We investigated the formation of track-etched membranes of poly(vinylidene fluoride) (PVDF), a type of fluoropolymer, in detail, using conductometry. A 25 µm-thick PVDF film was irradiated with a 450 MeV $^{129}$Xe or 2.2 GeV $^{197}$Au ion beam, and then the latent tracks were etched in a 9 mol dm$^{-3}$ aqueous potassium hydroxide solution at 80 ºC in a conductometric cell. This paper focuses on the theoretical basis of the conductometric method and the apparatus used in our study. Representative results are then given in terms of how the etching kinetics was affected by various experimental conditions including the irradiation parameters and cell voltages applied between the electrodes.

Key words: Heavy ions, Track etching, Conductometry, Nanopore, Poly(vinylidene fluoride) (PVDF)

1. INTRODUCTION

When heavy ions of MeV–GeV kinetic energies pass through an insulator, in particular an organic polymer, they create tracks of modified materials. These latent tracks can sometimes be developed into capillary channels with diameters ranging from nanometers to micrometers [1]. Figure 1 presents the principal steps in the preparation of a so-called track-etched membrane. Although the ion-track technique has mostly been studied for hydrocarbon polymers, such as polycarbonate (PC) and poly(ethylene terephthalate) (PET), our focus is on track-etched membranes of poly(vinylidene fluoride) (PVDF), a type of fluoropolymer [2-7], because of its superior chemical, mechanical, and ferro-electric properties. We previously prepared polymer electrolyte membranes for fuel-cell applications by filling the channel pores of PVDF-based track-etched membranes with proton-conductive polymer chains using $\gamma$-ray-induced graft polymerization [2,3]. This research spawned a renewed interest in precisely varying the pore diameter.

In order to produce visible tracks in irradiated PVDF films, researchers have used several kinds of etching solutions; in most cases [8,9], a concentrated aqueous potassium hydroxide (KOH) solution with a potassium permanganate ($\text{KMnO}_4$) additive was maintained at a high temperature. These severe etching conditions produced irreversible chemical damage over the entire film including the non-irradiated part. Thus, in our study, chemical etching was performed under much milder conditions, i.e., without any additives in the alkaline solution; however, it had to be achieved as rapidly as possible. Detailed knowledge of pore evolution during the entire etching process is indispensable for effective control of pore sizes.

It is known that the formation of a track core consisting of highly damaged material depends on the polymer and on the energy loss of the incident ion [10-12]. Outside the core region, the polymer matrix is also slightly modified, mainly as a result of cascades of secondary electrons. The diameter of this track halo can exceed several hundred nanometers. Conductometric etching of the latent tracks allows monitoring of pore evolution versus etching time by recording the electrical conductance through the membrane [13-15]. Changes in the etching rate with the increasing pore diameter reflect the spatial distribution of the ion-induced chemical and physical modifications in both the core and halo regions.

We investigated the evolution of etched ion tracks in a...
PVDF film using a conductometric method, expecting that attempts to clarify the mechanisms would lead to variations in the pore formation kinetics. Experiments were therefore performed under various conditions; different parameters (mass and velocity) of the bombarded ions and cell potentials applied between the electrodes were found to determine the etching rates. A major part of this paper is devoted to a description of our equipment and the techniques used for the conductometric analysis.

2. EXPERIMENTAL

2.1 Materials and irradiation

We used PVDF films of thickness 25 μm (Kureha KF Polymer) as the test material. The films were irradiated perpendicular to the surface with $^{129}$Xe at a total energy of 450 MeV from a cyclotron at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility, Japan Atomic Energy Agency (JA EA), and with $^{197}$Au at a total energy of 2.2 GeV from a linear accelerator, UNILAC, at GSI (Darmstadt), Germany. In all cases, the irradiation was carried out in a vacuum chamber at room temperature. The number of irradiated ions per square centimeter, i.e., the ion fluence, was fixed at $3 \times 10^{13}$ ions cm$^{-2}$.

2.2 Conductometric cell

Electrical measurements help to determine the structural parameters of the pores during track etching. They detect events in real time and enable one to study dynamic processes. This real-time method can reduce the number of required scanning electron microscopy (SEM) observations and cut cycle times in process optimization.

A computer-controlled hermetically sealed conductometric cell was used to etch the ion tracks and measure their electrical properties. As shown in Fig. 2, track etching was performed by tightly clamping a circular disk of the irradiated PVDF film (diameter 2.0 cm) between two compartments of a cell made of polytetrafluoroethylene (PTFE). Etching starts from both sides of the membrane, leading to double cone intersections at the very beginning.

