CO₂ separation using composites consisting of 1-butyl-3-methylimidazolium tetrafluoroborate/CdO/1-aminopyridinium iodide

Hyun Young Kim¹ & Sang Wook Kang¹,²*

1-Aminopyridinium iodide (iodine salt) was used in CO₂ separation composites consisting of CdO and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺BF₄⁻). Using iodine salt, the separation performance was largely improved. The CO₂/N₂ selectivity was 64.6 and the permeance of CO₂ gas was 22.6 GPU, which was about twice that of BMIM⁺BF₄⁻/CdO composites without addition of iodine salt. These results were due to the both effect of iodine salt on the transport of the N₂ molecules by the cyclic ring compound and the promoting transport of CO₂ molecules by the amine groups. Moreover, the oxide layer on the surface of the CdO could enhance the CO₂ solubility, resulting in the enhancement of separation performance. The mechanical and chemical properties were measured using SEM, Raman, TGA and FT-IR. The cross-section of coated membranes was confirmed by SEM. The coordinative interactions of iodine salts with BMIM⁺BF₄⁻/CdO composite were observed by Raman.

Most of the natural gas produced worldwide includes carbon dioxide. Carbon dioxide in nature gas occupies 70% of the total volume of gas¹. Unfortunately, carbon dioxide could cause corrosion of pipe lines in purification process and reduce the efficiency of natural gas¹,². Thus, separating and removing carbon dioxide from natural gas streams and flue gases have been major concern recently, since it could prevent pipeline corrosion and reduce global warming effects³–⁶. There were conventional carbon dioxide separation technologies to have been commonly used, such as carbon capture and storage (CCS) technology, solid adsorbent, adsorption and stripping using aqueous amine as liquid⁷–⁹. However, these existing technologies were economically costly and have the disadvantage of operating on a large scale¹⁰. On the other hand, for the case of membrane technology, it complements these disadvantages since it has many advantages such as being economically efficient, small scale operation, and being environmentally friendly¹¹–¹³.

Polymer-based membranes, especially with ether group in their chains, have contributed to strong coordination between CO and oxygen atoms of the polymer¹⁴–¹⁷. This strong coordination could enhance solubility of CO₂ molecules, resulting in the enhancement of CO₂/airy gas selectivity¹⁸. For example, Liu et al. arranged poly(ether block amide)/polysulfone (PEBA/Psf) composite hollow fiber membrane. That membrane achieved a CO₂ permeability up to 260 Barrer (1 Barrer = 7.5 × 10⁻¹⁵ m³ (STP) m⁻¹ m⁻¹ s⁻¹ K Pa) and 40–51.5 selectivity of CO₂/N₂¹⁹. However, since poly(ethylene oxide) (PEO) has a relatively large number of ether group, its mechanical properties were relatively weak even though it has high crystallinity.

For ionic liquid (IL)-based membranes, it has various advantages such as thermally stable and had long-term stability under pressurized conditions. Using these advantages, many researches on various gas separation membranes based on ILs have been reported²⁰–²². For example, membrane consisting of 1-hexyl-3-methylimidazolium nitrate (HmimNO₃)/Cu nanoparticles (CuNPs) showed a selectivity of 6.2 for CO₂/CH₄ and 7.4 for CO₂/N₂ selectivity²³.
In our previous study, we have studied the CO₂ permeance and CO₂/N₂ selectivity by preparing membranes by adding various metal oxides to ionic liquids. For example, for the BMIMBF₄/ZnO composite membrane, the CO₂ permeance was 101 GPU and the CO₂/N₂ selectivity was 42.1. The ZnO oxide layer has a strong affinity for CO₂ and has been shown to influence the increase in solubility of CO₂. The BMIMBF₄/CdO composite membrane had CO₂/N₂ selectivity of 32.5 and a CO₂ permeance of 57.1 GPU. As a result, when the metal oxide was introduced, the oxide layer could improve the CO₂ solubility, which has influenced the CO₂ transport by free ions in the ionic liquid.

In this study, BMIM⁺BF₄⁻/CdO composite membrane was used with an iodine salt containing amine group in metal oxide doped membrane. For these membranes, it was expected that the amine group in iodine salt will interact with CO₂ molecules for solubility enhancement. Furthermore, the CdO nanoparticles have strong affinity for CO₂ capable of enhancing the transport. It was also thought that the synergistic influence of the cyclic ring effect in iodine salt plays a role as barriers for N₂ transport, resulting in the increase of CO₂/N₂ selectivity.

Results and Discussion

SEM images analysis. As shown in Fig. 1, the morphology was examined by SEM and used to investigate the average thickness of the coating solution on the polysulfone microporous support. The average pore size of neat polysulfone was 0.1 μm and pore of surface state was also observed as microporous structure. SEM image showed that the polysulfone support was similar to the sponge like structure and the thickness of selective layer was about 8.7 μm.

Previous studies have shown that the CO₂/N₂ selectivity in the 1/0.007 in the composite membrane of BMIM⁺BF₄⁻/CdO on polymer support with finger-like structure was 32.5. In this study, the shape of the cross-section of the polysulfone support was sponge like structure.

