

# 1-Methyl-3-octylimidazolium tetrafluoroborate/AgO nanoparticles composite membranes for facilitated gas transport

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**Abstract**—AgO nanoparticles (NPs) were generated in ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate ( $\text{Moim}^+\text{BF}_4^-$ ). The formation of Ag NPs was attributable to the favorable interaction between the surface of particles and counteranions of ionic liquid. The generated AgO nanoparticles in  $\text{Moim}^+\text{BF}_4^-$  were confirmed by TEM, and the average size was 40 nm. Coordinative interactions of AgO NPs with  $\text{Moim}^+\text{BF}_4^-$  were investigated by FT-Raman spectroscopy. The prepared  $\text{Moim}^+\text{BF}_4^-/\text{Ag}$  NPs composites were utilized for  $\text{CO}_2$  separation membrane, and consequently,  $\text{CO}_2$  separation performance for composite membranes was improved compared with neat  $\text{Moim}^+\text{BF}_4^-$ . The ideal selectivity for  $\text{CO}_2/\text{N}_2$  was 23.4 with a  $\text{CO}_2$  permeance of 18.7 GPU was observed, while the neat  $\text{Moim}^+\text{BF}_4^-$  membrane showed a selectivity of 15.9 and a  $\text{CO}_2$  permeance of 12.7 GPU.

Keywords: Membrane, Facilitated Transport, Composite, Ionic Liquid, AgO

## INTRODUCTION

$\text{CO}_2$  emission in the atmosphere is mainly from coal-fired power plants. Especially, it causes global warming associated with climate change, and the topic that our world faces is arguably one of the most important environmental issues [1–3]. Furthermore, because the world's main sources of energy are coal, oil and natural gas,  $\text{CO}_2$  capture and separation has been essential. Carbon dioxide is often observed as an impurity in natural gas, including methane. So it can lead to degradation of natural gas due to the presence of carbon dioxide [4–7]. There are several technologies for the separation of  $\text{CO}_2$  from light gases, such as cryogenic separation, adsorption, absorption and membrane separation [8–10]. Among these, conventional absorption with amine-based has been the most promising and used to scrub the  $\text{CO}_2$  from gas streams [11–13]. However, it has drawbacks such as high cost and energy inefficiency since it demands a high temperature to regenerate the adsorbed gas and experiences degradation of the solvent [14]. Therefore, microporous metal-organic frameworks (MOFs) including the high flux, well-defined pore sizes, thermal stability, their versatility in chemical compositions and crystal structures have been recently proposed as promising novel separator for  $\text{CO}_2$  capture [15–17]. To increase the interaction strength between  $\text{CO}_2$  molecules and the MOFs with metal or metal oxide corners connected by organic linkers, unsaturated metal centers can help increase the  $\text{CO}_2$  capacity for MOFs. Besides high  $\text{CO}_2$  capacities, many MOFs must have high  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  selectivities which are essential for  $\text{CO}_2$  separation from flue gas and natural gas. Several research groups, including Thallapally, Denayer, Carreon, Rosi, and others have developed

