AJP FIZIKA 2021 volume XXVII №2, section: En

FREE STANDING AAO NANOPOROUS MEMBRANES FOR LIQUID FILTRATION

Sh.O. EMINOV, A.Kh. KARIMOVA, E.A. IBRAHIMOVA, J.A. GULIYEV
Institute of Physics NAS Azerbaijan, H.Javid ave., 131 Baku, Azerbaijan
e-mail:ayselkerimova00@mail.ru

The method for creation of membranes of alumina (AAO) films for water filtration by anodization of aluminum foils in oxalic acid was descripted. The obtained foils were characterized by SEM and optical microscopes. The permeability measurements of the membranes have shown that the membranes are suitable for precision separation of liquid and gaseous mixtures in laboratory conditions.

Keywords: Membranes, anodic oxidized aluminum, AAO, liquid filtration.
PACS: 61.46.Km

INTRODUCTION

Quasi-one dimensional nanostructures such as nanowires and nanotubes have attracted the attention from researchers due to their properties of the two dimensions being in the nanoscale and one dimension being in the microscale. Fabrication of ordered arrays of nanostructures is required in catalysis, sensing, electronics, energy harvesting and storage, and applications of materials with tailored magnetic and optical properties.

Membrane methods for the separation of liquid and gaseous mixtures refer to low-cost environmentally friendly technologies for the separation of substances and the treatment of various wastes. Owing their effectiveness in removing contaminants with sizes less than 1 μm nanoporous filtering membranes have been used for drinking water purification. Another quite important task in terms of the practical application of membranes is separation of organic macromolecules and proteins for hemodialysis and hemofiltration in biomedicine.

One of the promising materials for creating nanoscale membranes is nanoporous anodic aluminum oxide (AAO, alumina) [1-3]. This material has a precise, self-assembled honeycomb structure composed of parallel nanopores with no lateral crossovers between individual pores. AAO can be easily fabricated by simple anodization of aluminum in an acidic electrolyte. Different anodization regimes can be applied in the fabrication process, leading to different pore diameters in the range of 10-450 nm AAO is a very suitable template for immobilization of the biological molecules, due to the adjustable pore size and interpore distance. Furthermore, nanoporous AAO is optically transparent, electrically insulating, chemically stable, bioinert, and biocompatible. These outstanding properties are beneficial for various applications of AAO membranes in biotechnology and medicine ranging from biofiltration membranes, lipid bilayer support structures biosensing devices, and implant coatings to drug delivery systems with AAO capsules and scaffolds for tissue engineering. Furthermore, AAO also serve as widely used template for other biocompatible nanostructures such as gold and platinum nanopillars. For that reason over the past years, the development of novel biomedical applications has benefited immensely from the unique properties of AAO membranes. Despite the proven utility of those nanofabrication methods, there is still a lack for simpler and cheaper procedures to expand the usage of this nanotemplate.

