

## SECTION 2. APPLICATIONS OF NANOMATERIALS (ELECTRONICS, MECHANICS, BIOLOGY etc.)

### PROTON-CONDUCTING MEMBRANE WITH SPATIALLY HETEROGENEOUS STRUCTURE BASED ON POLYMER-SILICA NANOCOMPOSITES

*E. Trofimchuk<sup>1</sup>, N. Nikonorova<sup>1</sup>, I. Meshkov<sup>2</sup>, A. Muzafarov<sup>2</sup>,  
M. Gallyamov<sup>1</sup>, D. Kondratenko<sup>1</sup>, N Bakeev<sup>1,2</sup>*

<sup>1</sup>*Moscow State University, Russia*

<sup>2</sup>*Institute of Synthetic Polymeric Materials RAS, Russia, Moscow*

**Abstract** – An original approach for the preparation of ternary proton-conducting membranes consisting of high density polyethylene (PE), silicon dioxide, and phosphoric acid for the intermediate temperature (140–180 °C) fuel cell is presented. The base of this method is a template synthesis of silica phase using hyperbranched polyethoxysiloxane as a precursor by hydrolytic condensation reaction within the volume of the nanoporous polymer matrix with pore's diameter of about 10 nm obtained via the mechanism of delocalized solvent-crazing. The received polymer-silica nanocomposites containing up to 40 wt.% of SiO<sub>2</sub> were characterized by a structure of two interpenetrating networks, and silicon dioxide formed a rigid three-dimensional framework. Loading of composites by phosphoric acid was carried out by their heating in an environment of H<sub>3</sub>PO<sub>4</sub> at 160 °C that was above the melting point of PE. In this case, the polyethylene melt migrated from inner volume to surfaces of the composite while emerged pores were filled with acid. The amount of introduced acid increased linearly with a growth of silica phase in the composite and maximum content of H<sub>3</sub>PO<sub>4</sub> equaled to 50 wt.%. The proton-conducting membranes obtained are characterized by conductivity of 0.03 S/cm and the best performance of 0.4 V at current densities of 0.4 A/cm<sup>2</sup> at 160 °C.

#### I. INTRODUCTION

Today polymeric materials characterized by the high proton conductivity (10<sup>-3</sup>-10<sup>-1</sup> S/cm) attract the considerable interest because they are prospective as the proton-conducting membranes for fuel cells (FC). FCs are well known as a promising alternative power sources due to their high efficiency of energy conversion and low pollutant emission [1]. Conductive channels in the similar polymer membranes are usually formed via the microphase separation of the hydrophobic and hydrophilic regions as in Nafion, or via loading of a large amount of the conductive component (about 5 molecules of the filler per monomer unit) as in polybenzimidazoles.

In this paper the conductive channels are proposed to form using crazing mechanism, i.e. in the process of uniaxial stretching of polymer films in the liquid medium. It is known [2] that solvent-crazing allows to create a system of highly dispersed interpenetrating pores in the solid amorphous and semi-crystalline polymers, as well as filling the polymer matrices by substances of different nature, including thermodynamically incompatible with it (metal, oxides, salts, etc.).

The aim of this work is the development of an approach for the preparation of proton-conducting membranes based on high density polyethylene (HDPE) and phosphoric acid (PA) using a process of solvent-crazing.

#### II. RESULTS AND DISCUSSION

The matrices characterized by the open nanoporous structure were obtained on a base of the commercial film of high density polyethylene ( $M_w=2\times 10^5$ , degree of crystallinity 70%,  $T_{melt}=130^\circ\text{C}$ , thickness 75  $\mu\text{m}$ ) via the mechanism of delocalized crazing [1]. In order to give HDPE the proton conductivity, porous films were saturated by 85% solution of PA. These materials possessed relatively high proton conductivity of about  $1\times 10^{-4}$  S/cm (Fig. 1, curve 2), but they were not stable over time due to the exudation of a hydrophilic acid at the surface of hydrophobic HDPE.

