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Hybrid membranes based on short side chain perfluorinated sulfonic acid membranes (Inion) and heteropoly acid salts

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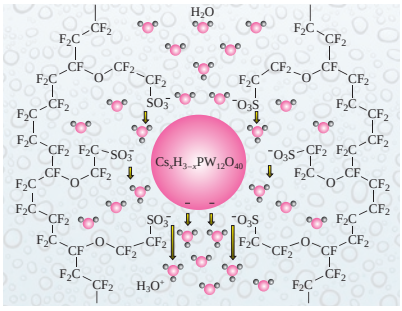
Transport properties of Inion, the new perfluorinated membrane containing short side chains, and of hybrid materials designed by the incorporation of nanoparticles of cesium hydrogen phosphotungstate into it were investigated. The Inion membranes possess a proton conductivity of 16.8 mS cm^{-1} upon a contact with water at 25 °C, while the modification with cesium hydrogen phosphotungstate (1.2 wt%) increases their conductivity up to 34.8 mS cm^{-1} accompanied by the simultaneously decreased diffusion permeability.



The environment pollution motivates the mankind to look for new renewable energy sources.[1,2] Fuel cells (FCs) are alternative energy devices demonstrating a high efficiency and releasing only water as the product.[3] Low-temperature FCs contain a proton-conductive polymer membrane as one of their key parts. Usually, FCs contain Nafion membranes based on perfluorinated sulfonic acid cationites.[4,5] However, their practical application brings up a number of problems, in particular, their operation requires a high humidity in order to maintain a high proton conductivity.[6,7] This problem is commonly resolved by membrane doping with nanoparticles of oxide materials that enhance the membrane conductivity at a reduced humidity.[8–10] Heteropoly acids and their salts are among the promising dopants.[11]

Considerable efforts were recently undertaken for obtaining membrane materials with improved properties. Most of hopes are put on membranes containing shortened side chains (*i.e.*, the chains that branch from the main chain and bear functional groups). There is an opinion that this facilitates the retention of membrane water and preservation of satisfactory conductivity at elevated temperatures (up to 130 °C),[12] which results in the especial attention paid to membranes with such shortened side chains.[13–16] Recently, the InEnergy company has already started the development of such membranes under 'Inion' brand in Russia.

Here we report the results of studies of the properties of new Inion membranes based on perfluorinated sulfonic acids and hybrid membranes designed by their doping with cesium hydrogen prosphotungstate.

Inion membranes† were prepared using the moulding method according to the known procedure.[17] Inion–CsHPWA hybrid membranes containing $Cs_xH_{3-x}PW_{12}O_{40}$ were synthesized *in situ*.[18] The dopant content in the resulting materials was 1.2 wt%, which is close to the reported optimum values.[11] The conductivity of the starting membrane is 16.8 mS cm^{-1} at 25 °C, which is much higher than that of Aquivion 870 under the same conditions (13.6 mS cm^{-1}).[18] The modification with cesium hydrophosphotungstate increases the conductivity almost twofold, *viz.*, up to 34.8 mS cm^{-1} (Figure 1).

According to the model of limited elasticity of membrane pore walls, the increase in the membrane conductivity upon its modification with cesium hydrogen phosphotungstate is caused by the widening of pores and, consequently, the channels in the membrane matrix that limit the membrane conductivity.[19,20] Furthermore, these insoluble salts of heteropoly acids are presented as nanosized particles on whose surfaces the cesium ions are replaced with protons possessing high acidity.[21] Therefore, this modification leads to an increased concentration of charge carriers, which provides an additional improvement of conductivity.

The results of proton conductivity measurements for the membrane samples at various relative humidities (RH) at 50 and

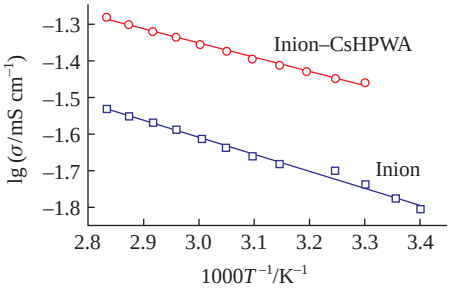


Figure 1 Conductivity of Inion-based membranes upon the contact with water.

