

SPECIFIC PERMEABILITY OF NANOPOROUS ALUMINA MEMBRANES STUDIED BY DIFFUSION CELL TECHNIQUE

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Abstract

The permeability and barrier properties of various solutes were studied through nanoporous alumina membranes by diffusion cell technique. Fabricated membranes were characterized by basic physic-chemical methods. The accurate thickness and roughness was determined by profilometry, the distribution of pores and pore size was detected by mercury intrusion porosimetry, textural properties were studied by scanning electron microscopy and specific surface area by BET analysis. The specific permeability was compared by determination of fundamental diffusion parameters such as diffusion flux and break-through time (lag time).

Results show, that the penetration ability and other important parameters such as thickness and the distribution of pores are strongly dependent on experimental setup within preparation of nanoporous alumina membranes. The most important parameters which influenced the final properties of membranes are time of anodization, type of electrolyte, applied voltage and current density.

Keywords: Nanoporous alumina membrane; diffusion; permeability; potassium chloride; preparation of nanoporous membranes

1. INTRODUCTION

1.1. Nanoporous alumina membranes

Nanoporous membranes are frequently used in sensorial applications for their unique properties - chemical stability, semitransparency, insolubility, inertia, biocompatibility and high ordered arrangement with large surface area [1, 2]. Membranes are extensively utilized for specific attaching of molecules from solution. Therefore, membranes are modified by various biomolecules or covered by metal layers [3]. Metal layers deposited on alumina surfaces can serve as electrodes for detection in nanopores or as matrix for attaching of molecules. Attaching of biomolecules into the nanopores and subsequent binding of compatible molecules, cause blockage of pores and change the measured signal [4]. Due to possibility to control morphology of nanopores (length and diameter) [5], alumina membranes are used for filtration purposes or for sorting of various substances [6, 7]. For these reasons it is necessary to know diffusion properties of membranes. Perusal of the relevant recent literature shows there is lack of information related to diffusional characterization of alumina membranes. Due to this fact, it is required to realize general characterization of alumina membranes with various thicknesses and pore diameters.

Nanostructured membranes based on anodic aluminium oxide with highly organized nanopores (nanocolumns) are studied because of their unique physical properties [8] and wide range of potential applications. Anodic aluminium oxide can be utilized in optical, electronic or electrochemical branches as a tool for sensing of gases, biosensors, catalysis, and selective separation of molecules, filtration or purification [9].

The physical properties of anodic alumina oxide membranes are strongly influenced mainly by the morphology of the final product. The change of physical-chemical properties such as permeability can be driven during the

anodization process [10]. The main parameters which are able to influence the permeability are pore size (alumina membranes obtained by anodization method have nanopores with diameter in range from 4 nm to 250 nm), thickness (in the range 1 - 200 μm) and density of pores (typically 10^9 - 10^{12} pores/ cm^2). Dimensions of pores can be easily controllable by changing of procedure conditions (current density, time of anodization, type of electrolyte or applied voltage) [1].

1.2. Permeability of nanoporous membranes

Growing interests about the usage of nanoporous membranes in sensor technologies is given mainly by their specific permeability for different solutes. This permeability is influenced primary by shape and size of nanopores in alumina membranes and also by the size of diffusing solutes. One of the most important facts for practical usage of anodic alumina oxide nanoporous membranes is the detailed knowledge of their transport (permeability) properties. Methodology, usually used for the determination of these fundamental penetration parameters, is well known and described in literature.

Kipke and Schmid [11] studied the diffusion processes realized through alumina membranes with pore size in range 20 - 200 nm. Organic dye crystal violet (C.I. 42555) encapsulated in the micelles of sodium dodecyl sulfate (SDS). They used horizontal diffusion cell (Franz diffusion cell) for the realization of the transport experiments. They observed absolutely no influence of the pore width on the delivery speed. Romero et al. [12] studied the penetration of sodium chloride through nanoporous membranes based on alumina. They studied mainly the interactions between diffusing probes (low molecular ionic compounds) with alumina membranes.