To prevent migration of the proton-conducting compound and to increase the stability of membranes, the phase of silica that is formed a hydrophilic backbone was synthesized within the

polymer films. Hyperbranched polyethoxysiloxane, HPEOS ( $M_w=3 \times 10^4$ , density  $1.17 \text{ g/cm}^3$ , viscosity  $18.8 \text{ cP}$ , effective diameter of molecule  $2\text{-}5 \text{ nm}$ ) was used as the precursor of  $\text{SiO}_2$ . HPEOS was introduced into the polymer matrix via crazing and then it was transformed into silicon dioxide directly in the pores' volume by hydrolytic condensation process (catalyst – 10% water solution of  $\text{HCl}$ ). The obtained silica-containing composite was loaded with concentrated PA at the room temperature. Although in this case the content of acid in the membranes did not exceed the 10 wt%, it is allowed to receive materials with a comparable level of conductivity (Fig. 1, curve 4) and significantly increase their stability in time (the conductivity of the membranes after a year of their storage under room conditions decreased by one order).

It should be noted that the level of conductivity of  $10^{-5} \text{ S/cm}$  is insufficient to obtain a proton-conducting membrane characterized by good performance. To increase the acid content, the polymer-silica composites were heated at  $160\text{-}170^\circ\text{C}$ , which is above the melting point of the polymer matrix, in the environment of PA during 0.5-2 hrs. After similar a thermal treatment, the content of acid in the samples was found to greatly rise and the amount of PA increased linearly with the growth of  $\text{SiO}_2$  content as shown in Fig. 2.

By scanning electron microscopy, it was found that the surface of a composite was coated with islands of polyethylene film thickness of  $3 \mu\text{m}$  after the heat treatment (Fig. 3a). Moreover, maps of the distribution of elements (C, Si and P), obtained by energy dispersion spectrometry, showed that carbon as part of a polymer was concentrated on the surface of a sample (Figs. 3b,d), silicon as part of silica and phosphorus as part of acid almost uniformly distributed over the whole volume (Fig. 3e). One can assume that a polymer melts and migrates from the bulk of the composite at the surface during the heating. Simultaneously, PA, which is well compatible with  $\text{SiO}_2$ , flows into a volume of a composite and fills the formed voids.

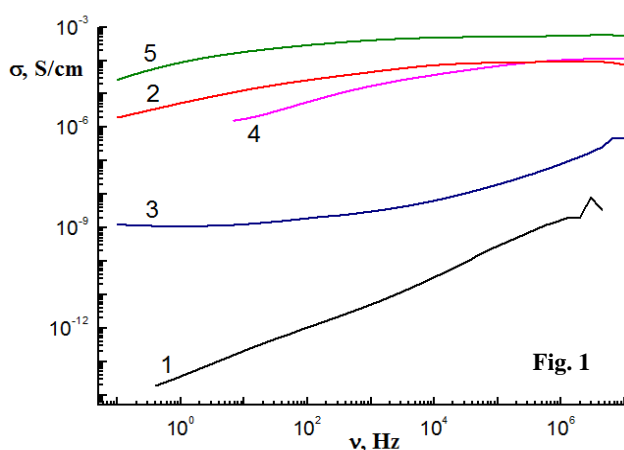


Figure 1 – Dependence of the conductivity of samples from frequency: (1) initial porous HDPE film, (2) HDPE- $\text{H}_3\text{PO}_4$ , (3) HDPE- $\text{SiO}_2$ , (4) HDPE- $\text{SiO}_2$ - $\text{H}_3\text{PO}_4$ , (5) HDPE- $\text{SiO}_2$ - $\text{H}_3\text{PO}_4$  after heat treatment

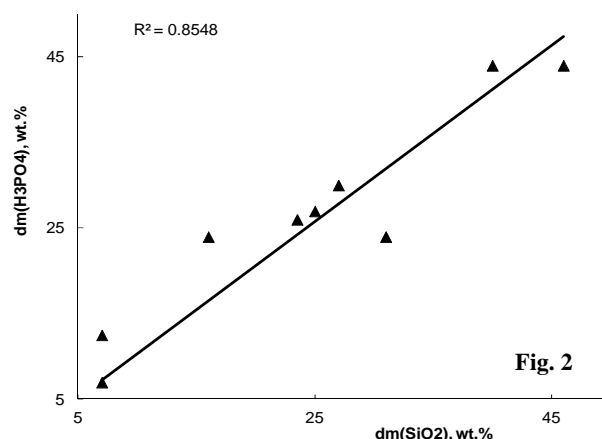


Figure 2 – Dependence of the amount of introduced acid from the content of  $\text{SiO}_2$  in the composite

