

## Hybrid Ionic Liquid Capsules for Rapid CO<sub>2</sub> Capture

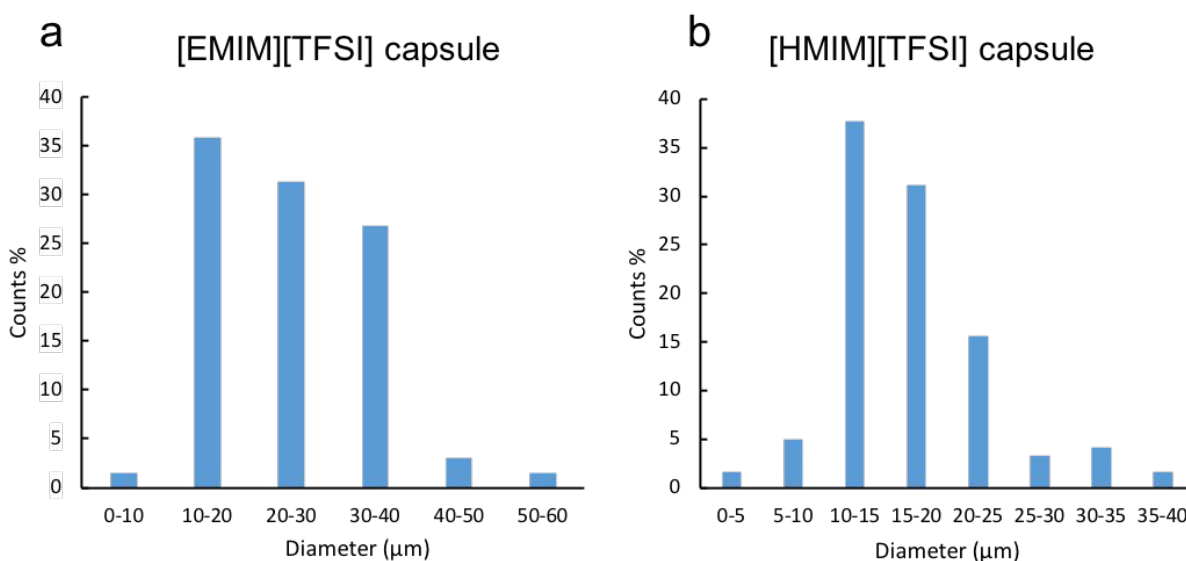
Qianwen Huang <sup>a</sup>, Qinmo Luo <sup>b</sup>, Yifei Wang <sup>b</sup>, Emily Pentzer <sup>\*b</sup>, Burcu Gurkan <sup>\*a</sup>

<sup>a</sup> Department of Chemical Engineering Biomolecular Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

