Facilitated Transport Membrane with Functionalized Ionic Liquid Carriers for CO₂/N₂, CO₂/O₂,

and CO₂/Air Separations

Yun-Yang Lee¹, Nalinda P. Wickramasinghe², Ruth Dikki¹, Darrell L. Jan³, Burcu Gurkan^{1,*}

- 1. Department of Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, OH
- 2. Northeast Ohio High Field NMR Facility, Case Western Reserve University, Cleveland, OH
- 3. Ames Research Center, National Aeronautics and Space Administration, Moffett Field, CA

Supporting information

Number of pages: 14 Number of figures: 11 Number of tables: 1

Content:

- Calculation of theoretical minimum work of DAC and PCCC
- ¹H-NMR and HSQC of studied IL (Figure S1)
- ¹H-NMR and HSQC of studied PIL (Figure S2)
- Pulse sequence used for ion diffusivities (Figure S3)
- ¹H-DOSY NMR of IL carrier (Figure S4)
- Viscosity and water content of IL as a function of CO₂ concentration and humidity. (Figure S5)
- DSC curves of PIL-IL (Figure S6)
- Photo images and SEM surface morphology of PIL-IL/GO on *b*PES/PET and PIL-IL/GO on UF (Figure S7)
- ¹H-NMR, HSQC, and HMBC of GO in DMSO-d₆ (Figure S8)
- CO₂ separation performance of PIL-IL/GO on *b*PES/PET and on UF substrate (Figure S9)
- FTM model fitting of CO₂ permeance data (Figure S10)
- The impact of temperature on FTM performance
- Fabricated FRTM compositions for testing under vacuum operation (Table S1)
- The dependence of self-diffusivities on humidity (Figure S11)

Calculation of theoretical minimum work of DAC and PCCC

From the perspective of thermodynamics, the theoretical minimum work (assuming ideal gas) required for flue gas (**Figure S1**) is the change of Gibbs free energy, as is given by **Equation S1**:

$$W_{min} = RT \left[X_{N_{2},2} \ln \left(\frac{x_{N_{2},2}}{x_{N_{2},1}} \right) + X_{N_{2},3} \ln \left(\frac{x_{N_{2},3}}{x_{N_{2},1}} \right) + X_{CO_{2},2} \ln \left(\frac{x_{CO_{2},2}}{x_{CO_{2},1}} \right) + X_{CO_{2},3} \ln \left(\frac{x_{CO_{2},3}}{x_{CO_{2},1}} \right) \right]$$
(S1)

where N_i is the quantity of component *i* in mole, R is ideal gas constant (8.3145 J mol⁻¹ K⁻¹), T is the absolute temperature (295 K, assuming ambient temperature), and x_i is the molar fraction of component *i*. Based on the scenario of post-combustion (20%, X_{CO2} =0.2), the minimum work is calculated as 4,495 J mol⁻¹. In comparison, it is estimated to be 19,130 J mol⁻¹ for DAC (410ppm, X_{CO2} =0.00041).



Scheme S1. Schematic of a hypothetical process that separates CO_2 from a gas mixture. Example shows the PCCC operation.



Figure S1. (a) ¹H-NMR and (b) HSQC of the synthesized [EMIM][2-CNpyr].



Figure S2. (c) ¹H-NMR and (d) HSQC of the synthesized P[DADMA][2-CNpyr].



Figure S3. (a) The schematics of the pulse sequence for ¹H-DOSY NMR. The first step excites the spins using a 90° radio frequency (RF) pulse. A gradient pulse of intensity g(z) and duration δ is applied, the molecules are let to diffuse during the drifting time interval Δ , and an effective opposite gradient pule rephases the spins. (b) Right: The ¹H-NMR recorded as a function of the gradient strength g(z) showing different attenuation rates for hydrogens. Left: The exponential attenuation of hydrogens at different chemical shifts plotted against the gradient step with increasing strength. The self-diffusivity (D) was calculated by **equation 1** using MestReNova. An example of the ¹H-DOSY spectra is given in **Figure S4b**. (c) The actual pulse sequence used for ¹H-DOSY.



Figure S4. (a) Example ¹H-NMR spectra of neat [EMIM][2-CNpyr], with the pulse gradient strength from 2% to 95% showing the attenuation of magnetization. (b) The calculated ¹H-DOSY spectra of [EMIM][2-CNpyr]. Note that there is no deuterated solvent in the characterized samples in these measurements; solvent is separated by an inner tube as illustrated in **Figure S3a**.



Figure S5. (a) Viscosity and (b) water content of [EMIM][2-CNpyr] as a function of CO₂ concentration and the humidity content in the gas (CO₂/N₂/H₂O) exposed to the IL. The viscosity of [EMIM][2-CNpyr] under RH 40% and 16-20% O₂ is plotted in red square symbols; very similar to the data in the absence of O₂.