The electrodes work by interacting with the ions in the electrolyte solution (containing positive and negative charges) and the electrons from an electric circuit. The transport of electrons at the electrode surface is associated with a change in the electrode potential. Special attention must be paid to this polarization effect. Electrode polarization was minimized by (a) using polarization-free electrodes, (b) keeping the accumulated charge low, and (c) using alternating-current (AC) measurements. The polarization-free electrodes typically consisted of platinum (Pt) plates, each having a total surface area of 0.28 cm$^2$. The Pt electrodes can be used for very small accumulated charge.

2.3 Phase sensitive detection

In order to avoid polarization, a sinusoidal voltage of 0.3 (typical), 1.0, or 2.0 V was applied between the electrodes, and the resulting current was measured by an LCR meter (HiTESTER 3522, HIOKI). Figure 3 shows an equivalent circuit of the electrode-solution-membrane-solution-electrode section of the conductometric cell with the membrane. The phase shift is determined by integrating the product of the voltage and current over one period of the applied AC voltage. This enables us to separate the capacitive and resistive components of the complex impedance. The deposited charge on the electrodes, and hence electrode polarization, can be kept to a minimum for sufficiently high frequencies, e.g., 1 kHz in this study.

The real part of the electrical impedance corresponds to the ohmic resistance, and thus includes the resistance of the solution ($R_s'' + R_m''$), which is small enough to be neglected in most cases. Accordingly, the resistive component comes from the resistance across the membrane, reflecting the geometry of the etched pores. The etching of the surface and the formation of etching pits should in principle lead to an increase in the capacitance of the solution-membrane-solution section corresponding to the imaginary part of the impedance. However, measurement of the time constant of the circuit showed that the capacitive component remained practically constant [14]. The phase-sensitive system suppresses the out-of-phase noise.

2.4 Experimental design for high-temperature etching

The etchant for the irradiated PVDF film was a 9 mol dm$^{-3}$ aqueous KOH solution maintained at 80°C. The conductometric cell was placed inside a hot-water bath, and upon reaching the required temperature, the solution was brought into contact with the membrane surface.

![Fig. 2. Cross-section of the conductometric cell used for track etching of the PVDF films: (1) membrane, (2) etching solution (9 mol dm$^{-3}$ KOH), (3) PTFE, (4) Pt electrode, and (5) LCR meter.](image)

![Fig. 3. Electrical equivalent circuit of the conductometric cell with membrane: $R_s'''$ and $R_m'''$ represent the resistances of the etching solution; $R_s$ and $C_m$ are the resistance and capacitance, respectively, across the membrane.](image)
The consumption of KOH during the track dissolution was negligibly low because the compartment volume was sufficient.

We have to be aware of the fact that the etching temperature was as high as 80 ºC in our case; this is in contrast to track etching of PET and PC, in which the alkaline solution is generally heated to temperatures of 60ºC or lower [14,15]. At high temperatures, one of the greatest problems is evaporation of water from the bath; an uncovered bath will lose all the water overnight. One option for covering the water here was to place a thin layer of paraffin oil on top of it. Water evaporation also occurs from the surface of the etching solution. As shown in Fig. 6, the entire etching period was sometimes more than 24 h, undoubtedly increasing the KOH concentration because of considerable water loss. Each aperture of both compartments was closed with a stopper to minimize evaporation and maintain the concentration. The detailed experimental setup is shown in Fig. 4.

2.5 Principle of analysis [15]

The electrical resistance across the membrane, $R_m$, was measured as a function of the etching time. Based on Ohm’s law, $R_m$ is proportional to the specific electrical resistivity of the solution, $\rho$, and the pore length (equal to the membrane thickness), $L$, and inversely proportional to the pore density, $N$, the analyzed surface area, $S$, and the pore diameter, $d$, as follows:

$$R_m = \frac{\rho L}{NS} \frac{1}{4d^2}$$  (1)

This equation can be used under the following assumptions:

(i) All the pores are cylindrical. Equation (1) can be rewritten to calculate the effective pore diameter, $d_{\text{eff}}$, from $R_m$:

$$d_{\text{eff}} = \left(\frac{4\rho L}{\pi NS R_m}\right)^{\frac{1}{4}}$$  (2)

(ii) All the pores are identical; otherwise, the calculated $d_{\text{eff}}$ is a mean value. Pore size disparity may be caused by inhomogeneity of the polymer film and variations in energy deposition.

(iii) The pore diameter is much smaller than the pore length ($L/d > 100$); for larger pores, distortion of the current streamlines at the pore entrance must be taken into account.

Finally, instead of the resistivity values, $\rho$ and $R_m$, in Equation (2), the specific conductivity, $K$, and the conductance, $g(t)$, can be used to express $d_{\text{eff}}$:

$$d_{\text{eff}} = \frac{4Lg(t)}{\pi KNS}$$  (3)

The conversion from $g(t)$ to $d_{\text{eff}}$ was essential for data analysis, in which comparisons were made between the measurements.

