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Ultem®/ZIF-8 mixed matrix hollow fiber membranes for CO_2/N_2 separations

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ABSTRACT

Organic–inorganic hybrid (mixed matrix) membranes can potentially extend the separation performance of traditional polymeric materials while maintaining processing convenience. Although many dense films studies have been reported, there have been few reported cases of these materials being successfully extended to asymmetric hollow fibers. In this work we report the first successful production of mixed matrix asymmetric hollow fiber membranes containing metal-organic-framework (MOF) ZIF-8 fillers. Specifically, we have incorporated ZIF-8 into a polyetherimide (Ultem® 1000) matrix and produced dual-layer asymmetric hollow fiber membranes via the dry jet-wet quench method. The outer separating layer of these composite fibers contains 13 wt% (17 vol%) of ZIF-8 filler. These membranes have been tested over a range of temperatures and pressures for a variety of gas pairs. An increase in separation performance for the CO_2/N_2 gas pairs was observed for both pure gas and mixed gas feeds.

1. Introduction

The impact on global warming caused by emissions of CO_2 from various sources is a major concern. According to the Environmental Protection Agency, the U.S. emitted 6.1 billion metric tons of CO_2 to the atmosphere in 2007 [1]. One large source of carbon dioxide is fossil fuel combustion. Alkaline-based sorbents and scrubbing solutions can be employed to remove CO_2 from various gas mixtures. These methods have critical drawbacks, however, due to the large volume and low pressure of flue gas. Carbon dioxide capture methods have been reviewed by a number of authors [2,3]. Membranes for the selective removal of CO_2 in the presence of CO, H_2, H_2O, and H_2S (fuel gas) or N_2, O_2, H_2O, SO_2, NO, and HCl (flue gas) would be potentially advantageous relative to other approaches [4,5].

The well-known challenges of low selectivity and permeability in polymer membranes are being addressed with some degree of success with advanced engineering polymers [6,7]. There is no guarantee, however, that these materials can be processed into cost-effective asymmetric hollow fiber membranes. The “spinnability” of a polymer is often undermined by the lack of adequate stability of the nascent fiber, which prevents extrusion and take up at economical rates [8].

In addition to challenges associated with the hollow fiber spinning, selectivity enhancement via the introduction of new polymers offers slow progress as is evidenced by rather marginal increases in selectivity and permeability over the previous decade [9]. In contrast to polymers, inorganic and carbon based molecular sieves offer very high selectivities and permeabilities. These materials are, unfortunately, prohibitively expensive to fashion into working membranes with current technology. A promising route to enhanced transport properties involves the formation of *hybrid* or *mixed matrix membranes* (MMM) combining the processibility of spinnable polymers with the excellent transport properties of molecular sieves. In principle, adhesion of a continuous polymer matrix to a dispersed zeolite can create a hybrid material with appropriate properties [10,11]. One class of inorganic materials that has been considered extensively for this purpose is zeolites. Two major drawbacks of zeolite-based MMM must be overcome. First, the number of zeolite types identified to produce successful MMM is limited. Second, the inorganic surface chemistry of zeolites leads to additional membrane formation challenges when attempting to create a defect-free morphology [12].

Metal organic frameworks (MOFs) are a relatively new class of microporous materials comprised of transition metals and transition metal oxides connected by organic linkages to create one-, two- and three-dimensional microporous structures. MOF particles offer an attractive alternative to zeolite particles in MMM applications. Like zeolites, MOFs have characteristically high surface areas, sorption capacities and selective affinities for gases. The “tailorability” or flexibility of the MOF structure introduces controlled pore sizes, surface functionalities and chemical properties which are very desirable properties in a hybrid membrane system [13–15]. In short, MOFs appear to be attractive fillers in MMMs [16,17]. Thousands of crystalline MOF structures have been identified [18,19]. *Zeolitic imidazolate frameworks* (ZIFs) are a class

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of MOFs with tetrahedral networks that resemble structure types of conventional zeolites. As one of the many different such structures, ZIF-8 crystallizes in the sodalite topology (SOD) and consists of Zn(II) tetrahedrally coordinated by four 2-methylimidazolate linkers [20]. The rate-limiting step for the diffusion of guest molecules is the passage through the six-membered windows connecting each cavity. The window size is estimated to be 3.4 Å by X-ray diffraction structure analysis [20,21]. ZIF-8 is currently the only ZIF that is commercially available.

ZIF-8 was predicted by Haldoupis et al. to have extraordinarily high membrane selectivity for CO_2/CH_4 mixtures in theoretical calculations based on a rigid crystal structure [22]. Bux et al. however have observed much lower actual selectivity in a pure ZIF-8 film [23]. This is consistent with the idea that internal vibrations in ZIF-8 are sufficient to enable the window between cages to allow molecules to pass through even though the molecules are "larger" than the pore size that would be assigned from a rigid crystal structure. Although flexibility in the windows of ZIF-8 has not been observed directly, Zhou et al. have shown the existence of a quasi-free rotational potential for CH_3 groups in the ZIF-8 structure [24]. Although a full description of the effect of framework vibrations on different molecules in ZIF-8 is not available, this material is nonetheless a reasonable candidate for membrane-based separation because of its relatively small pores. MOFs that have only large pores (i.e. when diffusion is controlled by constrictions 1 nm across or larger) are unlikely to show appreciable diffusion-based selectivity for CO_2/N_2 and are therefore not as interesting as smaller pore materials in membranes for this separation [22,25].

