The Flerov Laboratory of Nuclear Reactions

Category: Applied Physics Research

Title: Development of ion-selective track membranes for nanosensors and electrodialysis

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List of publications:

1. I.V. Blonskaya, O.V. Kristavchuk, A.N. Nechaev, O.L. Orelovich, O.A. Polezhaeva, P.Y. Apel. Observation of latent ion tracks in semicrystallime polymers by scanning electron microscopy. *J. Appl. Polym. Sci*. 138 (2021) art. 49869. (IF = 3.1)
2. П.Ю. Апель, И.В. Блонская, О.М. Иванов, О.В. Криставчук, Н.Е. Лизунов, А.Н. Нечаев, О.Л. Орелович, О.А. Полежаева, С.Н. Дмитриев. Получение ионоселективных мембран из облученных тяжелыми ионами ПЭТФ пленок: критические параметры процесса. *Мембр. Мембр. Технологии*, 10 (2020) 113-124. English version: Apel, P.Y., Blonskaya, I.V., Ivanov, O.M., O.V. Kristavchuk, N.E. Lizunov, A.N. Nechaev, O.L. Orelovich, O.A. Polezhaeva, S.N. Dmitriev. Creation of Ion-Selective Membranes from Polyethylene Terephthalate Films Irradiated with Heavy Ions: Critical Parameters of the Process. *Membr. Membr. Technol.* **2,** 98–108 (2020). (IF = 2.0)
3. Yu. Yamauchi, И. В. Блонская, П. Ю. Апель. Осмос в отрицательно заряженных нанокапиллярах и его усиление анионным поверхностно-активным веществом. *Кол. Журн*. 81 (2019) 125-136. English version: Yu. Yamauchi, I.V. Blonskaya, P.Yu. Apel. Osmosis in Negatively Charged Nanocapillaries and Its Enhancement by an Anionic Surfactant. *Colloid Journal*, 80 (2018) 792–802. (IF = 1.3)
4. P.Y. Apel. I.V. Blonskaya, N.E. Lizunov, K. Olejniczak, O.L. Orelovitch, M.E. Toimil-Molares, C. Trautmann. Osmotic Effects in Track-Etched Nanopores, *Small* 14 (2018) 1703327 (10 pp). (IF = 10.9)
5. I.V. Blonskaya, N.E. Lizunov, K. Olejniczak, O.L. Orelovich, Y. Yamauchi, M.E. Toimil-Molares, C. Trautmann, P.Y. Apel. Elucidating the roles of diffusion and osmotic flow in controlling the geometry of nanochannels in asymmetric track-etched membranes. *J. Membr. Sci*. 618 (2021) 118657. (IF = 8.7)

Abstract

This series of publications is dedicated to the development of ion-selective membranes, obtained using accelerated heavy ions, for two practical applications – for the separation of ions via electrodialysis and for nanosensors based on the resistive-pulse principle.

The work has been executed using basic facilities of the Flerov Laboratory of Nuclear Reactions (heavy ion accelerators U-400, IC-100) and the equipment park of the FLNR nanotechnology centre (scanning electron microscope Hitachi SU8020, IR and UV spectrophotometers, picoampere meters and others).

A deeper insight into the nature and structure of heavy ion tracks in polymers is needed for the development of new applications of ion-irradiated polymers. In [1], a method is developed which allowed, for the first time, direct observation of latent heavy ion tracks in a semicrystalline polymer using scanning electron microscopy. The method is based on the controlled soft photo-oxidation of amorphous phase of the polymer. As a result, the sample prepared by this technique exhibits a sharp contrast between the structure of pristine polymer and the amorphized and partially degraded track zone. Images of tracks of ions with energy losses dE/dx from 7 to 17 keV/nm in polyethylene terephthalate and polypropylene are obtained. The transverse size of the track halo is determined, which has not been accessible before to direct observation by other methods.

The properties of latent track as an amorphous inclusion that contains low-molecular radiolysis products are employed in [2] with the aim to develop a product of practical importance. It is shown that an ion-exchange membrane, selective to cations, can be fabricated from a monolithic polymer film using liquid extraction of radiolysis and photolysis products from tracks. The properties of the obtained membranes are shown to depend on the mass of bombarding ion, pH and temperature of extracting medium. Due to high concentration of carboxyl groups, capable of dissociation, the membrane possesses ionic selectivity in electrolyte solutions. The selectivity and permeability drastically change when halos of individual tracks overlap. Thus, it is shown that the latent tracks, being modified by the extraction, are responsible for the ionic transport. Two factors are determining for the ionic transport – free volume and high concentration of carboxyl groups. In fact, the modified tracks constitute nanosized chromatography columns filled with an electrically charged gel. The transport occurs through the subnanometer channels in the gel, due to which hydrated cations of a smaller size (K^+) migrate faster than Li^+ and Mg^{2+}. The results have shown that the “extracted” track membranes – in addition to conventional application areas of track-etched membranes (ultrafiltration and microfiltration) – have a potential for the use in electrodialysis, i.e. for the separation of ions. The possibility to separate Li^+ ions seems to be especially important, and therefore further research work on the optimization of ion-selective track membranes is in progress.

The results obtained in [3] have become a preparatory stage for the studies [4, 5]. For the first time, on the example of cylindrical track pores 10-25 nm in radius, osmotic phenomenon caused by ionic selectivity is demonstrated. It is revealed that not only monolithic semipermeable membranes (as it is customary to think) but also membranes with capillary pores can show pronounced osmotic behavior in diluted salt solutions. It is evidenced that, in the presence of electrolyte concentration gradient, the osmotic forces occur due to the electrostatic interaction between ions and charged surface of pores. Conclusions drawn in [3] are used in [4, 5] for finding out mechanisms of asymmetric pore etching in polymer films and for optimization of the process. Nowadays asymmetric nanopores are an object of great interest because of their unique properties (ionic selectivity and diode-like behavior) and versatile potential applications in nanosensorics, nanofluidics and medical diagnostics (see reviews by Zhang et al. 2016; Laucirica et al, 2021; Shiohara et al., 2021, in which the recent achievements, including the results obtained at FLNR JINR, are considered). In is shown in [4] that the concentration gradient under conditions of asymmetric etching generates osmotic flux of neutralizing solution opposite to the diffusion flux of etching agent. The study [5] was performed with the aim to find out interrelations that govern the pore formation. Electric current through single pores and through arrays of pores, diffusion flux of etching agent and osmotic counter-flux were measured in the course of asymmetric etching of heavy ion tracks in thin polymer foils. It is shown that on the initial stage the pore geometry is governed by the diffusion-controlled nonlinear gradient of etchant concentration in the nanopore. Later, an osmotic flux arises, and the change in the balance between the diffusion and convection leads to the modification of the longitudinal profile of the channel. Estimates of reflection coefficients responsible for the osmotic flow are obtained. Application of external electric field is one more factor for the control over the shape of asymmetric channel. Evolution of the nanochannel geometry is supported by electron microscopy images that outperform the state of the art quality. The main result of this study is the method that allows, within the frame of the same procedure, fabrication of asymmetric nanopores of different configurations on which the functionality of the obtained system depends. First of all, these nanopores are applicable in the technique of biosensors.

In summary, the presented publications is a series of interconnected research works in which the methods for the fabrication of practically important nanoporous systems – ion-selective membranes for electrodialysis and asymmetric membranes for nanosensors - are developed. Publications [1, 4, 5] are in Q1-journals.

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