High-quality AAO (anodic aluminum oxide) films provide ordered straight channels, with a diameter of 10–500 nm, pore density of 10^7–10^{11} pore/cm^2 , and thickness of 1–300 μm [1,2]. With large surface areas, high mechanical strength, and flexibility, AAO can be used in medical or energy applications, such as drug delivery and detection [3,4]. The large AAO surfaces can be utilized to absorb the bio-indicators or drugs, and the releasing behavior can also be controlled based on the heat sensitivity. AAO has also found applications in energy conversion between carbon dioxide (CO_2) and methanol (CH_4) [5,6]. By loading photocatalyst particles on the AAO surface, such photocatalytic systems can be used to recycle carbon dioxide into organic compounds. Based on the features of larger surface areas and nanochannels for mass delivery and gas diffusion, three-dimensional (3D) structure of AAO films have practical advantages over two-dimensional (2D) AAO films for medical and energy applications. AAO has a lower melting point than pure alumina because of the inclusions in the porous AAO structure. Spooner [7] presented the following compositions of alumina film anodized using sulfuric acid as electrolyte: Al2O3 (78.9 wt. %), Al2O3·H2O (0.5 wt. %), Al2 (SO4)3, and H2O (0.4 wt.%). According to Akahori's work [8], the melting point of AAO is near 1200 °C, and AAO template retains stable, at around 1000 °C [9], which is lower than that of bulk alumina (2017 °C for Al2O3(γ)). The AAO structure maintaining temperature of 1000 °C is stable enough to be a template for CaO-CaCO3 reaction at 894 °C. In the past, tubular AAO has attracted attention. Several methods were proposed for the fabrication and applications of tubular AAO films. According to Altuntas's report [10], the large area (50 cm^2) free-standing AAO membranes was obtained by sputtering carbon onto AAO surface for conductive AAO biosensor applications, especially tubular AAO for filtering. Belwalkar [11] showed that AAO tubular membranes were fabricated from aluminum alloy tubes in sulfuric and oxalic acid electrolytes, the pore sizes were ranging from 14 to 24 nm, and the wall thicknesses was as high as 76 μm, which increased the mechanical strengths for handing. The pore density can be calculated by determining the number of pores according to the area fraction: $P = Ap/[(\pi/4)\ D2\ ]$, where P is the number of pores, Ap is the area fraction of pores, and D is the average pore diameter. Gong [12] presented that AAO membrance was prepared in 0.2 M oxalic acid electrolyte under 25 to 40 V applied for 11 to 18 h; additionally, the control in drug delivery by using nanoporous alumina tube capsules with pores of 25 to 55 nm was demonstrated. Kasi1 [13] further reported that the purity of Al is also a matter of great concern for AAO fabrication. Some applications, such as nano-templates for semiconductor industry, require a regular pore arrangement with a honeycomb structure, which cannot be achieved from low grade Al. Moreover, AAO membrane in tubular form can further satisfy the demand in both diffusive and convective filtration of hemodialysis.

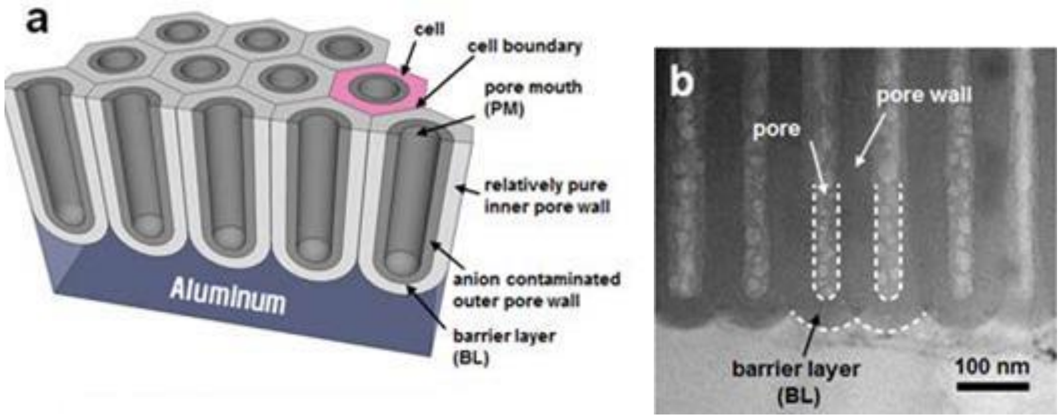

Fig. 1. (a) Schematic showing an idealized structure of porous anodic aluminum oxide (AAO) with a self-organized array of hexagon cells and convex-shaped geometry of barrier layer (BL) at the base of pores. The two different regions of anion contaminated (dark gray) and relatively pure oxide (light gray) are also presented. (b) Cross-section TEM image of bottom part of porous AAO.

1. EXPERIMENT TECHNIQUE

In this work, we present the development and optimization of low cost AAO membranes by galvanostatic anodization of commercial Al foils (99.5% purity), and their application as membrane filters in the UF process of drinking water.

