Permeability Asymmetry in Composite Porous Ceramic Membranes

I.M. Kurcharova, N.I. Laguntsov, V.I. Uvarovb, O.V. Kurchatovac

aNational Research Nuclear University MEPhI, Kashirskoe shosse 31, Moscow 115409, Russia
bInstitute of Structural Macrokinetics and Materials Science, BAS, ul. Akademika Osip'yan 8, Chernogolovka 142432, Moscow region, Russia
cJSC Aquaservice, Kashirskoe shosse 31, Moscow 115409, Russia

Abstract

The results from the investigation of transport characteristics and gas transport asymmetry in bilayer composite membranes are submitted. These membranes are produced by SHS method. Asymmetric effect and hysteresis of permeability in nanoporous membranes are detected. It’s shown, that permeability ratio (asymmetry value of permeability) increases up to several times. The asymmetry of permeability usually decreases monotonically with the pressure decrease.

Keywords: Assimetric gas transport, permeability ratio, selective layer, self-propagating high-temperature synthesis (SHS) method

1. Introduction

Nanoporous membranes are gradient porous structures, i.e., structures wherein the radius of pores varies in a chosen direction. Similar objects are widely used in the membrane gas separation, hydrogen energetics, and other hi-tech industries [1,2]. Particularly, composite and asymmetric membranes are related to such class of objects, in which the size of pores decreases from layer to layer. Selective layer is nonporous diffusion layer with the pores size is nearly equal to \(10^{2} \pm 10^{3}\) nm. This layer is formed on the nanoporous layer, wherein the size of pores is about \(10^{3}\) nm. Recent experiments showed that gas transport through such kind of structures can be asymmetric; i.e., the value

* Corresponding author. E-mail address: aquaserv@mail.ru
of the gas flow depends on the direction of the pressure gradient and its variation can reach several times (the great asymmetry of permeability) [3,4,5]

As it was shown in work [5] the experimentally observed anisotropy cannot be described in the context of existing models. It was established that this effect is observed when the free molecular component of the flow in a membrane is significant; this property occurs at pressures close to atmospheric in the nanometer range of pores size. The interaction of gas molecules with the surface is determinative in the free molecular gas flow mode; thus, it was assumed that the anisotropy of permeability appears, cause of a specific interaction of gas molecules with the walls of pores. The directional distribution of molecules becomes anisotropic. To describe the specific scattering of the gas on the rough surface, the "white noise" model is used [5], which is obtained by the methods of stochastic dynamics. According to this model, the directional distribution of gas molecules, escaping from the surface of a pore is given by the expression:

$$
\omega(\theta) = \frac{A \exp(-A \theta^2)}{\sqrt{\pi} \text{erf}\left(\frac{\sqrt{A}}{2}\right)},
$$

(1)

where $\theta$ is the molecule outlet angle to the surface normal and $A$ is the non-dimensional interaction parameter, determining the width of the distribution.

At $A \ll 1$, the directional distribution is isotropic, that corresponds to the diffusion model of the interaction of molecules with the surface (model of full accommodation). At $A \gg 1$, the range of outlet angles from the surface is limited.

Stochastic dynamics method has previously been used to describe the transport of photons, phonons and electrons in the channels with rough walls [6,7]. In these works, an approach to transport description involves the introduction of several parameters of the channel with a rough surface, which for a porous medium cannot be determined simultaneously for a porous structure.

Thus, the frequency of collisions with the surface depends on the parameter $A$, leading to the increase of molecules concentration on the inner surface of pores and, correspondingly, in the surface flow. Theoretical backgrounds from [8,9] indicate that the surface flow is the main reason for the appearance of the transport asymmetry in membranes with porosity gradient.

The theoretical approaches, describing the asymmetric gas transport in bilayer membranes with the surface flow proposed in works [8-11], but the experimental data is not presented.

In this work, the results of experimental studies of gas transport in bilayer composite ceramic membranes, produced by the SHS method, are presented.


The properties of a porous ceramic depend on the form of an initial material, porosity, and structure of a product. The characteristics of the structure are the total, open, and closed porosities, permeability, size of pores, pore size distribution, shape of pores, and specific surface. The most important characteristics of the structure are porosity and size of pores. This size can vary in wide ranges from the order of nanometer to several millimeters. Products with a porosity of 20–27% can be easily obtained. However, the production of the porous ceramic with high and particularly ultrahigh porosity requires the use of special procedures and processes. One of such processes, "solid flame phenomenon," was discovered in 1967 by Russian Academician A.G. Merzhanov with colleagues. It was used to develop a new method for producing materials in the combustion mode that was called the self-propagating high-temperature synthesis (SHS). This method is based on the fact that the synthesis and sintering reactions become exothermic with the temperature increase, ensuring the possibility of the propagation of a combustion wave in the self-support mode.

