Swift Heavy Ion Irradiated Polymeric Membranes for Gas Permeation

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ABSTRACT: Polycarbonate membranes of thickness 18 μm were irradiated by Ni^{7+} ion of 100 MeV at fluences 10^6–10^8 ions/cm^2. The permeability for hydrogen and carbon dioxide has been measured from the membrane with increasing etching time. Permeability of both the gases increases with etching time, but for hydrogen the permeability was higher than for carbon dioxide for all membranes. The selectivity of hydrogen increases as ion fluence of membrane increases, for 10^8 ions/cm^2 membrane was higher than the lower fluence membranes. The irradiated membranes were also etched by monitoring the current, which shows change in the etching time for membrane of different doses. Ion permeation measurements show that pores in polymeric membrane are charged or neutralized, which depends upon the variation in concentration of the solvent. The etched tracks of membranes were characterized by the scanning electron microscopy.
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Key words: ion irradiation; track etched membrane; critical etching time; gas permeation; ion permeation

INTRODUCTION

The effect of swift heavy ions on polymers has been studied from past few decades. The irradiation of swift heavy ions in polymers changes the physical and chemical properties.[1] The energy loss mechanism of an energetic ion in solid is described via two independent processes, i.e., ion–atomic nucleus interaction that dominates at low energies and ion–electron interactions, prevalent at high energies. For heavy ions in the MeV/amu range, the energy transfer occurs mainly through electronic excitation and ionization. The passage of an energetic ion in polymers produces the latent tracks of reduced density and molecular weight.[2] The tracks are enabled to pass the gas molecules or liquids so it is required to preferentially etch to enlarge the size. Both the track and bulk etching takes place in irradiated membrane. Etching temperature has an important role to determine the formation of permeating tracks.[3,4] Successful track etching requires that the damaged material along the track is preferentially etched at a much higher rate than the surrounding undamaged matrix; in another word the track etching rate V_t has to be higher than the bulk etching rate V_b. The ratio of the two etching rates V_b/V_t determines the geometry of the etched pores. The track etch rate depends on many factors like sensitivity of materials, irradiation conditions (bombarding particle, atmosphere, temperature), and the postirradiated conditions.[5,6] The productions of porous membranes stands out among other applications of track etch technique as nanofilter.[5]

Track etched membrane can be applicable in the versatile area of scientific and industrial research in particular gas purification. Irradiation of a polymer membrane by heavy ions and subsequent chemical etching creates a membrane having an array of nano channels.[5,7] Conduction nature of pores in PET membranes has been studied using I-V characteristics by Apel et al.[8]; this type of membranes were produced by one side etching of irradiated membrane while other side of membrane was protected by a stopping medium.[3,4] The distinctive properties of track-etched membrane are a very narrow pore size distribution and low sorption ability, which is especially important for the filtration of gas mixtures. For the present work, the polycarbonate membranes of thickness of 18 μm were irradiated by Ni^{7+} ion of 100 MeV at low flux of 10^6–10^8 ions/cm^2. The membranes were treated by UV radiations and etched chemically in 6*N* NaOH at (60 ± 1)°C. The membranes were characterized by hydrogen and carbon dioxide gas permeation. The conduction nature of asymmetric pores was studied using $FeCl_3$ solution of different concentration. The scanning electron micrograph (SEM) of the etched membranes shows etched pits of membranes.

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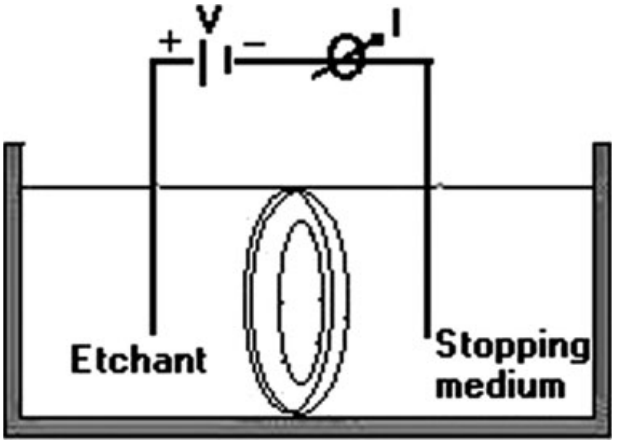

Figure 1 Schematic diagram of conductivity cell.

