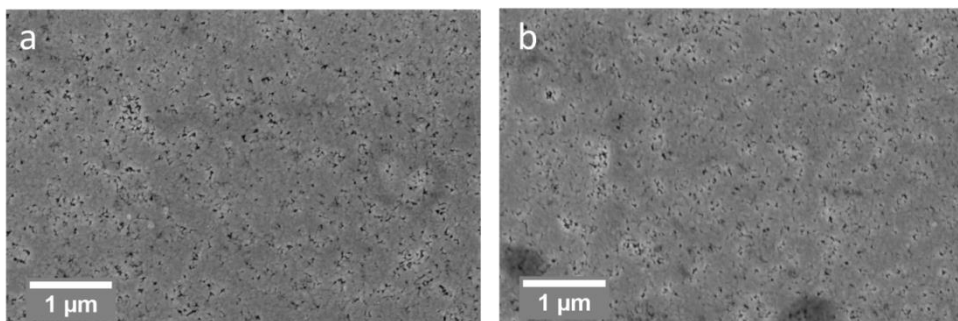


Figure 24. Surface structures of the gold at the contact area, untreated (a) and exposed to 0.5 M phosphoric acid for 30 min. (pore widening treatment) (b).

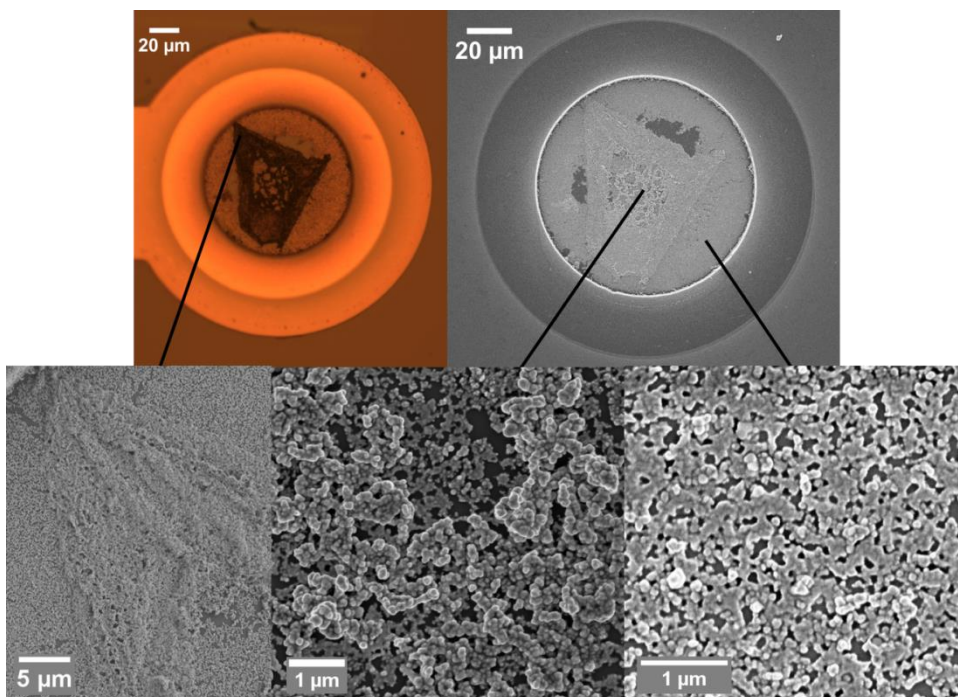


Figure 25. *Electrode anodized for 24 h in 0.5 M oxalic acid.*

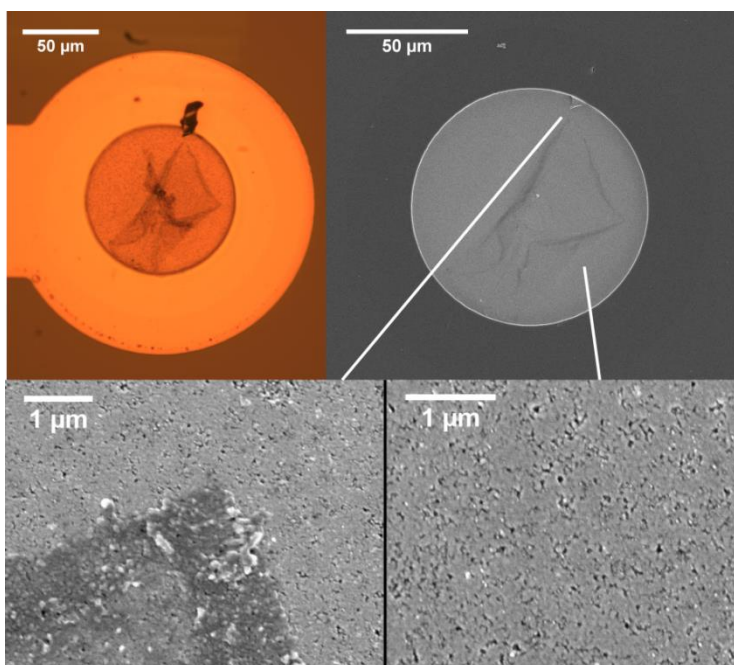


Figure 26. *Electrode that has not been anodized but treated with 0.5 M oxalic acid for 3 days.*

4.6 DAMAGES WHEN USING HIGH ANODIZING POTENTIALS

During experimenting it very soon became clear that high anodization potentials and currents can damage the electrodes. Different potentials were tried and even as low as 1.5 V causes substantial damage to the electrode. A common sight among the damaged electrodes is a hole where the gold and aluminum used to be. Three examples of this are shown in Figure 27. Prolonged treatment at high voltages caused even more severe damage to the gold conductor. Anodization at 1 V did not at all cause these kinds of damages.

