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# Large area $\text{Cl}^{9+}$ irradiated PET membranes for hydrogen separation

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## Abstract:

In the present case, Polyethylene terephthalate (PET) membranes of thickness 25 $\mu\text{m}$  were irradiated by 100 MeV  $\text{Cl}^{9+}$  ion beam with ion fluence of  $10^7$  ions/cm<sup>2</sup>. These membranes were etched in 6N NaOH at 60<sup>0</sup>C at different etching times to generate pores. The permeabilities of nitrogen, oxygen, methane, carbon dioxide as well as hydrogen were measured for etched membranes at various etching times. The permeability of gases was found to increase with etching time and a rapid increase was noticed after a critical etching time when the etched tracks meet at their vertexes. The selectivity of hydrogen gas over other gases was also observed.

**Key words:** Track etched membrane, ion irradiation, chemical etching, Gas permeability

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## **1. General Introduction:**

Gas separation is a major industrial application of membrane technology. Over the past two decades, it has drawn a great deal of interest due to its low cost and ease of operation. Hydrogen perm selective membranes are indispensable for practical use of fuel cells. The membrane based separation technology has emerged into a new era of advanced functional materials. It has grown from early diffusion experiments, through basic concepts of diffusion and permeation to industrially accepted products. At present, a variety of novel membrane materials are being used to separate gases from their mixtures, separation of small molecules like gases and vapors as well as the resolution of optical isomers, ions, or biological matter, and in catalytic membrane reactors and sensor systems [1- 5] . Membrane separation processes are often more capital and energy efficient when compared with conventional separation processes. The membrane based separation requires simple, easy to operate and compact equipment due to which it has acquired a significant role in the industrial scenario[6, 7] .

Membranes serve as an interphase between two adjacent bulk phases as a selective barrier. It is either a homogeneous phase or a heterogeneous collection of phases. The movement of any species across the membrane is caused by one or more driving forces. These driving forces arise from gradient of potential, concentration, pressure or electrical. Membranes can be made of any material that forms sufficiently thin and stable films like metal, glass, ceramics, polymers and well-ordered monomolecular layers of surfactant molecules in liquid membranes. So, a membrane can be homogeneous or heterogeneous, symmetric or asymmetric and dense or porous [8]. Membrane based separation technology has major application in chemical and petrochemical industries that includes natural gas processing, landfill gas recovery, olefin /paraffin separation, air separation and recovery of hydrogen from nitrogen, carbon monoxide and methane mixtures[4].

The gas transport capacity of a membrane is ascribed to its permeability *i.e.* gas flux and selectivity for a specific gas. Commercially several membranes are being used for gas separation like polymer membranes, metal membranes, ceramic membranes etc. Existing challenges of low permeability and selectivity in polymer membranes are being addressed with advanced nanomaterials. However, polymer membranes with both high gas permeability and permeation selectivity are desirable for practical applications.

Track etched polymeric membranes offer distinct advantages over conventional membranes due to tunable pore size and porosity that are independent of each other and can be varied in an easily controlled manner over several orders of magnitude. Pore size is a function of etching time while porosity is a function of irradiation process [9].

Swift heavy ion irradiation of polymers leads to bond breaking, formation of free radicals and various other phenomena that are induced by the complex secondary chemical processes along the trajectory of the ions [10, 11]. Swift heavy ions transfer energy to the polymer essentially by inelastic (electronic) process while elastic (nuclear) energy transfer is, in general negligible for pristine polymers. But nuclear energy loss gains importance with proceeding polymer destruction, when tracks start overlapping. The energy transfer leads to excitation and ionization of molecular chains leading to radical formation, to side or main chain bond scissioning and also to crosslinking of polymer chains. Due to the electrostatic repulsion, these ions repel each other, thereby creating vacancies and interstitials. The range of this atomic collision cascade defines the core of latent track and has a diameter of less than 10nm. The track core is surrounded by a much larger halo of about 100-1000 nm [12-14].

Thus, during irradiation by swift heavy ions, latent ion tracks are formed along the path of the ions. After irradiation, the material is subject to chemical etching resulting in transformation of latent ion track into a hollow channel. During this chemical stage of processing, the size and

shape of the etched ion track is determined. Their pore size, shape and density can be varied in a controlled manner so that a membrane with required transport and retention characteristics could be produced. Pore shape can be made cylindrical, conical, funnel-like, or cigar-like at will [15-18]. Many attempts have been made to characterize the ion irradiated polymer membranes for gas separation [19-29].

