Ion-Track Membranes of Poly(vinylidene fluoride): Etching Characteristics during Conductometric Analysis

Nunung Nuryanthi1,2, Tetsuya Yamaki1*, Hiroshi Koshikawa1, Masaharu Asano1, Shin-ichi Sawada1, Shin Hasegawa1, Yasunari Maekawa1 and Yosuke Katsumura2

1 Quantum Beam Science Directorate, Japan Atomic Energy Agency
1233 Watanuki, Takasaki, Gunma 370-1292, Japan
2 Department of Nuclear Engineering and Management, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
* Corresponding author: Fax: +81-27-346-9687, e-mail: yamaki.tetsuya@jaea.go.jp

A poly(vinylidene fluoride) film irradiated with 450 MeV 129Xe ions was etched in an aqueous potassium hydroxide solution at 80°C in a conductometric cell. The etching characteristics were investigated in situ at different applied voltages. The conductometric curves reached a plateau when the etching time was sufficiently long (up to 48 h); this plateau indicates that etching was complete in the damaged track and that the bulk etch rate was negligibly low. The applied voltage produced larger pores than the etching with no voltage. Higher voltages shortened the etching time; the voltage accelerated the etching before the pore breakthrough and during the pore growth. The increase in the etch rate was probably caused by the dissolved etching products being pulled away from the pores more efficiently at higher applied voltages. However, the effective pore diameter, \( d_{eff} \), at the end of the etching was not substantially affected by varying the applied voltage. The final \( d_{eff} \) values calculated from the conductometric measurements were not consistent with the results acquired by scanning electron microscopy observations. This can likely be explained by inhomogeneous etching at the edge of the membrane.

Key words: ion track, poly(vinylidene fluoride) (PVDF), chemical etching, conductometry

1. INTRODUCTION

When energetic heavy ions in the range of MeV to GeV pass through a polymer, they create a concentrated zone of macromolecular fragments as well as free radicals and excited or ionized chemical species along their trajectory. The resulting ion tracks can be etched in a suitable solution to produce nanometer- to micrometer-sized pores. These ion-track membranes have been widely used in industry and research as biological sensors and as templates for nanowire synthesis [1]. The pore diameter and shape need to be controlled as precisely as possible; the pore geometry is affected by the nature of the irradiation, the etching conditions, and the materials employed [2].

The ion-track etching technique has mainly been applied to a series of hydrocarbon polymers, such as polycarbonate (PC), polyethylene terephthalate (PET), and polyimide (PI) [3-8]. In contrast, we have focused on poly(vinylidene fluoride) (PVDF) ion-track membranes, because of the superior chemical and mechanical properties of fluoropolymers [9-17]. A very hot, concentrated alkaline solution with an oxidative additive, such as KMnO₄ or KIO₄, was mostly used to produce visible tracks in PVDF films [11,12]. However, these harsh etching conditions cause irreversible chemical damage to the film, and eventually dissolve it. Thus, we have performed the etching under much milder conditions, with no oxidative additive, which allowed the pore evolution in the PVDF-based ion-track membrane to be investigated in detail [13-17].

In order to investigate the track etching in PVDF films and the characteristics of the etched pores, we have used a conductometric analysis, in which the electrical conductance of the electrolyte solution was recorded across the perforated membrane [2]. In this analysis, the etching solution can be used as the electrolyte giving a method to etch out the tracks and simultaneously monitor the pore evolution [18]. The advantage of the in-situ conductometric analysis, sometimes referred to as conductometric etching, lies in the fact that the pore formation kinetics, including the etch rate during the initial stage and the time-dependent pore growth, can be determined. There has been a strong motivation to estimate the key track-etching parameters with this technique for optimizing the experimental conditions toward the formation of pores with a desirable size and shape [15-17].

The purpose of the present investigation is to study the etching behavior of energetic-heavy-ion-irradiated PVDF films during conductometric analysis. One of the variable conditions in the analysis is the voltage applied between the electrodes in the conductometric cell, which was previously examined for PC- or PET-based ion-track membranes [4,6,8]. Our recent studies of the PVDF-based ion-track membranes also demonstrated that the profile of the conductometric curves depended on the applied voltage from 0.3 to 2.0 V [16,17]. In this study, we extended the applied-voltage range and examined the changes in the etching characteristics to pursue a direction toward greater freedom in controlling the pore geometries.
2. EXPERIMENTAL

Poly(vinylidene fluoride) films with thickness of 25 µm (Kureha KF Polymer) were used as received. The potassium hydroxide (KOH) pellets (Wako Pure Chemical Industries, Ltd.) were used without further purification. The water was passed through a Milli-Q system (Millipore Corp.).

