

STUDY OF NANOPOROUS ALUMINA MEMBRANES BY ELECTROCHEMICAL METHOD

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Abstract

Nanoporous alumina is useful material for development of electrochemical sensors including filtration, molecule sorting and subsequent detection. Big advantage of alumina is possibility to reliably control size of nanopores and membrane thickness. For sensorial utilization, it is necessary to know diffusion properties of membranes and their permeability of various substances. Therefore, membranes with different pore diameter and thickness were prepared by two step anodization and modified by deposition of gold layers which serve as electrodes. Thereafter, their influence on changes of electrochemical impedance spectra was studied and compared in dependency on membrane morphology.

Keywords: Nanoporous membrane, anodization, alumina, gold layer, diffusion, electrochemical impedance spectroscopy

1. INTRODUCTION

Nanostructured membranes find application in many branches as catalysis, fuel cells, optics, electronics, fabrication of nanomaterials, filtering and purification purposes and especially sensorial applications [1-4]. Anodic oxidation is well established process and alumina membranes are widely used in construction of biosensors due to relatively low cost production, advantageous properties and excellent reproducibility. The most useful properties of anodic alumina are chemical stability, inertness, insolubility, high surface area and self-assembled highly ordered hexagonal arrangement. Nanoporous alumina contains nanopores with controllable diameter in range 10 - 200 nm and thickness in micrometers [2]. Nanopores in alumina are uniform, parallel and perpendicular to the surface of membrane [5, 6]. Many types of sensors containing alumina are based on attaching of substances in nanopores and subsequent detection of pore blockage by electrochemical impedance spectroscopy [7]. For these purposes, nanopores are often modified by various biomolecules e.g. DNA probes, antibodies, oligonucleotides etc. [8-11]. Membranes are also covered by thin layers of metals which are used for attaching of molecules (gold) [12]. Metal layers deposited on the membrane also serve as sensing electrode utilized for electrochemical detection of substances [13] or electrodes for detection of blockage of nanopores in the case of both sides coverage. Generally, membranes are modified by metals using thermal evaporation and sputtering methods. Unfortunately, the upper metal layer negatively affects diameter of nanopores and their permeability. Thicker layer even block nanopores completely. Despite of this problem, metal layer have to be sufficiently conductive to serve as electrode. Therefore, it is necessary to find optimal ratio between diameter of nanopores and thickness of metal layer. In this study, we covered alumina membranes by thin gold layer and observed changes in nanopores diameters. Changes in impedance spectra between electrodes separated by alumina membrane before and after gold covering were also investigated. Kipke at al. studied similarly changes in impedance spectra in dependency on various membrane thickness and variable pore diameters [14].

2. MATERIALS AND METHODS

Nanoporous alumina fabrication

Nanoporous alumina membranes were fabricated by two step anodization method (**Fig. 1**) of pure aluminium foil (99.0 %, Goodfellow, UK). The resulted morphology of membrane is dependent on set up of experimental conditions. Thickness of resulted membrane is dependent on time of the second anodization and thickness of anodized aluminium foil. Diameter of nanopores is controlled by type of acidic electrolyte such as applied voltage, time of anodization and temperature of solution.

At the beginning, aluminium foil was rinsed in acetone and then in demineralized water for degreasing of surface. The first anodization was performed in 0.3 M oxalic acid (COOH_2) under the anodization voltage of 40 V or 60 V. Electrolyte solutions were tempered to a 5°C and stirred because anodization is highly exothermic process. The first anodization lasted 3 hours to substitute electrochemical polishing which is considerably problematic in the case of large scaled samples. The nanoporous alumina created during the first anodization was etched away in mixture of phosphoric acid (H_3PO_4) and chromium trioxide (CrO_3) because alumina obtained during this step is highly disordered and non-perpendicular to the surface. The aluminium sample with residual dimples after the first anodization was obtained. The second anodization was done under the same conditions as the first step and the time of process took 15 hours in all cases. The time of process is important for thickness of final membrane. The subsequent step was etching of non-anodized aluminium in mixture of chloric acid (HCl), copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). The last part of fabrication was etching of barrier layer at the bottom of nanopores and the opening of nanopores. The homogeneity and morphology of fabricated alumina membrane were evaluated by scanning electron microscope (Tescan MIRA II, CZ).