There has been a growing interest in MMMs containing MOF fillers as seen in the literature reports [13,16,17,26–34]. Additionally, there have been a few reports in recent literature of MMMs containing a ZIF-8 [26,27,29,31,35]; moreover, a few reports exist in the open literature on asymmetric mixed matrix zeolite hollow fiber spinning for gas separations [28,36–42]. Only a single report was found on MOF/polymer asymmetric mixed matrix hollow fibers for H_2 separations [28].

The objective of this study was to create mixed matrix asymmetric hollow fiber membranes comprising ZIF type fillers in a commercially available glassy polymer matrix. In this work Ultem® 1000 (a polyetherimide) was chosen for the matrix because it is has acceptable intrinsic separation properties and has been used successfully for creating mixed matrix hollow fibers [37,38]. This publication, to the best of our knowledge, is the first report of successful ZIF/polymer mixed matrix hollow fibers for gas separation.

2. Experimental

2.1. Materials

Ultem® 1000 polymer was purchased from GE Plastics (Pittsfield, MA). Anhydrous *N*-methyl-2-pyrrolidione (NMP), tetrahydrofuran (THF), *iso*-propanol (IPA), methanol (MeOH), hexane, lithium nitrate ($LiNO_3$), heptane and ZIF-8 were all purchased from Sigma-Aldrich (Milwaukee, WI). Polydimethylsiloxane (PDMS, Sylgard 184) is produced by Dow Chemicals. All chemicals and polymers were used as received without any further purification.

2.2. Mixed matrix dense membrane preparation

ZIF-8/Ultem® dense membranes were made to study the concept prior to spinning hollow fibers. A 10 wt% ZIF-8/Ultem® dense MMM was fabricated by solution blending. Two mixtures were initially prepared: Ultem® 1000 (0.45 g) powder in chloroform (5 ml) and ZIF-8 (0.05 g) in chloroform (5 ml). The ZIF-8 suspension was stirred and sonicated in a bath alternately for 1 h to obtain a homogenous dispersion. The sonication bath used for indirect sonication was a VWR Ultrasonication Water Bath, operating at 120 W and 40 kHz. ZIF-8 crystals were first "primed" by adding a small amount, approximately 20%, of the Ultem® 1000 solution to the ZIF-8 mixture, after which the mixture was further stirred and sonicated for another 1 h. After thorough mixing, the remaining polymer solution was added gradually by pipette. Excess chloroform was evaporated to obtain a solution with the desired viscosity (~10 wt% polymer) for membrane casting. Membranes were cast onto a glass plate in a N_2 filled glove bag containing a small dish of chloroform using a fixed casting knife (Bird Film Applicators; Norfolk, VA). The resulting membrane was immediately covered with a watch glass, and kept for 2 days as the chloroform evaporated through a small vent into a hood. The membrane was then peeled off the glass plate and annealed in a vacuum oven at 100 °C for overnight.

Table 1
Pure polymer dope and dual layer core and sheath dope compositions (wt%).

Component	Pure polymer dope	ZIF-8/Ultem® core dope	ZIF-8/Ultem® sheath dope
Ultem® 1000	33.00	32.06	29.82
NMP	51.00	55.71	51.34
THF	10.00	10.02	13.23
Ethanol	4.70	–	–
$LiNO_3$	1.30	2.21	1.17
ZIF-8	–	–	4.44

2.3. MMM hollow fiber membrane preparation

For high rates of gas production, the dense separating layer of a membrane must be as thin as possible, yet strong enough to withstand the applied transmembrane pressure differential driving forces. Such an arrangement is ideally achieved with asymmetric hollow fibers, which consist of a very thin dense layer (skin) on a porous support layer. These membranes are typically formed in a single step via a dry jet-wet quench spinning process where phase separation within the wet quench bath occurs as rapidly as possible. Rapid phase separation traps in significant porosity for the support layer of the membrane, while a thin skin can be formed in the prior step via solvent evaporation in the air gap. Pure polymer dope preparation and the spinning procedure for the hollow fibers were performed following previous work [38].

2.3.1. MMM hollow fiber membrane dope preparation

2.3.1.1. Core dope preparation. Dried (convection oven, 110 °C, overnight) $LiNO_3$ was dissolved in NMP using a sonication bath. The salt is used as a pore-forming agent in this work wherein it controls the phase separation kinetics and morphology of the porous support layer. After the salt was dissolved, THF and dried polymer powder (vacuum oven, 110 °C, overnight) were added and the mixture was placed on a roll mill until the polymer was completely dissolved and the solution became transparent. An infrared heat lamp was used to aid dissolution of the polymer solution on the roll mill at 50 °C. Once fully dissolved, the solution was loaded into a 500 ml syringe pump (Model 500D; Teledyne Isco, Inc.; Lincoln, NE) 1 day prior to spinning to allow for degassing. The core dope composition used in this work is provided in Table 1.

2.3.1.2. Sheath dope preparation. The polymer and ZIF-8 were dried at 110 °C in a vacuum oven overnight prior to use. ZIF-8 was added to a portion of the required NMP and sonicated using the above mentioned ultrasonication water bath. The mixture was stirred and sonicated alternately for 1 h to obtain a well dispersed suspension containing 10 wt% ZIF-8. All of the THF (as per the dope