Study of long-term changes in visible-light transmittance of porous alumina membranes

E N Muratova, S S Nalimova and V A Moshnikov
Saint Petersburg Electrotechnical University "LETI", ul. Prof. Popova, 5, SaintPetersburg, 197376, Russia
E-mail: SokolovaEkNik@yandex.ru

Abstract. The paper presents a study of the optical properties of porous alumina membranes obtained by electrochemical anodizing in electrolytes based on sulfuric and orthophosphoric acids. The pore size was analyzed by SEM. The degradation of transmittance of membranes after one year and six years storage was studied. The change one year later in optical properties was explained by the adsorption of water molecules. Six years later, an increase in throughput is observed for all membranes. At present, there are no theoretical models that can explain obtained experimental results and additional studies in this area are necessary.

1. Introduction
Dielectric matrices based on porous anodic alumina (PAA) are an important material for photonic crystals [1-3]. Due to the unique ordered honeycomb structure of the array of channels located along the normal to the film surface [4, 5], spatial modulation of the dielectric constant can be realized on a scale comparable to the wavelength of light. Earlier studies of the optical properties [6, 7] showed that PAA is transparent in the visible wavelength range, while they well screen IR radiation[8-10]. By the shape of transmission spectrum, it is possible to determine the pore diameter and their uniformity in size qualitatively.

These studies were confirmed by thermal imaging measurements [11, 12]. Dielectric porous materials with such properties are widely used in many fields of science and technology [4, 5]. To date, no scientific papers devoted to the study of the degradation of the optical properties of PAA membranes are published. Only rare studies on a similar topic are presented in literature [13, 14].

Nowadays the degradation of optical properties over time is of great interest. In this work, we investigated PAA membranes with different geometric parameters obtained in electrolytes based on sulfuric and orthophosphoric acids.

2. Experiment
To study the changes in optical properties over time, PAA membranes with significantly different geometric parameters were prepared. The membranes were obtained by electrochemical anodizing in a single-chamber cell under the potentiostatic regime in electrolytes based on sulfuric (at U=25...30 V) and orthophosphoric (at U=100...120 V) acids. As a starting material, we used aluminum foil (thickness of 40 µm) pre-purified in acetone and isopropyl alcohol. Each sample, for the reliability of the results, was fixed in a fluoroplastic frame with the same hole.
The optical properties of the obtained samples were studied with an interval of 1 year and 6 years using a PE-5400UF spectrophotometer operating in the visible spectral range (190–1000 nm). During the entire time, the membranes were stored in separate identical sealed packages. A Tescan scanning electron microscope was used to study the morphology of PAA membranes.

3. Results and discussion
The analysis of SEM images of PAA (Figure 1) synthesized in electrolytes based on sulphuric and orthophosphoric acids showed that the pore diameters in samples differ by almost 10 times ($d_{por}(H_2SO_4)$ ~ 17-20 nm, $d_{por}(H_3PO_4)$ ~ 180-220 nm). The membrane thickness also differed: 15 µm for $H_2SO_4$ and 8 µm for $H_3PO_4$.

As can be seen from Figures 2 b and 2 c, the surface of membranes with large pores can sometimes have roughness caused by the piled up on top of each other thin walls of the pores of the aluminum oxide upper sacrificial layer. Most often, this roughness etched and a flat surface remains, but in some cases such a "grass" can be observed.

![Figure 1. SEM image of PAA membrane formed using $H_2SO_4$: top view (a) and cross-sectional view (b)](image1)

![Figure 2. SEM image of PAA membranes formed using $H_3PO_4$: top view of membrane with smooth (a) and rough surface (b), cross-sectional view of membrane with rough surface (c)](image2)

Figure 3 presents the transmission spectra in the visible range, taken at intervals of one year and six years, for membranes with different pore sizes and roughness. Studies of the optical transmission spectra after one year showed that for sulfuric acid-based membranes, the transmission of visible radiation significantly decreased, while for membranes based on orthophosphoric acid on the contrary...
the transmission value increased. While for membranes obtained in an electrolyte based on orthophosphoric acid, other technological conditions being equal, both an increase and a decrease in the transmission value are observed.

