

ISBN 978-5-9906777-6-0

# ION TRANSPORT IN ORGANIC AND INORGANIC MEMBRANES

*CONFERENCE PROCEEDING*



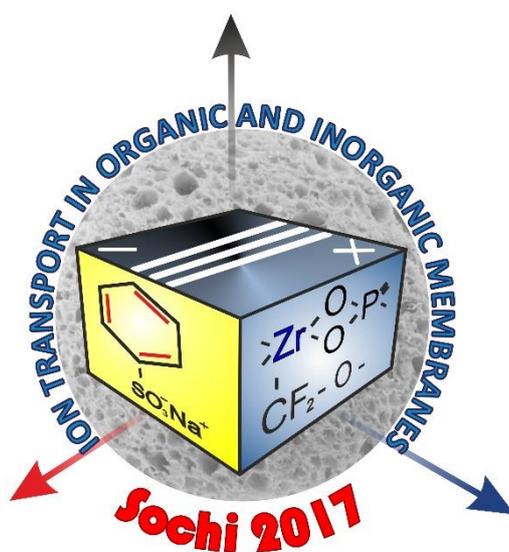
RUSSIAN ACADEMY OF SCIENCES  
SECTION "MEMBRANES AND MEMBRANE TECHNOLOGIES" OF D.I.  
MENDELEEV RUSSIAN CHEMICAL SOCIETY  
RUSSIAN FOUNDATION FOR BASIC RESEARCH  
FEDERAL AGENCY FOR SCIENTIFIC ORGANIZATIONS  
RAS SCIENTIFIC COUNCIL ON PHYSICAL CHEMISTRY  
RUSSIAN MEMBRANE NETWORK  
KUBAN STATE UNIVERSITY  
KURNAKOV INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY RAS  
«MEMBRANE TECHNOLOGY» INNOVATION ENTERPRISE

## INTERNATIONAL CONFERENCE

# *Ion transport in organic and inorganic membranes*

## Conference Proceedings

23 - 27 May 2017



Krasnodar 2017

## SCIENTIFIC/ORGANIZING COMMITTEE

**Chairman** YAROSLAVTSEV A.B. (*Russia*)  
**Co-chairman** ZABOLOTSKY V.I. (*Russia*)

POURCELLY G. (*France*)

NIKONENKO V.V. (*Russia*)

**Scientific secretary** KONONENKO N.A. (*Russia*)

AGEEV E.P. (*Russia*)

OZERIN A.N. (*Russia*)

BILDYUKEVICH A.V. (*Belarus*)

PISMENSKAYA N.D. (*Russia*)

BOBRESHOVA O.V. (*Russia*)

ROLDUGHIN V.I. (*Russia*)

CRETIN M. (*France*)

RUBINSTEIN I. (*Israel*)

DAMMAK L. (*France*)

SHAPOSHNIK V.A. (*Russia*)

FILIPPOV A.N. (*Russia*)

SHELDESHOV N.V. (*Russia*)

GRAFOV B.M. (*Russia*)

STAROV V.M. (*UK*)

GRANDE D. (*France*)

TSKHAY A.A. (*Kazakhstan*)

KHOHLOV A.R. (*Russia*)

VOLFKOVICH Yu.M. (*Russia*)

NOVAK L. (*Czech Republic*)

VOLKOV V.V. (*Russia*)

**Local organizing committee** (*Krasnodar, Russia*)

ACHOH A.R.

LOZA N.V.

BELASHOVA E.D.

LOZA S.A.

DOLGOPOLOV S.V.

MAREEV S.A.

ETEREVSKOVA S.I.

MELNIKOV S.S.

FALINA I.V.

NEBAVSKAYA K.A.

KOZMAI A.E.

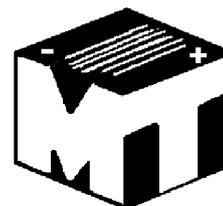
SHKIRSKAYA S.A.