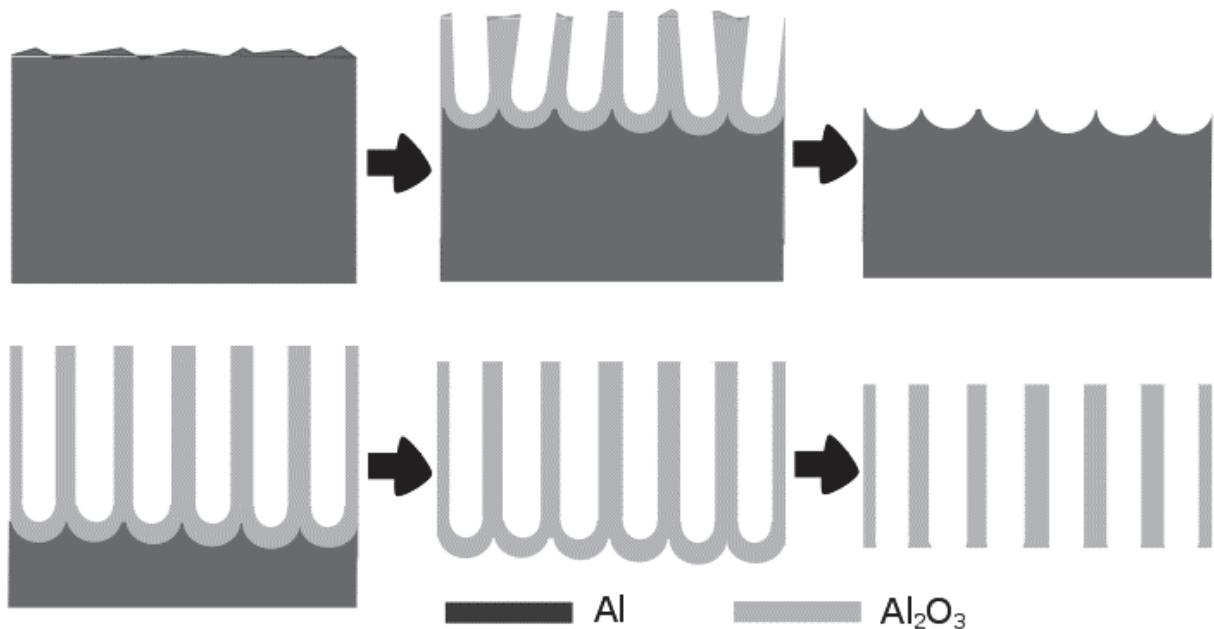


Fig. 1 Fabrication process of nanoporous alumina membranes

In subsequent step, part of fabricated alumina membranes were coated with thin gold layers with thickness of 25 nm on the both sides of membrane by ion beam sputtering method. Nickel chromium layer with thickness of 5 nm were used as adhesion layer. The gold modified membranes were contacted by wires on the both sides for possibility to engage gold layers in measurements as electrodes. All types of membranes were placed into homemade Teflon potting cell and potted using acrylic resin ViaFix (Struers) to define the area of membrane 5 mm in diameter. In this way, four types of alumina membranes were obtained (two pure alumina membranes and two membranes modified by gold).

Measurements

The measurements were performed using µAUTOLAB III/FRA2 in connection with NOVA 1.10. software (Metrohm Autolab, NL). Three-electrode cell with Pt auxiliary electrode and Ag/AgCl/3M KCl reference electrode and glassy carbon working electrode (all Metrohm AG, CH) were used for experiments. In the second part of study, gold layers on the both sides of membranes were used as working electrodes. The impedance spectroscopy was measured in a frequency range from 500 kHz to 0.1 Hz and amplitude of 20 mV. Electrochemical characterization of membranes was done in 0.1 M potassium chloride (KCl) solution. The sample was placed into home-made diffusion cell which consists of two beakers separated by nanoporous alumina membrane.

3. RESULTS AND DISCUSSION

Two types of nanoporous alumina membranes were successfully made by two step electrochemical anodic oxidation under the similar experimental conditions. In this way, membranes with various pore diameters have been obtained (**Fig. 2**). Part of fabricated membranes were covered by thin gold layers on the both sides, contacted by wires and potted into acrylic resin to define reproducible area of samples. The dimensions of samples, thickness of gold layers and anodization conditions are listed in the table below (**Table 1**).