† Inion membranes were provided by the InEnergy company (Russian Federation).

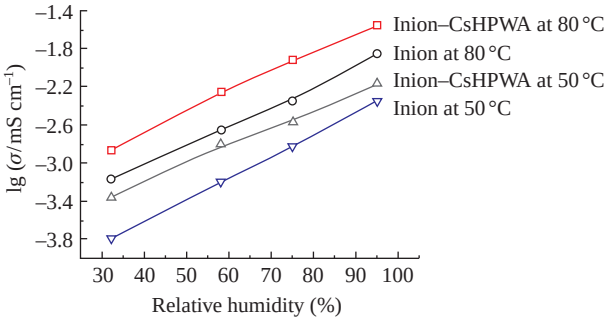


Figure 2 Dependence of membrane proton conductivity on the RH at 50 and 80 °C.

80 °C are shown in Figure 2. Their modification with cesium hydrogen phosphotungstate results in the increased conductivity for the entire RH range (from 95 to 32%). For example, at 80 °C and RH of 32%, the modified Inion membranes demonstrate a threefold growth in the proton conductivity, from 0.43 to 1.36 mS cm^{-1}.

The dopant particles occupy a part of pore volume in the hybrid membranes, which prevents their constriction. On the other hand, this creates narrow zones inside the pores that restrict proton transfer.[22] Furthermore, the proton transfer at a high humidity occurs between water molecules that possess the equal proton affinity, while functional groups with considerably lower proton-accepting capability are almost not involved in it. A decreased humidity results in the dehydration of membrane and transition of protons into a weakly hydrated state, up to $H_5O_2^+$ ions. The direct proton transfer between these ions is nearly excluded due to the high proton transfer enthalpy. The considerable increase in the distance between oxygen atoms with similar proton-accepting capability is not less important. Under these conditions, the proton conductivity is limited by proton jumps,[22] thus the role of pore wall surface in the transfer rises inevitably. In the meantime, the pores of hybrid membranes bear additional oxygen-containing moieties that can participate in the proton transfer. This can also decrease the proton jump length and hence raise the conductivity of hybrid membranes at the low humidity.

The diffusion permeability characterizes the diffusion rate of anions through the membranes. Since the concentration of cations and hence, the rate of cation transfer, are much higher inside the cation exchange membranes, the protons are much more quickly transferred to the membrane surface contacting with pure water because their activity is lower there. However, due to the electrical neutrality requirement, their further transfer is impossible without the charge compensation, which leads consequently to the limitation of this process by the anion transfer rate.

Transformation of original Inion membrane into the membrane doped with cesium hydrogen phosphotungstate leads to a considerable decrease in its permeability for 0.1 M HCl solution at 25 °C from 4.5×10^{-7} to 3.3×10^{-8} cm^2 s^{-1}. The membrane pore walls are charged negatively since they are covered with SO_3^- ions. On the other hand, owing to electrostatic interactions, the majority of oppositely charged counter-ions are localized near these walls. As a result, the double electric layer with a typical thickness of *ca*. 1 nm is formed.[4,7] Almost all the counter-ions are localized within that layer. Conversely, the anions are displaced from that layer. An electrically neutral solution containing nearly equal amounts of mobile cations and anions is located in the pore centers. It is believed that its concentration is almost equal to that of solution that surrounds the membrane. The proton conductivity of cation exchange membranes is predominantly determined by the transfer in the Debye layer along the pore walls. At the same time, anions primarily move through the electrically neutral solution localized in the pore centers. The nanoparticles of heteropoly acid salts are formed directly in the membrane pores. Since their surface is also charged negatively, they create the similar double electric layer around themselves and are localized near the membrane pore center, thus displacing the 'electrically neutral' solution with anions and nonpolar molecules localized in it. This establishes the increased selectivity of hybrid membranes obtained.