The stages of AAO processing are shown in the Fig.1. Pure aluminum (99.95%) foil with a thickness of 100 μm was used as a starting substrate for anodization. In order to promote long-range ordering in aluminum by limiting the number grain boundaries the foil was annealed at 500°C in air for 3 hours. Then the annealed foil was cut into approximately 3.0 cm by 3.0 cm rectangles and ultrasonically degreased in acetone and ethanol for 5 minutes on an each. The native oxide layer of the Al foil was removed in 1 M NaOH solution and rinsed in distilled water (Stage A).

The anodization was carried out in a home made two-electrode cell using ice-bath for keeping temperature of solution in the range of 0-5°C during anodization. Before anodization the area of the foil intended for the membrane has been delaminated (Stage B). Then the foil (anode) was mounted to an electrolytic cell via an O-ring and on copper plate which was connected to the power supply by a conducting wire. (Stage C). The plate was continuously cooled by means of ice water bath. The counter electrode (cathode) was a piece of platinum (Pt) sheet. The distance between the two electrodes was approximately 2 cm.

The AAO were prepared by two-step anodization experiments. The defective microstructure of the Al metal surface prior to anodization affects the ordering of the subsequent oxide film. For that reason in accordance with the “Masuda method”; the first oxide film (called the sacrificial layer) is selectively dissolved. As proposed in the literature this step removes the non-ordered pores and lets a dimple array to the second anodization stage. Thus second oxidated film has a much more regular structure due to the pre-patterning of the substrate by the first anodization.

The first anodization step was carried out for 1 h under galvanostatic conditions (U =40 V, T=5°C) in 4% water solution of oxalic acid ($C_2H_2O_4$. During this operation, the layer with non-ordered pores structure was created. Then this layer was completely stripped away from the Al substrate by dissolution i.e. wet chemical etching in a solution containing 6 wt% phosphoric acid and 1.8 wt% chromic acid ($H_2Cr_2O_7$) at 60◦C for 1h under stirring (Stage D).

The second anodization step (Stage E) was carried out under condition similar with the Stage C for 3h. After this step the aluminum back side of the electrode was chemically etched in 0.1 M solution of $CuCl_2$ in 20% HCl to reveal the AAO barrier oxide layer (Stage G).To provide stable mechanical support to the AAO membrane, was performed in a reduced area compared with the anodized side of the Al foil (stage E). The barrier layer was removed in 5%H_3PO_4 water solution at temperature 45-50°C during 15 min over the barrier layer, which was then rinsed with deionized water, and then dried with Nitrogen gun under ambient conditions (stage H).