<sup>b</sup> Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

### Supplementary Information

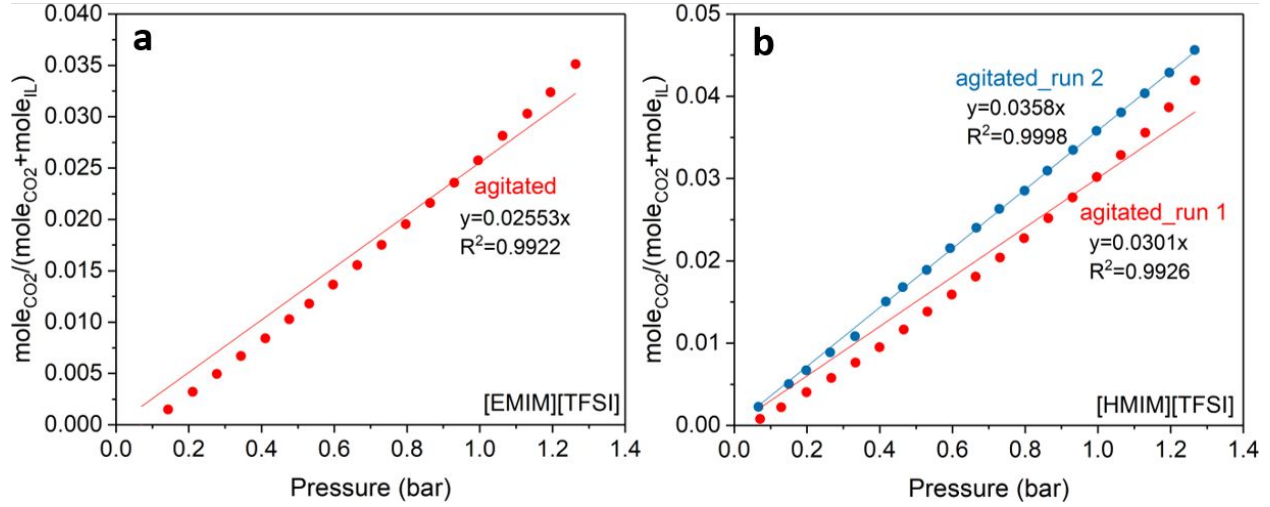
#### Particle size analysis of capsules



**Figure S1.** Particle size distribution of (a) [EMIM][TFSI] capsule (b) [HMIM][TFSI] capsule.

#### CO<sub>2</sub> uptake of neat ILs

Within the pressure range studied in this paper (0 to 1.26 bar), the CO<sub>2</sub> uptake isotherms for [EMIM][TFSI] and [HMIM][TFSI] exhibited nearly linear behavior (**Figure S1**). The Henry's law constants were obtained from the inverse of the slopes of the linear fits shown in **Figure S1a** for [EMIM][TFSI] and in **Figure S1b** for [HMIM][TFSI]. Repeated experiments are also shown; the uncertainties are obtained to be roughly 10 %; see example propagation of error analysis below.



**Figure S2.** CO<sub>2</sub> absorption in [EMIM][TFSI] (a) and [HMIM][TFSI] (b) with agitation at 1000 rpm and at 19.5 °C. Henry's law constants (inverse of fitted line slopes) for CO<sub>2</sub> in [EMIM][TFSI], [HMIM][TFSI] run 1 and [HMIM][TFSI] run 2 are 39 bar, 33 bar and 28 bar, respectively.

### Propagation of Error Analysis

The absorbed CO<sub>2</sub> is calculated from the ideal gas law (**Equation 1**).

$$PV = nRT \quad \text{Eq. 1}$$

In which, P is the pressure, V is the volume, n is the amount of gas, R is the gas constant, and T is the temperature. Experimentally, we introduce an amount of CO<sub>2</sub> by regulating the inlet pressure  $\Delta P$  (Equation 2).

$$\Delta P = P_2 - P_1 \quad \text{Eq. 2}$$

In which, P<sub>1</sub> is the initial pressure which is 0 mmHg at vacuum, and P<sub>2</sub> is the pressure after applying CO<sub>2</sub>. Substituting **Equation 2** into **Equation 1** yields:

$$n_{\text{CO}_2} = \frac{\Delta PV_F}{RT} \quad \text{Eq. 3}$$

In which,  $n_{\text{CO}_2}$  is the amount of CO<sub>2</sub> (mol), and  $V_F$  is the free space (cm<sup>3</sup>). Therefore, the error in  $n_{\text{CO}_2}$  can be expressed as:

$$\frac{\delta n_{\text{CO}_2}}{n_{\text{CO}_2}} = \sqrt{4\left(\frac{\delta(\Delta P)}{|\Delta P|}\right)^2 + 4\left(\frac{\delta(V_F)}{|V_F|}\right)^2 + 4\left(\frac{\delta(T)}{|T|}\right)^2} \quad \text{Eq. 4}$$