Figure 1 shows the microstructure of the produced sample.
To obtain membranes with nanopores (2–3 nm), an oxide system based on mixed oxides and nitrides with the general formula AlSiN$_3$0$_3$C$_2$P or P$_{0.03}$Ti$_{1.97}$O$_2$ was formed on the synthesized samples by the “spin-coating” method. The installation is used for analyzing the temperature and pressure dependences of gas permeability for various types of membranes, in particular, composite, ceramic, and polymeric. The installation can be used also for investigation of various porous structures.

The bench was designed to study the asymmetry of gas transport in composite membranes and allows investigating of the samples permeability at different directions of the gas flow without rotation of the sample.

3. Discussion Of The Experimental Data

As it was mentioned above, the interaction parameter $A$ characterizes the effect of the specific interaction of gas molecules with the surface of pores on the gas flow through the porous membrane. In order to determine the interaction parameter $A$, the dependences of the relative flow on the interaction parameter of gas molecules with the surface of the porous structure were plotted within the white noise model for all membrane samples. The relative flow is the dependence between the gas flow at given interaction parameter and the flow calculated within the diffusion scattering model. Gas flows in the free molecular regime through the membrane samples under study were experimentally measured. Using the theoretical dependences of the relative flow on the interaction parameter of gas molecules with the surface of the porous medium within the white noise model, the interaction parameters for all samples were determined.

Permeability was studied and the interaction parameter for monolayer samples of three porous materials was determined. The parameters of the samples and the results of the study are summarized in Table 1. It is noteworthy that the interaction parameter correlates with the hydraulic radius of pores. This can be qualitatively explained by the fact that if the channel radius is reduced, gas molecules will longer stay in the potential field of the surface, i.e., the interaction of gas molecules with the surface will be stronger. Furthermore, a decrease in the radius of pores reduces the number of intermolecular interaction events, thus increases the effect of the anisotropic directional distribution of molecules in the porous structure.

| Material of the membrane sample | Hydraulic radius $\rho$, nm | Porosity $\varepsilon$, % | Interaction parameter $
\begin{array}{|c|c|c|c|}
\hline
\text{Material of the membrane sample} & \text{Hydraulic radius } \rho, \text{ nm} & \text{Porosity } \varepsilon, \% & \text{Interaction parameter} \\
\hline
\text{Al}_2\text{O}_3 & 470 \pm 20 & 35 & 0.62 \pm 0.03 \\
\text{SiC} & 110 \pm 20 & 50 & 1.63 \pm 0.07 \\
\text{BN} & 80 \pm 30 & 30 & 2.8 \pm 0.1 \\
\hline
\end{array}$

In this work, boron nitride membranes, obtained by SHS technology, were studied. A 10-\mu m-thick mesoporous P$_{0.03}$Ti$_{1.97}$O$_2$ coated with pores of an average diameter of $<d>$ ~3 nm and a porosity of 7% was formed on the geometric surface of the first layer (a thickness of 4 mm, a porosity of 38%, a pore size of 50 nm, and a specific surface of 50 m$^2$/g). These membranes were chosen for studies cause they have a developed inner surface and a narrow pore size distribution, which makes it possible to determine easily the average hydraulic radius of pores of
these membranes.

The measurements were performed with three gases: light, poorly adsorbed He; heavy, easily adsorbed CO₂; and intermediate N₂; hydrogen was also used to study the hysteresis of the permeability of SHS porous structure.

The results of the studies are shown in Figs. 2 and 3.

![Graphs showing temperature and pressure dependences for nitrogen and carbon dioxide](image)

Fig. 2. (Left panel) Temperature and (right panel) pressure dependences from the value of asymmetry of membrane permeability for nitrogen.

![Graphs showing temperature and pressure dependences for nitrogen and carbon dioxide](image)

Fig. 3. (Left panel) Temperature and (right panel) pressure dependences from the value of asymmetry of membrane permeability for carbon dioxide.

In Figs. 2 and 3, direct supply \( J_{dir} \) means that the gas was supplied on the side of the membrane with a size of pores of 3 nm and reverse supply \( J_{rev} \) means that the gas was supplied on the porous side of the membrane.

According to figures 2 and 3, the value of asymmetry of permeability decreases with an increase in both pressure and temperature. As a temperature increase reduces the surface component of the flow and a pressure increase is accompanied by an increase in the volume component of the flow, the appearance of asymmetric gas transport is conditioned due to the effect of the surface flow.