EXPERIMENTAL

Membrane preparation and irradiation

The polycarbonate material is obtained in granular form Goodfellow UK. The membranes of thickness 18 μm were prepared by solution cast method. The detail of solution cast method has been given elsewhere.[9] Membranes were dried in low vacuum at 50°C for 10 h to completely remove the solvent.

The membranes were irradiated by Ni^{7+} ion of 100 MeV in General Purpose Scattering Chamber (GPSC) at Inter University Accelerator Centre, New Delhi. The fluence of ion beam was kept 10^6–10^8 ions/cm^2, which was reduced by Rutherford scattering to mount the samples at different angles. The uniformity was achieved using rotating flywheel attachment, the details has been given elsewhere.[10] After the irradiation, the samples were stored in air conditions.

Chemical etching

The irradiated membranes were etched chemically in 6*N* NaOH at (60 ± 1)°C. The etching time increased with the step of 30 s, and after every etching, the membrane was washed thoroughly. The etchant was changed periodically, so that the concentration of the etchant remains same during the experiment. By a proper choice of etchant, temperature, and etch time, the diameter of resulting pores can be adjusted to be between 10 nm and 10 μm.[11] To etch the track from one side, the irradiated membrane was placed between the two chambers of conductivity cell, one chamber of the cell was filled with the etchant (6*N*, NaOH) at (60 ± 1)°C while the other side of membrane was protected by a stopping medium. For PC, an acidic solution (e.g., a mixture of 2*M* KCl and 2*M* formic acid) is used as a stopping medium. The schematic diagram of conductivity cell is shown in Figure 1.

Permeability measurements

The permeability of hydrogen and carbon dioxide has been measured from the membrane. The product of diffusion coefficient and solubility coefficient gives resultant permeability. The gas permeability is calculated using another form of Fick's formula according to the following relation

$$P = K(d^*s)/(\Delta P^*t)$$

The symbols have their usual meanings, i.e., K refers for cell constant depending upon the permeate area and cross-sectional area of the flow rate meter, d for the thickness of the membrane, s for the displacement of Hg slug, t for time, and ΔP for pressure gradient.[12] The Schematic of gas permeability setup is shown in Figure 2.

Conduction nature of etched pores

The electrolytic conduction studies through etched pores were also carried out in electrochemical cell, under symmetric bath conditions, which measure the ion current across the membrane. The electrolytic solution of $FeCl_3$ of different concentration is used for conduction measurements through etched pores of PC. Double distilled and carrier free deionized water will be used as a standard solvent, which were obtained from Millipore ultra pure water system. The voltage current characteristics were measured by stepping 0.1 V between −5 V and +5 V. The ion current is recorded responding to the voltages with help of Keithley 238 high current source measure unit.[8]

Scanning electron microscope

The fully etched samples were cut to the lengths of 5–5 mm using a fresh razor blade and were snapped under liquid nitrogen, which gives a generally clean break. The samples were then mounted on sample stubs and sputtered with gold, before a

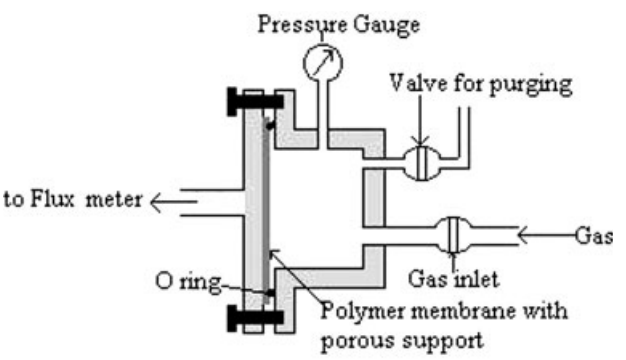

Figure 2 Schematic diagram of gas permeability setup.