3. RESULTS AND DISCUSSION

3.1 SEM observations

Although $N$ generally corresponds to the ion fluence, the fluence is stochastic. Correlation between the fluence and $N$ was checked microscopically. Figure 5 shows SEM images of the surfaces of track-etched membranes obtained by irradiation with (a) 450 MeV $^{129}$Xe and (b) 2.2 GeV $^{197}$Au ions, and subsequent 48-h chemical etching. The surface pore diameters were 138 ± 11 and 220 ± 11 nm, respectively. This clearly confirms that, for a given etching time, irradiation with a higher-LET beam led to larger pores in PVDF track-etched membranes.

3.2 Typical conductometric results

Figure 6 presents a typical record of the converted $d_{\text{eff}}$ values versus time during the course of the etching of the PVDF film irradiated with 2.2 GeV $^{197}$Au ions at an applied voltage of 0.3 V. All the curves followed the general trend described in the next three paragraphs; there are three characteristic stages.

During the first stage, the plateau at nearly zero represents the process of etchant penetration into the tracks and approach of the etched cones from both sides of the film. The period up until these two approaching cones make contact with each other is called the breakthrough time [15], $T_B$. The track-etching rate, $V_T$, for which severe damage in the core region results, is calculated by dividing the half thickness of the films by $T_B$ [15]. As indicated by the arrow in Fig. 6, we obtained $T_B = 1.0$ h, corresponding to $V_T = 13$ µm h$^{-1}$.

Fig. 4. Photograph of the track-etching experiments using PVDF. The aqueous KOH solution in the conductometric cell was heated at 80°C using a water bath.

Fig. 5. Surface SEM images of PVDF-based track-etched membranes. The membranes were prepared by chemical etching for 48 h after irradiation with (a) 450 MeV $^{129}$Xe and (b) 2.2 GeV $^{197}$Au ions.
After $T_B$, we found growth of the pores in the transverse direction. However, only the beginning of the second stage might be influenced by the perforation of additional pores. This possibility can be considered because all the tracks in the film are not simultaneously perforated. In this sense, $T_B$ or $V_T$ refers to the first pore.

Lastly, the curve reached a second plateau, meaning that pore growth almost stopped. Chemical etching in the unmodified area, i.e., bulk etching, occurred beyond the width of the latent track.

3.3 Effects of different experimental conditions

As demonstrated in Section 3.2, we were able to recognize etching of the damaged zone, enabling easy estimation of its size, from the $d_{eff}$ value versus time curves. Our interest is in comparing the track-etching characteristics, such as $V_T$ and pore growth after breakthrough, for different ions. We made the following three observations. (i) The $T_B$ value for the $^{129}$Xe-irradiated film was 4.2 h, about four times longer than that for the $^{197}$Au-irradiated one, at an applied voltage of 0.3 V. This means that $V_T$ for the former (3.0 $\mu$m h$^{-1}$) increased at the same rate as the $T_B$. (ii) The slope of the curve after the $T_B$ also appeared to be smaller for $^{129}$Xe than for $^{197}$Au. This corresponds to slower pore growth for the former. (iii) $^{125}$Xe beam irradiation decreased the final plateau $d_{eff}$ by 1.7 times compared with that for $^{197}$Au, producing smaller track-etched pores. These $d_{eff}$ values agreed, within the experimental error, with the surface pore sizes obtained using SEM observations, indicating cylindrical pores, as assumed in Section 2.5.

We compared the conductometry results obtained at different applied voltages. These comparisons were limited to the $^{129}$Xe-irradiated samples. When the applied voltage was increased from 0.3 to 1.0 V, we did not see any significant changes in the curve. When we further increased the voltage to 2.0 V, the curve exhibited a significantly shorter $T_B$ and time taken until the $d_{eff}$ value started to level off, although it still showed an invariant growth rate and final $d_{eff}$. In other words, the etching was accelerated at higher voltages. Similar results have been reported by a few research groups including Cornelius et al. [16], and the details were discussed elsewhere [7].

Conductometric analysis allowed us to examine the effects of the mass and velocity of the bombarding ions and of the cell voltages applied between the electrodes. The results will be useful for optimization of etching conditions.

4. CONCLUSIONS

PVDF films were irradiated with 450 MeV $^{129}$Xe and 2.2 GeV $^{197}$Au ions. We then investigated their track-etching behavior in a 9 mol dm$^{-3}$ KOH aqueous solution conductometrically. The apparatus and method described here made it possible to determine the $V_T$ (or $T_B$) and pore diameter reached in the final plateau under different experimental conditions including the parameters (mass and velocity) of the irradiated ions and the cell voltages applied between the electrodes.

5. REFERENCES


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