TEM images analysis. To investigate the CdO nanoparticles in BMIM⁺BF₄⁻/CdO/iodine salt composite, TEM was observed as shown in Fig. 2. TEM image showed that the average size of generated CdO nanoparticles were ranged from 100 to 200 nm and the aggregation phenomena was observed.

Separation performance. Figure 3 showed the separation of CO₂/N₂ using a BMIM⁺BF₄⁻/CdO containing CdO particles and iodine salt. The weight ratio of BMIM⁺BF₄⁻/CdO was fixed at 1:0.007 and membranes with increasing mole ratio of iodine salt were tested at room temperature using a single gas (CO₂ and N₂). These experiments were tested three times and the single gas permeances measured for CO₂ and N₂ were described as shown in Fig. 3(a). As the mole ratio of iodine salt increased, the permeance of CO₂ increased to 0.05 mole ratio of salts and decreased above that ratio due to the aggregation phenomena of iodine in composite. These aggregation phenomena of iodine salts prevented the gas molecules from being transported through membrane, diminishing the permeance. Thus, CO₂ permeance decreased with increasing iodine salt to 0.05 mole ratio of salts. Thus, the best separation performance was observed at 0.05 mole ratio of iodine salts as shown in Fig. 3(b).

The single gas permeance and selectivity of the composite membranes: 1/0.007 BMIM⁺BF₄⁻/CdO and 1/0.007/0.05 BMIM⁺BF₄⁻/CdO/iodine salt membranes were compared as shown in Table 1. Table 1 indicated that BMIM⁺BF₄⁻/CdO composite membranes showed the CO₂ permeance of 22.9 GPU and the selectivity of 17.6 (CO₂/N₂) while the CO₂ permeance of 22.6 GPU and the selectivity of 64.6 for BMIM⁺BF₄⁻/CdO/iodine salt composite membranes. These results were attributable to that the iodine salt acts as a hindrance to the moving of gas molecules, resulting in the decrease in overall permeance (‘barrier effect’). However, the transport of CO₂ could be accelerated by the amine group of iodine salt. In addition, the interaction between the oxide layer formed from the dissociated CdO nanoparticles and the CO₂ molecule also could improve the solubility of CO₂.

Raman analysis. Raman was measured to investigate the interaction of iodine salt molecule in BMIM⁺BF₄⁻/CdO composite. The Raman spectrum BMIM⁺BF₄⁻/CdO (1/0.007) was described in Fig. 4(a), and the addition of 0.05 mol of iodine salt was shown in Fig. 4(b). The three different ionic species for various BF₄⁻ states such as ionic aggregates, ion pairs, and free ions were observed at 777, 770, and 765 cm⁻¹, respectively. Table 2
compared the deconvolutions of BMIM$^+$/BF$_4^-$/CdO (1/0.007) and BMIM$^+$/BF$_4^-$/CdO/iodine salt (1/0.007/0.05) for each area of BF$_4^-$ species. In the case of BMIM$^+$/BF$_4^-$/CdO/iodine salt, the region of free ions was extended from 35% to 45.7%. These results suggested that new binding of BMIM$^+$ and iodine salt of BMIM$^+$/BF$_4^-$/CdO weakened the interaction between BMIM$^+$ and BF$_4^-$, leading to the increase in free ions of BF$_4^-$.

TGA analysis. The TGA of Fig. 5 was measured at room temperature up to 600 °C. In particular, the thermal stability of the BMIM$^+$/CdO composite and BMIM$^+$/CdO/iodine salt composites was compared using a TGA analysis. In the case of BMIM$^+$/CdO composite, the weight loss occurred at 390 ~ 530 °C while BMIM$^+$/CdO/iodine salt composite lost the weight at 200 ~ 500 °C. The overall graph showed that when CdO and iodine salt were added, the stability of BMIM$^+$/BF$_4^-$ was gradually reduced. When CdO was added, the CdO particles were well dispersed in BMIM$^+$/BF$_4^-$, resulting in that the interactions between BMIM$^+$/BF$_4^-$ and

![Image](100 nm)

Figure 2. Transmission electron microscopy (TEM) image of CdO particles in BMIM$^+$/BF$_4^-$/CdO/iodine salt composite.

![Graph](CO2 Permeance Vs N2 Permeance)

Figure 3. Separation performance of the BMIM$^+$/BF$_4^-$/CdO/iodine salt composite membranes: (a) single gas permeance and (b) CO$_2$/N$_2$ selectivity.

|                | CO$_2$ Permeance (GPU) | N$_2$ Permeance (GPU) | Selectivity (CO$_2$/N$_2$) |
|----------------|------------------------|------------------------|-----------------------------|
| 1/0.007 BMIM$^+$/BF$_4^-$/CdO [finger-like] | 57.1                    | 1.8                    | 32.5                        |
| 1/0.007 BMIM$^+$/BF$_4^-$/CdO [sponge-like] | 22.9                    | 1.3                    | 17.6                        |
| 1/0.007/0.05 BMIM$^+$/BF$_4^-$/CdO/iodine salt [sponge-like] | 22.6                    | 0.35                   | 64.6                        |

Table 1. Single gas permeance and selectivity of the composite membranes: 1/0.007 BMIM$^+$/BF$_4^-$/CdO and 1/0.007/0.05 BMIM$^+$/BF$_4^-$/CdO/iodine salt membranes.
CdO generated the decrease of thermal stability. Furthermore, the addition of iodine salt caused the iodine salt to be interacted with BMIM$^+$BF$_4^−$/CdO, further reducing thermal stability.

