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Palladium nanoparticle binding in functionalized track etched PET membrane for hydrogen gas separation

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ABSTRACT

In this work, track-etched poly (ethylene terephthalate) (PET) membranes having different pore sizes were functionalized by the carboxylic groups and the amino groups. Palladium (Pd) nanoparticles of average diameter 5 nm were synthesized chemically and deposited onto pore walls as well as on the surface of these pristine and functionalized membranes. Effect of Pd nanoparticles binding on these membranes were explored and aminated membrane were found to bind more Pd nanoparticles due to its affinity. The morphology of these composite membranes is characterized by Scanning Electron Microscope (SEM) for confirmation of Pd nanoparticle deposition on pore wall as well as on the surface. Gas permeability of functionalized and non-functionalized membranes for hydrogen and carbon dioxide has been examined. From the gas permeability data of hydrogen (H_2) and carbon dioxide (CO_2) gases, it was observed that these membranes have higher permeability for H_2 as compared with CO_2. Due to absorption of hydrogen by Pd nanoparticles selectivity of H_2 over CO_2 was found higher as compared to without Pd embedded membranes. Such type of membranes can be used to develop hydrogen selective nanofilters for purification/separation technology.

Introduction

For justify the world's energy necessities, enhancements in fuel cell and environmental issues, pure hydrogen is one of the most assuring solutions of such problems [1–6]. For producing an enormous amount of hydrogen and it can use as clean energy, the performance of hydrogen perm selective membrane should be improved. For hydrogen separation, membrane-based gas separation has fascinated awareness due to the intrinsic reimbursements like cost effective, energy efficient, eco-friendly and ease to operate over the other well-established separation process [7–11]. Polymer also proposed many appropriate abilities like lightweight, ductility, robustness, etc. [12–14]. There are several types of membranes such as polymer membrane, metal membrane, ceramic membrane, etc. that are used for gas separation [15]. But among them

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track etched polymeric membrane are the best suitable choice for application in gas separation due to its tunable pore size and shape as well as the preference of ion [16–20]. During ion irradiation process, ion fluence is the crucial element by which porosity can be varied in a controlled way [19]. Track etched PET membranes are widely used for the several applications because of its superb mechanical strength, inertness and thermal resistance [21]. But these membranes suffers low permeability as go for high selectivity [22]. Pore size of the membrane and interaction ratio between gas molecule with the membrane, both are the fundamental fact which plays an important role in gas permeation [23,24].

Functionalization is the advanced technique by which surface properties of the required material can be altered [25,26]. The functionalized pores of the membrane are effectual for depositing various nanoparticles as per required applications. After treating with functionalization, these membranes proposed benefit over unfunctionalized membrane as several functionalization processes can proceed and afterwards nanoparticles or nanotube can be inserted into the pores [27,28]. Functionalization of the porous membrane appearances complication while for planar surface it is more significant. Due to the chemical modification of the surface and pore walls, the effect of functionalization leads considerable effects in the gas separation. The functionalization of pore walls and deposition of nanoparticles is an efficient procedure for gas separation since with various functionalities; chosen nanomaterials can be integrated into the pore walls [29,30]. As per required shape, size and charge of the nanomaterial can be altered in functionalized membrane [31]. Sign of the surface charge can be varied by modifying the membrane with different functional groups, e.g., hydroxyl, carboxyl, amino, etc.

Pd nanomaterials are being used for gas separation applications since they have a high hydrogen diffusivity and are relatively resistant to oxidation. In the area of metal-based hydrogen system, palladium is an expressive catalytic metal which can be used for hydrogen storage and also for hydrogen sensing [32,33]. Due to having the outstanding ability to separate and dissolve hydrogen, metallic elements like nickel [34], palladium [35], platinum [36], copper [37,38], silver [39], iron, etc. can be chosen. Pd nanocomposite membranes are one of the most promising technologies for hydrogen separation. With having some advantages such as highly potential of separation efficiency and high permeability, these membranes can proceed to significant improvements in the separation of H_2 from the gas mixture. Pd-based metallic or composite membranes show an extraordinary talent to hydrogen transportation and purification because of its much higher solubility and absorption properties [40]. Palladium composite membranes have much high hydrogen permeability than CO_2 and N_2, and such membranes have improved hydrogen selectivity [41–43]. In membranes, the permeability of hydrogen is controlled by diffusion of hydrogen through the metal [44]. A thin metal layer always has lower mechanical strength than a self-supporting metallic membrane. So, for encounter the challenge of achieving high selectivity and good mechanical strength, metallic membranes have been deposited on the inorganic supports such as glass, ceramics, and metals by electroless plating [40], spray pyrolysis [45,46], sputtering [47] and chemical vapor deposition [48].

An effort has been made by Urch et al. [49], by depositing functionalized calcium phosphate nanoparticles on track etched PET membrane and found that there was no particle adsorption on the unfunctionalized surface while functionalized surface binds the nanoparticle. Palladium nanotubes have deposited into the pores of track-etched polycarbonate (PC) membrane by electroless plating technique by Yu et al. [50]. It was observed that nanotubes with having high surface area due to its granular surface which shows high sensitivity and the small detection limit for hydrogen sensing. Friebe et al. demonstrated a controlled way for pore functionalization of PET membrane by surface-initiated atom transfer radical polymerization. However, they grafted polymer layer on the track etched PET membrane [51]. Gupta et al. had reported Pd nanoparticles synthesis by polyol solution chemistry technique and studied for hydrogen sensing at different temperatures, 35 °C–75 °C [52].

To prepare an ultra thin membrane of Pd is quite challenging and fascinates innovative applications for separation technology. By introducing palladium nanoparticles on the surface and pore walls of modified membranes, it can be make beneficial for separation applications. The controlled functionalization of porous material is more difficult in comparison to planar surface but it is more relevant for advanced functional materials such as membranes. Here we report the interaction of functionalized PET track etched membranes with the palladium nanoparticles which is deposited on pore walls as well as on the surface of the membrane for gas separation. This procedure is followed due to easy deposition of nanoparticles over complex shapes, large surface to volume ratio and low cost. We demonstrated that the functionalization of track-etched PET polymeric membrane with deposition of nanoparticles plays an influential role in controlling the adsorption. Pd is chosen in our case due to having high diffusivity of hydrogen, and also it is not easily oxidised. Schematic diagram for the process is shown in Fig. 1.

Experimental details

Materials

The track etched PET polymeric membranes having higher pore density with different pore sizes i.e., 0.1 μm and 0.2 μm were purchased from Sterlitech Corporation. The chemicals used for the functionalization of the porous PET membranes were potassium permanganate ($KMnO_4$, Merck Millipore, India), hydrochloric acid (HCl, Merck Millipore, India), sulfuric acid (H_2SO_4, Merck Millipore, India), palladium chloride ($PdCl_2$, Sigma–Aldrich, India), sodium citrate ($Na_3C_6H_5O_7$, Sigma–Aldrich, India), sodium borohydride ($NaBH_4$, Sigma–Aldrich, India), dicyclohexylcarbodiimide ((DCC) $C_{13}H_{22}N_2$, Sigma–Aldrich, India), 1-Hydroxybenzotriazole ($C_6H_5N_3O$, Himedia, India), N,N-dimethylformamide ((DMF) C_3H_7NO, Sigma–Aldrich, India) tetraethylenepentamine ((TEPA) $C_8H_{23}N_5$, Sigma–Aldrich, India), Whatman 0.2 μm PTFE filter (GE Healthcare, USA) and ethanol (Emsure, Germany). All chemicals used as received without any further purification.