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Fabrication of different pore shapes by multi-step etching technique in ion-irradiated PET membranes

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ABSTRACT

A method for the fabrication of different pore shapes in polyethylene terephthalate (PET)-based track etched membranes (TEMs) is reported. A multi-step etching technique involving etchant variation and track annealing was applied to fabricate different pore shapes in PET membranes. PET foils of 12-μm thickness were irradiated with Bi ions (kinetic energy 9.5 MeV/u, fluence 10^6 ions/cm^2) at the Heavy Ion Research Facility (HIRFL, Lanzhou). The cross-sections of fundamental pore shapes (cylinder, cone, and double cone) were analyzed. Funnel-shaped and pencil-shaped pores were obtained using a two-step etching process. Track annealing was carried out in air at 180 °C for 120 min. After track annealing, the selectivity of the etching process decreased, which resulted in isotropic etching in subsequent etching steps. Rounded cylinder and rounded cone shapes were obtained by introducing a track-annealing step in the etching process. Cup and spherical funnel-shaped pores were fabricated using a three- and four-step etching process, respectively. The described multi-step etching technique provides a controllable method to fabricate new pore shapes in TEMs. Introduction of a variety of pore shapes may improve the separation properties of TEMs and enrich the series of TEM products.

1. Introduction

Tack-etched membranes (TEMs), thin porous polymer films manufactured by a combination of irradiation and chemical etching, have attracted significant attention owing to their utility in laboratory and industrial filtrations [1,2], biosensing [3], nanofabrication [4,5], and other highly specific applications. In contrast with conventional membranes, TEMs have three distinct advantages: (i) raw material abundance in terms of their preparation; (ii) well-defined pore shape; (iii) good structural controllability. Because of these merits, a growing number of facilities [6–8] have been built for mass production of TEMs. In addition, numerous reports detailing studies of the track formation mechanism [9–17], pore formation [18–25], and transport properties [26,27] abound in the literature. Several experiments have been carried out to control pore morphology; in particular, TEMs with various pore shapes such as cylindrical, conical, funnel, and cigar, have been fabricated in the last decade. These novel pore shapes may be promising for filtering, particle translocation and nanofluidic applications. For constant track etch rate, the shape of etched track is a Mach cone, wherein the cone angle is dependent on the etch rate ratio ($\boldsymbol{V_t}/\boldsymbol{V_b}$). When the track etch rate $\boldsymbol{V_t}$ is much larger than the bulk etch rate $\boldsymbol{V_b}$ track-etched pores should be cylindrical throughout their depths. Several pore-shaping methods have been achieved by modifying the etch-rate ratio, normally by variations in raw material or etchant conditions. UV-light and track-annealing treatments have also been employed for etch-rate modification [9,13]. Additionally, the pore shape profiles can be tailored in a controlled manner by adding surfactant to the etchant [18,21].

The multi-step etching technique, offers the possibility of fabricating new pore shapes in TEMs. One of the successful examples of this type of modification is the funnel-shaped pore. Berndt et al. [25] fabricated funnel-shaped pores in CR-39 by a two-step etching process. Trautmann et al. [24] prepared funnel-shaped pores in polyimide substrates. In the present paper, we focused on the fabrication of different pore shapes in polyethylene terephthalate (PET)-based TEMs by multi-step etching technique. Two methods, including etchant variation and track annealing, were used. The commercially available PET foils, as one of the most widely used ion-track materials, was selected as the raw material in this work. Scanning electron microscopy (SEM) was utilized to observe etched samples.

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2. Experimental

PET foils (FS301, KaiLi) of 12-μm thickness were irradiated with Bi ions (kinetic energy 9.5 MeV/u, fluence 10^6 ions/cm^2) at the Heavy Ion Research Facility (HIRFL) in Lanzhou. Irradiation was performed under vacuum at room temperature. Irradiated PET foils were etched with methanol-free or methanol-containing alkaline solutions at different etching steps. An electrochemical cell, consisted of two compartments, was employed for mounting the irradiated samples. In order to avoid electrode polarization, an AC voltage (amplitude, 0.1 V; frequency, 100 Hz) was applied across the membrane using two Pt electrodes. The electrical conductance or resistance was monitored with a PC-controlled LCR-meter (HIOKI 3522-50).

Three different etching conditions (Table 1) were used for etching PET samples. The bulk etch rate was calculated from thickness measurements by double-sided etching in a large beaker. The track etch rate was determined experimentally by measuring sample thickness and breakthrough time; the samples were etched from one side in selected etching solution and the other side was filled with 1 M KCl solution. To obtain a conical shape, irradiated PET foils were etched with an etch solution of 9 M NaOH in methanol/water mixture with a volume ratio of 1:1 at 20 °C (condition 1). To obtain a cylindrical shape, PET foils were etched in a 5 M NaOH solution at 20 °C (condition 2) or 60 °C (condition 3). Only condition 3 required temperature control. In order to maintain a temperature of 60 °C, the electrochemical cell was embedded in a heating jacket. Both electrochemical cell and etching solution were preheated for 1 h.

