Supporting Information

for

High-Permeance Room-Temperature Ionic-Liquid-Based Membranes for CO_2/N_2 Separation

Jinsheng Zhou,[†,] * *Michelle M. Mok,*[†] *Matthew G. Cowan,*[‡, §] *William M. McDanel,*[‡] *Trevor K. Carlisle,*[‡] *Douglas L. Gin,*[‡, §] *and Richard D. Noble*[‡]

Materials

Poly(vinylhexylimidazolium bis(trifluoromethylsulfonyl)imide) (**1**)[1] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**2**)[2] were synthesized according to previously published procedures and conformed to the chemical and structural purity data previously reported.[1, 2] Cylinders of CO_2 and N_2 gas were purchased from either Airgas (Randor, PA) or the Oxygen Service Company (St. Paul, MN) and were of at least 99.99 % purity.

TFC membrane gas permeance testing with bubble flow meter

A schematic figure of the bubble flow meter test apparatus is shown in Figure S1 below.

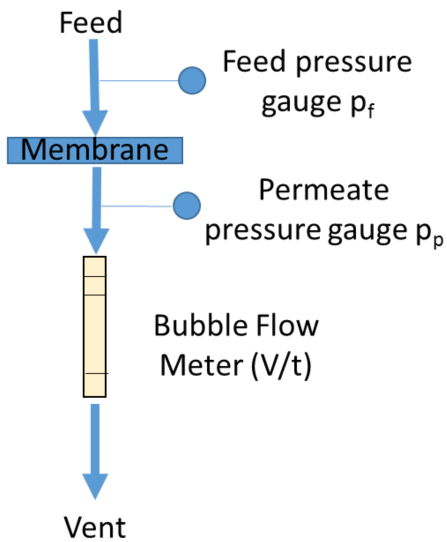

Figure S1. Schematic of the testing apparatus used to test membranes with a bubble flow meter.

For testing, 47-mm-diameter discs were punched from the produced membrane line and were designated as membranes **A–D**. After loading each membrane in the testing apparatus, the unit was evacuated (< 0.1 torr) for 10 min. The apparatus was isolated from dynamic vacuum, and the feed volume was then connected to a gas cylinder of either CO_2 or N_2. The gas was allowed to flow for sufficient time to completely flush the permeate volume and bubble flow meter with the target gas (at least 3 times the permeate and bubble flow meter volume). Once the system reached steady state (5 min), the bubble flow meter was used to determine the gas flux (volume/time) through the membrane sample. At least 3 gas flux measurements were performed for both CO_2 and N_2 and averaged for each membrane sample tested. The permeance ($\mathbb{P}$) was then calculated with the equations shown below; where J_x = the flux of gas x, $\Delta p = p_{feed} - p_{perm}$ (transmembrane pressure drop), V is the volume of gas measured via bubble flow meter, A is the membrane area, t is the amount of time required for gas to flow volume V, and $\alpha_{i/j}$ is the permeance selectivity.

$$\mathbb{P}_{CO_2} = \frac{J_{CO_2}}{\Delta p}$$

$$\text{and } \mathbb{P}\ [=] GPU, \qquad 1GPU = 10^{-6}\frac{cm^3\ (STP)}{cm^2 * s * cmHg}$$

$$J_{CO_2} = \frac{V}{t * A}\left(\frac{cm^3\ (STP)}{cm^2 * s}\right)$$

$$\propto_{CO_2/N_2} = \frac{\mathbb{P}_{CO_2}}{\mathbb{P}_{N_2}}$$

Gutter support gas permeance testing with dead-end cell set-up

The testing was conducted on a constant volume-variable pressure set-up equipped with gas source (CO_2 and N_2), feed gas reservoir, membrane cell, permeate pressure transducer, permeate gas reservoir, and vacuum pump. All gases were tested in duplicate with a feed pressure of 10 psi and static vacuum on the permeate side at room temperature to determine the ideal single-gas permeances of the composite membranes as follows:

$$\mathbb{P} = \frac{\overline{(\frac{\Delta p^*}{\Delta t})} * V_0}{R * T * A * \Delta p} * V(STP)$$

$\overline{\Delta p^* / \Delta t}$, average pressure increment in the permeate

V_0 , the fixed volume of the permeate side

R , gas constant

T , testing temperature

A , membrane test area

ΔP , transmembrane pressure

$V(STP)$, gas molar volume at standard temperature and pressure

The CO_2/N_2 selectivity (α) is calculated from the ratio of the permeances of single gases.

$$\alpha = \frac{permeance(CO_2)}{permeance(N_2)}$$

SEM imaging

Membrane samples were cross-sectioned by cutting under liquid nitrogen and coated with a thin layer of Pt. SEM imaging was conducted using a Hitachi S-4700 Field Emission Scanning Electron Microscope at the 3M Company.

Discussion regarding the calculated CO_2 permeability of the poly(RTIL)/RTIL active layer of the TFC membranes

Previous data from Ref. 15 in the main manuscript reports a CO_2 permeability of 105 barrers for a fully infused membrane of poly(RTIL) **1** containing 20 mol % RTIL **2** (i.e., ca. *23 wt %* **2**) in a porous poly(ether sulfone) support. In contrast, the top layer thickness and CO_2 permeance data observed for the TFC membrane in this work (which contains *58 wt %* **2** in the poly(RTIL)/RTIL layer) suggest an active layer CO_2 permeability of at least 600 barrers. We believe that this permeability difference is due largely to the different RTIL loadings in the poly(RTIL)/RTIL materials used. It may also be due in part to small-scale phase heterogeneities in the poly(RTIL)/RTIL (see Ref. 10 in the main manuscript) and/or differences in gas permeability behavior between an ultrathin supported poly(RTIL)/RTIL film vs. the same material infused through a porous poly(ether sulfone) support. These two configurations afford different surface area-to-volume ratios for the poly(RTIL)/RTIL and its amount of interfacial contact with the support, both of which could affect gas transport.

References for the Supporting Information

(1) Carlisle, T. K.; Wiesenauer, E. F.; Nicodemus, G. D.; Gin, D. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2012,** *52*, 1023-1032.

(2) Finotello, A.; Bara, J. E.; Camper, D.; Noble, R. D. *Ind. Eng. Chem. Res.* **2007,** *47*, 3453-3459.