In this study, the permeability of different alumina membranes was determined by the change of concentration of chosen diffusing probes through membranes. Potassium chloride as a representative of low molecular ions compounds and methylene blue as a representative of basic organic dyes were chosen as a suitable diffusion probes. The change of concentration of potassium chloride was determined by conductivity measurements and the change of methylene blue (C.I. 52015) was measured by UV-Vis spectroscopic measurements. Methylene blue, as cationic organic dye, was chosen purposefully, because the authors have wide experience with the usage of this dye for penetration experiments. Further papers [13-15] studied the mobility of methylene blue through hydrogels samples with addition of humic acids. This cationic dye is able to interact with anionic supramolecular humic acids and fundamental diffusion parameters such as effective diffusion coefficient, break-through time (lag time) and sorption capacity of agarose hydrogel with/without addition of humic acids can be calculated.

2. EXPERIMENTAL PART

2.1. Materials and methods

Aluminium foil (99.999 %, Goodfellow, UK), sulphuric acid (H_2SO_4 , 96 % p.a., Penta), oxalic acid ($(\text{COOH})_2$, p.a. Penta, CZ), absolute ethanol (p. a., Penta, CZ), perchloric acid (HClO_4 , 70 % p.a., Penta CZ), phosphoric acid (H_3PO_4 , 84 % p.a., Penta CZ), chromium trioxide (CrO_3 , p., Penta, CZ), chloric acid (HCl , 35 % p.a., Penta CZ), copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, p.a. Penta CZ). Deionized water (18.2 $\text{M}\Omega$) was obtained from Millipore Synergy UV system (Merck Millipore Corp., USA). All chemicals were used as purchased without any purification.

2.2. Fabrication process of alumina membranes

Self-assembled nanoporous alumina membranes are produced by anodization of aluminium foil with high purity (99.999 %) performed in acidic solution. Production process consists from three main parts: pre-treatment, anodization and posttreatment. Pre-treatment include rinsing in acetone for decreasing and electrochemical polishing in mixture of perchloric acid and ethanol under the voltage 20 V [16]. After that, flat aluminium foil is prepared for anodization step. Then, polished aluminium film is transformed by anodization

to nanoporous alumina (Al_2O_3) with the hexagonally ordered nanopores perpendicular to the surface. Anodization is made as two-step. During the first anodization nanopores grow disorderly. Therefore, alumina created in the first step is etched away and the aluminium sample with small dimples is obtained. During second anodization, the nanopores grow in bases of dimples and newly created alumina with ordered structure is obtained. Experimental conditions strongly influence morphology of resulted membranes. Diameter of nanopores depends on type of acidic solution (oxalic acid, sulphuric acid, phosphoric acid), concentration of solution and value of voltage. Electrolyte solution has to be cooled because anodization is highly exothermic process. The length of nanopores is mainly determined by time of process. The last fabrication process is posttreatment. During this step, the non-anodized aluminium is dissolved in hydrochloric acid and copper sulphate. At the end, bottom part of nanopores is dissolved and nanoporous alumina membrane is obtained [17]. If the barrier layer etching is longer than it is necessary, the solution penetrate into nanopores and nanopores are etched and expanded from the inside. Pore diameter is usually in range from 4 nm to 250 nm and thickness from a few micrometres to tens of micrometres [1].

2.3. Characterization of nanoporous alumina membranes

First of all, alumina membranes were characterized by fundamental physical-chemical methods. The exact thickness of membranes was measured by profilometry (DektakXT, Bruker), the measurement of roughness was performed by elipsometry (Uvise, Horina JobinYvon). Homogeneity, shape and the pore size was studied by scanning electron microscopy (Tescan FE MIRA II LMU with detectors EDX and WDX). Applied voltage during SEM measurements was 12.5 kV, magnification was 100 000 \times . Specific surface area values were determined by using a Quantachrome NOVA 2200 analyser (Quantachrome Instruments). The samples were degassed and evacuated. The evacuated chamber with sample was filled by pure nitrogen. The measurements were repeated three times. The penetration experiments were realized in the water-jacketed horizontal diffusion cells (PermeGear, Inc.).

