Composite membranes with a highly selective polymer skin for hydrogen separation

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ABSTRACT

This study reports the fabrication of a highly hydrogen selective cross-linked polymer skin on a highly permeable mixed matrix membrane. Selective polymer skins were prepared by spin coating a thin layer of 6FDA-durene polymer onto ZIF-8/6FDA-durene mixed matrix membranes followed by subsequent cross-linking of the 6FDA-durene layer with ethylene diamine (EDA) vapor. Resultant membrane yielded significantly high gas pair selectivities for the separation of H_2/CO_2, H_2/N_2 and H_2/CH_4 of 29, 341, and 278, respectively, while also maintaining a high hydrogen permeability of 500 Barrers. The superior separation performances of this system surpass the current permeability–selectivity tradeoff limits (Robeson 2008 upper bound) for H_2/CO_2, H_2/N_2, and H_2/CH_4 separations. The present work elucidates the potential of fabricating a highly selective layer (thin skin) on a highly permeable membrane to obtain high permeability and high selectivity simultaneously.

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1. Introduction

As the world-wide availability of petroleum resources decline, there is a need for sustainable and green energy sources to fulfill the growing energy demand. A hydrogen based economy is a potential solution to this energy crisis which opens up path for the development of efficient and environmentally benign hydrogen purification processes [1]. As compared to conventional separation methods such as pressure swing adsorption and distillation, membrane based gas separations/purifications have attracted tremendous attention due to the low capital cost, and high energy efficiency [2]. The performance of membranes is evaluated based on gas permeability and selectivity where permeability is a measure of membrane productivity, and selectivity is a measure of separation efficiency. High gas permeability and high selectivity are of significant importance for the commercial viability of membranes [3]. However, there is a tradeoff between the permeability and selectivity in polymeric membranes, which requires new approaches to overcome this limitation [3–6]. Current membrane research is focused on fabricating stable, high performance membranes with permselective properties above the current permeability–selectivity trade-off limit (Robeson upper bound) [7]. Several strategies have been employed to overcome this tradeoff, such as

polymer cross-linking, polymer blending, and adding inorganic particles to form mixed matrix membranes [7].

Cross-linking has proved an effective way of increasing gas pair selectivity, usually at the expense of gas flux. Different cross-linking methods have been employed [8–11], and several blend membranes are reported in literature [12]. Mixed matrix membranes (MMMs) [13–16] containing zeolites [17,18], activated carbon [19], carbon molecular sieves [20–22], mesoporous materials [23–25], carbon nanotubes [26], and metal–organic frameworks (MOFs) [27–32] are reported. As compared to zeolite MMMs having poor polymer–particle interfacial contact [13] MOF [33] containing MMMs offer good polymer–particle compatibility, arising from the organic nature of the linkers [30] Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs with structures similar to zeolites, offering unprecedented surface areas and high thermal stability [34,35]. Therefore, recently, ZIF containing continuous membranes [36–40] and ZIF/MMMs [30–32] have been studied for gas separations. The main problems associated with ZIF membranes are the framework flexibility of the ZIFs [41] and particle aggregation [42], which limit their performance. Due to these reasons reported ZIF MMMs mainly show improved gas permeability with little or no improvement in gas pair selectivity, and therefore require novel methods to improve the performance of these MMMs. One strategy to overcome the permeability selectivity tradeoff by simultaneously increasing gas permeability and selectivity is to combine the advantages of cross-linking and mixed

matrix membrane approach [3]. Only a few studies have been published so far on cross-linked MMMs for gas separation.

In a study by Koros and co-workers, cross-linkable co-polyimide 6FDA–DAM–DABA having a pendant carboxylic group, has been cross-linked using diols with different lengths, which increased the CO_2/CH_4 separation factor [43,44]. Hillock et al. has reported on cross-linking MMMs by first adding zeolite SSZ-13 to PDMC, a cross-linkable polymer with a pendant ester group, and then cross-linking the bulk MMM at elevated temperatures under vacuum [17]. Following a discovery on diamine cross-linking of polyimides [45], the cross-linking of polyimide membranes using a wide variety of diamines and polyimides have been reported for gas separations [8,12,46–51]. Chung and co-workers cross-linked the surface of 6FDA-durene membranes with ethylenediamine (EDA) vapor, yielding a very high H_2/CO_2 separation factor of 102 and a moderate hydrogen permeability of 32 Barrers [52]. Since the gas flux of these cross-linked membranes is inadequate to be commercially viable [53], we explored novel flat MMM fabrication and modification methods to improve the gas flux while utilizing diamine cross-linking to improve the gas pair selectivity.

Porous asymmetric membranes with a thin selective skin are ideal for gas separations as the porous structure increases gas flux and the thin selective skin increases the gas pair separation factor [54]. Hollow fiber membranes with this morphology are the most preferred form of membranes for industrial applications due to the good performance and low cost [55]. Several asymmetric flat membranes have been reported using different methods of fabrication. The most popular form is dry–wet phase inversion yielding asymmetric membranes with a porous substructure and a selective skin [56]. Thin polymeric membranes have also been fabricated on porous substrates using spin coating, where the porous substrate mainly provides mechanical stability for the membranes [57].