### Sponsors:

RUSSIAN FOUNDATION  
FOR BASIC RESEARCH

FEDERAL AGENCY FOR  
SCIENTIFIC ORGANIZATIONS

«MEMBRANE TECHNOLOGY»  
INNOVATION ENTERPRISE



Мероприятие проводится при финансовой поддержке Российского фонда  
фундаментальных исследований, Проект № 17-08-20100

---

# SYNTHESIS AND PREDICTION OF TRANSPORT PROPERTIES OF HYBRID BILAYER ION-EXCHANGE MEMBRANES ON THE BASE OF MF-4SC, HALLOYSITE AND PLATINUM

Anatoly Filippov

Gubkin University, Moscow, Russia, *E-mail: filippov.a@gubkin.ru*

## Introduction

It is well-known that American cation-exchange perfluorinated membrane Nafion-117<sup>®</sup> (DuPont de Nemours, USA) and its Russian analogue MF-4SC (LTD Plastpolymer, Russia) are among the most widely used as separators in various devices like fuel cells, electrolyzers, electrolysers, sensors and investigated ion-exchange materials. Surface and spatial modification of ion-exchange membranes by incorporation of different inorganic dopants allows to change their stability and structural properties as well as ion and molecular transport. Polyaniline, nanoparticles of noble metals, oxides of zirconium and silicon [1], carbon and halloysite nanotubes [2] and other materials that can transform transport properties of the membranes in the preferred direction are frequently used as such dopants. This poses the priority problem of a reliable characterization of the newly created hybrid nanocomposites membranes. Here we propose an attempt to solve this problem for bilayer hybrid membranes, based on a theoretical examination of the electrodiffusion transport and our own experimental data for monolayer membranes. As a dopant, halloysite and platinum nanoparticles were used. Halloysite nanotubes of 2% by weight were added to one of the membrane layers during its synthesis by casting method. Halloysite clay is a natural tubule material formed by rolled kaolin sheets. Halloysite is aluminosilicate which is chemically identical to kaolin but typically contains minor amount (less than 1 wt%) of iron ions. Prior to synthesis, nanoparticles of platinum were deposited on the external surface of halloysite nanotubes [3]. A similar attempt to membrane characterization was made in our recent work [4] for the surface-modified MF-4SC membranes in low-temperature plasma. Thus, halloysite nanotubes are used not only as a container for the delivery of metallic nanoparticles inside the membrane matrix, but also as a hydrophilic object, which increases the moisture content of the membrane. Ion-exchange membranes with enhanced water uptake are interesting for fuel cells applications because make it possible to improve the properties of fuel cells.

## Experiment

Composite (hybrid) bilayer membranes based on the perfluorinated matrix MF-4SC, halloysite nanotubes and platinum nanoparticles were synthesized by a two-stage casting process: first a thicker layer of unmodified polymer, then a thin layer of polymer with the added halloysite nanotubes and platinum nanoparticles embedded on their outer surface (membrane No 1). A bilayer composite was also synthesized in a different order - a thinner, halloysite-modified layer was first cast, followed by a layer of pure polymer without dopant (membrane No. 2). When casting the membrane No. 1, a solution of polymer LF-4SC (manufactured by JSC "Plastpolymer", St. Petersburg, Russia) and a solvent of dimethylformamide were used. Initially, the first layer was cast from a pure polymer solution (thickness of 160  $\mu\text{m}$ ). The membrane was dried according to a standard procedure developed and described in detail in our work [3]. Then, after the first layer completely dried out, the second layer (thickness of 40  $\mu\text{m}$ ) was cast from a modified polymer solution of LF-4SC (using dimethylformamide as a solvent) with the addition of 2% wt. of halloysite nanotubes with platinum nanoparticles encapsulated on the outer surface of nanotubes. When casting membrane No. 2 we used a solution of polymer LF-4SC and two solvents: dimethylformamide and isopropyl alcohol. Primarily, the first layer was cast from a modified polymer solution of LF-4SC (isopropyl alcohol solvent) with the addition of 2% wt. of halloysite nanotubes functionalized by platinum nanoparticles on their outer surface (the thickness of the modified layer was 40  $\mu\text{m}$ ). The membrane was dried according to the standard procedure described in [3]. Then, after complete drying of the first layer, the second layer (160  $\mu\text{m}$  thick) was cast from a pure polymer solution of LF-4SC (a solvent was dimethylformamide). Thus,

reproducible homogeneous and resistant to aggressive media double-layer membranes without microdefects (microcracks), having a constant thickness were synthesized. The obtained hybrid nanocomposites No. 1 and No. 2 were studied by electron microscopy (Figs 1, 2) and characterized.

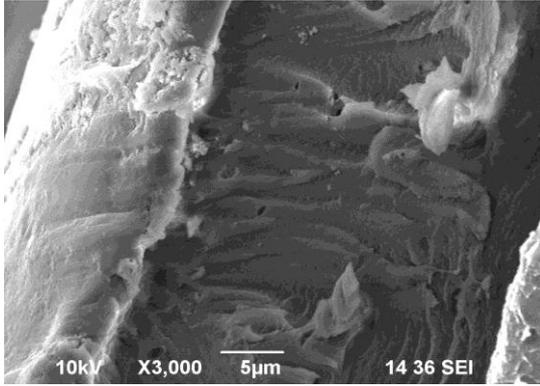


Figure 1. Microphotography of the cross section of bilayer hybrid membrane No. 2.