Ovchinnikov et al. [19] investigated the efficiency of the separation of some inert gases (helium, nitrogen, argon, krypton, xenon) and hydrogen by nuclear track etched membranes of polyethylene terephthalate (PET) with pores of size of 2-10 nm and found membranes with pores over 6 nm in diameter to have an ideal size for gas separation. Schmidt et al. [20] have shown the separation factor as a function of the pore diameter. They found that after grafting with styrene the separation factor can be increased. Sudowe et al. [21] have used the gas mixture CO/CO<sub>2</sub> as a model system for the gas separation and the results show that a separation of the gas mixture is possible. Kulshrestha et al. have investigated permeability for Hydrogen and CO<sub>2</sub> of track etched membranes at different etching times and with different geometry of etched pores [22-24]. Ensinger et al. [25] have investigated gas permeability of CO and CO<sub>2</sub> gas mixture for 10<sup>8</sup> pores/cm<sup>2</sup> and showed that CO penetrates faster through the membrane than CO<sub>2</sub>, leading to gas separation. Gas permeability of ion irradiated polymer blend membranes has been reported and it was found that selectivity is reduced as the concentration of polycarbonate in polysulphone increases [26-27]. Acharya et al. [28] has deposited Ti on track etched polycarbonate membranes and found selectivity 4.72 for H<sub>2</sub> over CO<sub>2</sub>.

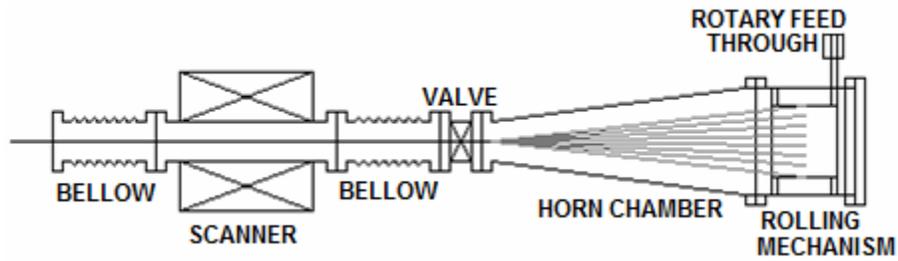
The aim of present article is to prepare and characterize large area track etched membranes based on swift heavy ion irradiation and subsequent chemical etching. The gas permeability and selectivity of different gases has been measured at different etching times for ion irradiated PET membranes.

## **2. Experimental:**

### *2.1. Irradiation*

The role of PET membrane (Mylar) having density  $1.39\text{g/cm}^3$ , dimension of 12 cm x 120 cm and thickness of 25  $\mu\text{m}$  was purchased from Garware Polyester Ltd., Mumbai (India). Swift heavy ion irradiations of PET films were carried out under collaboration with Tata Institute of Fundamental Research, Mumbai, India. PET membrane was irradiated by 100 MeV  $\text{Cl}^{9+}$  ion beam at fluence  $10^7$  ions/ $\text{cm}^2$  at BARC-TIFR pelletron accelerator facility, Mumbai (India). For even distribution of swift heavy ions (SHI) on the film a beam scanner was used to scan the SHI from the accelerator in horizontal direction. The beam scanner is an electromagnet which gives a peak magnetic field of 1.35 KG at 15 Amps. The deflection depends on the charge state of the desired ions which were produced using post stripper. The deflection, at the exit of the scanner was few centimeters which can be widened using a horn chamber of one meter length. Thus, deflection up to 25 cm was achieved at the end of the scanner.

The film was wound on a Perspex shaft which was continuously unwound on to another roller, driven by a D.C motor from outside the chamber. This coupling was done with a vacuum rotary feed through. Thus, polymer film was moved in vertical direction by using this rolling mechanism. The linear speed of the film was kept at 60 cms/min which was achieved at 10 rpm. The beam was defocused in vertical direction to get almost uniform particle distribution. The particles passing through the polymer membranes were stopped by a metallic plate to read the beam current. The ion beam was optimized on quartz mounted on the stainless steel (SS) plate in the center. The particles will fall on the S.S plate only when scanner magnet was energized. By using this facility, at the BARC – TIFR Pelletron Accelerator facility, polymer film up to 15 meters long and 20 cm wide in one roll can be irradiated in single run [29]. A schematic diagram is shown in figure 1.