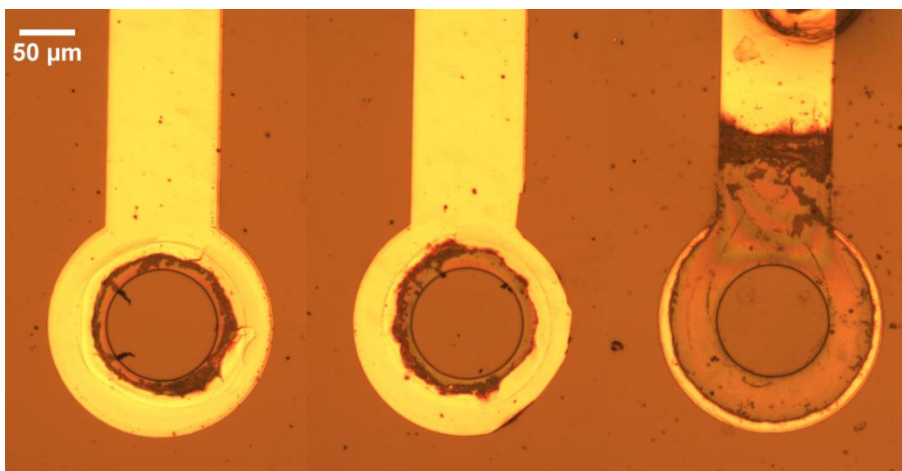


Figure 27. Three electrodes anodized at high potentials. From the left: Anodization at 5 V for 20 s, 10 V for 20s and 20 V for 12 min. The circles in the middles are the edges of the SU-8 layers.

5 DISCUSSION

SEM investigations of the evaporated aluminum layer showed a grainy surface structure. This was not the case for the surface of the aluminum foil, which was more even. The grains could be part of the explanation to why the aluminum layer seems to drift off when electrodes are exposed to oxalic acid for an extended time period. As seen in Figure 17 the grains are present on the aluminum covering gold as well as SU-8. This indicates that the grains are not a consequence of a lattice mismatch between gold and aluminum. Pore widening seems to even the aluminum surfaces but the pattern appearing as a white net, seen in Figure 18, is probably the boundaries in between the grains. These boundaries are also visible in the edges of holes in the aluminum layer after pore widening, indicating that the grainy structure goes deeper than the surface. During fabrication the wafer was transferred to another building to perform the aluminum evaporation and it is possible that an oxygen plasma treatment just prior to evaporation could have given a better surface for the aluminum to grow. Since a high aspect ratio is desired for the final application the aluminum layer was made thick and at a high growth rate. The high growth rate, and the high temperature required to achieve it, may also be part of the explanation behind the non-uniform layer. A too high growth rate would mean there is not enough time for diffusion to a lattice point before new material arrives to the surface and builds up.

The surface structures of aluminum on untreated electrodes (Figure 17) is similar to the ones seen on electrodes which have only been anodized, but not pore widened (Figure 20). The surface structure changes when electrodes are pore widened, and the surface structure seems to be independent of anodization in this case as well, compare Figure 18 and Figure 21. This clearly indicates that the aluminum has not been affected in the desired way by the anodization. It is likely that the anodizing potential has been too low to push the ions through the oxide layer. As mentioned in section 2.1.2 the barrier oxide thickness is 1.4 nm/V. This means that for each 1.4 nm of oxide 1 V is needed to push ions through, and probably the native oxide layer on the aluminum already exceeds 1.4 nm. The anodizing potentials have not been higher than 1 V due to the damages done to the electrodes when exceeding this value. Still, there is a drop in current during

the first seconds of potentiostatic anodization (Figure 13) indicating an increasing resistance. It is possible that there is some growth of oxide on the aluminum despite the low anodizing potential, or there are other processes taking place in the electrode or the acid altering the total resistance. The corresponding resistance change is also seen during galvanostatic anodization, Figure 15. The current-time curves for potentiostatic anodization in near-neutral electrolyte is also similar to the ones obtained when anodizing in oxalic acid. When comparing with theory the expected differences would be a higher final current in the case with anodization performed in oxalic acid due to a thinner barrier oxide layer at the bottom of the pores, allowing for a higher current, and a slight increase in current before reaching this stable level. The increasing current is assigned to the increasing surface area during pore formation, something that has not happened during these experiments. With the grainy surface of the electrodes used here an increase in current would probably not be seen even if there were formation of pores, since the surface is already large and uneven and pores would probably form in between the grains. In the near-neutral case the current is a little lower, but still on the same order of magnitude. The difference could be caused by properties of the electrodes on this particular chip or be an effect of the electrolyte, but it is probably not an effect of the aluminum structure.