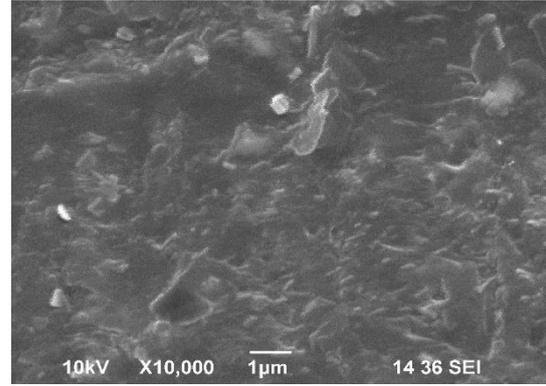


Figure 2. Microphotography of the modified surface of bilayer hybrid membrane No. 2.

### Theoretical prediction of diffusion permeability and comparison with experiment

Earlier in [3], we obtained data on the magnitude of physico-chemical parameters (diffusion coefficients of ions  $D_{m\pm}$  and the equilibrium ion-pair distribution coefficient  $\gamma_m$ , Table 1) of a single-layer membrane MF-4SC cast from a solution of a pure polymer and a membrane spatially modified by halloysite nanotubes (2% wt.) with platinum nanoparticles. On their basis, a priori to the experiment, the weak asymmetry of the diffusion permeability of the two-layer membrane No. 2 was quantitatively predicted. The calculation based on the model of the bilayer membrane developed earlier by us [5] showed a good agreement between the theoretical and experimental values of the diffusion permeability of the bilayer membrane over a solution of hydrochloric acid. This makes it possible to create bilayer hybrids with a predetermined diffusion permeability.

Table 1. Parameters of pure and hybrid single-layer membranes MF-4SC [3].

Membrane	$\gamma_m$	$D_{m+}, \mu\text{m}^2/\text{s}$	$D_{m-}, \mu\text{m}^2/\text{s}$	$D_m, \mu\text{m}^2/\text{s}$
initial MF-4SC, $i=2$	0.481	1417	15.4	30.1
MF-4SC/Hall+Pt, $i=1$	0.442	990	6.2	12.3

To find the theoretical values of diffusion permeability coefficients, the following formulas obtained in the above-mentioned work [5] were used:

$$P_s = \frac{(\bar{D}_{m1}/\gamma_1)(1+h_2/h_1)}{\sqrt{(|\bar{\sigma}_2| + \sqrt{\bar{\sigma}_1^2 + 4})^2 + 4(\bar{v}^2 - 1) + (|\bar{\sigma}_2|\bar{v} + \sqrt{\bar{\sigma}_1^2 + 4})}}, \quad (1)$$

$$P_w = \frac{(\bar{D}_{m1}/\gamma_1)(1+h_2/h_1)}{\sqrt{(|\bar{\sigma}_2| + \bar{v}\sqrt{\bar{\sigma}_1^2 + 4})^2 - 4(\bar{v}^2 - 1) + (|\bar{\sigma}_1| + \bar{v}\sqrt{\bar{\sigma}_2^2 + 4})}}, \quad (2)$$

where  $\bar{\sigma}_i = \gamma_i \left| \frac{\bar{\rho}_i}{C_0} \right| > 0$ ,  $\bar{D}_{mi} = \frac{2D_{mi+}D_{mi-}}{D_{mi+} + D_{mi-}}$ ,  $\gamma_i = \sqrt{\gamma_{i+}\gamma_{i-}}$ ,  $i = 1, 2$ ,  $\bar{v} = \frac{\bar{D}_{m1}h_2\gamma_2}{\bar{D}_{m2}h_1\gamma_1}$ ,  $i$  – number of the membrane layer (1- modified, 2- unmodified layer),  $\bar{\rho}_i$  – layer exchange capacity,  $\bar{D}_i$ ,  $D_{mi\pm}$ ,  $\gamma_i$ ,  $\gamma_{i\pm}$  – diffusion and equilibrium distribution coefficients of the electrolyte molecule and ions in the membrane,  $C_0$  – electrolyte concentration,  $h_i$  – thickness of the  $i$ -layer. Exchange capacities of both layers were considered equal to 0.98 M, and the ratio of the layer thicknesses  $h_2/h_1 = 4$ . The remaining parameters used are shown in Table 1. A comparison of the predicted

theoretical concentration dependences (curves) of the diffusion permeability coefficients of the bilayer membrane and their measured values (circles) is shown in Fig. 3 and 4. We note that the curves are drawn without any fitting of the physicochemical parameters of the membrane. The agreement between experiment and theory for a membrane facing the modified side to water is slightly better than when this side is turned to an acid solution.