**Figure1:** Set up for large area irradiation [29]

### 2.2. Chemical etching

The irradiated membranes were etched chemically in 6N NaOH at 60 °C [6]. The etching time was increased with a step of 5 min and after every etching step the membranes were washed thoroughly with double distilled water. To keep the concentration of etchant the same, the etchant was changed periodically and the temperature of etchant was kept constant throughout the process.

### 2.3. Permeability measurements

The permeabilities of the nitrogen, oxygen, methane, carbon dioxide and hydrogen were measured for etched membranes at different etching time by pressure increase measurements at GKSS Research Centre Geesthacht (Germany). Feed pressure was 1 bar while pressure increase (permeate) was 0.2-2 mbar. The unit of permeability is defined by the volume ( $m_N^3$  STP) per time unit (h) which penetrates a defined membrane area ( $m^2$ ) by a pressure difference (bar). The value of the permeability of a membrane with an unknown thickness of the selective layer is called flux density and is defined as

$$\frac{m_N^3 \text{ (STP)}}{m^2 \cdot h \cdot \text{bar}}$$

Finally permeability was calculated by using following relation:

$$L = \frac{V \cdot 22,413600}{R \cdot T \cdot A \cdot t} \cdot \ln \left( \frac{p_F - p_b}{p_F - p_{F(1)}} \right) \cdot \frac{m_N^2 \text{ STF}^2}{m^2 \cdot h \cdot bar}$$

Selectivity can be calculated by taking the ratio of permeabilities of two gases.

#### 2.4. Surface Morphology:

High resolution scanning electron microscopy was performed using a Zeiss Ultra 55 Gemini scanning electron microscope with an accelerating voltage of 3kV. For preventing charging, gold sputtering was carried out for 20 seconds.

### 3. Result and discussion:

The bombardment on amorphous polymer with energetic heavy ions results in the change in the free volume properties and chemical properties of the material. The permeability of membrane is directly related with the chemical composition and free volume available in the polymer matrix. If the range of energetic ions is less than the thickness of membrane then all the energy of ions is lost within the material, and in this case track etching proceeds from one side although for an irradiated membrane both the bulk and track etching takes place simultaneously. The track etching is faster than the bulk etching and depends on the amount of energy deposition and formation of chain fragments from radicals in the material due to the irradiation. In present case, the projectile range has been calculated by SRIM [30] for  $Cl^{9+}$  ion beam in PET film and found to be 33  $\mu m$ , which is much larger than the thickness of film. Hence, track etching takes place from both sides of irradiated membranes. The schematic for preparation of etched tracks in a polymer film is shown in figure 2.

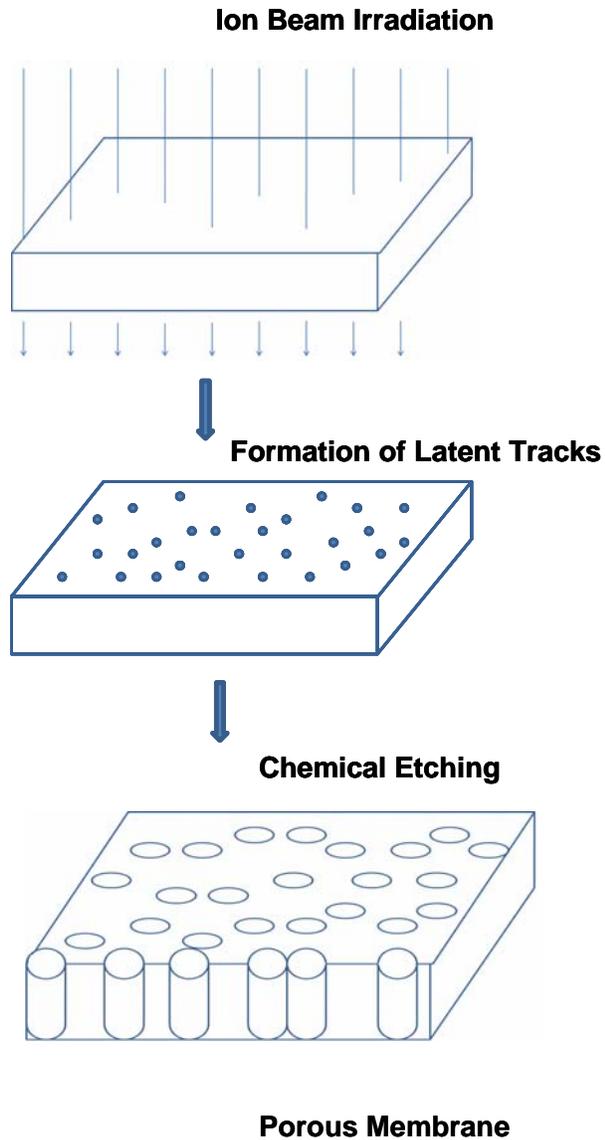
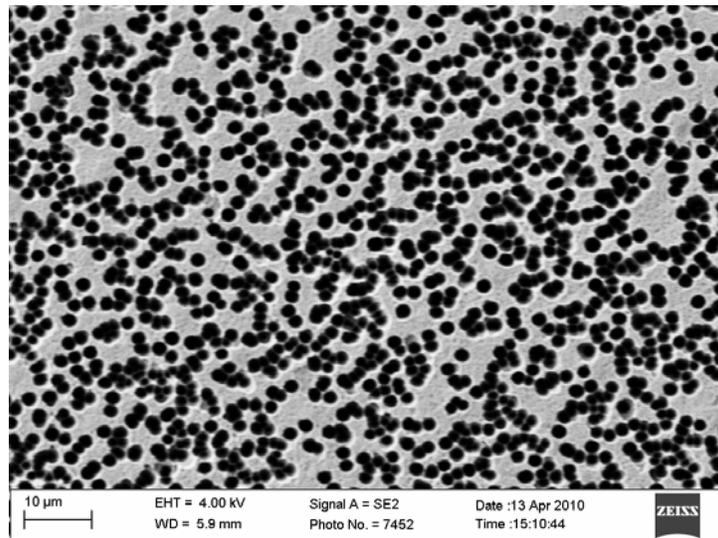