Potassium chloride (> 99.0 wt. %, Sigma Aldrich®) was used as suitable diffusion probes without further purification. The cell volumes were 50 cm³ in each compartment of diffusion cell. All experiments in diffusion cells were realized at constant temperature 25°C. The temperature was controlled and maintained at constant value by circulating water bath. The stirring of both solutions (acceptor and donor compartment of diffusion cell) was arranged by magnetic stirrer (constant rate 350 rpm).

Table 1 Experimental setup for preparation of alumina membranes

Alumina membranes	Applied voltage	Anodization solvent	Time of anodization
Sample 1	40 V	oxalic acid	20 hours
Sample 2	40 V	oxalic acid	6 hours
Sample 3	20 V	sulfuric acid	8 hours

3. RESULTS AND DISCUSSION

3.1. Thickness and roughness of alumina membranes

The thickness of alumina membrane can be varied by changing of experimental conditions during preparation of membranes. The highest impact on the thickness of alumina membrane has the applied voltage and the time of anodization. If we will compare sample 1 (40 V, oxalic acid, 20 hours) with sample 2 (40 V, oxalic acid, 6 hours), it is obvious, that the thickness of alumina membranes increase with increasing time of anodization.

The roughness of alumina membranes can be varied especially by changing of anodization solvent. Sample 4 was prepared by anodization process in sulfuric acid instead of other samples, which were prepared by anodization in oxalic acid. Sample 3 have lower roughness (at least 6 \times) in comparison with all other samples.

The knowledge of roughness is one of the most important parameter for the accurate description of diffusion processes.

Table 2 Thickness and roughness of alumina membranes

Alumina membranes	Thickness (μm)	Roughness (μm)
Sample 1	160 ± 5	3.4
Sample 2	43 ± 2	4.4
Sample 3	103 ± 2	0.5

3.2. Scanning electron microscopy of alumina membranes

Nanoporous alumina membranes were characterized by scanning electron microscopy to determine the morphology and mainly the distribution of pores. The main purpose for this characterization was to determine the influence of anodization solvent for the morphology of fabricated membranes.

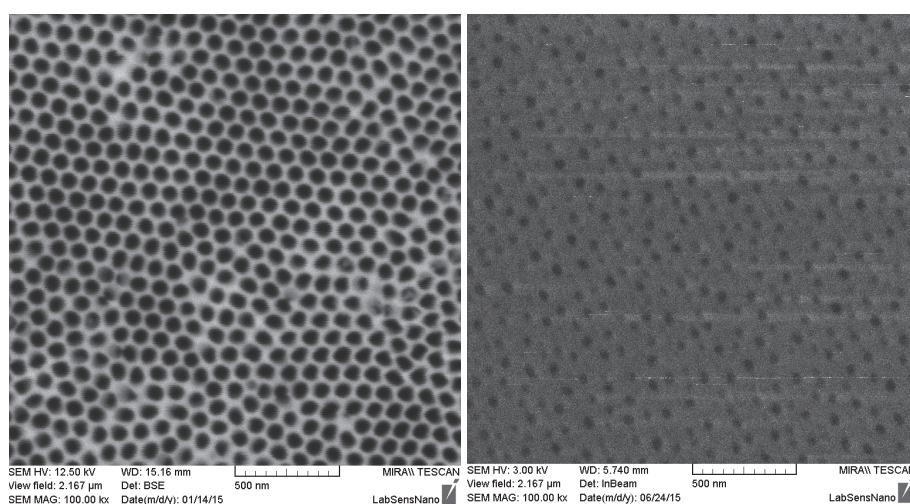


Fig. 1 Scanning electron microscopy of nanoporous alumina membranes anodized in oxalic acid (left) and sulfuric acid (right)

It is obvious, that the alumina membranes anodized in oxalic acid (**Fig. 1** on the left) dispose higher pore size in comparison with alumina membranes anodized in sulfuric acid (**Fig. 1** on the right). But the differences in pore size are not so significant. The barrier properties of alumina membranes are influenced mainly by distribution of pores. Density of pores for alumina membranes anodized in oxalic acid is much higher in comparison with membranes anodized in sulfuric acid (see **Fig. 1**)

3.3. Ionic permeability tests

Simple through-diffusion experiments in diffusion cells were performed in order to evaluate permeability of the prepared membranes for model low-molecular ions. Break-through curves, determined for the diffusion of potassium chloride, are presented in **Fig. 2**. Obviously, structural differences of the tested membranes resulted in a correspondingly altered barrier properties. Regression of the linearly increasing part of a breakthrough curve provides two important parameters which allow evaluation of membranes' transport properties in a quantitative way.

