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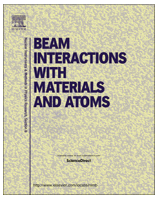

Diode-like properties of single- and multi-pore asymmetric track membranes

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ABSTRACT

In this work, we investigated the ionic transport properties of asymmetric polyethylene terephthalate (PET) track membranes with the thickness of 5 μm. The samples containing single pores and arrays of many pores were fabricated by irradiation with accelerated ions and subsequent physicochemical treatment. The method of etching in the presence of a surface-active agent was used to prepare the pores with highly-tapered tip. The transport of monovalent inorganic ions through the nano-scale holes was studied in a conductivity cell. The effective pore radii, electrical conductance and rectification ratios of pores were measured. The geometric characteristics of nanopores were investigated using FESEM.

1. Introduction

Track membranes (TM) are used in a variety of areas, such as environmental analytics, biotechnology and medicine. During the past few years, nanopores in TM have attracted much interest due to their potential applications as resistive-pulse sensors and the fact that they can mimic biological ionic channels [1–4]. Designing nanopores in artificial membranes is associated with the weak mechanical robustness of biological nanopores. The alpha-hemolysin, mainly used for the detection of various analytes, tends to rupture within a few hours [5,6]. This disadvantage precludes its use as sensor elements. In contrast to the reproducible biological nanopores, the creation of reproducible artificial ones is not an easy task. Pores having the same shape, size of both openings and surface charge density are desirable. The irradiation of PET films with heavy ions and etching of the latent tracks allow the preparation of nanopores, which usually differ slightly from each other. In order to receive identical pores the appropriate ion-track etching method is still sought. The issue of reproducibility and uniformity of pores in many-pore membranes has been widely studied [7–9]. It was found that the symmetric, i.e. cylindrical, track-etched pores are highly uniform while both asymmetric pores with highly-tapered tip and conical pores produced using one-step pore-etching procedure are characterized by the large scatter of constriction diameter [8,13].

The development of single pore systems plays an important role in the creation of prototype resistive-pulse sensing devices [10–14]. In contrast to pores in many-pore membranes, the issue of single pores reproducibility has not been studied extensively. Because of this the single pores require in-depth studies in order to provide a better understanding of processes occurring in nanopores with charged walls. The previous studies [13] show that the best track etching method to obtain a reproducible sensor elements based on conical nanopores is the two-step etching process used by the Martin Research Group. The construction of the cone-shaped pores of well-defined base and tip diameter sizes was carried out in two stages. First, the well-known method of one-step pore-etching was used [10,14]. During the track etching process the etchant (sodium hydroxide solution) was placed on the one side of the membrane and the stopping solution (formic acid) was placed on the other side of the membrane. As a result, the conical pores with a uniform base diameter only were prepared. The problem of irreproducibility of tip diameter was solved by using an additional etching. It was performed on both sides under mild conditions. This two-step pore-etching procedure allows control with good reproducibility over both the base and tip diameters of the conical nanopore.

In this work we investigated the suitability of the method of etching in the presence of a surface-active agent to obtain reproducible asymmetric single nanopores with highly-tapered tip.

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2. Experimental

2.1. Preparation of the nanopores

Polyethylene terephthalate foils with a thickness of 5 μm (Hostaphan RE 5) were irradiated with Au and Xe ions at the UNILAC linear accelerator (GSI, Darmstadt) and with Kr ions in the U-400 cyclotron of the Flerov Laboratory of Nuclear Reactions (Dubna). The energy of ions was in the range of 1–11.4 MeV/u. Samples containing single track, 2500 tracks and samples with a track density of 5×10^7 tracks/cm^2, respectively, were prepared. For single-ion irradiation, a metal mask with a 1 mm aperture in the center was placed in front of the sample so that the location of ion track was pre-determined. During the irradiation with Xe ions, a regular pattern of 2500 single tracks spaced at a 5 μm interval was produced in the center of specimens [15]. In the case of membranes prepared in the U-400 cyclotron, the 320 mm wide and several meters long film was transported at a constant speed across the scanning ion beam that contacted the film through rectangular window. A scanning system provided a homogeneous distribution of ions over the target.

The tracked films were first subjected to one-sided UV exposure for 16.5 h and then etched. The etching conditions were selected to keep a compromise between the increase in rectification and the broadening of pore size distribution with increasing etchant concentration [8]. They were as follows: surfactant-doped 5 mol/L NaOH, temperature of 60 °C, time 6 min 30 s. After etching the samples were rinsed with ultra-pure water and air-dried.

2.2. Characterization of the nanopores

The etched membranes with high pore density (5×10^7 pores/cm^2) were examined using scanning electron microscope LEO-1530. The image of the pore profiles was obtained by the fracture technique, a special procedure for this type of samples [16].