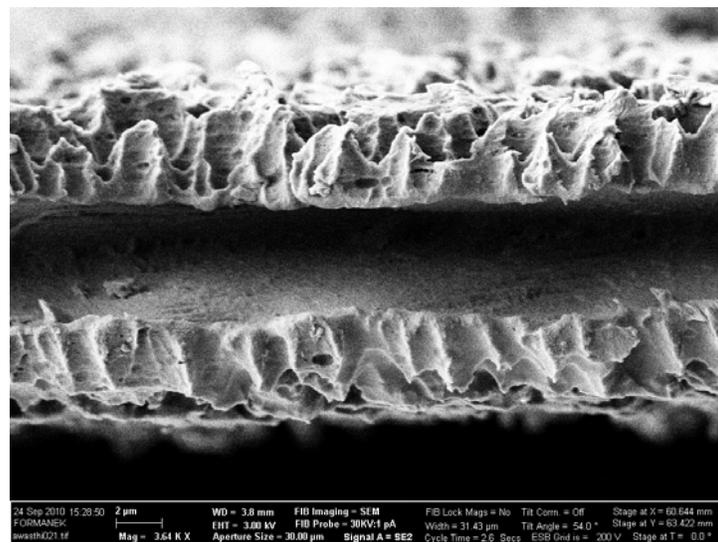
Figure 2: Schematic for preparation of etched tracks in polymer membrane

Figure 3 shows the scanning electron micrograph of the surface of PET membrane after chemical etching. The etched tracks in the form of pores are circular in shape having outer diameter 2  $\mu\text{m}$ . It is clear from figure 3 that individual ion tracks are not fully identical with respect to etching even for ions of the same masses and energies. It is due to the statistical nature of interaction between the ionizing particle and the penetrated matter and the heterogeneous structure of the

polymer. The pore diameters are found 70 ( $\pm 10$ ) nm, 120( $\pm 10$ ) nm and 210( $\pm 10$ ) nm for 15 min, 30 min and 45 min etched samples. The pore diameters are found to grow almost linearly after 15 min and are consistent with reported literature [31, 32]. During chemical etching, the material is removed along the latent track from both sides of membrane with higher velocity than the bulk etch rate resulting etch pit cones. As etching time increases, the double cone structure becomes a cylinder like structure. The number of pores per unit area ( $10^7$  ions/cm<sup>2</sup>) corresponds to the fluence of ions received by the polymer film. We cut the membrane for analyzing the shape of 45 minute etched pores by scanning electron micrograph. Figure 4 shows the cross sectional part of one of the fully etched pores in PET membrane and it can be concluded that after complete etching from both side of membrane, the shape of etched tracks are nearly cylindrical but not with sharp boundaries. Etching might not be homogeneous leading to irregular pore walls and the damage induced by fast ions could be not homogeneously distributed around and along the track due to many reasons e.g., from the localization of secondary electrons, producing multiple ionization events in a small volume or from Auger decay of created inner cell vacancies [3]. Also, the cutting of membrane may lead to deformation of pores and thus, to irregularities. Therefore, the ion track within damage region does not have sharp boundaries as shown in figure 4.