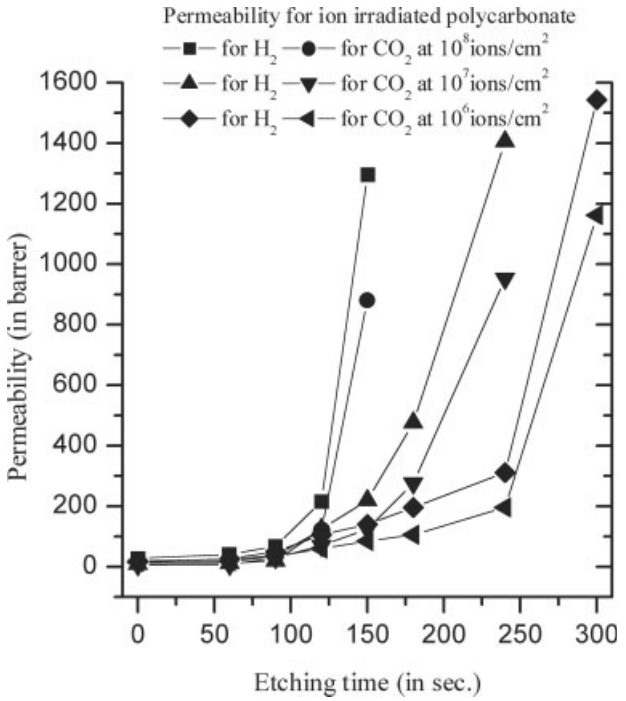

Figure 3 Graph of permeability versus etching time.

surface scanning investigation using scanning electron microscope (SEM) of KYKY-1000B.

RESULTS AND DISCUSSION

The polycarbonate can be used to develop the track-etched membrane. When the range of an energetic ion is higher than the thickness of the membrane

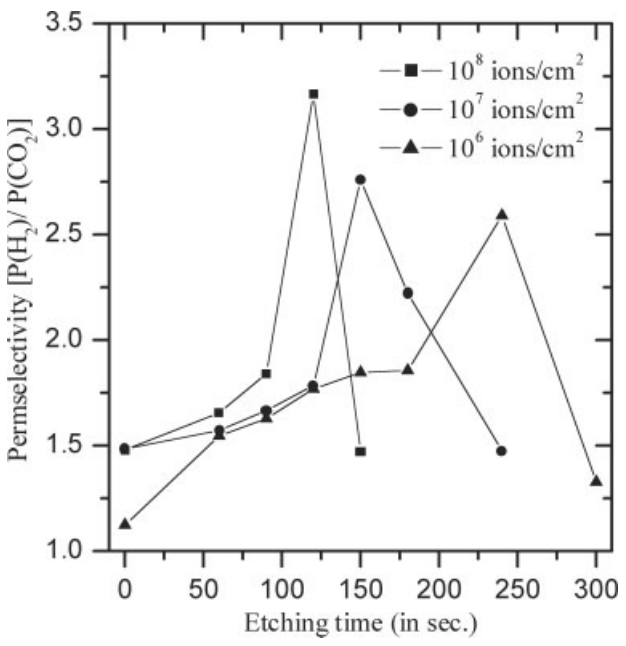

Figure 4 Graph of permselectiviity versus etching time.

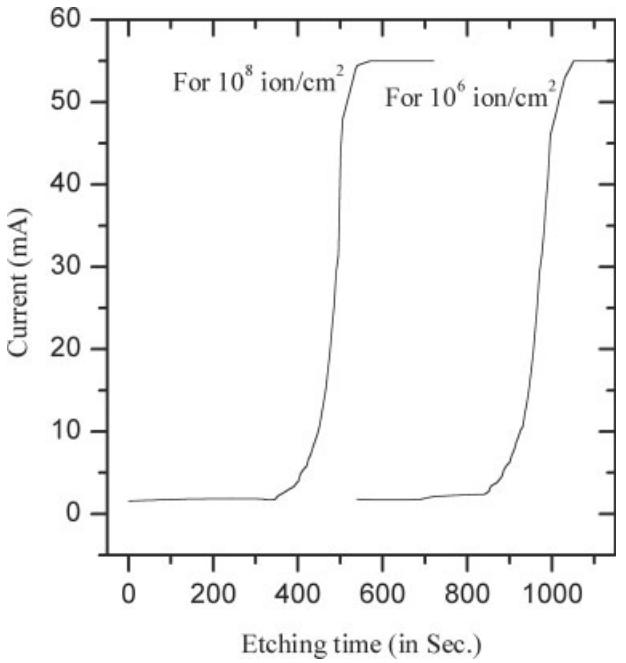

Figure 5 Graph of the ion current versus etching time.