In a previous study we incorporated 33 wt% zeolitic imidazolate framework-8 (ZIF-8), porous nano particles into highly permeable polymer 6FDA-durene to obtain highly permeable MMMs, and cross-linked the surface layers (top and bottom) of these MMMs by reacting the membranes with EDA vapor [58]. Although this method improved the hydrogen separation properties the full potential enhancement in selectivity was not realized. ZIF-8 (Fig. 1) is a tetrahedral porous framework formed by the coordination of N atoms in methylimidazolate (MIm) ligands to Zn (II) ions [34]. ZIF-8 has a pore aperture of 0.34 nm [59], chemical and thermal stability (>400 °C), and high surface area (1630 m^2/g). 6FDA-durene (Fig. 1) is a polyimide with a high H_2 permeability of 600 Barrers [52] and a high thermal stability indicated by a glass transition temperature (T_g) of 422 °C [60].

In this study we prepared composite membranes with a highly selective polymer skin by spin coating a thin layer of the cross-linkable polymer 6FDA-durene onto highly permeable ZIF-8/6FDA-durene MMM substrates followed by subsequent cross-linking of the 6FDA-durene polymer layer with EDA vapor to enhance

gas pair selectivity. This method is an attempt to combine the high permeability of the ZIF-8/6FDA-durene MMMs and the high selectivity of the cross-linked polymer layer. The casting solvent, polymer concentration, and spinning conditions were optimized to obtain a thin defect-free polymer layer. The gas transport properties of the resultant membranes were studied by varying the ZIF-8 loading in the MMM. To the best of our knowledge this is the first study of a composite membrane with a selective cross-linked polymer skin on a ZIF mixed matrix substrate for gas separation. This work demonstrates the potential of combining a highly selective thin layer and a highly permeable layer in a membrane to obtain high gas flux and high gas selectivity simultaneously.

2. Materials and methods

2.1. Materials

Anhydrous N-methylpyrrolidinone (NMP, 99.8% purity) was obtained from Fisher Chemicals Inc. 4,4-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, >99% purity) was purchased from Akron Polymer Systems and was dried under vacuum at 150 °C prior to use. 2,3,5,6 tetramethyl-1,3-phenyldiamine (durene-diamine, 99% purity), acetic anhydride (Ac2O), and triethylamine (TEA, 99% purity), were acquired from Sigma–Aldrich. Durene-diamine was purified by recrystallization from methanol.

Chloroform ($CHCl_3$), methanol (MeOH), dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were acquired from Fisher Inc. All solvents were dried over activated 4A molecular sieves purchased from Sigma–Aldrich prior to use. ZIF-8 (Basolite™ Z1200) was obtained from Sigma–Aldrich and was activated at 100 °C under vacuum for 24 h. Ethylenediamine (EDA, 99.5%) was acquired from Sigma–Aldrich, and Mylar® A92 thin films were purchased from Active Industries.

2.2. Synthesis of 6FDA-durene

The synthesis of 6FDA-durene was carried out using chemical imidization following literature procedures [8,58].

2.3. Mixed matrix membrane fabrication

The 33.3 wt% and 50 wt% ZIF-8/6FDA-durene MMMs were prepared using 0.20 g of 6FDA-durene with 0.10 g of ZIF-8 in $CHCl_3$ and 0.20 g of 6FDA-durene with 0.2 g of ZIF-8 in $CHCl_3$, respectively. The polymer solution and ZIF-8 dispersion were prepared separately in two vials using 3 mL and 5 mL of chloroform, respectively, and stirred and sonicated for 4 h (alternating 1 h stirring followed by 1 h sonication). After adding 10% of the polymer solution to the ZIF-8 dispersion (precoating), the mixture was again stirred and sonicated for 4 h, before adding the remaining polymer. Next, the mixture was stirred and sonicated for further 4 h, and left stirring
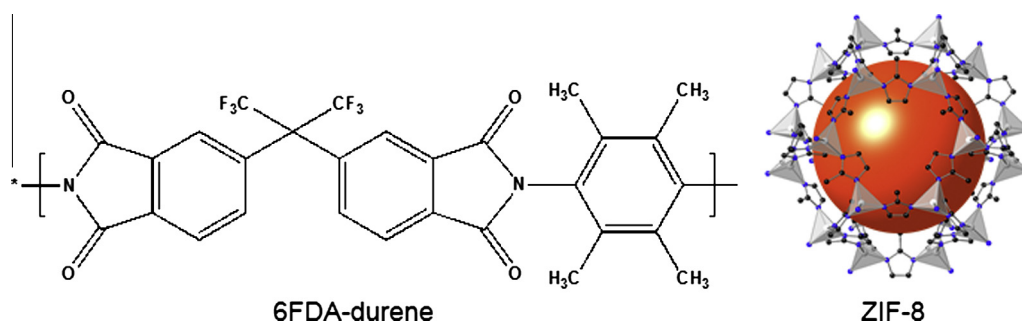

Fig. 1. Structures of 6FDA-durene and ZIF-8.