Novel nanocomposites MF-4SC/halloysite/Pt (Fe) and new method of membrane characterization

<u>Filippov A.N.</u>^{*}, Afonin D.S., Kononenko N.A. and Shkirskaya S.A. *Gubkin University, Moscow, Russia*

*e-mail: filippov.a@gubkin.ru

We synthesized novel hybrid materials from freshly prepared monolayer membranes modified spatially by halloysite nanotubes (mass fraction of 2%) and embedded platinum or iron nanoparticles. The original pure membrane MF-4SC was cast from a polymer solution (7% by weight LF-4SC solution in dimethylformamide, exchange capacity of 0.98 mgEq/g). New nanocomposites are stable against their physicochemical and mechanical properties and promising for use in fuel cells. To determine the physicochemical parameters of the listed membranes the special method developed in our recent paper [1] was used. Through minimizing the deviation between experimental and theoretical values of the integral diffusion permeability coefficient [2], using Mathematica-10 software, the average diffusion $D_m = 2D_{m-}D_{m+}/(D_{m-} + D_{m+})$ and equilibrium distribution $\gamma_m = \sqrt{\gamma_{m+}\gamma_{m-}} < 1$ coefficients as well as the ratio of individual ions diffusivities $v_m = D_{m-}/D_{m+}$ for the 1:1 electrolyte molecules inside the membrane matrices were calculated. We found that average diffusivity of the electrolyte molecule (HCI) in the pure membrane is largest and approximately 2 times greater than that in the halloysite membrane with iron nanoparticles, and 4 times greater than in the halloysite membrane is also largest, and γ_m of the membrane with iron particles greater than that of

the membrane with platinum. Reducing γ_m indicates an increase in positive sorption of counter-ions (protons) in the membrane matrices. Minimization of the functional of errors has allowed establishing that the proton mobility in the membrane exceeds of chlorine ion mobility by several orders.

To check the validity of the obtained values of physicochemical properties of investigated membranes, we used the formula for the electric conductivity, provided in [1]. The functional of errors for conductivity was minimized using only parameter v_m ; the other two parameters (D_m, γ_m) were chosen from the calculations

on the diffusion data. This is the essence of our new characterization method. Independent measurements of conductivity confirmed the fact of the dominance of the proton mobility in the membranes. The same is confirmed implicitly by values of proton transport numbers (close to 1 inside all membranes) which were measured in the third series of independent experiments. We can conclude that there is a good agreement for their diffusion permeability and acceptable agreement for electrical conductivity. The study of electroosmotic permeability of the composites investigated made it possible to determine a significant impact of modifying agent (nanoparticles of Pt and Fe in halloysite nanotubes) on the water transfer by protons. When introducing Pt and Fe nanoparticles (20 nm) into the membrane MF-4SC/halloysite, there is a decrease of electroosmotic permeability of 40-50%. This suggests that the structure of membranes becomes more crosslinked and water transfer occurs only by hydronic complexes.

Thus, it is proved that a sample of perfluorinated membrane MF-4SC/halloysite/Pt possesses the greatest electrical conductivity and the limiting current value and has a reduced diffusion and electroosmotic permeability while maintaining high proton selectivity. We note that the results obtained can theoretically predict diffusive permeability and electrical conductivity as well as current-voltage curve [3] of bilayer membranes of any thickness, consisting of unmodified layer and modified layer with halloysite containing iron or platinum nanoparticles.

Acknowledgements This work was supported by the Russian Science Foundation, project no. 14-19-01045.

- [1] A. Filippov, D. Afonin, N. Kononenko, and S. Shkirskaya, AIP Conf. Proc., 2015, 1684, 030004.
- [2] A.N. Filippov, E.Yu. Safronova, A.B. Yaroslavtsev, J. Membr. Sci., 2014, 471, 110.
- [3] A.N. Filippov, Colloid J., 2016, 78, 397.