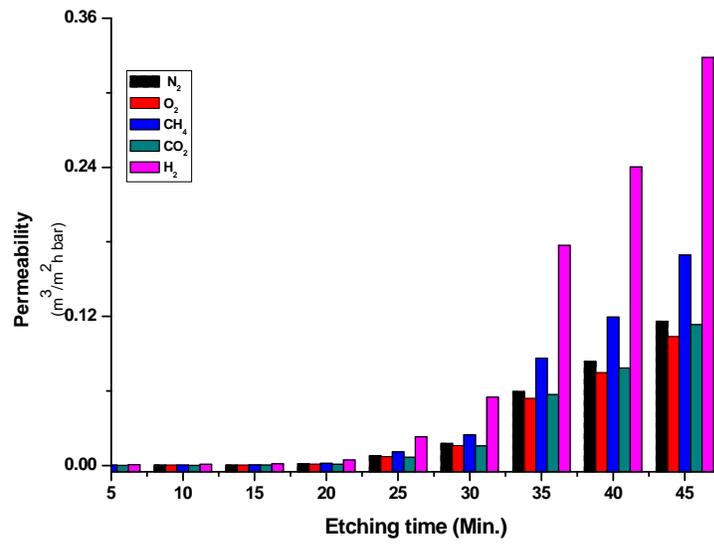
**Figure 3:** SEM of etched tracks



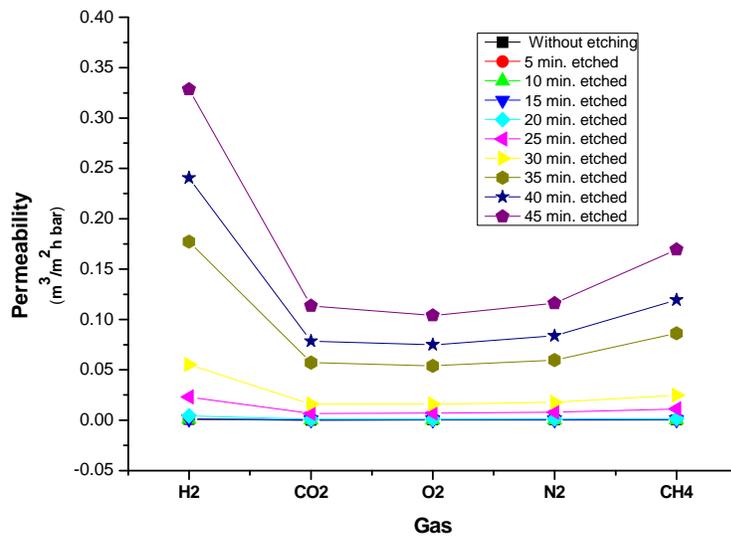
**Figure 4:** Cross sectional SEM of etched track

The permeability of the membrane for a penetrant is defined as the amount of penetrant that passes through the membrane with respect to time. Size selective, polymer membranes preferentially enable diffusion of small molecules such as hydrogen relative to larger ones. The results of gas permeability experiment are shown in figure 5. The simple solution diffusion model of permeation involves (i) dissolution (or sorption) of the penetrating gas through membrane at