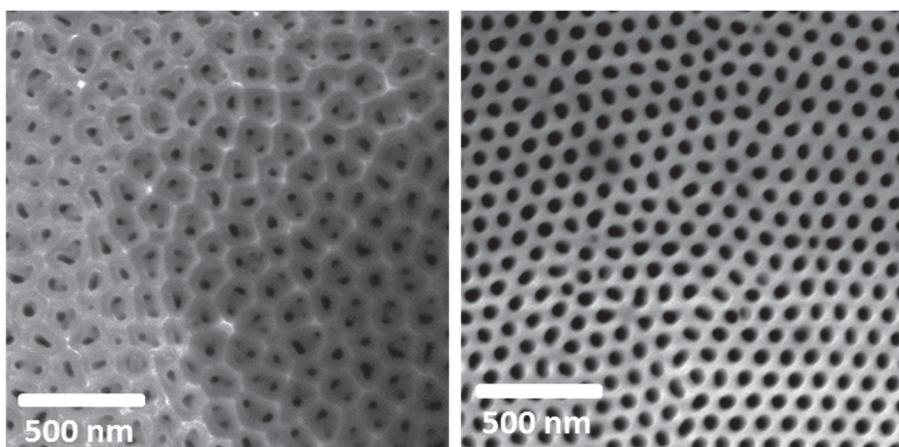


Fig. 2 Fabricated alumina membranes: sample 1 (left) and sample 2 (right)

Table 1 Dimensions of prepared membranes and fabrication conditions

	Anodization	Pore diameter	Pore length	Modification
Sample 1	(COOH) ₂ , 40 V	40 nm	75 µm	-
Sample 2	(COOH) ₂ , 60 V	70 nm	75 µm	-
Sample 3	(COOH) ₂ , 40 V	40 nm	75 µm	5 nm NiCr/25 nm Au
Sample 4	(COOH) ₂ , 60 V	70 nm	75 µm	5 nm NiCr/25 nm Au

Measurements were performed in the cell consisting of two beakers with 0.1 M potassium chloride separated by alumina membrane in various electrode arrangements. Initially, efficiency of nanopores filling by electrolyte was evaluated. Despite of fact that anodic alumina is hydrophilic material several tests of nanopores filling by electrolyte were made before impedance characterization. It was very important to determine ability of solution to penetrate into nanopores. Impedance measurements were performed three times in one week intervals. The first measurements were carried out immediately after placing into the diffusion cell and rinsing into the electrolyte. The next measurements were performed after one and two weeks dipping. The differences were not observed in these time-dependent measurements. The influence of application of high voltage (600 V) on electrodes placed on the both sides of membrane was also tried. It was expected better filling of nanopores by

electrolyte after high voltage application. However, no changes in impedance measurements were observed. Therefore, excellent fulfilment of nanopores was considered.

A several type of electrodes arrangements considering to the membrane were suggested. Firstly, three standard electrodes were placed on the one side of membrane and changes in measured impedance spectra were observed when working and reference electrodes were separated by alumina membrane (**Fig. 3**). In all measurements, alumina membranes caused slight increasing of impedance values especially in the field of local maxima of impedance curve when the electrodes are separated by alumina membranes. Increasing is larger in the cases of sample 1 and sample 3 as a result of smaller nanopores in membrane. It is obvious; change is most evident at high frequencies of impedance spectra while the diffusion part of impedance is unchanged.