then incident ion comes out from the membrane by losing some energy. In this case track etching takes place from both the side of the membrane. The stopping range of Ni^{7+} ion of 100 MeV in polycarbonate is 22 μm. For 18-μm thick membrane, the track etching takes place from both the sides. At this stage, the gas passes through the conical tracks that are just meeting at their vertexes. The gas permeability of the same membrane for hydrogen is greater than that of

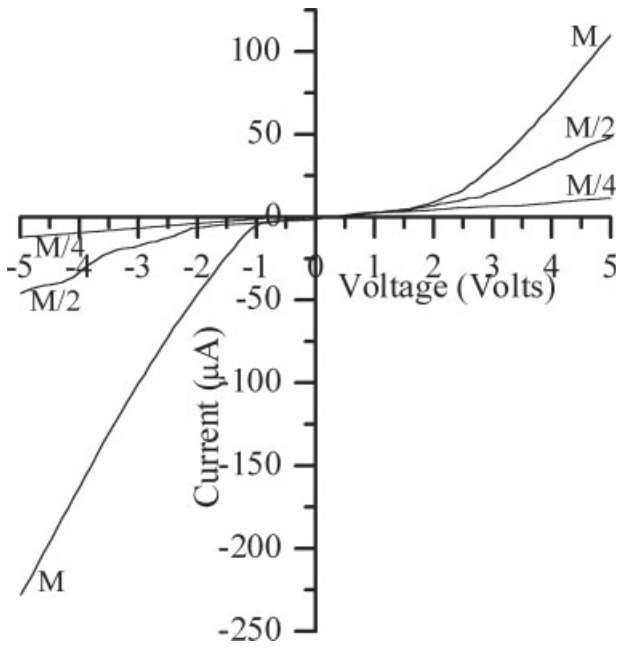

Figure 6 Voltage-current characteristics of 10^8 ions/cm^2 irradiated polycarbonate membrane.

carbon dioxide due the difference of their molecular sizes for H_2 it is 0.2 nm and for CO_2 it is 0.4 nm.

The ion fluence also alters the gas permeation rate. The permeability of hydrogen and carbon dioxide increases with increasing etching time. After a particular etching time (critical etching time, τ_c), the rapid enhancement in permeability is observed; this indicates the generation of permeating tracks as shown in Figure 3. The higher fluence membranes having less critical etching time than the lower fluence membranes due to variation in the number of tracks. The ion fluence also alters the gas permeation rate. The critical etching time for 10^8 ions/cm^2 irradiated membrane is found about 120 s, whereas for 10^6 ions/cm^2, it is about 240 s. The permselectivity of hydrogen over carbon dioxide is also found to increase with increasing etching time and reach to a maximum and on further etching it reduces, which shows that after critical etching the membrane allows passing both the gases as shown in Figure 4, at this time the diameter of tracks is more than the diameter of gas molecules.

For conical pores, membrane was etched from one side by monitoring the ion current. Figure 5 represents a graph between current versus time showing the breakthrough moment. The breakthrough is characterized by a sudden increase in current, when two chambers of cell become connected through the pores generated in the membrane. Using the stopping medium and a positive voltage on etchant side ensured that after breakthrough the current dose not change significantly for few time. The critical etching time for 10^6 ions/cm^2 irradiated membrane was higher than the critical etching time of 10^8 ions/cm^2 irradiated membranes due to the ion fluence.

Conduction measurements were carried out for conical pores by electrical conduction (V-I characteristics) behavior of electrolytes in PC. At an alkaline pH of electrolyte solution forming the bulk phases of the membrane, the internal surface of conical pores carries negative charges formed by ionic group.[11] The protons of these groups dissociate above a characteristics pH value leaving behind their immobile negatively