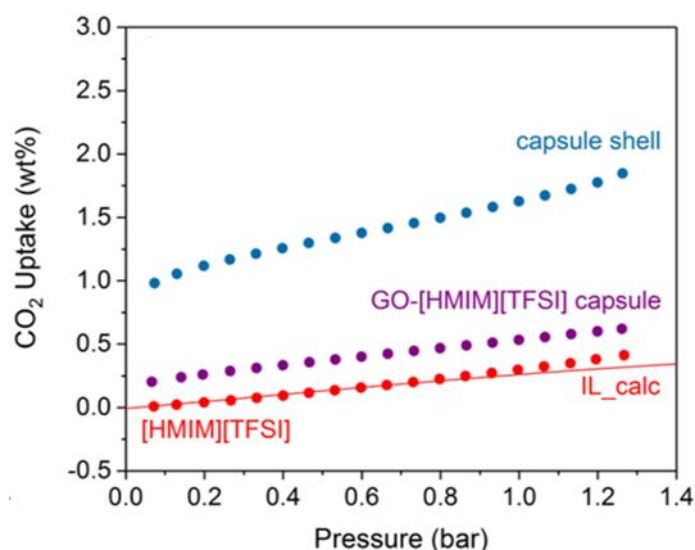
where  $\delta(\Delta P)$  is the uncertainty of the pressure gauge (0.05 mmHg),  $\Delta P$  is the maximum pressure applied experimentally,  $\delta(V_F)$  is the uncertainty of the free space measurement,  $V_F$  is the free space of the experiments,  $\delta(T)$  is the uncertainty of the lab temperature (1 °C), and  $T$  is the measurement temperature (19.5 °C).

In agitated [HMIM][TFSI], for example,  $\Delta P$  is 950.6 mmHg,  $\delta(V_F)$  is assumed to be 0.003 cm<sup>3</sup> (estimated from two separate measurements), and  $V_F$  is 31.4 cm<sup>3</sup>. Therefore the estimated uncertainty is calculated as:

$$\frac{\delta n_{CO_2}}{[n_{CO_2}]} = \sqrt{4\left(\frac{0.05}{950.6}\right)^2 + 4\left(\frac{0.003}{31.4}\right)^2 + 4\left(\frac{1}{19.5}\right)^2} = 0.1026 = 10.3\% \quad \text{Eq. 5}$$

The estimated error of CO<sub>2</sub> uptake measurement in agitated [HMIM][TFSI] is 10.3 %, which is expected to be similar for all other measurements

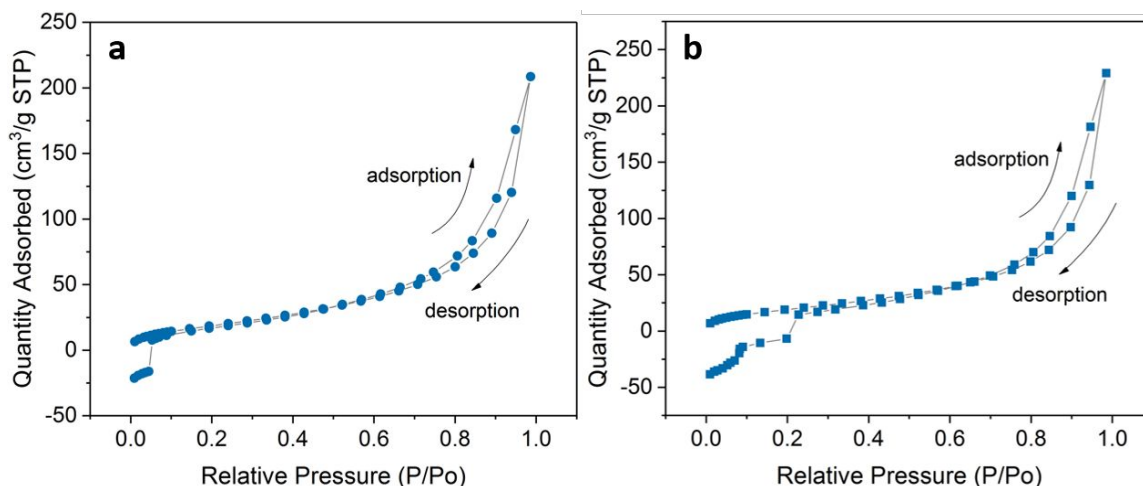
### CO<sub>2</sub> uptake of GO-IL capsules