a variety of MOFs [18–22]. However, because most MOFs have been designed with very large pore sizes or channels to achieve maximum loadings, it has a lack of selectivity, which is required for gas separation applications. The cost of bulk synthesis and the stability toward water vapor have been also challenging problems. As another alternative, ionic liquids have been of interest as reusable adsorbent [23,24]. Especially, it is known that the solubility of carbon dioxide in imidazolium-based room-temperature ionic liquids is relatively high. Furthermore, to increase the  $\text{CO}_2$  solubility and gas separation performance in ionic liquids, a carrier that can be reversibly complexed with  $\text{CO}_2$  has been introduced for facilitated  $\text{CO}_2$  transport. For example, separation performance was reported for 1-butyl-3-methyl imidazolium tetrafluoroborate ( $\text{BMIM}^+\text{BF}_4^-$ )/copper nanoparticles (Cu NPs). [25] Imidazolium cations with an amine group and the surface of Cu NPs partially polarized by  $\text{BF}_4^-$  anions cause an increase in copper- $\text{CO}_2$  complexation, enhancing the solubility of  $\text{CO}_2$  [25]. This improved separation performance resulted in a  $\text{CO}_2$  permeance of 25 GPU (1 GPU =  $1 \times 10^{-6} \text{ cm}^3 \text{ (STP)} / (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})$ ) and the ideal selectivity of 11 for  $\text{CO}_2/\text{N}_2$ . Very recently, we reported that dissociated silver(II) oxide particles in ionic liquids ( $\text{BMIM}^+\text{BF}_4^-$ ) have a strong affinity for  $\text{CO}_2$  because of the oxide layer and imidazolium cations, resulting in silver(II) oxide as a carrier used to selectively remove  $\text{CO}_2$  [26]. Accordingly in a series of studies, 1-methyl-3-octylimidazolium tetrafluoroborate ( $\text{Moim}^+\text{BF}_4^-$ ) with more free ions than  $\text{BMIM}^+\text{BF}_4^-$  was chosen for facilitated  $\text{CO}_2$  transport. The longer the alkyl chain in the imidazolium cations was expected to stabilize the metal oxide nanoparticles for a long time. Also, if the length of the alkyl chain is short, such as  $\text{BMIM}^+\text{BF}_4^-$ , both cations and anions in ionic liquids could tend to be aggregated each other because of hydrogen bonding. Thus,  $\text{Moim}^+\text{BF}_4^-$  originally known as more free ions was expected to show high  $\text{CO}_2$  solubility, resulting in the improvement of  $\text{CO}_2$  separation performance with AgO particles.

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## EXPERIMENTAL SECTION

### 1. Materials

1-Methyl-3-octylimidazolium tetrafluoroborate ( $\text{Moim}^+\text{BF}_4^-$ ) was purchased from C-tri Co., Ltd. AgO was purchased from Sigma-Aldrich Chemical Co. Ethyl alcohol (greater than 94.0%) was purchased from Daejung Chemicals & Metals. All initial solvents and materials were used as received.

### 2. Membrane Preparation

The membranes were prepared using  $\text{Moim}^+\text{BF}_4^-$ , silver(II) oxide and ethanol. First, silver(II) oxide was sonicated to disperse in ethanol for 5 min. Then,  $\text{Moim}^+\text{BF}_4^-$  was added to the mixtures of silver(II) oxide and ethanol. The solution was heated at  $60^\circ\text{C}$  for 24 h to evaporate the ethanol. The final solution was coated onto a polysulfone support (Toray Inc., Ltd., Tokyo, Japan) and then cast using a RK control coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). The best performance of  $\text{Moim}^+\text{BF}_4^-/\text{silver(II) oxide}$  was observed at 1/0.001 (weight ratio).

### 3. Gas Separation Performance

Gas permeance values were measured with a bubble flow meter at upstream  $2\text{ kgf}\cdot\text{cm}^{-2}$  and atmospheric downstream pressure. Gas permeance is expressed as units of GPU ( $1\text{ GPU}=1\times 10^{-6}\text{ cm}^3\text{ (STP)/ (cm}^2\text{ s cmHg)}$ ). Selectivity was defined as ideal selectivity ( $\text{CO}_2$  permeance/ $\text{N}_2$  permeance).