Changes in color seen in electrodes anodized for longer periods of time indicate that something happens with the material. The changes could be the result of light interference caused by two or more layers with different refractive index. Colors shifting with the anodizing time would then suggest that the thickness of at least one of these layers is changing, or that there is a change in refractive index. This would mean that there is a process going on in the electrode throughout the experiment. Since the colors seem to change with different anodizing times this process does not stop after the initial drop in current, as would be the case if only a barrier type oxide layer is formed since the thickness of barrier type oxide layers is determined solely by the anodizing potential. Without cross-sectional images of the electrodes it is difficult to determine what has happened during anodization. To obtain a good cross sectional image the electrodes need to be split into two pieces, which has proven difficult using this chip design. Dicing the chip is not an option since this would grind and destroy

the structures of interest. Some attempts were made at cutting a small portion of the chip along the gold conductor using diagonal cutting pliers, hoping the electrode would split, but when the crack reached the electrode it made a turn around the aluminum. An alternative would have been to use a manual scribe, but it is unclear whether the silicon would have been enough affected by this to break along the intended line since it is protected by the SU-8 layer. If further studies were to be made to realize this fabrication technique it might be worth the effort to re-design the devices to open up for cross sectional views. On the other hand, it is not desirable to move too far from the final design since the process may have different outcome based on the device structure. One solution could be to use an elongated electrode which would be easier to break straight across. Lines aiding the aiming could also be incorporated and made together with the gold structures. It will then become important to pay attention to the crystal orientation of the silicon wafer used.

Due to the poor quality of the aluminum layer the option to achieve surface enlargement with PEDOT deposited in a porous anodic alumina layer cannot be ruled out completely. Further experiments would require a more homogenous aluminum layer and preferably more robust electrodes to enable use of higher anodizing potentials. If this cannot be achieved it is not likely that the method will prove successful. The damages done to the electrodes at high anodizing potentials are caused by the current rather than the potential and electrodes based on the same design have in previous experiments been able to withstand higher currents than the electrodes used during these experiments have. It is possible that these chips were of inferior quality, due to poor adhesion of gold to the substrate or impurities. As seen in Figure 24 the gold in the contact area has some holes and has not formed a smooth layer, and this is seen for gold that has not been exposed to any acids, as well as for gold that has been exposed.

Another option for surface enlargement on the electrodes has presented itself during this work. Rather than placing polymer wires on top of the gold surface it may be possible to modify the gold surface itself. The structure of the material in Figure 25, where a potential has been applied, is different from the one in Figure 26. Assuming this material to be gold, exposed when the aluminum layer has drifted off, it is possible that the

gold has been anodized. Anodization of gold has been performed by Nishio and Masuda and they report on a nanoporous material formed by anodization of gold in oxalic acid.[25] In their work they used a variable potential reaching 1.8 V at most. This porous material consists solely of pure gold and thus it differs from anodic alumina, which is an oxide structure. Not very much has been published about this porous gold apart from Nishio and Masuda's study but it is not unlikely that the properties of the porous material can be influenced by the processing parameters, such as temperature, pH, time and anodizing potential. The mechanical and electrical properties must also be investigated before use on the actual electrodes.

6 CONCLUSIONS AND FUTURE WORK

Attempts to anodize aluminum in 0.5 M oxalic acid have been made. The electrodes used have shown a grainy aluminum surface structure and this has probably reduced the resistance to the acid, causing the aluminum layer to drift off when electrodes have been exposed to oxalic acid for extended periods of time. Pore widening in 0.5 M phosphoric acid has altered the surface structure, and pore widened electrodes tend to show the same surface characteristics, whether they have been anodized or not. Correspondingly, an electrode which has been anodized but not pore widened shows the same surface characteristics as does a completely untreated electrode. From these observations it is possible to draw the conclusion that the anodization has not been successful. Probably there is a need for a higher anodizing potential to induce necessary ion movements, but it has not been possible to go above 1 V, since this damages the electrodes.

With a more homogenous aluminum layer it may be possible to fabricate a porous alumina membrane to use as scaffold for electrodeposition of PEDOT. Due to the poor quality of the evaporated aluminum layer the anodization technique cannot be fully disregarded.

Electrodes where the aluminum seems to have drifted off showed different surface characteristics depending on whether the electrodes had been anodized or not. It is possible that the anodization has altered the surface of the gold. Another option for increasing the surface area is thus to use anodization of the gold electrode to form a porous film. This would be a procedure with fewer processing steps than the suggested electrodeposition of PEDOT in a porous membrane, which is attractive. The effect of processing parameters and the mechanical as well as electrical properties of the resulting film need to be investigated further.

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