



# High performance polybenzimidazole based asymmetric hollow fibre membranes for H<sub>2</sub>/CO<sub>2</sub> separation

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## ABSTRACT

We demonstrated for the first time the development of polybenzimidazole (PBI) based asymmetric hollow fibre membrane for H<sub>2</sub>/CO<sub>2</sub> separation at high temperatures. High molecular weight PBI was synthesised in-house by a solution polycondensation method. Hollow fibre membranes were fabricated by conventional dry-jet wet spinning technique. Defect free asymmetric PBI hollow fibre membranes were successfully produced, which eliminated the step of silicone rubber coating and were tested in the high temperature range of 100–400 °C. The effect of bore fluid chemistry was found to have a significant effect on the morphology as well as gas performance of the hollow fibre membranes. Suppressing the formation of macrovoids was found to show improvement in the mechanical properties of the fibres produced. The PBI fibres showed an increment in H<sub>2</sub> permeance with up to ~8 folds, but with relatively small increment in CO<sub>2</sub> permeance of up to ~2 folds at 400 °C. Present PBI hollow fibre membranes showed H<sub>2</sub> permeance of about  $2.6 \times 10^{-6}$  cm<sup>3</sup> (STP)/cm<sup>2</sup> s cmHg and H<sub>2</sub>/CO<sub>2</sub> selectivity of about 27. Ability to show the good separation characteristics at elevated temperatures depicts the potential of the present high performance PBI membranes for high temperature applications.

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## 1. Introduction

Gas separation using membranes has been the area of extensive research [1–3] because it is considered to be one of the energy efficient separation processes. Gas separation at high temperatures using membranes would be advantageous and highly beneficial as it would eliminate the step of cooling and prevent energy loss. Using polymeric membranes for such an application would be highly challenging due to the limitation of the thermal and mechanical stability for most of the existing commercial polymers.

Hydrogen as a high-quality and clean energy carrier has attracted attention around the world in recent years, mainly due to the development of fuel cells as well as environmental pressures including climate change issues [4,5]. Hydrogen is primarily produced by steam reforming of hydrocarbons followed by water–gas shift reaction. In order to obtain high purity hydrogen from either syngas or the products of the water–gas shift reaction, separation of H<sub>2</sub> from either CO or CO<sub>2</sub> is necessary [6]. The H<sub>2</sub>-permeable inorganic membranes composed of a porous ceramic such as zeolite, a dense perovskite [7], or a dense metal have been reported [8]. They show promises in membrane reactors involving water–gas shift reaction due to their high temperature stability and durabil-

ity in harsh environment [9]. Zhang et al. studied the hydrogen permeation behaviour of dense palladium membranes prepared by micro-fabrication technique [10]. According to their study, this technique offers high durability to the membrane for operation at elevated temperatures. However, inorganic membranes are associated with complexities of fabrication and require high production costs [10]. On the other hand, the advantageous properties of polymeric membranes such as ease of processing and low cost may dominate the application of organic membranes over inorganic membranes. Polymeric membranes would be most accessible due to the more versatile chemical approaches, synthetic feasibility, large-scale production, processibility, and cost in comparison to other membranes [11,12]. However, the main drawback of polymeric membranes for hydrogen separation compared to inorganic ones is their limitation in operating temperature ranges. In addition, it is well shown that CO<sub>2</sub>-induced plasticization severely deteriorates the separation performance of membranes prepared from glassy polymers [13,14]. As a consequence there is a compelling need of a polymeric material which can operate in such a harsh environment and retain the performance of commercial significance. High performance polymers with rigid structures, high thermal and mechanical stability can be best suited for H<sub>2</sub>/CO<sub>2</sub> separation at elevated temperatures. A heterocyclic polymer polybenzimidazole (PBI), is well known for its many excellent properties such as high thermal stability (over 550 °C, [15]), excellent mechanical properties and chemical stability, making it an outstanding candidate over other common polymers. Due to

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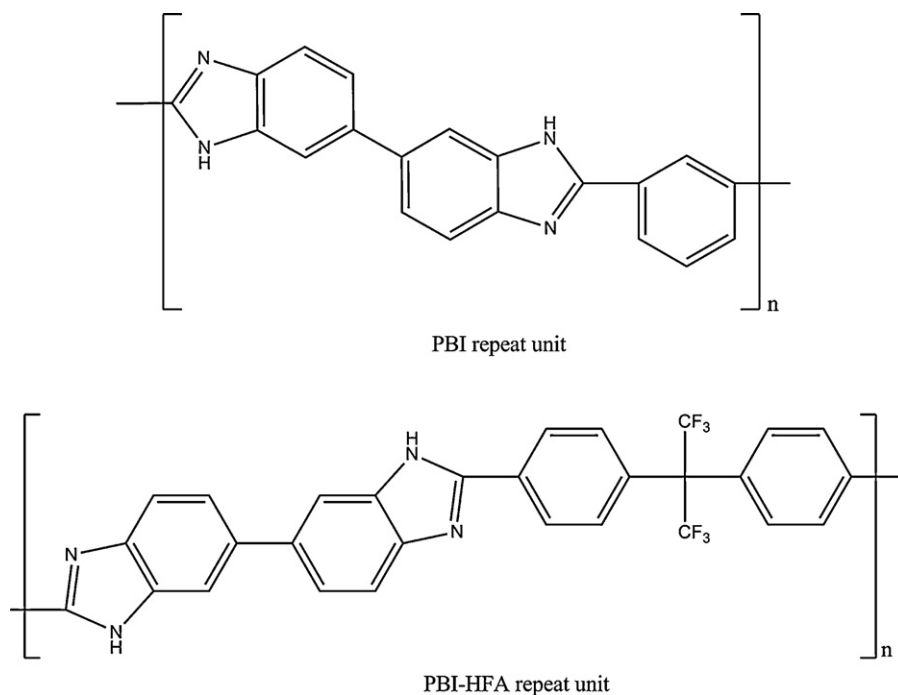


