SMALL-ANGLE SCATTERING ON PROTON-CONDUCTING MEMBRANES WITH NANODIAMONDS

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In order to create more efficient and economical hydrogen fuel cells, new proton-conducting membranes based on Nafion® and Aquivion® matrices (perfluorinated copolymers with different side chain lengths) modified with detonation nanodiamonds have been developed [1, 2]. The method of preparing membranes with enhanced conducting properties has been improved by introducing into the polymer solution small amounts (≤ 1 wt. %) of detonation nanodiamond particles 4–5 nm in size with groups (H, OH, COOH, SO_3H) grafted to the surface, removing the solvent, and precipitating the mixture on a solid substrate.
The combined mechanism of conduction is most successfully implemented in the presence of protonated diamonds (positively charged, Z+ type) [3] or diamond particles with sulfonic acid groups. According to small-angle neutron scattering (SANS) data, the structure of membranes in the presence of diamonds demonstrates the ionomer peak is retained at a scattering vector value of q ~ 2 nm^{-1}, which means that the main structural elements in the polymer matrix - hydrophilic conducting channels and their mutual arrangement - are preserved (Fig. 1). Similar structural data were obtained for a series of Nafion® type membranes with Z+ nanodiamonds. However, the proton conductivity of these membranes is significantly reduced in the presence of 2-3 wt. % of diamonds.
For a deeper integration of diamond particles into the polymer matrix, an experiment was carried out on the preparation of a copolymer (emulsion copolymerization, [4]) of the Nafion® type in a mixture with Z+ nanodiamonds. The obtained composite membrane demonstrates a narrowed ionomer peak on the X-ray scattering curves, shifted to higher q (Fig. 2). Such changes reflect an increase in channel ordering with a decrease in the distance between neighboring channels under conditions of high diamond content (4.1 wt. %) due to a more uniform distribution in the membrane material, which showed good conducting properties.

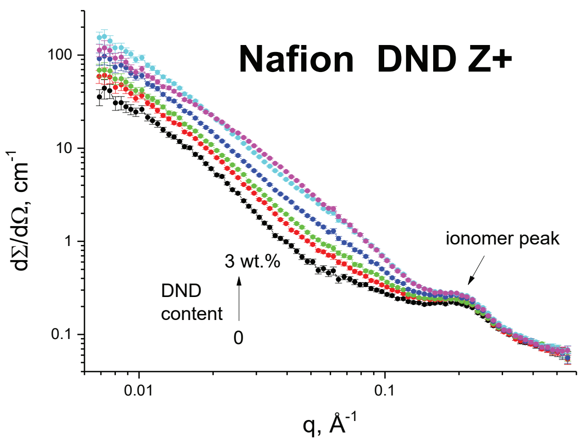

Fig. 1. SANS on Nafion®-type compositional membranes with DND Z+ in air-dry condition.

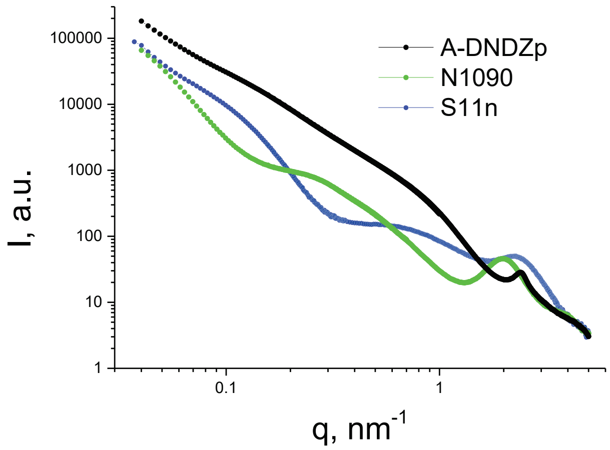

Fig. 2. SAXS on an A-DNDZp composite membrane obtained by copolymerization in the presence of diamonds and comparison with other membranes of Nafion®-type (N1090) and Aquivion®-type (S11n) without diamonds.

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[3] Yu.V.Kulvelis (2021). Modification of the mechanism of proton conductivity of the perfluorinated membrane copolymer by nanodiamonds. Russ. Chem. Bull. 70,1713-1717.
[4] O.N.Primachenko (2021). Influence of sulfonyl fluoride monomers on the mechanism of emulsion copolymerization with the preparation of proton-conducting membrane precursors. J. Fluor. Chem. 244,109736.