Slope of the increasing part of the breakthrough curve represents a major experimental outcome as far as the membrane permeability is concerned. Furthermore, the slope should be crucially affected by the structure of the material, mainly its porosity. This expectation was experimentally confirmed. The slope increases with specific surface area of the membranes as it is shown in **Fig. 3** - i.e. with their increasing microporosity.

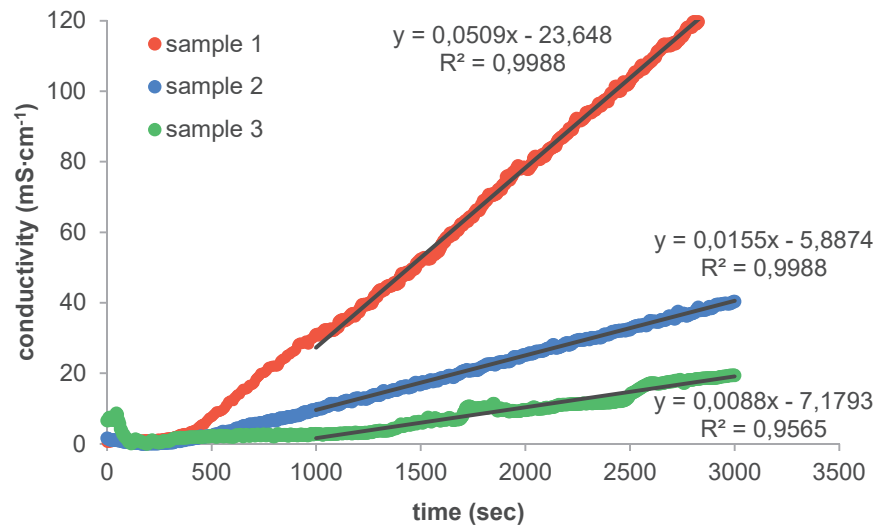


Fig. 2 The change of conductivity as the time function. Break-through curves determined for the diffusion of potassium chloride

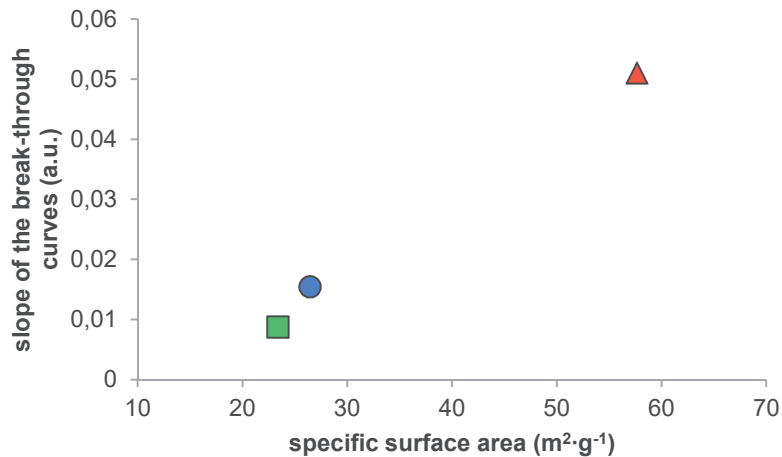


Fig. 3 The slope increases with specific surface area of the membranes

4. CONCLUSION

Specific permeability of nanoporous alumina membranes was studied by diffusion of potassium chloride in horizontal diffusion cells. Penetration ability of potassium chloride through membranes is strongly dependent on the specific surface area (the linear increase of the slope of the break-through curve with increasing specific surface area was observed). The permeability is also strongly dependent on the pore size and the distribution of pores in the structure of membrane. This expectation was experimentally confirmed by correlation of images from scanning electron microscopy with diffusion experiments (the slope of the break-through curve is the lowest for membrane anodized in sulfuric acid. This sample disposes totally different distribution of pores in comparison with samples anodized in oxalic acid).

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