The PVDF film was irradiated with 129Xe ions at a total energy of 450 MeV using the cyclotron at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility of the Japan Atomic Energy Agency (JAEA). The ion fluence was fixed at 3 × 10^7 ions/cm², and the irradiation was carried out in a vacuum chamber at room temperature. Then, the irradiated films were etched in an aqueous 9 mol dm⁻³ KOH solution at 80°C in a conductometric cell made of Teflon [17]. The electrical conductance was monitored under a sine AC voltage with a frequency of 1 kHz using an LCR meter (HiTESTER 3522, HIOKI). The amplitude of the voltage between the electrodes was varied from 0.1 to 3.0 V.

Assuming cylindrical pores, we calculated the effective pore diameter, \(d_{eff}\), at any given time [18]:

\[
d_{eff} = \frac{4Lg(t)}{πKNs},
\]

where \(L\) is the membrane thickness, \(K\) is the specific conductivity of the KOH etching solution [19], \(N\) is the pore density (which corresponds to the ion fluence), and \(S\) is the area of the samples, which were 0.85 cm² in diameter.

For comparison against etching without an applied voltage, track etching was also performed in the same etching solution without stirring but not in the conductometric cell. Surface observations were carried out by scanning electron microscopy (SEM; JSM-5600, JEOL) after the samples were coated with a 20-nm-thick gold layer to determine the diameter of the pores.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the PVDF-based ion-track membranes obtained after 48-h etching at different applied voltages and without an applied voltage. The membrane etched without an applied voltage exhibited pores of 149 ± 39 nm in diameter, whereas the membranes etched at 0.1, 0.5, 2.0, and 3.0 V showed pores of 237 ± 44, 163 ± 46, 164 ± 30, and 161 ± 18 nm in diameter, respectively. Applying a voltage to the conductometric cell increased the size of the pores. Etching for 48 h was long enough to etch beyond the latent track under the applied voltages; bulk etching was achieved for the membranes in Figures 1 (b) to (e). However, the track etching was not complete in the membrane with no applied voltage (Figure 1 (a)); it may take much longer than 48 h to reach the bulk etching stage.

Figure 2 shows representative conductometric curves obtained under the different applied voltages. Three stages were seen in all the curves, as previously reported [17]. The first stage corresponded to the plateau at a conductance of nearly zero, which represented the penetration of the etching solution into the tracks from both sides of the film, and meant no current was recorded. The time required for the first stage is called the breakthrough time, \(T_b\). Once the cone-shaped etching fronts made contact with each other, the conductance suddenly increased. During the second stage, the conductance increased rapidly, mainly because of the growth of the pores in the transverse direction. In the final stage, the rate of the pore growth became negligibly low, and the diameter reached a second plateau. At this stage, the etching was complete and the ion tracks were entirely dissolved away. Therefore, the diameter at the end of the etching was the final \(d_{eff}\).

The time for completing the etching decreased as the applied voltage was increased, although the final \(d_{eff}\) was not substantially affected. This suggests that the pore growth was faster at higher voltages, which was consistent with the larger slope of the curve during the second stage of etching. The constant value of the final \(d_{eff}\) also supported our interpretation of the conductometric curves, where the final \(d_{eff}\) corresponded to the pore diameter at the end of the etching, that is, the track size of the bombarding 129Xe ions for all the
membranes.

The inset in Figure 2 shows an enlarged view of the initial stage of the track etching, clearly representing the influence of the varied applied voltages on $T_b$. The breakthrough time was 1.6-fold shorter at 2.0 V than at 0.3 V (results not shown), which appears to be quantitatively consistent with our previous study demonstrating a 2.8-fold reduction in $T_b$ as the applied voltage was decreased from 0.3 to 2.0 V [17]. This might be within the margin of experimental error, which was unavoidably large owing to the inhomogeneous etching in the conductometric cell in this study. However, the decrease in the $T_b$ at higher voltages agreed qualitatively with our previous results. The higher applied voltages accelerated the track etching before $T_b$.

According to previous studies, there are three possible ways that the applied voltage could have affected the track etching in PVDF. Apel et al. reported that the conductometric etching could be influenced by the migration of ions or polar materials in the electric field gradient, and thus the polarity of the applied voltage could stop or promote the track etching process [4]. However, this can be ruled out because we used a sine AC voltage. On the other hand, the polarization of the electrodes could play a major role under DC voltages.

Higher applied voltages could also cause resistive heating of the etching solution inside the nanopores during the etching [6]; the local heating would increase the etch rate and the pore diameter. To test this hypothesis, Harrell et al. estimated the theoretical temperature rise in the solution to be approximately 9°C when a voltage of up to 30 V was applied [6]. However, we applied voltages of 0.1 to 3.0 V, which were low enough to avoid resistive heating.

