Influence of the drying method on the structure of aluminum oxide capillary-porous nanomembranes

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Abstract. Porosity characteristics are widely used to assess the internal structure of nanomembranes. The membrane was considered complex in the analysis of the structure. The membrane was presented in a simplified way as a system interacting with a dispersion medium, for example, water. A physicochemical model of the membrane has been proposed, which allows one to study the logical and structural similarity between systems, the properties of which are known, with similar systems, but with unknown properties. We have chosen a simple mechanical model of a membrane permeable to liquid and gas molecules. Permeability was determined by the characteristics of the porosity, shape, and size of the pores.

1. Introduction
The structural features of nanomembranes based on anodic alumina lead to irreversible changes in their structure during drying and heat treatment after the completion of the synthesis [1–3]. These changes are caused by the following circumstances. Associates of membrane macromolecules consist of a spatial network of “cross-linked” macromolecules, in the cells of which there is moisture freely communicating with an external solution. The molecules of the liquid and the ions in it can move inside the matrix.

Inside the associates there is a dispersion medium with ions dissolved in it, released into the medium as a result of the dissociation of functional groups under the action of an electric field during the synthesis of nanomembranes. The article presents the study results of the effect of the drying membranes method after the anodizing process on the structure of the resulting porous system.

2. Experimental part
Nanoporous alumina was synthesized using a simple and low-cost anodizing process in acidic electrolytes. By changing the basic parameters of anodizing, such as the composition of the electrolyte, etching voltage, etching duration, and others, you can change the morphology of the layers [2–4]. The research methodology was based on a comparative analysis of the microstructure of the original membranes and those dried under different modes (table 1). In the course of the experiments, the decrease in moisture and the change in the size of the samples were recorded. The initial membranes structure was fixed by rapid freezing of the samples at temperatures from 253 to 213 K. The processing of the porous structure of thin sections and replicas photographs was carried out by a linear statistical method based on the Cavalieri-Acker principle.
3. Results and discussion

With an initial moisture saturation $W_o = 6.2$ kg/kg, a massive texture is formed in the sample after freezing. The results of the replica photographs analysis have showed that the membrane samples had a homogeneous microstructure (figure 1a). Ice inclusions are distributed in macropores in the form of isometric nests and separate lenses and do not form a coherent set. They are separated by the matrix of the membrane skeleton. The results of data processing for determining the pore sizes are presented in the graph form of the pore volume distribution by diameter (figure 1b, curve 1) and a summary curve expressing the percentage of pores (figure 2, curve 1).

![AFM images of membranes based on nanoporous alumina (a); pore volume curves of distribution by diameter (b). Numbers of curves on the graph correspond to the drying modes in table 1.](image)

From the analysis of these plots, it follows that the pore sizes of the initial “frozen” membrane vary from 8 to 80 nm, which makes it possible to attribute it mainly to a nanoporous mesostructure with finely porous elements. As can be seen from figure 1b, distribution curve 1 has a maximum corresponding to the pore size in the range from 32 nm to 48 nm. The characteristics of the original sample porous structure are shown in table 1.

![Table 1. Influence of dehydration modes on the porous structure parameters.](table)

The resulting pore size distribution curve characterizes the inter-associative pore space. The coefficient of heterogeneity for large pores $f$ characterizes the ratio of such equivalent diameters, more than which the membrane structure contains, respectively, 10% and 60%. Its value for the original membrane is given $f = 2.96$.

3.1. Radiation convection drying

Let us consider the regularities of structural changes in membranes during their radiation-convective drying in a drying oven at 378 K. The processing results (figures 1b, 2, curve 2) show that, in
comparison with the initial sample state, there was an increase in the pore size interval in the coarse-
porous region of the meso-structure. From curves 1, 2 (figures 1b, 2a) it follows that during the drying
process there was a significant change in the material structure in comparison with the initial one. Due
to the absence of capillary contraction, the structure of the dehydrated vacuum-sublimation method
(sample 6, table 1) practically does not differ from the original (sample 6, table 2). This makes it
possible to recommend this drying mode for obtaining samples, the structure of which will be close to
the original in the moisture-saturated membrane. This is confirmed by the data of experiments to
determine the moisture absorption of membranes obtained under different drying modes. Figure 2b
shows the dependences of the kinetics of the relative moisture absorption of samples sublimated at
atmospheric pressure (curves a, b) and dried under radiation-convective mode (curve c) samples.