After etch rates (Table 1) were confirmed, different pore shapes were obtained by etching over a certain time for each different etching step. All etching times were calculated according to track etch rates under the specified etching conditions (Table 1). One-sided etching was performed in the electrochemical cell at 20 °C (without heating); double-sided etching was performed by immersing the samples in a large beaker containing the etchant. After every etching step, the membranes were washed in distilled water for several minutes. Track annealing was used to decrease the selectivity of the etching process. The annealing process was carried out in air at a temperature of 180 °C for 120 min. Cross-sections of etched PET membranes were observed using SEM; a thin gold film (20 nm) was first deposited on the sample surface to improve surface conductivity. In order to observe fine profiles of etched pores, PET samples were embrittled by exposing to UV light for 48 h.

3. Results and discussion

The main goal of fabricating TEMs with different pore shapes is to acquire different technical parameters according to different product performance needs. Sample reproducibility as one of the key technical problems needs to be solved. To avoid problems occurring from different ion-energy loss, all PET foils were irradiated under the same conditions. However, adverse effects caused by heating cannot be avoided. Therefore, heating was applied over a few steps. To achieve high-quality TEMs, we needed to set the precise etching time at different etching steps. Although present methods can be well applied to measure the bulk etch rate, it is still difficult to precisely measure the track etch rate in porous TEMs. Typically, etching processes are monitored via current (or conductance) versus etching time curve [5,17]. This monitoring system has succeeded in the direct measurement of the track etch rate of single-pore TEMs. The conductance versus etching time curve, which was used to measure the track-etching rate under condition 2, is given in Fig. 1a. For porous TEMs, the drawback of this method is that only some first pores are observed. Oganessian et al. [16] performed resistance measurements on porous PET TEMs (fluence 3.7×10^3 ions/cm^2); they developed a "track-by-track" method, which has been used to investigate the break-through time of individual pores. The resistance versus etching time used in our experiment is shown in Fig. 1b. The break-through started with a value of 10,500 s (Fig. 1a and b) and ended with a value of 11,500 s (Fig. 1b). Relying on these two methods, we can estimate the track break-through time distribution around 1000 s (~17 min). Zhu et al. [14] proposed that the break-through probability of tracks can be taken as a Gaussian function. The break-through time distribution is directly related to the pore-size distribution. In this context, considering the bulk etching rate for condition 2 is 1 nm/min, the pore-size distribution for samples etched at room temperature was around 17 nm, which was in accord with SEM observations (±20 nm) for sample etched at 20 °C. However, the pore distribution appeared to be seriously affected (±50 nm), if heating was introduced. The dilemma of uneven temperature controlling still remains and needs to be solved.

3.1. Analysis of pores displaying fundamental shapes

Cylindrical, conical, double-cone and cigar-like morphologies are fundamental shapes found in TEMs. Fig. 2a shows the pore morphology in PET TEMs fabricated using the double-sided etching method under etching condition 3 as having a cylindrical shape. As the track etch rate (1200 nm/min) was much larger than the bulk etch rate (35 nm/min), well-defined cylindrical pores were obtained. The pore diameter (1410 ± 50 nm) obtained from Fig. 2a was in accordance with the calculated result (1400 nm). The cylindrical pore shape is the most commonly found in TEMs; it follows that the separation properties of TEMs with cylindrical pores are strongly dependent on both pore density and pore diameter. The conical pore was obtained by etching from the top side under etching condition 1 (see Fig. 2b). The tip diameter was around 530 nm. Based on the track etched (400 nm) and bulk etch rate (43 nm/min); the calculated tip diameter was 516 nm; The double-cone shape was fabricated by double-sided etching (see Fig. 2c); the width at narrowest point was around 650 nm, and the calculated width at narrowest point was 688 nm. It was concluded that the calculated results were in basic agreement with the experiment results. A conical shape can effectively improve filtering efficiency, allowing the filtering process to be performed accurately and rapidly. A number of reports devoted to the control of pore geometry in commercial track-etched polycarbonate membranes have appeared in the literature [18–25]; the typical etching process for a conical shape is terminated right after pore breakthrough. The high reproducibility of the etching process makes mass production of TEMs possible. Based on the measured bulk

Table 1
Etching conditions for track developing in PET membranes.

Etching condition	Etchant solution	Temperature (°C)	Bulk etch rate (nm/min)	Track etch rate (nm/min)
Condition 1	9 M NaOH (methanol/water 1:1)	20	42	400
Condition 2	5 M NaOH	20	1	68
Condition 3	5 M NaOH	60	35	1200