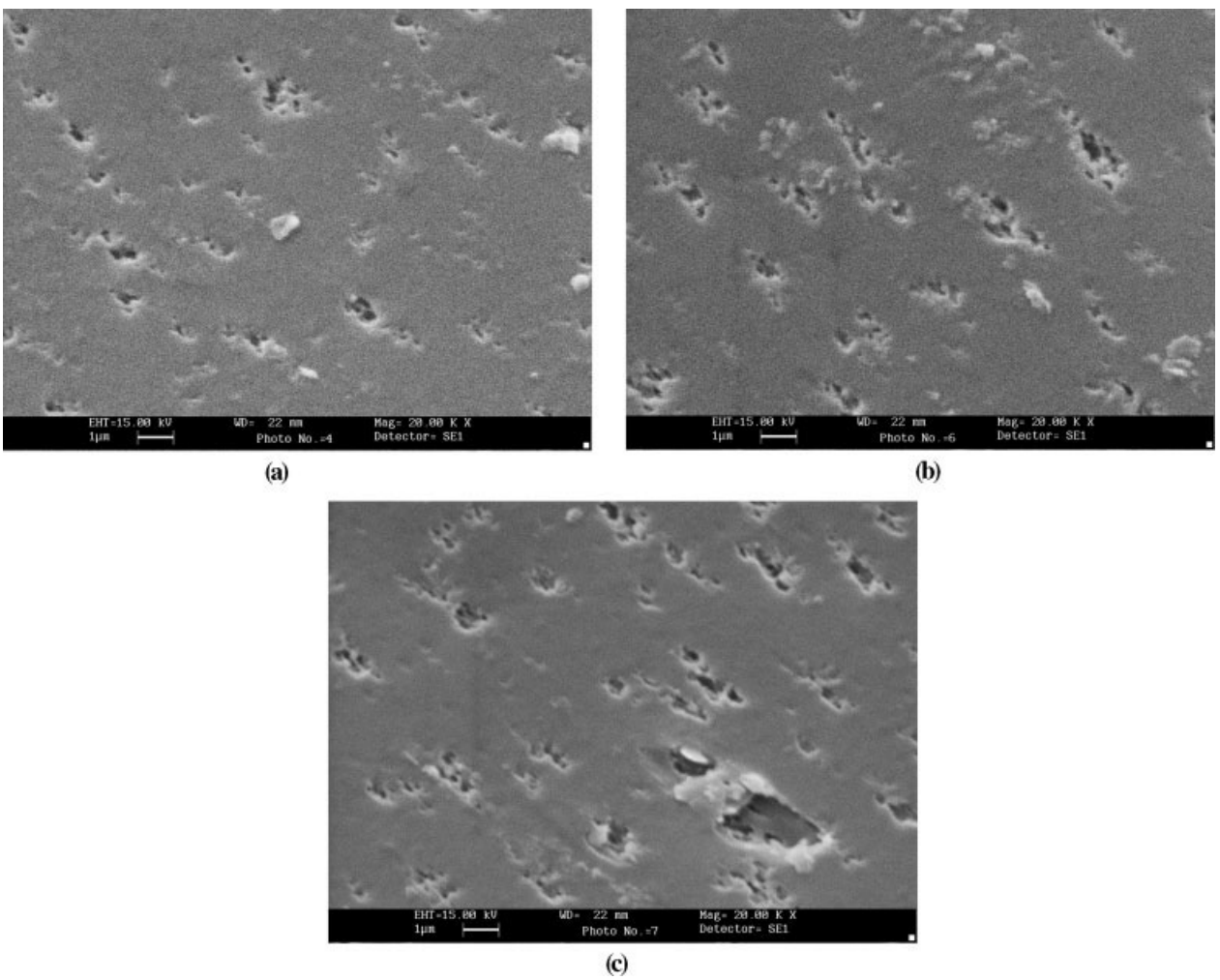

Figure 7 Scanning electron micrographs (SEM) for (a) 10^6 ions/cm^2, (b) 10^7 ions/cm^2, (c) 10^8 ions/cm^2 irradiated and fully chemical etched membranes.

charged COO^- part. The V-I characteristics obtained are that of an electronic diode, such a behavior of pores due to their conical geometry as shown in Figure 6.[13] Conduction measurement shows the nature of etched conical pores, which depend on the concentration of electrolyte. At concentration M, the pores rectify the ion current while at concentration $M/4$, pore losses its rectifying nature and becomes linear. The ion channels that function as a diode for ionic current have preferential direction of ion flow and block almost completely ions moving in the other direction. The SEM micrographs of fully etched tracks were shown in Figure 7(a–c).

CONCLUSION

The present study concludes that permeability of polymer membrane can be improved by irradiation; the chemical etching also helps to increase the permeability by a large factor. The selectivity of hydrogen over carbon dioxide also increases with etching time but at the critical etching time the selectivity found to be maximum. The rectification behavior observed for the pores in PC was an additional indication of the nanometer size of the pore opening. These membranes can be used for controlled gas release devices and fabrication of nanofilters.

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