### 4. Characterization

A sonifier (Branson 450, Branson Ultrasonics Corporation, Danbury CT, USA) with a standard tip was used. Thermogravimetric analysis (TGA) was obtained by using a Universal V4.5A TA. The TEM images were obtained with a JEOL JEM-3000 operating at 300 kV. Raman spectra were taken by a Horiba Jobin Yvon Labram Aramis with a diode laser beam at an excitation radiation wavelength of 785 nm. The spectral resolution was approximately  $0.5\text{ cm}^{-1}$ . The frequency of the Raman lines was calibrated by using the c-Si wafer at  $521\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### 1. Thermal Analysis

Fig. 1 shows the thermal decomposition characteristics of the  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  composite. The small weight loss between 80-

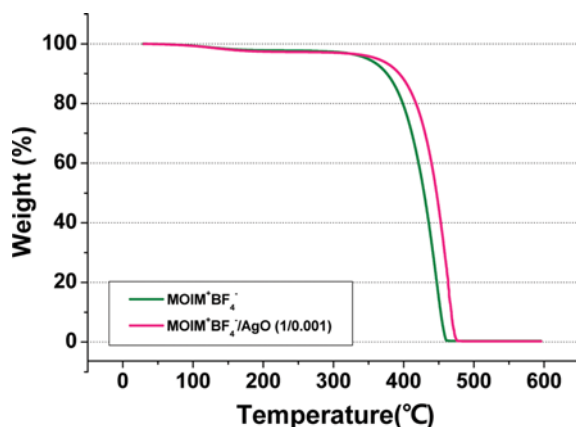


Fig. 1. TGA curves of  $\text{Moim}^+\text{BF}_4^-$  and  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  composite.

$280^\circ\text{C}$  appeared due to the loss of the adsorbed water or the residual ethanol solvent. The major weight loss occurred in the temperature range of  $280\text{--}465^\circ\text{C}$ . In the neat  $\text{Moim}^+\text{BF}_4^-$  and  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  composite, thermal decomposition showed a similar thermal stability. Also, in the  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  composite, decomposition temperature range was smaller than neat  $\text{Moim}^+\text{BF}_4^-$ . The little enhancement of thermal stability in  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  was attributable to the dispersion of AgO particles into ionic liquids.

### 2. FT-Raman Spectroscopy

Coordinative interactions of dissociated AgO particles with  $\text{Moim}^+\text{BF}_4^-$  were investigated by FT-Raman spectroscopy. The Raman spectra in the regions of the  $\text{BF}_4^-$  stretching bands for the  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  (1/0.001) are shown in Fig. 2. The  $\text{BF}_4^-$  bands at 765, 770 and  $774\text{ cm}^{-1}$  were assigned to free ions, ion pairs and ion aggregates, respectively [25]. As the silver oxide is finely dispersed in the ionic liquid, the distance of interaction between silver oxide and an ionic liquid is kept constant. Thus, main peak of free ions  $765\text{ cm}^{-1}$  was unchanged and broadening of Raman line shapes only differed.

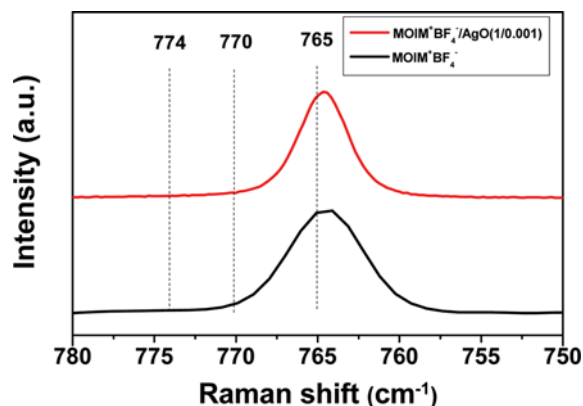


Fig. 2. FT-Raman spectra of neat  $\text{Moim}^+\text{BF}_4^-$  and  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  in the  $\text{BF}_4^-$  stretching region.

