Formation of ordered nanoscale capillary membranes based on anodic alumina

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Abstract. Membranes of nanoporous aluminum oxide (alumina) have been obtained using the electrochemical etching technique under varying technological regimes. The basic geometrical parameters including the thickness of the membrane, the average pore size, and the pore size distribution were determined by measuring the ultraviolet-infrared transmittance spectrum. The process of the charged particles transmission through nanoporous alumina membranes with a pore diameter of about 20 nm was studied.

1. Introduction
Currently, the methods of creating nanostructured materials using processes of formation and self-formation are being actively developed [1–4]. One of such materials interesting from a practical point of view is the porous anodic alumina. Membranes based on nanoporous alumina are required in nanotechnology, microbiology, and nuclear physics, because they have unique properties, such as mechanical strength, thermal stability, and chemical resistance.

To form oxide structures based on Si, Al, Ti, and other materials the electrochemical anodization is commonly used. This process is characterized by the availability, as well as the compatibility with the traditional process of micro- and nanoelectronics. However, the electrochemical method of forming micro- and nano-porous alumina most often presented in the literature is realized in thin aluminum films (~1 μm). These films are deposited onto the surface of a foreign substrate. The obtained structures are characterized by a large variance in pore size and a nonuniform pore distribution on the surface. The complexity and, in some cases, the impossibility to separate such porous anodic films from substrates limits the possibility of their use as free membranes (masks, matrices) with the required geometrical parameters of the pores.

Thus, formation of mechanically strong membranes based on porous alumina with ordered capillary structure on micro- and nano-scale in a thin (~10 μm) aluminum foil is the actual problem.

The main peculiarity of the proposed method is using the thin aluminum foil as an initial substrate for the formation of the autofixed porous alumina membrane. In this case the whole foil is anodized and an additional complex process of the separation of a membrane from a substrate leading to a membrane degradation is not required.

2. Experiment
A well-known mechanism of the ordered honeycomb por-Al₂O₃ formation [1, 5] was taken as a basis in the present work. The main reason for the forces arising between cells is a mechanical stress associated with an increase in alumina volume. The alumina volume expansion can occur only vertically. As a result, the new layer is formed on the pores bottom at the boundary between the aluminum and the oxide layer. Due to this, variations of the voltage and the electrolyte type allow one
to increase the aluminum oxide volume by 1.2–1.4 times. The basis for the pore formation effect and subsequent growth of pores is a balance between the electrochemical processes of the local growth and dissolution of aluminum oxide taking place simultaneously on the pore bottom.

In order to obtain a porous anodic alumina membrane [6] the electrochemical anodization of aluminum foil (40 μm) was applied in a potentiostatic mode in electrolytes based on aqueous solutions of phosphoric (H₃PO₄) and sulfuric (H₂SO₄) acids for 10–60 min at temperatures from 0 to 15°C. When using electrolytes with different acidities, the speeds of an anions introduction into the porous layer are different. This effect determines the voltage of the pore formation process and consequently the pore diameter. The anodizing voltage was within the range of 15-30 V (for H₂SO₄) or 130-160 V (for H₃PO₄) depending on the electrolyte type.

The basic structural parameters, such as the pore diameters \( a \) (see figure 1), the distances between pores \( b \), the thickness of the porous layer \( c \) and the barrier layer \( d \) of the obtained samples were studied using the scanning electron microscopy (SEM) at low accelerating voltages (10–20 kV) under high vacuum, that allowed us to study the insulating samples without a prior metal deposition.

**Figure 1.** SEM and schematic images of the por-Al₂O₃ membranes.

**Figure 2.** SEM images of the por-Al₂O₃ membranes obtained in an electrolyte based on solutions of H₃PO₄.
The SEM images of the membranes used in the experiments are shown in figure 2. When the electrolyte based on sulfuric acid is used, the membranes have a thickness of 12–18 μm, the average pore diameter is 20 nm, the barrier layer has a thickness of ≈ 200 nm, and the pore concentration is 350 μm⁻². The membranes formed in orthophosphoric acid have the following geometrical parameters: the average pore diameter is 80 nm, the layer thickness is 4–7 μm, the barrier layer thickness is ≈ 200 nm, and the pore concentration is ≈ 50 μm⁻². The barrier layers exist in all samples, but they are not etched since high-energy beams were employed in the experiments.