In conclusion, the perfluorinated Inion membranes containing the short side chains demonstrate the high proton conductivity values exceeding those of both Nafion and Aquivion. The present work has revealed that their modification with cesium hydrogen phosphotungstate can enhance their conductivity even more, both in contact with water and at low humidity, and simultaneously decrease the rate of anion diffusion. The reported membranes also possess the high selectivity, which makes them a promising material for various practical applications, including the fuel cells and other electrochemical devices.

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References

1 N. L. Panwar, S. C. Kaushik and S. Kothari, *Renew. Sustain. Energy Rev.*, 2011, **15**, 1513.
2 H. Hu, N. Xie, D. Fang and X. Zhang, *Appl. Energy*, 2018, **211**, 1229.
3 I. A. Stenina and A. B. Yaroslavtsev, *Pure Appl. Chem.*, 2017, **89**, 1185.
4 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535.
5 A. Kusoglu and A. Z. Weber, *Chem. Rev.*, 2017, **117**, 987.
6 A. Chandan, M. Hattenberger, A. El-Kharouf, S. Du, A. Dhir, V. Self, B. G. Pollet, A. Ingram and W. Bujalski, *J. Power Sources*, 2013, **231**, 264.
7 E. Yu. Safronova and A. B. Yaroslavtsev, *Petr. Chem.*, 2016, **56**, 281 (*Membr. Membr. Tekhnol.*, 2016, **6**, 3).
8 T. Xu, *J. Membr. Sci.*, 2005, **263**, 1.
9 Y. Zhang, H. Zhang, C. Bi and X. Zhu, *Electrochim. Acta*, 2008, **53**, 4096.
10 A. V. Parshina, E. Yu. Safronova, E. A. Ryzhkova, S. S. Chertov, D. V. Safronov, O. V. Bobreshova and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2016, **26**, 505.
11 E. Gerasimova, E. Safronova, A. Ukshe, Y. Dobrovolsky and A. Yaroslavtsev, *Chem. Eng. J.*, 2016, **305**, 121.
12 J. Li, M. Pan and H. Tang, *RSC Adv.*, 2014, **4**, 3944.
13 K. D. Kreuer, M. Schuster, B. Obliers, O. Diat, U. Traub, A. Fuchs, U. Klock, S. J. Paddison and J. Maier, *J. Power Sources*, 2008, **178**, 499.
14 A. Stassi, I. Gatto, E. Passalacqua, V. Antonucci, A. S. Arico, L. Merlo, C. Oldani and E. Pagano, *J. Power Sources*, 2011, **196**, 8925.
15 Y.-C. Park, K. Kakinuma, H. Uchida, M. Watanabe and M. Uchida, *J. Power Sources*, 2015, **275**, 384.
16 X. Luo and S. Holdcroft, *J. Membr. Sci.*, 2016, **520**, 155.
17 S. S. Ivanchev, V. S. Likhomanov, O. N. Primachenko, S. Ya. Khaikin, V. G. Barabanov, V. V. Kornilov, A. S. Odinokov, Yu. V. Kulvelis, V. T. Lebedev and V. A. Trunov, *Petr. Chem.*, 2012, **52**, 453 (*Membr. Membr. Tekhnol.*, 2012, **2**, 3).
18 E. Yu. Safronova, A. K. Osipov and A. B. Yaroslavtsev, *Petr. Chem.*, 2018, **58**, 130 (*Membr. Membr. Tekhnol.*, 2018, **8**, 34).
19 A. B. Yaroslavtsev and Yu. P. Yampolskii, *Mendeleev Commun.*, 2014, **24**, 319.
20 D. V. Golubenko, E. Yu. Safronova, A. B. Ilyin, N. V. Shevlyakova, V. A. Tverskoi, G. Pourcelly and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2017, **27**, 380.
21 E. Yu. Safronova, A. K. Osipov, A. E. Baranchikov and A. B. Yaroslavtsev, *Inorg. Mater.*, 2015, **51**, 1157 (*Neorg. Mater.*, 2015, **51**, 1249).
22 A. B. Yaroslavtsev, *Russ. Chem. Rev.*, 2016, **85**, 1255.

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