![Figure 2](image_url)

**Figure 2.** Total pore diameter distribution curves (a). The numbers of the curves on the graph
correspond to the drying modes in table 1. Kinetics of the relative moisture absorption of membranes
(b): sublimated membrane (a, b); dried (c). Drying modes: (a) T = 273 K, v = 1.25 m/s, W_o = 7.77
kg/kg; (b) T = 268 K, v = 0.35 m s, W_o = 8.30 kg/kg; (c) T = 293 K, v = 1.25 m/s, W_o = 6.25 kg/kg.

In the material during the sublimation of ice, almost completely restore the original moisture-
absorbing properties, in contrast to the dried sample, where the irreversibility of structural changes
significantly affects the moisture absorption of the material. The specific surface area practically did
not change (table 2).

**Table 2.** Changes in the characteristics of the dehydrated membrane porous structure
in relation to the original.

| Dehydration mode * | Inner zone | Outer zone |
|--------------------|-----------|-----------|
|                    | n_i       | D_i       | S_i       | f_i | n_i | D_i | S_i | f_i |
| 2                  | 1.74      | 1.78      | 1.15      | 1.47 | -- | -- | -- | -- |
| 3                  | 1.55      | 1.71      | 1.04      | 3.10 | -- | -- | -- | -- |
| 4                  | 1.52      | 4.18      | 0.42      | 1.18 | -- | -- | -- | -- |
| 5                  | 1.15      | 0.73      | 1.63      | 1.52 | 2.12 | 1.53 | 1.90 | 1.69 |
| 6                  | 0.87      | 0.79      | 1.06      | 1.69 | 1.46 | 1.05 | 1.26 | 1.17 |
| 7                  | 1.60      | 0.82      | 2.29      | 1.39 | 2.06 | 1.55 | 1.43 | 2.03 |
| 8                  | 2.37      | 1.12      | 3.15      | 1.08 | 3.30 | 1.48 | 4.07 | 1.14 |

* Modes of dehydration are similar to those presented in table 1 and figures 1–2.

Changes in the processes of structure formation, composition and microstructure transformation at
high temperatures (T = 378 K), i.e. in the “hard” mode of radiation-convective drying, have a direct
connection with the mechanism of external and internal heat and mass transfer. In the process of
drying a moisture-saturated membrane, heat transfer is complicated by mass transfer, as a result of
which the intensity of the process increases significantly. Moisture is transferred near the surface in a
molecular way. The vapor turbulizes the boundary layer intensively leaving the sample evaporation
zone, as a result of which the hydrodynamic conditions near the sample surface change. At the same time, the maximum development of shrinkage processes is observed (figure 2a, curve 2).

At the stage of constant drying rate (figure 3a, curve 2) to moisture content in the range from 3.0 kg/kg to 2.5 kg/kg, when capillary moisture is removed, shrinkage occurs under the action of capillary pressure. As the moisture evaporates, the curvature of the menisci increases and the resulting Laplace pressure is transferred through the films connected with the meniscus.

![Figure 3](image)

**Figure 3.** Dependence of the average evaporation rate on the moisture content at various modes of drying nanomembranes. Figures – drying modes in table 1.

Continuous steam-conducting channels intensify the process of moisture removal in the range of moisture contents 1 <W <3 kg/kg. At this stage, moisture is transferred in the vapor phase.

In the range of moisture contents up to W ≈ 1 kg/kg, the growth of capillary pressure lags behind the growth of the membrane structure resistance to compression. At a moisture content of W <1 kg/kg, shrinkage occurs under the action of intermolecular forces, which leads to strengthening of the membrane structure. Cracks are formed at the time of a significant decrease in the moisture content of the surface layer. Thus, during the drying process, the pore space changes and large pores are formed. This leads to an increase in their average size and porosity (tables 1, 2). However, significant shrinkage of the material practically compensates for the change in specific surface area, it always increased by 15%. Due to the non-uniform pore size distribution, the f coefficient increased by a factor of 1.47 compared to the initial structure.

### 3.2. Vacuum drying

Let us consider the structure of samples that were dried in vacuum at temperatures from 298 K to 274 K from moisture content (where W varied from 6.73 kg/kg to 0.4 kg/kg). Then they were further dried in a radiation-convective mode at T = 378 K in a drying oven to an absolutely dry state. During vacuum drying at the first stage, cracks were also formed due to the development of shrinkage stresses. From figures 1b, 2a (curve 3) follows that the number of small (from 8 nm to 80 nm) pores has significantly decreased and large pores (from 80 nm to 500 nm) have formed. The distribution curve had three maxima. One weakly expressed in the fine-pored area and two in the large-pore area. There is an increase in the average pore size, porosity and coefficient of heterogeneity (table 2).