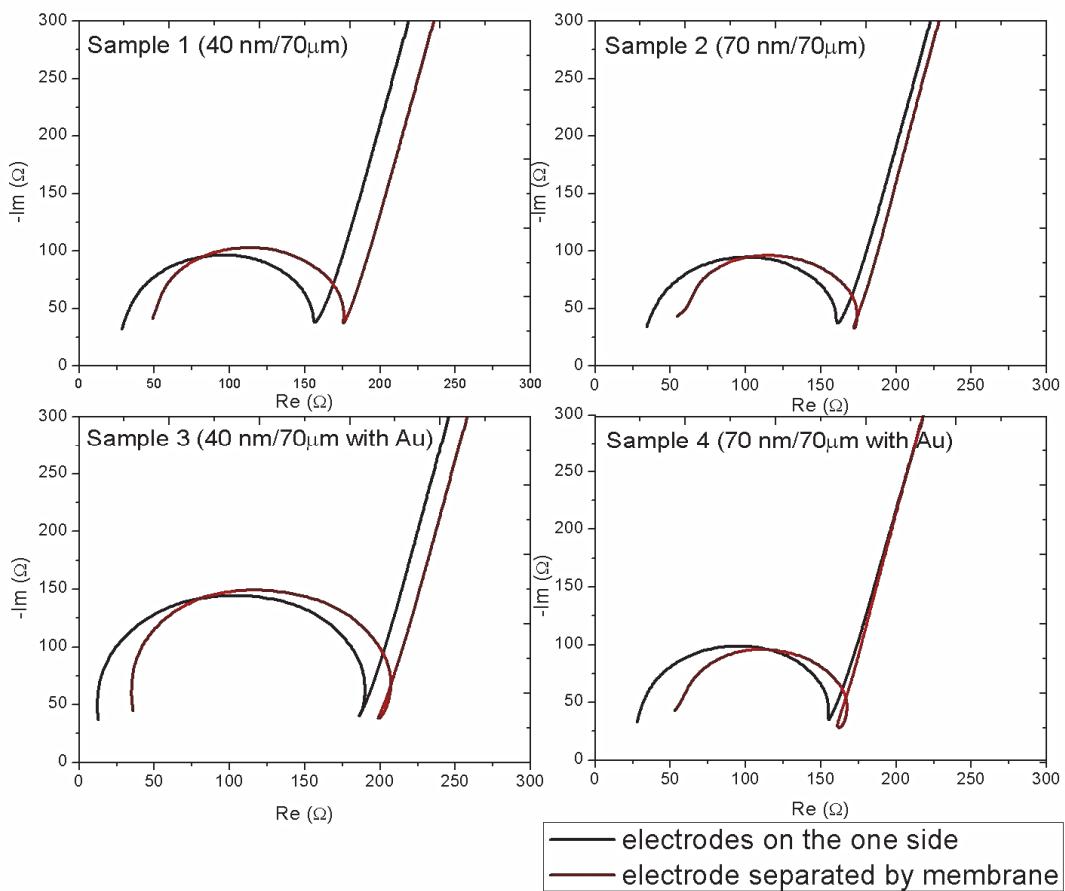


Fig. 3 Detail of impedance measurements with standard commercial electrodes

Analogical experiments were performed in the next part. However, standard commercial working electrode was replaced by thin gold layer deposited on the membrane (**Fig. 4**). Moreover, in this case increasing of impedance values in the part of local maxima (charge transfer resistance) is a more significant and achieved hundreds of ohms. Differences are again significantly greater in the case of sample 3. Nanopores in sample 3 are more blocked by deposited gold layer because initial size of nanopores was smaller (40 nm in diameter). Generally, electrodes deposited on the membranes have substantially higher impedance than standard electrode (area of electrode considered) because electrode is formed by thin gold layer.

All measurements were performed on three samples of one type and reproducibility of measurement was good. All measurements were performed three times.

Differences between impedance spectra for individual membranes were also compared. Unfortunately, the impedance changes are very small in the first part of study (using standard electrodes).