For studying the membranes using the Rutherford backscattering (RBS) and channelling the integral yield of the backscattered ions was measured with the step of 0.1°. The optical transmission measurements were performed using a PE-5400UV spectrophotometer (LLC “Ekohim”) in the wavelength range of 190–1000 nm.

3. Results and discussion

The study of the optical transmission spectra have showed that for any membrane the transmission spectra have a similar form [7]: the membrane starts to pass radiation at a certain wavelength. A comparison of the transmission spectra for different membranes shows that the wavelength at which the membrane starts to pass radiation depends on the type of electrolyte used in its production. Figure 3 presents the combined transmission spectrum of a porous alumina membrane in a wide optical range. There are several major regions, and this allows us to make the complete analysis of the porous membrane properties.

![Figure 3](image_url)

**Figure 3.** Transmission spectrum in a wide wavelength range. Different regions of spectrum characterize parameters of membranes: 1 – the average size and the dispersion of the pore diameter, 2 – the Al₂O₃ modifications, 3 – the thickness of membranes, 4 – anions of the used acid and the concentration of glycerol in the electrolyte.

Such spectra do not allow one to determine correctly the geometric parameters of a membrane. We can only state that the transmission spectrum shape corresponds to the geometric parameters of membrane determined by SEM.

Thus, the experimental data generalization gives a possibility to determine the average size and the dispersion of the pore diameter by measuring the UV–visible transmittance spectrum. The presence of different regions in the IR range of the transmission spectrum allows one to characterize the thickness of the membrane, the presence of residual products, as well as to identify the membrane material as alumina.

The RBS technique was used for in situ determination of the optimal geometry of the experiment. First, the position of a semiconductor detector at which the yield of the backscattered ions is uniform and minimal was found. This case corresponds to the situation when the pores in the target are through. It is worth noting that the above-mentioned ion-beam method of controlling the quality of nanoporous membranes structures is nondestructive.

The RBS spectra (figure 4) show the dependence of the number of passed particles on the slope angle of the target for the membrane containing pores of about 20 nm in diameter.
The intensity of the passing beams is nearly constant within 2.5°. A halving in the signal corresponds to a 3° slope of the target. This proves that the charge accumulation on the inner face of the nanoporous membrane results in the guiding effect. The maximum transmission factor is measured to be 0.625.

4. Conclusions

Thus, the technology of producing self-forming porous membranes has been proposed. The porous membrane is a system of ordered nanoscale (pore diameter of 20 nm or more) alumina capillaries with an aspect ratio of 500. It was established that the optical spectroscopy of nanoporous membranes in a wide wavelength range (from 200 nm to 15 microns) provides a rapid characterization of their basic geometrical parameters including the membrane thickness, the average pore size and the pore size distribution. It is shown that the nanoporous membranes based on alumina containing a nanoscale capillaries system provide the transport of high-energy flow of helium ions with energy of 1.5–2 MeV.

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References

[1] Eftekhari A 2008 Nanostructured Materials in Electrochemistry (Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA)
[2] Piao Y, Lim H, Chang J Y, Lee W-Y and Kim H 2005 Nanostructured materials prepared by use of ordered porous alumina Electrochimica Acta 50 2997
[3] Gracheva I E, Moshnikov V A, Karpova S S and Maraeva E V 2011 Net-like structured materials for gas sensors Journal of Physics: Conference Series 291 012017
[4] Foss C A, Hornyak G L and Stocker J A 1993 Optically Transparent Nanometal Composite Membranes Advanced Materials 5 135
[5] Afanas’ev A V, Il’in V A, Moshnikov V A, Sokolova E N and Spivak Yu M 2011 Synthesis of nanoporous and microporous structures by the electrochemical methods Biotekhnosfera, in Russian Issue 1–2 pp 20–26
[6] Muratova E N, SpivakYu M, Moshnikov V A, Petrov D V, Shemukhin A A and Shimanova V V 2013 Influence of technological parameters of nanoporous Al2O3 layers’ preparation on their structural characteristics Glass Physics and Chemistry 39 320
[7] Matyushkin L B and Muratova E N 2013 Investigation of the optical properties of nanoporous membranes based on Alumina Smart Nanocomposites 4 86
[8] Shemukhin A A and Muratova E N 2014 Investigation of transmission of 1.7-MeV He+ beams through membranes of porous Alumina JETP Letters 40 219

Figure 4. The energy spectrum of backscattered He+ ions with the energy of 1.7 MeV for the scattering angle of 120°. A – the structure of aluminum without etching, B – after electrochemical etching [8]