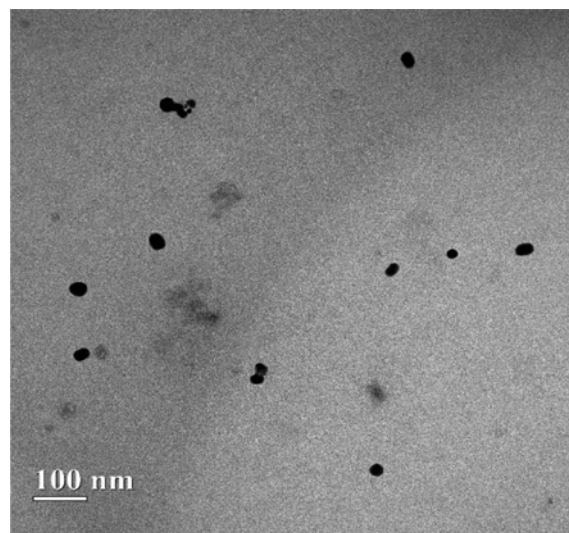


Fig. 3. Transmission electron micrograph of the dissociated AgO particles by the ionic liquid. Weight ratio of  $\text{Moim}^+\text{BF}_4^-/\text{AgO}$  = 1/0.001.

**Table 1. Permeance and selectivity of neat Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> and Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>/AgO (1/0.001, weight ratio)**

	Permeance (GPU)		Selectivity
	N <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
Neat Moim <sup>+</sup> BF <sub>4</sub> <sup>-</sup> [27]	1.8	20.3	11.8
Neat Moim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0.8	12.7	15.9
Moim <sup>+</sup> BF <sub>4</sub> <sup>-</sup> /AgO	0.8	18.7	23.4

\*Finger-like shaped polysulfone support (Woongjin Chemical Co., Ltd.) was used in our previous report [27]. However in this study, the sponge-like shaped polysulfone support (Toray Chemical Korea Inc.) was used. Compared to previous finger-like support, the gas permeation performance showed relatively low value because of conformational differences.

### 3. AgO Particles in Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>

The TEM image of ionic liquids composite with AgO nanoparticles is shown as Fig. 3, revealing a particle size of approximately 40±10 nm. The TEM images show AgO aggregates were very well dissociated as nanoparticles in ionic liquids Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>.

### 4. Separation Performance

The dissociated AgO particles in the ionic liquid Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> were applied to CO<sub>2</sub> separation. The separation performance for CO<sub>2</sub> permeance and selectivity (CO<sub>2</sub>/N<sub>2</sub>) is shown in Table 1. Neat Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> and Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>/AgO composite membranes were investigated. It is known to exist as more free imidazolium in the ionic liquids Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> unlike BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Thus, it was expected that the generated AgO particles could cause the CO<sub>2</sub> solubility to be enhanced by the increased oxide layer. Consequently, CO<sub>2</sub> separation performance for Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>/AgO composite membranes was improved compared with neat Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> as shown in Table 1. The ideal selectivity for CO<sub>2</sub>/N<sub>2</sub> was 23.4 with a CO<sub>2</sub> permeance of 18.7 GPU was observed, while the neat Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> membrane showed a selectivity of 15.9 and a CO<sub>2</sub> permeance of 12.7 GPU.

## CONCLUSION

We have succeeded in stabilizing AgO nanoparticles by employing an ionic liquid Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Furthermore, because an ionic liquid Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> has a longer alkyl chain in the imidazolium cations, the ionic liquid Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>/AgO composite membrane could show high facilitated transport between more free ions Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup> and CO<sub>2</sub>, improving CO<sub>2</sub> separation performance with the effect of AgO nanoparticles capable of increasing CO<sub>2</sub> solubility. As a result, the ionic liquid Moim<sup>+</sup>BF<sub>4</sub><sup>-</sup>/AgO composite membrane showed increased CO<sub>2</sub> separation performance in both CO<sub>2</sub>/N<sub>2</sub> selectivity and CO<sub>2</sub> permeance by both facilitated CO<sub>2</sub> transport and enhanced CO<sub>2</sub> solubility. Moreover, it was expected that such a facile nanoparticles synthetic strategy could be further applied into specific applications.

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