Table 2 presents the flows ratio of helium/carbon dioxide and helium/nitrogen gas pairs at the direct supply of the gases at an excessed pressure of 8 atm. It can be seen that the flows ratio for both gas pairs increases with the temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>He/N₂ flow ratio</th>
<th>He/CO₂ flow ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>((M_{hel}/M_{atm})^{0.5})</td>
</tr>
<tr>
<td>340 K</td>
<td>2.222±0.009</td>
<td>2.645</td>
</tr>
<tr>
<td>370 K</td>
<td>2.597±0.008</td>
<td></td>
</tr>
<tr>
<td>420 K</td>
<td>2.667±0.008</td>
<td></td>
</tr>
</tbody>
</table>

It is important that the ratio of nitrogen and helium flows at high temperatures is nearly equal to the inverse ratio of the square roots of the molar masses of these gases. This is characteristic of the free-molecular gas flow mode.
This fact confirms again, that asymmetric gas transport phenomena in composite membranes is conditioned by the influence of the surface flow. It can be assumed that the flows ratio for easily adsorbed carbon dioxide gas reaches the ratio of the square roots of the molecular masses at higher temperatures.

The effect of the surface flow on the gas flow in an asymmetric channel was considered in work [14]. The calculated degrees of transport asymmetry in the case of the anisotropic distribution of molecules over directions of motion ($A > 0$) the value of asymmetry is qualitatively equal to the value observed experimentally. Asymmetry is conditioned by increase of the number of collisions of molecules with the surface, and, as a result, by increase of the number of molecules adsorbed on the surface. Cause of the gradient of the surface density, a flow of adsorbed molecules toward decreasing surface density is occured at the interface of change in the radius of a pore; this flow has the same direction and doesn’t depend on the pressure gradient. Consequently, the total flow increases, when the gas flow is supplied from the layer in which the directional distribution of molecules is asymmetric and decreases on the reverse direction.

As it was shown in work [14], that the surface diffusion coefficient in the layer with an anisotropic distribution of molecules is larger, than the flow at the interface is larger and, correspondingly, the value asymmetry of permeability is larger, also.

When the parameter $A$ in the layer with the narrow cross section of a pore is larger than that in the layer with the wide cross section, direct asymmetry is observed, whereas inverse asymmetry is observed in the opposite case. At equal interaction parameters, observed asymmetry is occured only at the surface diffusion and does not exceed 10%, which is confirmed by the reported data [15].

It is noteworthy that the simulation was performed under the assumptions of thermal equilibrium and small pressure gradient. The model under consideration involved statistically average quantities, which can be used only if the system is ergodic [16, 17]. As the scattering of molecules on the surface is described by a stochastic equation for change in the direction of motion of the molecule at collision with the surface, $\Theta'_{n+1} = -\Theta'_{n} + \zeta(t)$, where $\zeta(t)$ is the white noise function [5], the dynamic system under consideration has the stirring property; consequently, the system is ergodic because stirring is a more general property [16].

The description of scattering of molecules on the surface should satisfy the detailed balance principle. It can be easily seen that the scattering of the form $\Theta'_{n+1} = -\Theta'_{n} + \zeta(t)$ has this property, because this scattering for a large number of particles and, thereby, at time averaging (cause of the ergodicity of the system) becomes mirror scattering that satisfies the detailed balance principle. We also note that the form of scattering used in this work is in good agreement with the experimentally observed scattering profiles [18].

It should be taken into account that the molecules adsorbed on the surface can change the character of scattering, assumingly leading to the smearing of the anisotropic directional distribution of molecules; thus, the parameter $A$ is the effective parameter of interaction of molecules with the surface and with adsorbed gas molecules.

It should be noted, that an abrupt change in the number of collisions of molecules with the surface of the channel at the interface of change in the radius of a pore is due to the rough representation of the channel in the form of the sequence of cylindrical channels with different radius. The boundary characteristics in a real object, particularly, the number of collisions of molecules with the surface of a pore, are obviously smooth continuous functions. Within the model under consideration, abrupt changes in the parameters are expected at a length of about several lengths of free paths of gas molecules.

**Conclusions**

Asymmetric gas transport in bilayer composite membranes, produced by the self-propagating high-temperature synthesis, has been studied experimentally as a function of pressure and temperature. The experimental data, obtained in this work, indicates that the asymmetry of gas transport is caused by the surface flow, which is intensified by the specific interaction of gas molecules with the inner surface of pores. Under this condition the directional distribution of molecules becomes anisotropic.
Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation (project no. 14.579.21.0046).

References