It is obvious that, despite the difference in drying modes (figure 3a, curves 2, 3), the structure-forming processes in them are similar. Although the intensity of the process during evacuation decreased by almost 5 times (figure 3a, curve 3). This is due to the fact that the transfer of moisture from the inner layers to the outer is determined not only by the temperature gradient, but also by the pressure of moisture vapor. As a result, the binding energy increases. Compared with drying at T = 378 K, the number of pores decreased in the range from 5 to 30 nm. In addition, large pores were formed in the range from 300 nm to 500 nm (figure 2a, curves 2, 3). This is associated with an increase in the coefficient of inhomogeneity f.
Subsequent drying at $T = 378$ K of the evacuated sample causes significant transformations of the formed structure. The pores are isometric, and the density of compact aggregates increases. Figures 1b, 2a curves 3 and 4 show that the number of small pores has decreased (from 8 nm to 100 nm) and the number of pores has increased in the range from 100 nm to 400 nm. However, larger pores over 400 nm are absent. There is a shift of 2 maxima in the large-pore zone of the structure to the left.

3.3. Freeze drying
Freeze drying [5–6] is one of the approaches to reduce the irreversibility of structural changes in strongly shrinking materials during drying. The samples were preliminarily frozen at a temperature from 253 K to 213 K to obtain a homogeneous cryogenic structure and placed in a sublimator. Experiments in a sublimator were carried out under isothermal conditions at temperatures of 272 K and 267 K at atmospheric pressure and evacuation ($P = 0.33$ Pa). The inner zone undergoes a process of moisture removal and compaction due to its migration to the outer zone. The parameters of the porous structure obtained under different conditions of sublimation are shown in table 1 (5–8). The characteristics of the porous space and the distribution curves were obtained separately for the inner and outer zones (curves 5, 6 and 5 ', 6', respectively). Analysis shows that frost drying under vacuum does not cause significant changes in the microstructure of the samples even at $T = 272$ K. The outer and inner zones of the samples have a similar structure. In the inner zone of the sample, a slight increase in the proportion of small pores is observed (figure 2a, curves 5, 6) and the maximum of the pore diameter distribution shifts to the left compared to the distribution curve of the original sample (figure 1b, curves 1, 5, 6). As follows from the analysis of the distribution curves (figures 1b, 2a curves 5 ', 6') here the transformation of the structure is more significant than in the inner zone. From tables 1, 2 (samples 5, 6 and 7, 8) it follows that sublimation at atmospheric pressure leads to a more significant deformation of the porous space.

Thus, the preservation of the membrane framework original structure is due to the crystallization of pore moisture during freezing. This excludes the manifestation possibility of the material shrinkage capillary mechanism in the process of subsequent sublimation. Vacuum – freeze drying allows ice to be removed from highly shrinking capillary-porous systems without disturbing their structure. This can be used both for reliable information on the porous structure of the initial membranes and for a differentiated assessment of various properties of the structure components. The membranes structure changes after heat treatment.

4. Conclusions
With an increase in the coating thickness (more than 1 μm), internal stresses increase, and microcracks are formed between the pore channels. Therefore, there is an optimum thickness in which small internal stresses with a high relaxation rate are possible during drying. The entire set of data obtained indicates that the formation of nanomembranes with highly elastic properties is possible at thicknesses from 0.5 to 1.0 μm. Thus, the drying process of nanomembranes is multi-stage. At the stage of removing liquid from the space between the pore channels, surface tension forces and the action of capillary pressure are of great importance.

References
[1] Yazdizadeh M, Yelon A and Ménard D 2020 Journal of Porous Materials 27 995–1002
[2] Kadir M F, Alpysbayeva B E, Batalova M S and Korobova N E 2020 Materials today – Proceedings 25(1) 101–5
[3] Batalova M S, Alpysbayeva B E and Korobova N E 2020 Russian Young Researchers in Electrical and Electronic Engineering (EIConRus) 2020 2115–8
[4] Batalova M, Alpysbayeva B, Kadir M, Yskak M, Kalkozova Zh and Korobova N 2019 Russian Young Researchers in Electrical and Electronic Engineering (EIConRus) 1999–2002
[5] Roy M L and Pika M J 1989 PDA J Pharm Sci Technol. 43 60–6
[6] Genin N, Rene F and Corrieu G 1996 Chem Eng Process 35 255–63