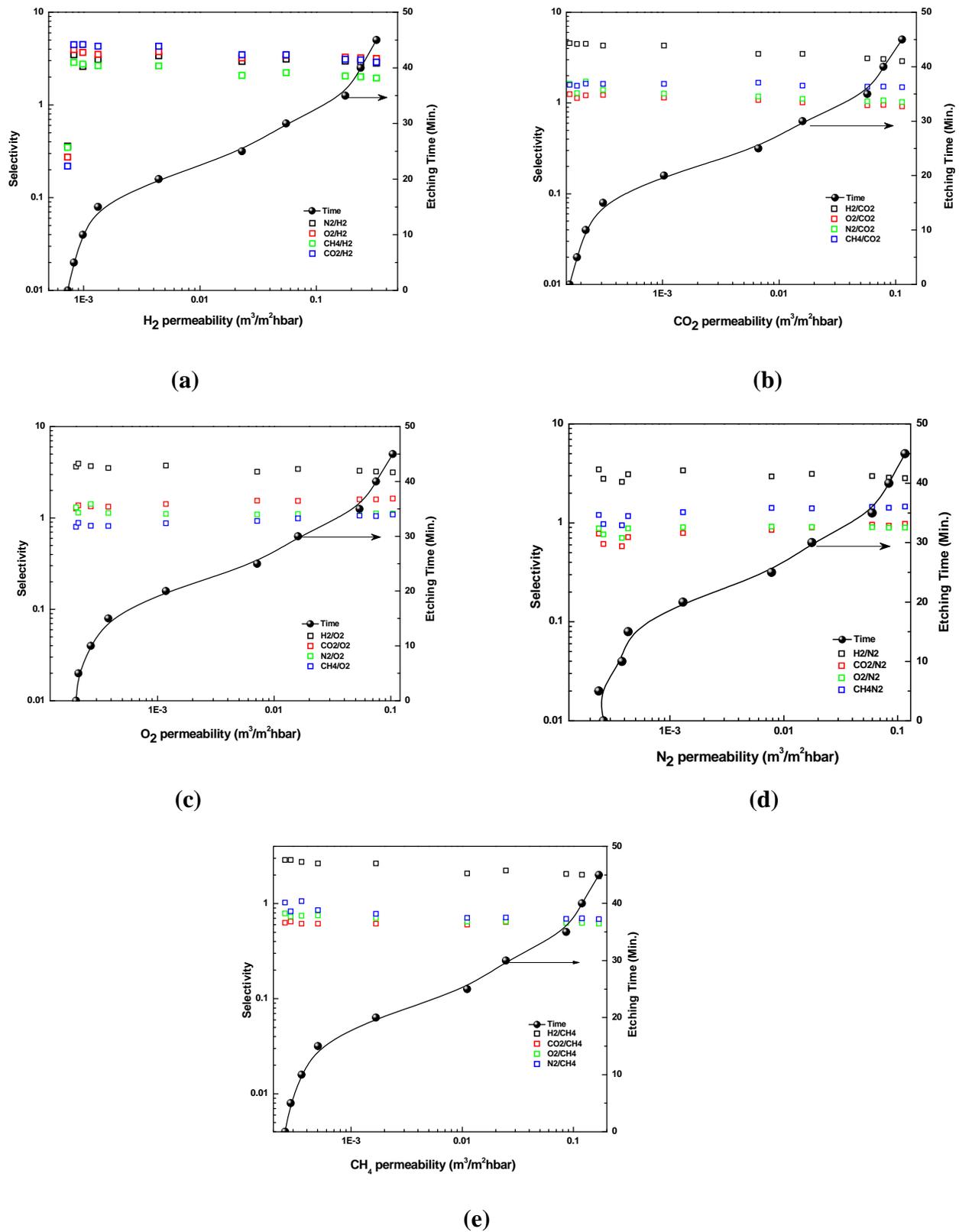
high pressure side, (ii) diffusion through membrane and (iii) desorption at the lower pressure side. The permeabilities of nitrogen, oxygen, methane, carbon dioxide and hydrogen gas have been measured for etched membranes at different etching time. The permeability of gases increases with increasing etching time. The permeability increases rapidly after a particular etching time as shown in Figure 4, at which the etched tracks meet at their vertexes. The estimated molecular diameters of H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> are found to be 2.89 Å, 3.3 Å, 3.46 Å, 3.64 Å and 3.8 Å respectively. The absolute magnitude of diameters of gas molecules is not important but ratio of diameters can give a good estimate of relative diffusion coefficient of different gas pairs. As hydrogen molecules are smaller in size than carbon dioxide molecules, so higher flow rate and correspondingly higher permeability has been observed at every step of different etching times as shown in figure 6. Sudowe et al. observed similar results in polyimide irradiated by Ar ions and concluded that carbon monoxide permeates faster through the membrane than carbon dioxide [21]. The selectivity of one gas over another for a membrane is given by the ratio of their permeabilities. The selectivities for H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> for different gas pairs and at different etching time are shown in figure 7. It can be concluded that these track etched membranes have reasonable selectivity but have to be used at low permeability. Further etching for higher permeability causes loss of selectivity due to overlapping of pores as shown in figure 7 and also in table 1. So, the dose of ion beam (ion fluence) also plays an important role to overcome the problem of overlapping of pores.