Cornelius et al. suggested that the dissolved etching products attached to the pore wall could affect the etching during the formation of PC-based ion-track membranes [7]. They proposed that the ionic or polar etching products on the pore walls could decrease the susceptibility of the materials to chemical attack. These etching products can be effectively removed from the pores by electrophoretic migration during the conductometry, which would reduce the effect of adsorption on the inner pore wall and accelerate the etching.

Figures 1 (b) to (e) can be used to compare the final $d_{eff}$ for different applied voltages, because the etching time was sufficiently long. The final $d_{eff}$ was plotted as a function of the applied voltage using the conductometry and SEM results (Figure 3). The pore diameters calculated from the conductometric analysis were larger than those observed by SEM, except at the lowest voltage, 0.1 V. Hiroki et al. reported a similar result in a study of the track etching of PET [5]. They suggested the formation of a gel layer on the pore wall. This gel layer could contain crosslinked polymers that would reduce the solubility and could also have high ion conductivity because of its swelling state. Accordingly, they assumed that the conductometry always overestimated the pore diameter. However, this would be an unlikely explanation for our results. The difference in the pore diameter was not observed at 0.1 V, and the final $d_{eff}$ was independent of the applied voltage in the results obtained by both methods. Thus, the creation of the ion-conductive gel layer is not plausible. Therefore, irregular and unexpected effects might be involved.

Conductometry provides information about the etching characteristics averaged over all the pores in the membrane, whereas SEM provides information about only the observed part of the membrane. Therefore, the etching may have been inhomogeneous during the conductometry. To verify this assumption, we examined surface SEM images from different parts of the membrane. Figure 4 (a) shows a photograph of a representative etched membrane, which was 1.5 cm in diameter. The membrane was clamped between two Teflon cells, and the central area (0.85 cm in diameter, corresponding to $S$ in equation (1)) was subjected to chemical etching. Figure 4 (b) shows the SEM image of the track-etched membrane obtained at an applied voltage of 0.5 V. The pore diameter here was completely different from that in Figure 1 (c) (although the same membrane was observed). Most parts of the membrane had diameters of 120 to 210 nm (Figure 3 (b)). However, a small region, at several micrometers from the membrane edge, exhibited much larger pores, which reached a diameter of around 350 nm.

The shape of the pores in Figure 4 (b) may explain the difference in pore sizes. The pores were not round, in contrast to the uniform round cylindrical pores observed in most other areas (Figure 1 (c)). The pore shape implies that the membrane was deformed by stress concentrated at its edge when it was installed in the conductometric cell. This local stress may contribute to

![Figure 3](image-url) **Figure 3.** Dependence of the final $d_{eff}$ on the applied voltage in the range of 0.1 to 3.0 V. A comparison is made between the results obtained by (a) the conductometric analysis and (b) the SEM observations.

![Figure 4](image-url) **Figure 4.** (a) Photograph of a representative PVDF-based ion-track membrane prepared in the conductometric cell. The pale-brown etching area, corresponding to $S$ in equation (1), was 0.85 cm in diameter. (b) An SEM image of the membrane obtained at an applied voltage of 0.5 V, taken several micrometers from the membrane edge.
the inhomogeneous etching, although other factors that affect the etching process cannot be ruled out. The SEM observations from the membrane edge were excluded when plotting Figure 3 (b). The diameters calculated from the conductometry results were larger than those from the SEM observations in Figure 3, because the former were averaged over all the pores. The conductometric analysis combined with the SEM observations revealed an unexpected inhomogeneous pore distribution in the track etching of PVDF films.

4. CONCLUSIONS
We irradiated 25-µm-thick PVDF films with 450 MeV 129Xe ions, and investigated their etching characteristics with an aqueous 9 mol dm⁻³ KOH solution in a conductometric cell at voltages of 0.1 to 3.0 V. The SEM images showed that the pore diameter was larger when a voltage was applied during the conductometric etching than when no voltage was applied. In the conductometric curves, the plateau in the effective pore diameter, \(d_{ef}\), was observed when the etching ended, indicating the bulk etching beyond the width of the damaged track was negligibly slow. The application of the voltage shortened the \(T_b\) and the time to reach the final \(d_{ef}\) value; however it did not strongly affect the final \(d_{ef}\). There was inconsistency in the final \(d_{ef}\) values measured by conductometry and SEM observations. This difference was explained by the inhomogeneous etching observed at the edge of the membrane; this inhomogeneity probably resulted from local stress-induced deformation.

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