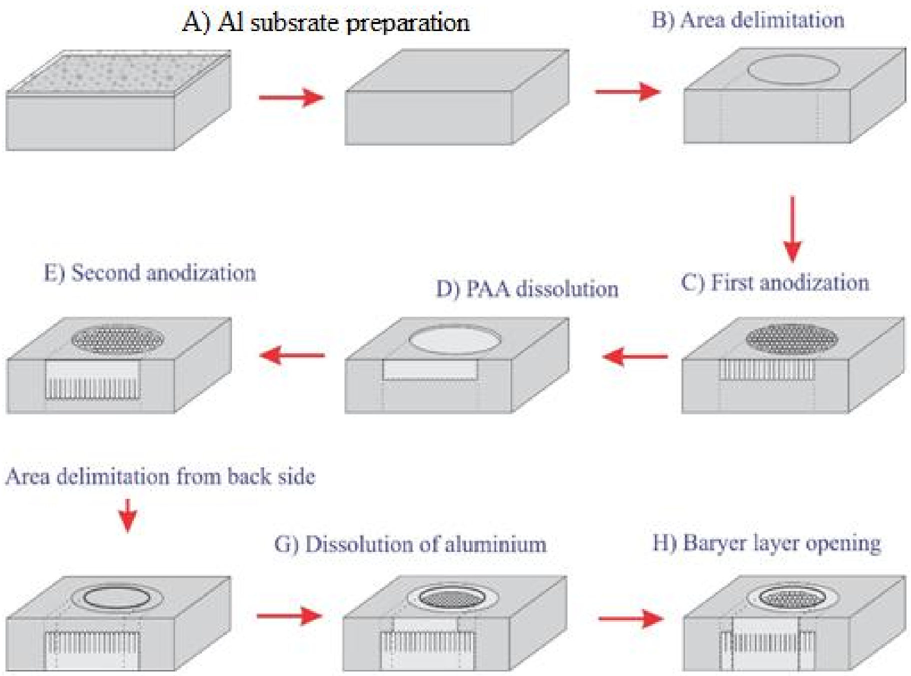

Fig. 2. The stages of AAO processing A)Preparation of the foil , irregular AAO film after 1st anodisation, stage C; b) dimple array on Al surface stage D ; c) homogeneus porous film after 2nd step anodization , Stage G;

2. RESULTS AND THEIR DISCUSSION

The optical photographs of the AAO film taken by microscope MBS-22 (x 54) after first anodisation is shown in Fig.2.

Fig. 3. View of the AAO film under optica microscope MBS-22 (x 54), photographs after first anodization.

SEM images of AAO (Fig.4) confirmed the creation of an array of highly ordered hexagonal cell structures with pores about 40-60 nm in diameter.

EDAX Spectrum of obtained film shown on figure 5. In this figure shows major elements such as Al and O is a main part of film. Ni sputtered on the sample used as a contact for measure of film and minor elements such as P and Si which were due to contamination.

Digital photographs of the membrane taken before and after removing barrier layer are showing correspondently on left and right sides of the figure 6. To guarantee the mechanical stability, as well as to inhibit solution leakage during the filtration, metallic aluminum on our membrane was maintained at the edge of AAO samples. The partially transparent region at the center of the image corresponds to the PAA membrane itself and the white ring is the supported membrane on the Al base.

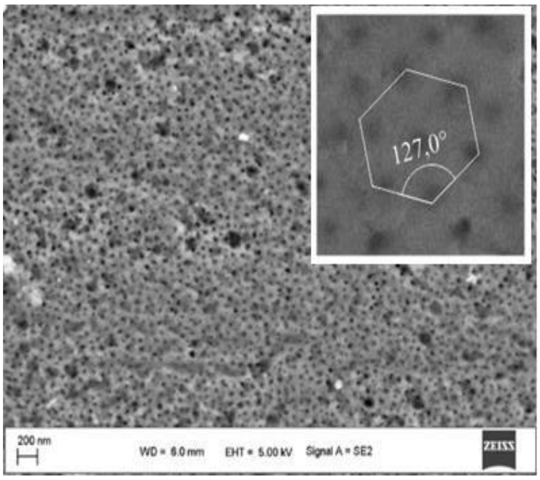

Fig. 4. The SEM image of the AAO film (left) and its an enlarged fragment (right).