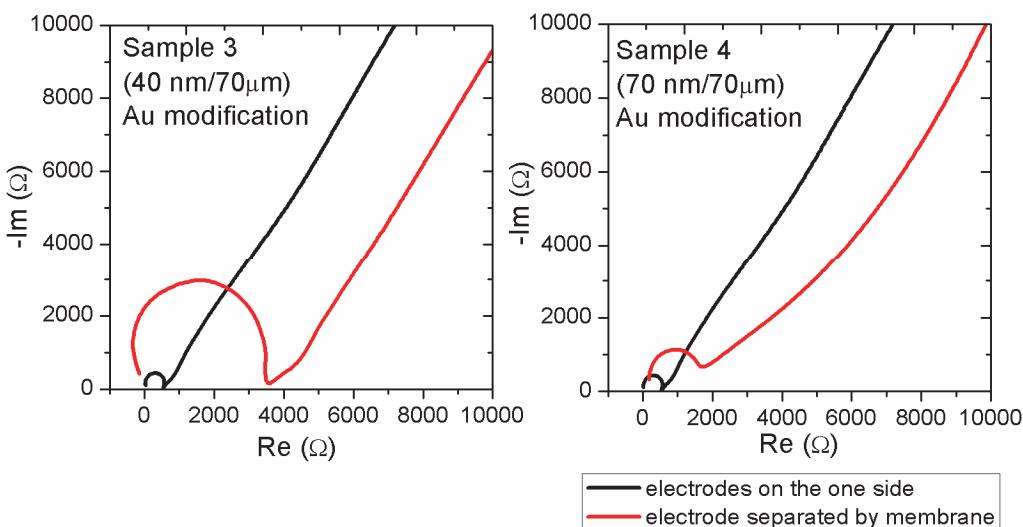


Fig. 4 Detail of impedance measurements involving gold layer deposited on membrane as working electrodes

4. CONCLUSION

Two types of nanoporous alumina membranes with different morphology were made by two-step anodization method and characterized by scanning electron microscopy. Subsequently, part of fabricated membranes was modified by deposition of thin gold layers on the both sides. Deposited layers were designed to serve as electrodes for future detection of substances in nanopores. The influence of placing of alumina membrane between working and counter electrodes on impedance measurement was observed. Electrodes placed on membrane surface were also involved in measurements and proved bigger changes in impedance spectra. These electrodes unfortunately had higher impedance values because are form by thin layer of metal. It is obvious, thicker layer has better conductivity but cause more blocked nanopores. In the future studies, optimal ratio in nanopores size and thickness of deposited layers will be investigated.

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REFERENCES

- [1] BOSS, C., et al. Size-selective diffusion in nanoporous alumina membranes for a glucose affinity sensor, *Journal of Membrane Science*, 2012, 401, p. 217-221.
- [2] STROEVE, P. and ILERI, N. Biotechnical and other applications of nanoporous membranes, *Trends in Biotechnology*, 2011, 29, p. 259-266.
- [3] HRDY, R., et al. Electrochemical Impedance Spectroscopy Behaviour of Guanine on Nanostructured Planar Electrode, *International Journal of Electrochemical Science*, 2013, 8, p. 4384-4396.
- [4] KYNCLOVA, H., et al. Nanostructured Surface Effect of Electrode on Doxorubicin Determination. In BABU, A.S., Mechanical Design and Power Engineering, Pts 1 and 2, 2014, vol. 490-491. Stafa-Zurich: Trans Tech Publications Ltd, pp. 262-266.
- [5] POINERN, G.E.J., et al. Progress in Nano-Engineered Anodic Aluminium Oxide Membrane Development, *Materials*, 2011, 4, p. 487-526.
- [6] TRECCANI, L., et al. Functionalized ceramics for biomedical, biotechnological and environmental applications, *Acta Biomaterialia*, 2013, 9, p. 7115-7150.

- [7] DENG, J.J. and TOH, C.S. Impedimetric DNA Biosensor Based on a Nanoporous Alumina Membrane for the Detection of the Specific Oligonucleotide Sequence of Dengue Virus, *Sensors*, 2013, 13, p. 7774-7785.
- [8] PEH, A.E.K. and LI, S.F.Y. Dengue virus detection using impedance measured across nanoporous alumina membrane, *Biosensors & Bioelectronics*, 2013, 42, p. 391-396.
- [9] DE LA ESCOSURA-MUNIZ, A., et al. Nanochannels for diagnostic of thrombin-related diseases in human blood, *Biosensors & Bioelectronics*, 2013, 40, p. 24-31.
- [10] KOH, G., et al. Development of a membrane-based electrochemical immunosensor, *Electrochimica Acta*, 2007, 53, p. 803-810.
- [11] RAI, V., et al. Electrochemical nanoporous alumina membrane-based label-free DNA biosensor for the detection of Legionella sp, *Talanta*, 2012, 98, p. 112-117.
- [12] LIN, K.C., et al. Biogenic nanoporous silica-based sensor for enhanced electrochemical detection of cardiovascular biomarkers proteins, *Biosensors & Bioelectronics*, 2010, 25, p. 2336-2342.
- [13] CHEOW, P.-S., et al. Transport and separation of proteins across platinum-coated nanoporous alumina membranes, *Electrochimica Acta*, 2008, 53, p. 4669-4673.
- [14] KIPKE, S. and SCHMID, G. Nanoporous alumina membranes as diffusion controlling systems, *Advanced Functional Materials*, 2004, 14, p. 1184-1188.