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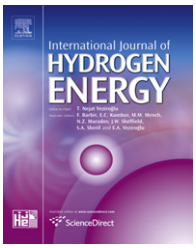

Large area Cl^{9+} irradiated PET membranes for hydrogen separation

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ABSTRACT

In the present case, Polyethylene terephthalate (PET) membranes of thickness 25 μm were irradiated by 100 MeV Cl^{9+} ion beam with ion fluence of 10^7 ions/cm^2. These membranes were etched in 6N NaOH at 60 °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.

1. 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

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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 10 nm. 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_2 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_2 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_2 gas mixture for 10^8 pores/cm^2 and showed that CO penetrates faster through the membrane than CO_2, 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_2 over CO_2.

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 (Myler) having density 1.39 g/cm^3, dimension of 12 cm × 120 cm and thickness of 25 μm 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 Cl^{9+} ion beam at fluence 10^7 ions/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 1 m 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 cm/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