**Figure S3.** CO<sub>2</sub> uptake of (a) GO-[EMIM][TFSI] capsule (purple circle), capsule shell (blue circle) and agitated [EMIM][TFSI] (red circle); (b) GO-[EMIM][TFSI] capsule (purple circle), capsule shell (blue circle) and agitated [EMIM][TFSI] (red circle). The red line reflects the calculated CO<sub>2</sub> uptake of the IL alone (calculated by subtracting the contribution from the shell material based on mass ratios). The measurements were conducted at 19.5 °C.

### Surface Area and Porosity of Capsule Shells

In order to characterize the capsule shell material, the IL core was extracted from the capsule with acetone. Nitrogen adsorption and desorption isotherms of capsule shells were measured at -196 °C (in liquid nitrogen) with a Micromeritics TriStar II analyzer. The samples were degassed at 80 °C under vacuum overnight and allowed to cool to room temperature before measurements (**Figure S3**). The N<sub>2</sub> isotherm showed a combination of Type III and Type V for both capsule shells, indicating that the GO-IL shell is has both macroporous and mesoporous features.<sup>1</sup>



**Figure S4.** N<sub>2</sub> adsorption-desorption isotherms at -196 °C of (a) [EMIM][TFSI] capsule shell (circle) and (b) [HMIM][TFSI] capsule shell (square). The grey lines are to guide the eye.

The Brunauer-Emmett-Teller (BET)<sup>2</sup> method was used to calculate the multi-layer adsorption surface area of N<sub>2</sub> at -196 °C. In this calculation, it was assumed that the area occupied by one N<sub>2</sub> molecule is 0.162 nm<sup>2</sup>.<sup>3</sup> The linear region of the isotherms, including data points between 0.05 to 0.3 relative pressure (P/Po), was used for the BET surface area calculation. The external surface area was calculated by the t-plot analysis according to the Harkins and Jura thickness equation<sup>4</sup> (**Equation 6**). The linear region of relative pressure (P/Po) between 0.08 and 0.3 was used for the analysis,

$$t = \left[ \frac{13.99}{0.034 - \log(P/P_o)} \right]^{0.5} \quad \text{Eq. 6}$$

where  $t$  is the thickness,  $P$  is the pressure applied and  $P_o$  is the saturation vapor pressure of N<sub>2</sub> at -196 °C.

Dubinin-Astakhov equation (**Equation 7**)<sup>5</sup> was used to estimate microporosity.

$$\log W = \log W_o - D(\log P_o/P)^n \quad \text{Eq. 7}$$

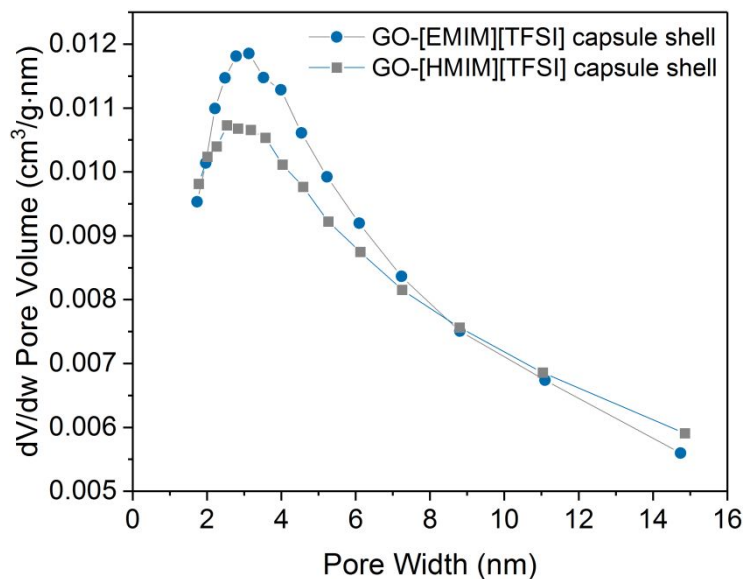
In **Equation 7**,  $W$  is the amount of gas adsorbed,  $W_o$  is the micropore volume, and  $n$  is the Astakhov exponent. The three parameters were optimized using the analyzer within TriStar II software. It should be noted that microporosity could not be quantified for the cases where external surface area is larger than the BET surface area. This may happen in cases where pores smaller than 2 nm are not accessible. The computed surface area and pore size are summarized in **Table S1**.