**Figure 5:** Gas permeability of PET membrane at different etching time



**Figure 6:** Permeability as a function of molecular diameter of different gases



**Figure 7:** Double logarithmic plots of selectivity versus permeability along with different etching time for (a) H<sub>2</sub> (b) CO<sub>2</sub> (c) O<sub>2</sub> (d) N<sub>2</sub> and (e) CH<sub>4</sub> gas

**Table 1: Selectivity of Hydrogen gas over other gases**

Etching Time (Minutes)	Selectivity			
	$N_2/H_2$	$O_2/H_2$	$CH_4/H_2$	$CO_2/H_2$
0	2.79397	3.64723	2.87006	4.45621
5	3.46764	3.94733	2.88143	4.46366
10	2.59539	3.68789	2.74763	4.48473
15	3.09361	3.51248	2.64626	4.30374
20	3.38549	3.75124	2.63964	4.29535
25	2.93982	3.21188	2.07768	3.46995
30	3.1213	3.43378	2.22877	3.47189
35	2.9726	3.28268	2.05276	3.10444
40	2.86921	3.21456	2.01443	3.06242
45	2.82692	3.16193	1.93984	2.89564

#### 4. Conclusion:

The large area irradiation of PET membranes has been described and irradiated samples are characterized by gas permeability measurement and scanning electron microscopy. Membranes with small circular pores have been formed. The number of pores per unit area corresponds to the fluence of ion beam. It is concluded that permeability of a polymer membrane can be improved by ion beam irradiation followed by chemical etching, however selectivity is lost as permeability increases. This technique is useful to prepare large area membrane filters for various applications. Further development in this direction will be preparation of membranes with smaller pores of large aspect ratio, functionalization of pores walls and combination of membranes in a stack for improving hydrogen selectivity at higher permeability.

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**References:**

1. Paul, D. R., Yampol'skii, Y.P., Polymeric Gas Separation Membranes; CRC Press, Florida, 1994.
2. Baker, R. W., Membrane Technology and Applications, 2nd ed., Wiley, New York, 2004.
3. Fink D., Transport Process in Ion Irradiated Polymers, Springer, Berlin, 2004.
4. Yampolskii, Y., Pinnau, I., Freeman, B. D., Materials Science of Membranes for Gas and Vapor Separation, Wiley, Chichester, 2006.
5. Vijay Y. K., Dhayal Marshal, Awasthi Kamendra, Kulshrestha Vaibhav, Acharya N. K., Choi J. S., Surface Modification and Synthesis of Polymeric Membrane for Energy and Biological Applications, Journal of Biomedical Nanotechnology 2 (2006) 144-151.
6. Kulshrestha V, Acharya N. K., Awasthi K., Singh M., Avasthi D. K., Vijay Y.K., Study of Gas Permeation for Asymmetric Track Etched Polymer Blends, International Journal of Hydrogen Energy 31 (2006) 1266-1270.
7. Pandey Pratibha, Chauhan R.S., Membranes for Gas Separation, Progress in Polymer Science 26 (2001) 853-893.

8. Maier Gerhard, Gas Separation with Polymer Membranes, *Angewandte Chemie International Edition* 37 (1998) 2960-2974.
9. Awasthi Kamendra, Kulshrestha V., Acharya N.K., Singh M., Vijay Y. K., Ion Transport Through Track Etched Polypropylene Membrane, *European Polymer Journal* 42 (2006) 883-887.
10. Fleisher, R. L., Price, P. B., Walker, R. M., *Nuclear Tracks in Solids: Principles and Applications*, University of California Press, Berkeley, 1975.
11. Awasthi Kamendra, Kulshrestha Vaibhav, Avasthi D. K., Vijay Y. K., Optical Chemical and Structural Modification of Oxygen Irradiated PET, *Radiation Measurements* 45 (2010) 850-855.
12. Fink D., *Fundamentals of Ion Irradiated Polymers*, Springer, Berlin, 2004.
13. Awasthi Kamendra, Kulshrestha Vaibhav, Nathawat Rashi, Acharya N. K., Avasthi D. K., Vijay Y. K., Conduction Nature of Conical Pores in PET Membrane, *Polymer Bulletin*, 57 (2006) 723-728.
14. Steckenreiter T., Fuess H., Stamm M., Trautmann C., Solvent-induced sensitization of ion tracks in PET analyzed by small-angle X-ray scattering and differential scanning calorimetry, *Nuclear Instruments and Methods in Physics Research B* 105 (1995) 200-203.
15. Spohr R., *Ion Track and Micro technology: Principles and Applications*, Vieweg & Sohn Verlagsgesellschaft mbH, Braunschweig 1990.
16. Apel P., Swift Ion Effects in Polymers: Industrial Applications, *Nuclear Instruments and Methods in Physics Research B* 208 (2003) 11-20.
17. C. Trautmann, S. Bouffard, R. Spohr, Etching Threshold for Ion Tracks in Polyimide, *Nuclear Instruments and Methods in Physics Research B* 116 (1996) 429-433.

