Optical transmission spectra of porous aluminamembranes with different pore size

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Abstract. Membranes of nanoporous aluminum oxide (alumina) have been obtained using the electrochemical etching technique by varying technological regimes. The surface morphology and cleavages of obtained experimental samples are studied using scanning electron microscopy (SEM). The optical transmission measurements were performed on a spectrophotometer in the wavelength range of 190–1000 nm. It is possible to determine the average size and the dispersion of the pore diameter by UV-visible transmittance spectrum measuring.

1. Introduction

The electrochemically produced porous alumina (por-Al2O3) membranes have been widely used as catalyst carriers and templates for the fabrication of ordered nanostructures [1-5], owing to regular nanoscale structures and relatively easy and low-cost processing. Of considerable interest is the por-Al2O3 for the problems of biomedicine [6, 7], for various types of sensors [8, 9], in MEMS-devices [10, 11]. A special attention is paid to the study of the optical properties of both the porous structures [12, 13] and various composites based on them [14]. Due to their structure, these membranes have potential in various optical device applications, such as optical filters and photonic crystals [15]. It is known that aluminum anodized in acidic electrolytes may occur at different rates, efficiency, and stability, in general, depend on the nature and concentration of the electrolyte, temperature and anodic current density [16].

It is important to be able to give a quick characteristic of the porous structure parameters, to evaluate the pore diameter, size distribution and order. Therefore, the aim of this work is to study the dependence of the transmission spectrum of the porous alumina membranes of their structural parameters.

2. Experiment

In order to obtain a porous anodic alumina membrane electrochemical anodization of aluminum foil (40μm) was conducted in potentiostatic mode in electrolytes based on aqueous solutions of phosphoric (H3PO4) and sulfuric (H2SO4) acids. Geometric parameters of membranes obtained in different electrolytes are presented in Table 1.

Usually the investigation of the structure and basic parameters (diameter of pores, interpore distance, porous layer thickness) of the samples obtained are carried out with the help of scanning electron microscopy (SEM). As shown in figure 1, anodic alumina membranes contain many columnar pores with diameters are about of 20-90 nm.
3. Results and discussion

It was found that porous alumina layers produced in different electrolytes (based on H$_2$SO$_4$, H$_3$PO$_4$) have different colors. For example, samples produced in the sulfuric acid solution have yellow color, while the samples produced in the phosphoric are usually blue. The study of optical transmission spectra have been shown that for any membrane the transmission spectrum has the same form (figure 2): the membrane starts to pass radiation with a certain wavelength.

A comparison of the transmission spectra for the different membranes (figure 3) shows that the wavelength at which the membrane starts to pass radiation depends on the type of electrolyte in the presence of which it was produced. The band gap of alumina is too large ($\approx 9$ eV) to observe the size effects in this optical range.
So this phenomenon can be related to a) the pore size or b) the type of anion incorporated into the anodized alumina lattice (SO$_4^{2-}$, PO$_4^{3-}$). However, since it is acid or anion type, determine the pore size; we can assume that both of these explanations are interrelated. We found the following pattern: the smaller the pore diameter, the smaller the critical wavelength $\lambda_c$. It is important to note there is always a values range of the pore diameter, which could be described by a Gaussian function (figure 4).

Analysis of experimental data showed some correlation between $\lambda_c$ and type of porous structure due to electrolyte. Summary of the experimental data presented in Table 1.

| Acid        | Diameter of pore, nm | Thickness of membrane, nm | Thickness of the barrier layer, nm | Concentration of pores, pcs/μm$^2$ | $\lambda_c$, nm |
|-------------|----------------------|---------------------------|-----------------------------------|------------------------------------|-----------------|
| sulfuric    | 20-30                | 12-18                     | 500                               | 350                                | 210…280         |
| phosphoric  | 80-100               | 4-7                       | 200                               | 50                                 | 450…750         |

Thus, the presented of experimental data generalization allows to determine the average size and the dispersion of the pore diameter by UV-visible transmittance spectrum measuring.
Furthermore, it was noted that increasing of the anodizing time leads to improved transmission of the membranes (figure 5). This is because the longer the process is the more aluminum ions move from the bottom of alumina foil to alumina and the membrane is transparent.

![Figure 5. Transmission spectra porous alumina membranes obtained during different time anodization.](image)

4. Conclusions
It is established that increasing of the anodizing time leads to improved transmission of the membranes. Investigations have shown that the membrane starts to pass radiation with a certain wavelength, which depends on the type of electrolyte in the presence of which membrane was produced. Thus, it is possible to determine the average size and the dispersion of the pore diameter by UV-visible transmittance spectrum measuring. It could be put in the basis of the non-destructive express control technique for the determination of pore size in por-Al$_2$O$_3$. The observed optical behavior of membranes may be used for cheap optical filters limiting the predetermined range radiation.

Acknowledgments
The reported study was supported by RFBR, research project No. 14-08-31609 mol_a.

The work was performed under the Russian Ministry of Education. Task (goszadanye) № 16.2112.2014/K (in the technological part, as well as the results of the influence of preparation conditions of the structure of porous layers).

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