**Table S1.** Measured surface area and pore size of IL capsule shells (after IL is extracted). The micropore surface area was calculated with Dubinin-Astakhov method, and average pore size width was estimated from BJH adsorption branch (shown in **Figure S4**).

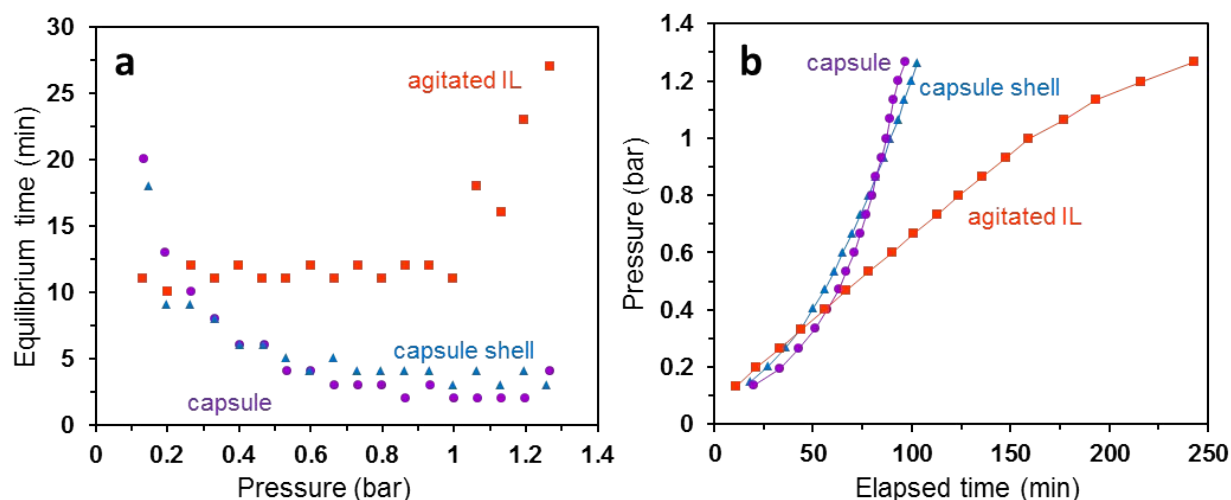
| GO-IL capsule shell | Surface Area (m <sup>2</sup> /g) |                 |           | Pore Size (nm) |
|---------------------|----------------------------------|-----------------|-----------|----------------|
|                     | BET                              | t-Plot External | Micropore |                |
| GO-[EMIM][TFSI]     | 74.55                            | 98.65           | 62.23     | 5.82           |
| GO-[HMIM][TFSI]     | 75.37                            | 97.24           | 63.42     | 6.24           |

The pore size distribution was derived using the Barrett-Joyner-Halenda (BJH)<sup>2</sup> method with the corrected Halsey's equation (**Equation 8**) at the adsorption branch (**Figure S4**).