The obtained materials HDPE- $\text{SiO}_2$ - $\text{H}_3\text{PO}_4$  were tested in a membrane-electrode assembly as proton-conducting membranes. Hydrogen as a fuel and air as an oxidant were supplied without excessive pressure and without humidification. It was found that these membranes at  $160^\circ\text{C}$  have a conductivity of about  $3 \times 10^{-2} \text{ S/cm}$  and the performance of  $0.4 \text{ V}$  at current density of  $0.4 \text{ A/cm}^2$ .

### III. CONCLUSION

Thus, the proton-conducting membranes based on silica-containing polyethylene and phosphoric acid can compete with commercial membranes. The combination of sufficiently good electrical conductivity, performance, mechanical properties at a relatively low price makes these materials economically attractive.

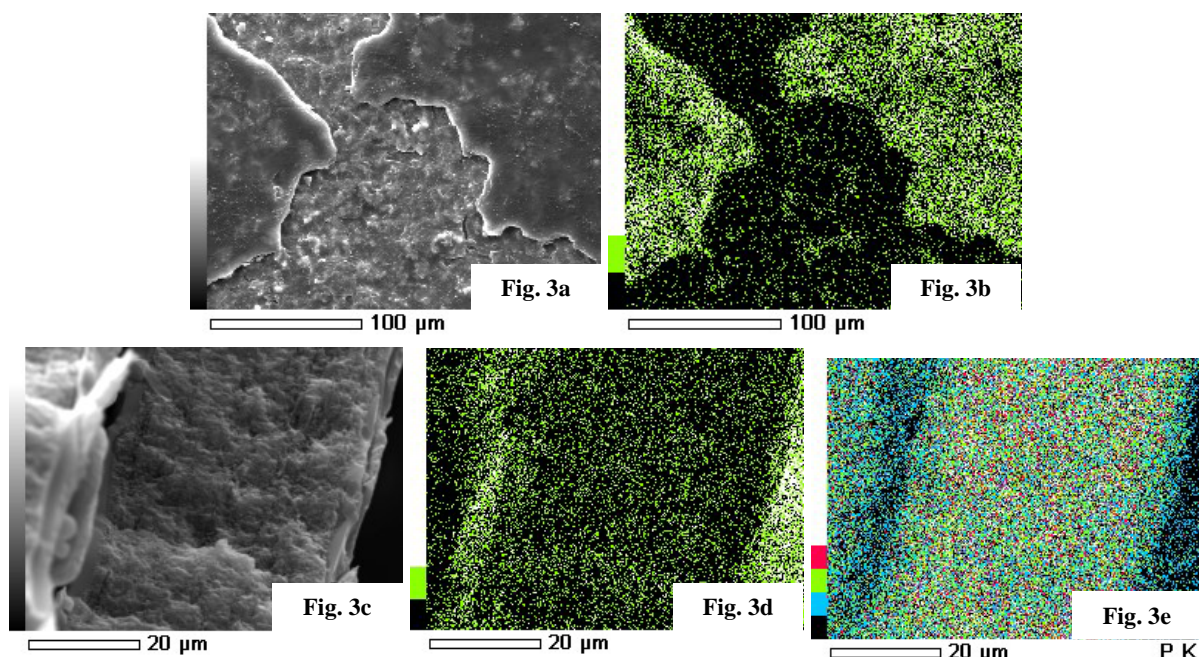


Figure 3 – SEM-micrographs of HDPE-SiO<sub>2</sub>- H<sub>3</sub>PO<sub>4</sub> after heat treatment.

#### ACKNOWLEDGEMENTS

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