The electrical properties of the samples were determined using a conductivity cell (Fig. 1) with Ag/AgCl electrodes. The cell was composed of two compartments filled with KCl solution (symmetric electrolyte conditions) and separated by the investigated membrane. The voltage between −2 and +2 V was applied across the membrane. The transmembrane ionic current was recorded at room temperature with a HIOKI 5322 RCL-meter. A shunt resistor was connected to the electrodes in parallel to prevent overflow in case the membrane electrical resistance is beyond the range of the instrument.

Electrolyte solutions with a concentration ranging from 0.2 to 3 mol/L were prepared using the reagent-grade KCl. The solutions were non-buffered (pH 5.6 ± 0.2) in order to avoid additional ionic species in the system.

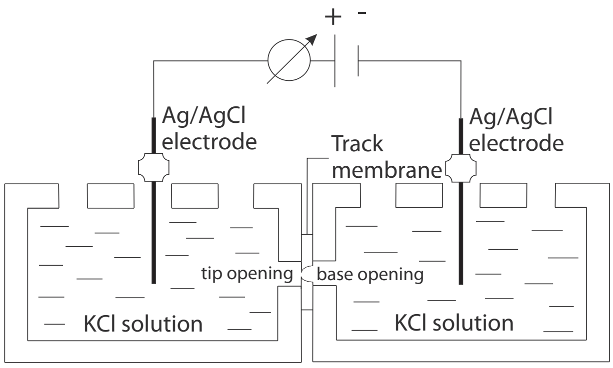

Fig. 1. Schematic representation of the experimental setup with the conductivity cell.

3. Results and discussion

The shape of the pore channels produced in the ion-irradiated PET film with the thickness of 5 μm is shown in Fig. 2. It is seen that process of track etching in the presence of a surface-active agent allowed to produce asymmetric nanopores with a bullet-shaped mouth. In order to obtain a detailed description of the highly-tapered pore shape, the relationship between the pore radius a and the distance x from the surface was determined using the procedure described earlier [8] (Fig. 3). The pore radii on both sides of the membranes were determined from SEM images of the samples with a pore density of 5×10^7 pores/cm^2. The base radius of the nanopores has a narrow distribution and was found equal to 139 ± 8 nm. The distribution of the tip radii in the investigated membrane is presented in Fig. 4. The nanopores with a tip radius of 23–30 nm predominated while the whole populated range extends from about 11 to 48 nm.

At electrolyte concentrations of 0.2 and 0.4 mol/L, the individual pores with bullet-like tip exhibit non-linear current–voltage characteristics. The I–V curves for single-pore membranes recorded at 0.2 mol/L KCl are shown in Fig. 5a. The asymmetry in the ion transport properties under the symmetric electrolyte conditions is caused by the asymmetric shape of the prepared pores and indicates that the nanopores possess ion-current rectifying ability. At electrolyte concentrations of 1 and 3 mol/L, symmetric I–V responses were recorded (Fig. 5b). For the 2500-pore membranes in the electrolyte solutions of high concentrations the drops of ionic current were observed on the negative part of I–V curves (Fig. 6). At first glance, this phenomenon looks like the nanoprecipitation observed before for single nanopores in the high-conductance state [17]. However, in our case the effect was observed for many-pore membranes but did not show up with single pores. Therefore, the interpretation of this observation is difficult; probably the abrupt decrease of ionic current could be caused by concentration polarization due to high conductance of the array of many pores.

A comparison of electro-conductivity data for single- and 2500-pore membranes made it possible to estimate the level of heterogeneity of the asymmetric nanopores. Table 1 presents the values of the rectification ratios $r = I(-1\ \mathrm{V})/I(+1\ \mathrm{V})$ at different KCl concentrations and effective pore radii a_{eff} for all investigated samples. The effective pore radius is defined as the radius of a cylindrical pore having the same electrical conductance G in 1 mol/L KCl at ±0.1 V:

$$a_{\mathrm{eff}} = \sqrt{\frac{l \cdot G}{\pi \cdot N \cdot k}} \tag{1}$$

where l is the thickness of the membrane, N is the number of pores, k is the specific conductivity of 1 mol/L KCl.

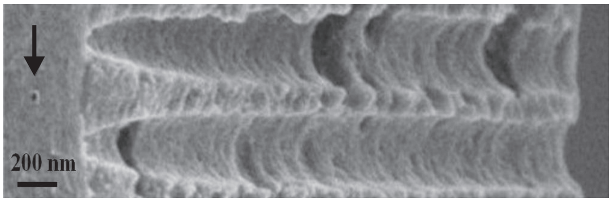

Fig. 2. FESEM image of a fractured PET membrane with pore density of 5×10^7 pores/cm^2. The tip and base openings of the pores are on the left and right side of the image, respectively. The arrow indicates a pore entrance on the selective side of membrane. The sample was tilted to make visible both the upper surface and the cleaved pore channels.