Figure 3. Transmission spectra in the visible range taken at intervals of one year and six years for PAA membranes obtained in electrolytes based on sulfuric acid (a) and orthophosphoric acid (with smooth (b) and rough (c) surface)

Initially, the semi-transparency of thin PAA membranes can be explained by several mechanisms of light scattering [7]: a) at the grain boundaries and at the boundaries of grains with pores, b) on inclusions of another phase, c) on the membrane surface roughness.

The latter component, diffuse light scattering on the membrane roughness, is negligible since PAA membranes are obtained by electrochemical anodizing, after pretreatment of the surface. As a result the size of the inhomogeneities becomes comparable to the size of the pores.

Grain boundaries and pores are the most important causes of light scattering in PAA membranes. The light scattering associated with the birefringence effect at the grain boundaries is comparable to the light scattering at the pores only for membranes with very low porosity. Therefore, for porous membranes, the scattering at the pores significantly influence the transmission of light. The smaller the pores are formed in membranes, the wider the transmission range in the visible region can be reached.

It was found that, due to air humidity, over time, water is adsorbed on a porous surface. Despite the important role of light scattering by pores in the transmittance of porous membranes, the adsorbed water molecules also make their contribution. It was found that in the case of PAA with a large pore diameter, water molecules penetrate inside pores and change their shape, thereby reducing light scattering and increasing the transparency of membranes. For PAA with a small pore diameter (Figure
1) as well as membranes with very rough surfaces (Figure 2, b, c), water molecules are adsorbed on
the surface, forming a continuous thin layer that reduces the transparency of the membrane.

Six years later, an increase in throughput is observed for all membranes. The possible causes of
observed phenomenon can be the change in some reflective features inside the pores, the change in the
roughness and the fractal properties of the pore surface, as well as electron density redistribution.
However, at present, there are no theoretical models that can explain obtained experimental results and
additional studied in this area are necessary.

4. Conclusions
At intervals of 1 year, the optical properties of PAA membranes were studied and their changes were
analyzed. Water is adsorbed on the porous surface over time due to the humidity of the air. Despite the
fact that the light scattering at the pores plays a crucial role in the transmission of light in porous
membranes, the adsorbed water molecules also influence this process. In the case of large pores (in
this paper ~ 200 nm), water molecules, penetrating inside, begin to change their shape, thereby
reducing the light scattering. For PAA with a small pore diameter, water molecules are adsorbed on
the surface, forming a solid thin layer that reduces the transparency of the membrane.

Acknowledgments
This work was supported by the grant of the President of the Russian Federation MK-2268.2020.8:
agreement No. 075-15-2020-520 of 13.04.2020.

References
[1] Wang B et al 2007 Nanotechnology 18 365601
[2] Fu X X et al 2011 Opt. Express 19 A1104
[3] Masuda H, Ohya M, Asoh H, Nakao M, Nohtomi M and Tamamura T 1999 Jpn. J. Appl. Phys 38 L1403
[4] Muratova E N et al 2017 Glass Phys. Chem 43 163
[5] Luchinin V V and Tairov Yu M 2006 Nanotechnology: physics, processes, diagnostics, devices
(Moscow: Fizmatlit)
[6] Matyushkin L B et al 2014 J. Phys. Conf. Ser 572 012031
[7] Matyushkin L B, Muratova E N and Panov M F 2017 Micro & Nano Letters 12 100
[8] Tajima S 1977 Electrochim. Acta 22 995
[9] Yao Z, Zheng M, Ma L and Shen W 2008 Nanotechnology 19 465705
[10] Apetz R and van Bruggen M P B 2003 J. Am. Ceram. Soc 86 480
[11] Muratova E N et al 2017 J. Phys. Conf. Ser 872 012020
[12] Muratova E N et al 2018 Inorg. Mater 54 593
[13] Nahar R K 2000 Sens. Act. B 63 49
[14] Bley K et al 2018 Adv. Funct. Mater 28 1706965