18. Hermsdorf N., Stamm M., Förster S., Cunis S., Funari S. S., Gehrke R., Müller-Buschbaum P., Self-Supported Particle-Track-Etched Polycarbonate Membranes as Templates for Cylindrical Polypyrrole Nanotubes and Nanowires: An X-ray Scattering and Scanning Force Microscopy Investigation, *Langmuir* 21(2005) 11987-11993.
19. Ovchinnikov V.V., Seleznev V. D., Surguchev V. V., Tokmantsev V. I., Investigation of efficiency of gas separation on nuclear track membranes with ultra-small pores, *Journal of Membrane Science* 55 (1991) 311-323.
20. Schmidt K., Friese K., Angert N., Trautmann C., Selective capillary diffusion of equimolar H<sub>2</sub>/D<sub>2</sub> gas mixtures through etched ion track membranes from polyethylene terephthalate and polyimide, *Nuclear Instruments and Methods in Physics Research B* 107 (1996) 381-383.
21. Sudowe R., Vater P., Ensinger W., Vetter J., Penzhorn R.D., Brandt R., Basic research on nuclear track microfilters for gas separation, *Radiation Measurements* 31 (1999) 691-696.
22. Kulshrestha Vaibhav, Awasthi Kamendra, Acharya N. K., Singh M., Vijay Y. K., Swift Heavy Ion Irradiated Polycarbonate Membranes for gas separation, *Journal of Applied Polymer Science* 102 (2006)2386-2390.
23. Kulshrestha Vaibhav, Awasthi Kamendra, Acharya N. K., Singh M., Avasthi D. K., Vijay Y. K., Gas and ion transport through a track etched large area polymeric film, *Desalination* 195 (2006)273-280.
24. Kulshrestha Vaibhav, Acharya N. K., Awasthi Kamendra, Nathawat R., Singh M., Vijay Y. K., Characterization of asymmetric polymeric membranes by gas permeation, *Micron* 38 (2007) 326-329.

25. Ensinger W., Sudowe R., Brandt R., Neumann R., Gas separation in nanoporous membranes formed by etching ion irradiated polymer films, *Radiation Physics and Chemistry* 79 (2010) 204-207.
26. Kulshrestha Vaibhav, Awasthi Kamendra, Vijay Y. K., Swift heavy ion irradiated polymer blend membranes for hydrogen permeation, *International Journal of Hydrogen Energy* 32 (2007) 3105-3108.
27. Acharya N. K., Kulshrestha Vaibhav, Awasthi Kamendra, Jain A. K., Vijay Y. K., Hydrogen separation in doped and blend polymer membranes, *International Journal of Hydrogen Energy* 33 (2008) 327-331.
28. Acharya N.K., Kulshrestha V., Awasthi K., Kumar R., Singh M, Avasthi D. K., Vijay Y. K., Gas permeation study of Ti coated track etched polymeric membranes, *Vacuum* 81 (2006)389-393.
29. Nair J. P., Surendran P., Sparrow Hillary, Ninawe N.G., Nathawat R., Vijay Y. K., Bhagwat P.V., Kailas S., Large scale production of track etch membrane (TEM) filters, *Proceedings of Indian Particle Accelerator Conference, Mumbai, 2006.*
30. <http://www.srim.org>
31. Apel P. Yu., Blonskaya I. V., Didyk A. Yu., Dmitriev S. N., Orelovitch O. L., Root D., Samoilova L. I., Vutsadakis V. A., Surfactant-enhanced control of track-etch pore morphology, *Nuclear Instruments and Methods in Physics Research B* 179 (2001) 55-62.
32. Apel P. Yu., Blonskaya I. V., Oganessian V. R., Orelovitch O. L., Trautmann C., Morphology of latent and etched heavy ion tracks in radiation resistant polymers polyimide and poly(ethylene naphthalate), *Nuclear Instruments and Methods in Physics Research B* 185 (2001) 216-221.