Figure S6. DSC curves of PIL-IL, with a scanning rate of 10 °C/min under N₂. The glass transition temperatures are marked with an arrow.



Figure S7. (a) SEM images of PIL-IL/GO and GONF on the two substrates studied. Bottom images show the visual appearances of the membranes as labeled. (b) FTIR spectra comparing the PIL-IL/GO and GONF on the two substrates. The PIL-IL/GO on UF corresponds to **i** in **Table 1**, whereas the PIL-IL/GO on *b*PES/PET corresponds to **ii**.



Figure S8. (a) 1 H-NMR, (b) HSQC, and (c) HMBC of GO in DMSO-d₆.



Figure S9. (a) Permeance of PIL-IL/GO on *b*PES/PET and PIL-IL/GO on UF (**i** and **ii** in **Table 1**) under $CO_2/N_2/H_2O$ (filled symbol) and $CO_2/N_2/O_2/H_2O$ (hollowed symbol). (b) CO_2/N_2 and CO_2/O_2 selectivities. (c) $CO_2/(N_2+O_2)$ separation ratio. Notice that for $CO_2/N_2/H_2O$, the $CO_2/(N_2+O_2)$ separation ratio is the same as their CO_2/N_2 selectivity. All of the mixtures have a humidity level of 40% RH at 22 °C; 10.6 mbar moisture.



Figure S10. CO₂ permanence PIL-IL/GO on *b*PES/PET (red data points) and PIL-IL/GO on UF (gray data points) under CO₂/N₂/H₂O (filled symbols) and CO₂/N₂/O₂/H₂O (hollow symbols) at 22 °C; RH 40%; 10.6 mbar moisture. The solid and dashed lines are the best fits of the data based on **equation 6**. The fitted parameters are listed in the inset table. The η value is related to the diffusion and reaction equilibrium of IL-CO₂ complex. The lower the diffusion and higher the equilibrium constant, the higher the value of η is. The *p**value describes the condition where CO₂ transport is hindered due to carrier saturation in a kinetically controlled mass transfer process.

The impact of temperature on FTM performance

The transport of CO_2 across FTM consists of three consecutive steps as depicted in our TOC graph, modified, and labeled for clarity in the below illustration:

(1) CO₂ binding: CO₂ absorption from gas to the carrier on the membrane surface

(2) CO_2 transport: CO_2 (and IL- CO_2 complex transport) via the three pathways (vehicular motion, hopping, and diffusion)

(3) CO₂ desorbing: CO₂ dissociation from the IL-CO₂ complex



The rate determining step (RDS) of our FTM is (2), which means (1) and (3) are all faster. Therefore, when temperature increase, the net transported CO_2 across membrane (CO_2 permeance) will decrease only if the reduction of (1) CO_2 binding is so profound to a point that there is not enough CO_2 to be supplied to step (2).

That being said, increasing temperature (to a point) in FTM will result in increase in CO_2 permeance; and only when the temperature reaches and passes over certain threshold, where (1) the formation of IL-CO₂ complex is really unfavored and insufficient in quantity, then we will start to observe a decrease in CO_2 permeance.

Trial #	PIL-IL/GO loading			PIL:IL		
	(mg)			(molar	Remarks	
	PIL	IL	GO	ratio)		
1	0.2	20	0.2	1:100	ii in Table 1	Leak
2	10	10		50:50	-	
3	20	0		100:0	-	Leak; Cracks observed
4	0.4	40	0.4	1:100	iii in Table 1	Leak
5	0.2	20	0.5	1.100	-	
6	0.5	50		1:100	iv in Table 1	Leak
7	10	10		50:50		
8	50	50			-	
9	50	0		100:0	-	Leak; Cracks observed
10	0.2	20	0.8	1:100	-	- Leak
11	0.8	80			-	
12	10	10		50:50	-	
13	40	40			-	
14	80	0		100:0	-	Leak; Cracks observed
15	1.25	3.75		25:75	-	Leak
16	0.2	20	1	1:100	-	Leak
17	2.5	2.5		50:50	-	
18	10	10			-	No CO ₂ Permeance
19	50	50			-	
20	100	0		100:0	-	Leak; Cracks observed
21	1.25	3.75		25:75	v in Table 1	Result in Figure 8a

Table S1. FTM-BS with different compositions and loadings for vacuum operation tests. To confirm the failure of FTMs, we tested at least two membranes for each composition.



Figure S11. The dependence of self-diffusivities of [EMIM]⁺ (filled symbol) and [2-CNpyr]⁻ (hollowed symbol) on the humidity content.