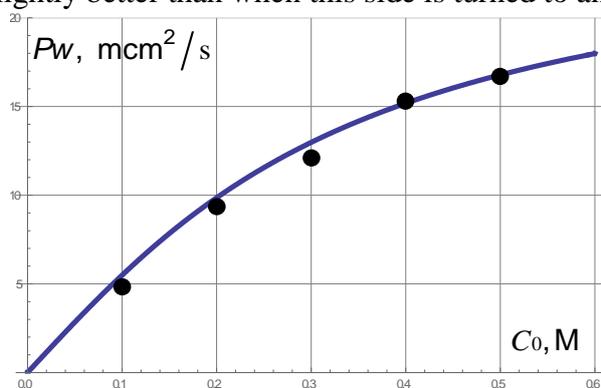


Figure 3. Dependence of the coefficient  $P_w$  on the concentration of HCl.

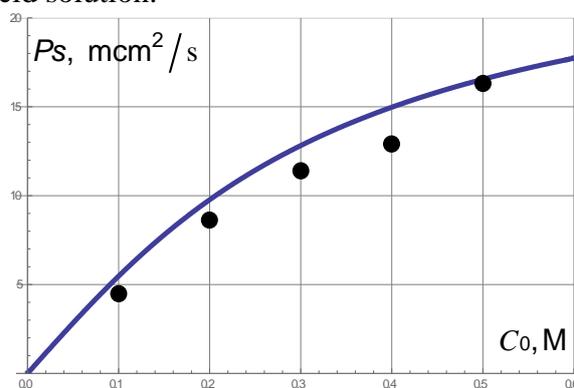


Figure 4. Dependence of the coefficient  $P_s$  on the concentration of HCl.

### Conclusion

The study of the transport characteristics of perfluorinated membranes after their spatial modification with halloysite nanotubes and platinum nanoparticles showed that the diffusion permeability of hybrid membranes is somewhat lower in comparison with the initial (pure) membrane. In this case, the integral coefficient of diffusion permeability of the membrane modified by halloysite nanotubes covered with platinum nanoparticles decreases by 50-55%. This suggests that under the operating conditions of the fuel cell the crossover through the modified membranes will be lower. The electric conductivity of membranes increases after modification. The greatest effect of increasing the electric conductivity (by about 30%) was noted again for a sample modified with halloysite and Pt. Since the observed changes in the structural characteristics cannot cause such an increase in the conductivity of the samples, the possible cause of this effect can be the contribution of the electronic conductivity of the metal. Thus, the modification of the perfluorinated membrane by the halloysite nanotubes with metal nanoparticles deposited on their outer surface does not lead to a noticeable change in the structure of the membranes and does not worsen their transport properties. This makes it possible to predict the effective use of hybrid membranes based on MF-4SC and halloysite nanotubes with platinum nanoparticles, not only as separating diaphragms in fuel cells and electromembrane devices, but also as promising catalytic systems.

This study was supported by the Ministry of Education and Science of the Russian Federation (Grant No 14.Z50.31.0035).

### References

1. Filippov A.N., Safronova E.Yu. Yaroslavtsev A.B. // *J. Memb. Sci.* 2014. V.471. P.110–117.
2. Filippov A., Khanukaeva Daria, Afonin D., Skorikova G., Ivanov E., Vinokurov V., Lvov Yu. // *J. Mater. Sci. & Chem. Eng.* 2015. V.3. P.58-65.
3. Filippov A., Afonin D., Kononenko N., Lvov Yu., Vinokurov V. // *Colloids Surf. A.* 2017. V.521. P.251-259.
4. Filippov A., Afonin D., Kononenko N., Shkirskaya S. // *AIP Conference Proceedings.* 2015. V.1684. P.030004-1–030004-9.
5. Filippov A.N., Starov V.M., Kononenko N.A., Berezina N.P. Asymmetry of diffusion permeability of bi-layer membranes // *Adv. Colloid Interface Sci.* 2008. V.139. P.29–44.