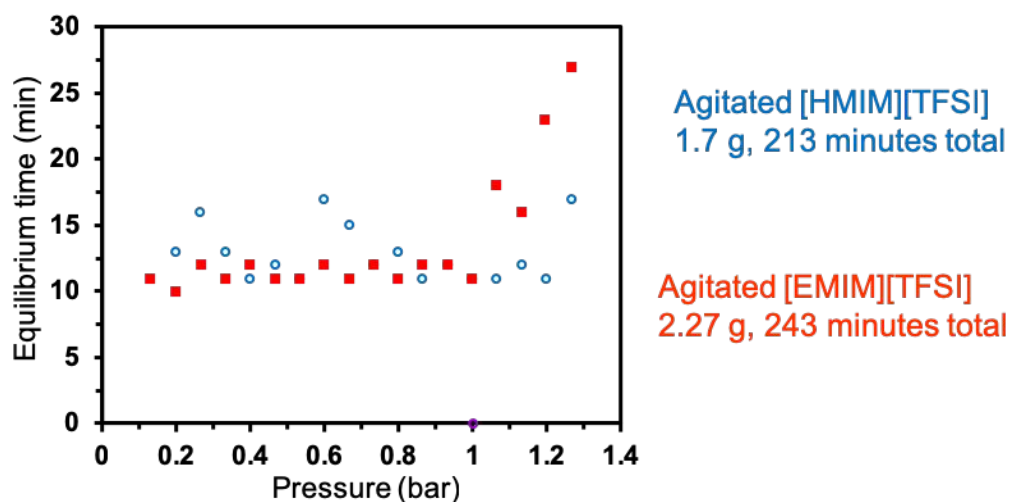
$$t = 3.54 \left[ \frac{-5}{\ln(P/P_0)} \right]^{0.333} \quad \text{Eq. 8}$$



**Figure S5.** BJH pore size distribution of (a) [EMIM][TFSI] capsule shell (circle) and (b) [HMIM][TFSI] capsule shell (square).



**Figure S6.** a) Equilibrium time between each pressure set point for agitated [EMIM][TFSI] (red squares), [EMIM][TFSI] capsules (purple circles) and capsule shell (blue triangles) as pressure is increased; b) Total elapsed time for equilibration of [EMIM][TFSI] (red squares), [EMIM][TFSI] capsules (purple circles), and capsule shell (blue triangles) as pressure increased in about 0.066 bar steps. Solid lines are to guide the eye.



**Figure S7.** Equilibration time between each pressure set point for agitated [EMIM][TFSI] (2.27 g, 243 minutes) and [HMIM][TFSI] (1.71 g, 213 minutes). These amounts of IL are the same as that encapsulated in the capsules discussed in the paper (based on the capsules being 80% IL).

## References

- (1) Alothman, Z. A. A Review: Fundamental Aspects of Silicate Mesoporous Materials. *Materials (Basel)*. **2012**, 5 (12), 2874–2902.
- (2) Kruk, M.; Jaroniec, M.; Sayari, A. Application of Large Pore MCM-41 Molecular Sieves To Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. *Langmuir* **1997**, 13 (23), 6267–6273.
- (3) Mirzaei, M.; Mokhtarani, B.; Badiei, A.; Sharifi, A. Improving Physical Adsorption of CO<sub>2</sub> by Ionic Liquids-Loaded Mesoporous Silica. *Chem. Eng. Technol.* **2018**, 41 (7), 1272–1281.
- (4) Kruk, M.; Jaroniec, M. Accurate Method for Calculating Mesopore Size Distributions from Argon Adsorption Data at 87 K Developed Using Model MCM-41 Materials. *Chem. Mater.* **2000**, 12 (1), 222–230.
- (5) Clarkson, C. R.; Bustin, R. M. Effect of Pore Structure and Gas Pressure upon the Transport Properties of Coal: A Laboratory and Modeling Study. 1. Isotherms and Pore Volume Distributions. *Fuel* **1999**, 78 (11), 1333–1344.