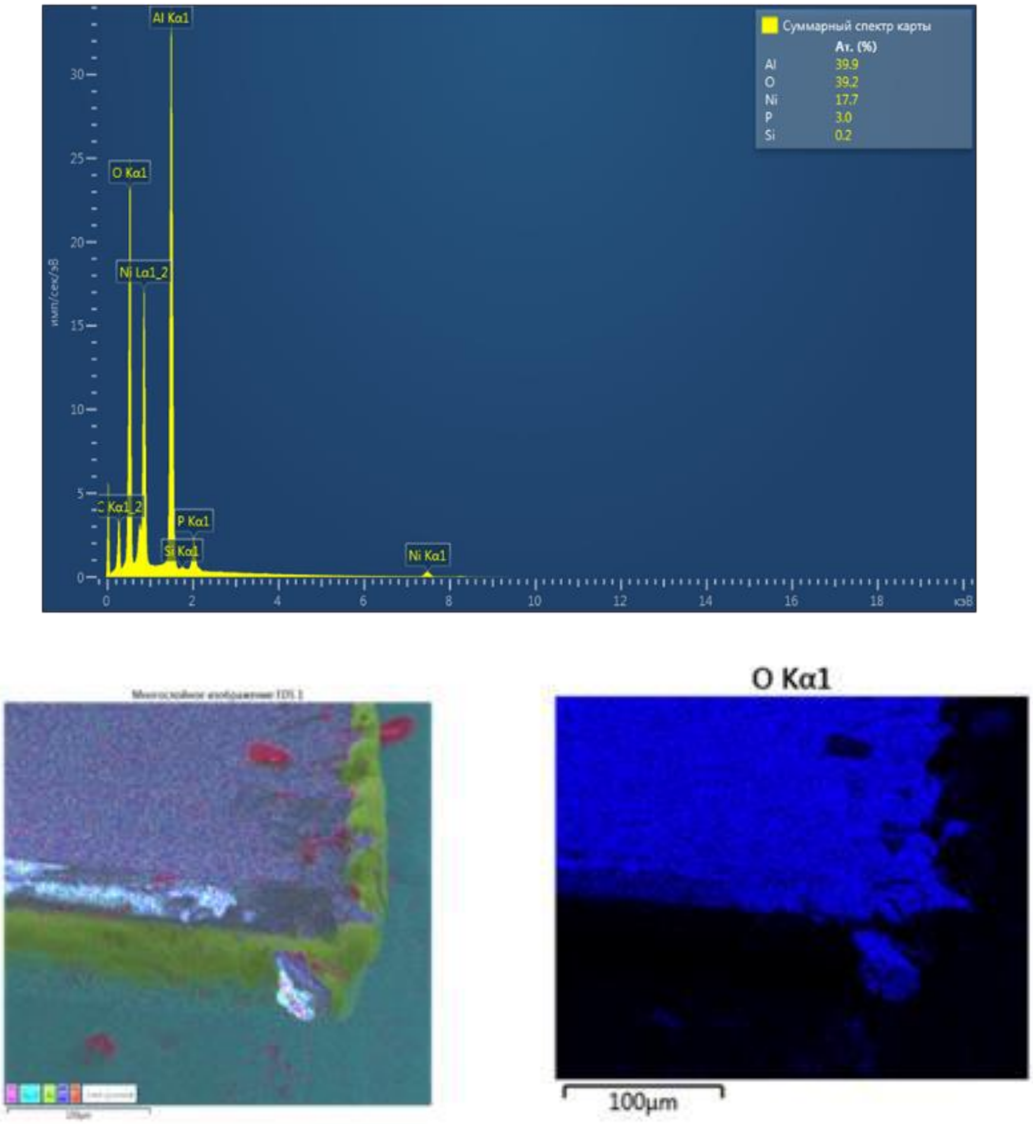

Fig. 5. EDAX spectrum and elemental maps of film.

Fig. 6. Digital photographs of the membrane before (left) and after (right) removing barrier.

The liquid permeance measurements membranes were performed using a home made device based on a large medical plastic syringe at a temperature of 25 ± 2 °C. The devise used for these studies is shown in the Figure 7.

The permeability was calculated from the pressure difference measured by pressure transducers and the mass of accumulated permeate. These studies have shown that the membranes are suitable for precision water purification in laboratory conditions.

Fig.7. Device for liquid permeance measurements.

[1] *M. Galizia, W.S. Chi, Z.P. Smith, T.Ce. Merkel et al.* 50th Anniversary perspective: Polymers and mixed matrix membranes for gas and vapor separation: A review and prospective opportunities. Macromolecules, 2017, *50*, 7809–7843.

[2] *Dmitrii I. Petukhov, Dmitrii A. Buldakov, Alexey A. Tishkin, Alexey V. Lukashin and Andrei A. Eliseev.* Liquid permeation and chemical stability of anodic alumina membranes Beilstein J. Nanotechnol. 2017, *8*, 561–570.

[3] *Alexsandro Mendes Zimer, Maria Manuela P. Machado1 et al.* Optimized porous anodic alumina membranes for water ultrafiltration of pathogenic bacteria (E. coli) Journal of Nanoscience and Nanotechnology Vol. 15, 1–9, 2015.

Received: 12.04.2021