Fig. 1. Structure for repeat unit of PBI and PBI-HFA.

these properties PBI have been extensively investigated for various applications such as polymer electrolyte membranes [15], thermo-insulating materials, composites, fire-fighting suits, etc. [16]. Owing to its rigid structure ( $T_g = 420^\circ\text{C}$ , [17]) and stability at high temperatures, PBI could be best suited for  $\text{H}_2/\text{CO}_2$  separation application at high temperatures. It has been studied for gas permeability at  $200\text{--}270^\circ\text{C}$  and show  $\text{H}_2/\text{CO}_2$  selectivity of about 20 [18]. Its extremely rigid structure as evident from its high  $T_g$  ( $420^\circ\text{C}$ ) is anticipated to show resistance towards  $\text{CO}_2$  plasticization and thus, unlike other polymers, may not lose its separation performance even at elevated temperatures. Recently, work on carbon membrane derived from PBI/polyimide blend was reported [19]. The selectivity of  $\text{H}_2/\text{CO}_2$  was increased as the PBI content in the blend increased and was attributed to the rigidity and high packing density of PBI [19]. Dual-layer hollow fibre prepared from PBI and Matrimid<sup>®</sup> after silicone rubber coating showed the  $\text{H}_2/\text{CO}_2$  selectivity of about 11.11 [20]. PBI/Matrimid (75/25 wt.%) blend membranes cross-linked with *p*-xylene diamine showed the  $\text{H}_2/\text{CO}_2$  selectivity of 26 with  $\text{H}_2$  flux of 3.6 Barrer [21]. Moreover, PBI has excellent mechanical properties [16] as a result it can withstand high compression stresses from high pressure feed streams. Scientists at Department of Energy's Los Alamos National Laboratory have developed PBI-metallic composite membrane. The membranes maintain a commercially attractive selectivity between  $\text{H}_2$  and  $\text{CO}_2$  even at  $370^\circ\text{C}$  [22]. However these membranes were based on coating of PBI on to a porous metallic sheet substrate, which would increase the capital cost as well as induce limitations on the fabrication of membrane system (such as compatibility of very thin top selective skin layer with the hard metal mesh).

A few reports were available for asymmetric PBI membranes or its blend that demonstrated its applicability for nanofiltration [23,24], reverse-osmosis [25,26], forward osmosis [27] ultrafiltration [28], pervaporation [29] and gas separation [19–22]. However, to the best of our knowledge, no literature was available for the PBI asymmetric hollow fibre membranes for  $\text{H}_2/\text{CO}_2$  separation at high temperatures. The objectives of the present study were to fabricate asymmetric PBI hollow fibre membranes and to investigate the effect of temperatures on the  $\text{H}_2$  and  $\text{CO}_2$  separation performances.

## 2. Experimental

### 2.1. Materials

3,3'-Diaminobenzidine (DAB, >99.9%), isophthalic acid (>99%), 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (98%), polyphosphoric acid (PPA, 115%  $\text{H}_3\text{PO}_4$ ), sodium bicarbonate and *N,N*-dimethylacetamide (DMAc, >99.5%) were procured from Sigma-Aldrich and used as received. Lithium chloride anhydrous (LiCl, Acros organics) was used to facilitate the PBI dissolution and reagent grade ethanol and hexane used as solvent exchange fluid was purchased from VWR chemicals.

### 2.2. Polybenzimidazole synthesis

Two different polybenzimidazoles viz., PBI (based on isophthalic acid) and PBI-HFA (based on 4,4'-(hexafluoroisopropylidene)bis(benzoic acid)) were synthesized in house by solution polycondensation method using PPA [15]. The chemical structures of the repeat unit of these PBIs are shown in Fig. 1. PBI-HFA was used for blocking the area of PBI membrane that is not participated in gas permeation at high temperature. The relevant details will be described in the subsequent section.

Typically, a three-necked flask equipped with a mechanical stirrer,  $\text{N}_2$  inlet and  $\text{CaCl}_2$  drying tube was charged with 50 g of PPA, 2 g (0.0093 mol) of DAB and temperature was elevated to  $120^\circ\text{C}$ . Then 0.0093 mol of corresponding carboxylic acid was added, temperature was elevated to  $170^\circ\text{C}$  and maintained for 4 h under constant flow of nitrogen. The temperature was further raised to  $200^\circ\text{C}$  and maintained for another 4 h. The highly viscous reaction mixture was then precipitated in stirred water. The polymer was neutralised with sodium bicarbonate followed by water washing till neutral to pH. The crude polymer was then soaked in acetone for 5 h and then dried in oven at  $100^\circ\text{C}$  for 12 h. The polymer was further purified by dissolving in DMAc (5% w/w), removing undissolved material, if any, by centrifugation followed by re-precipitation in water. The precipitate of the polymer was then soaked in acetone (5 h) and then dried at  $100^\circ\text{C}$  for 12 h. The polymer was charac-

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