FT-IR analysis. Figure 6 showed the FT-IR spectra for the neat BMIM$^+$BF$_4^−$/CdO and BMIM$^+$BF$_4^−$/CdO/iodine salt composites. The C-H stretching band in the alkyl group of neat BMIM$^+$BF$_4^−$ was known to be observed at 2966 cm$^{-1}$. However, when iodine salt was added to neat BMIM$^+$BF$_4^−$, it shifted from 2966 to 2962 cm$^{-1}$, due to the new coordinative interaction.

As shown in Fig. 7, with the new combination of BMIM$^+$ and iodine salt, the existing C-H stretching band was weakened. This also indicated BF$_4^−$ became more free ions when iodine salt was added to BMIM$^+$BF$_4^−$/CdO in the raman spectra.

Conclusions
We have succeeded in preparing high selective carbon dioxide membranes consisting of BMIM$^+$BF$_4^−$/CdO/iodine salt composite to facilitate the CO$_2$ transport for high separation performance. The features and interactions in BMIM$^+$BF$_4^−$/CdO/iodine salt composites were characterized by SEM, Raman, TGA, and FT-IR. The separation performance of BMIM$^+$BF$_4^−$/CdO/iodine salt composite membrane was significantly increased compared to BMIM$^+$BF$_4^−$/CdO composite. When CdO and iodine salt were incorporated into BMIM$^+$BF$_4^−$, the CO$_2$/N$_2$ selectivity was 64.6 and the permeance of CO$_2$ molecules was 22.6 GPU. These results were due to the both
Methods
Materials. Cadmium oxide (CdO) was supplied from Sigma-Aldrich Chemical Co. 1-Aminopyridinium iodide (Iodine salt, 97%) was supplied from Sigma-Aldrich Chemical Co. 1-Butyl-3-methyl imidazolium tetrafluoroborate (BMIM\(^+\)BF\(_4^-\)) was supplied from Merck KGaA (Darmstadt, Germany). Ethyl alcohol (≥94.0%) was supplied from Daejung Chemicals & Metals. The microporous polysulfone support (average pore size = 0.1 μm) for the enhancement of mechanical property was provided by Toray Chemical Inc., Korea. All the chemicals were used without purification.

Preparation of membranes. The membranes were prepared utilizing BMIM\(^+\)BF\(_4^-\), cadmium oxide, iodine salt and ethanol. As first step, the cadmium oxide was sonicated to be dispersed in ethanol for 5 minutes. Then, BMIM\(^+\)BF\(_4^-\) and iodine salt were added to the ethanol mixture with cadmium oxide dispersed. The solution was heated at 85 °C for 24 hours to evaporate the ethanol. Then, solution was coated onto a polysulfone microporous support and cast using a RK control coater (Model K202, Control Coater RK Print-Coat Instruments Ltd., UK). The best performance of BMIM\(^+\)BF\(_4^-\)/CdO/iodine salt was observed at 1/0.007/0.05 (The ratio of BMIM\(^+\)BF\(_4^-\)/CdO was described by weight ratio while BMIM\(^+\)BF\(_4^-\)/iodine salt was mole ratio).

Gas separation experiments. The all gas flow rates represented by gas permeance were determined using a bubble flow meter at the steady-state. Gas flow rates were measured with a mass flow meter at an upstream with
various pressure of psig and atmospheric downstream pressure. The permeances of CO$_2$ and N$_2$ were measured in gas permeance units (GPU), where 1 GPU = $1 \times 10^{-6}$ cm$^3$ (STP)/(cm$^2$·s·cmHg) and the ideal selectivity was defined as CO$_2$ permeance divided by N$_2$ permeance.

**Characterization.** The scanning electron microscope (SEM; JSM – 5600 LV, JEOL) characterized prepared membranes. The transmission electron microscope (TEM; Tecn F20 G2–200 KV, FEI) was used to characterize the CdO nanoparticle ranges in composite. The weight loss was collected using a thermogravimetric analysis (TGA; Q50 TA Instrument) of the composite membrane in flowing N$_2$. Raman spectra of for BMIM$^+\text{BF}_4^−$/CdO/iodine salt solution were obtained using a BRUKER RAM II instrument at a resolution of 4 cm$^{-1}$ at room temperature. The IR measurements were used on a VERTEX 70 FT-IR spectrometer; 16–32 scans were done at a resolution of 8 cm$^{-1}$. A sonifier was used Branson 450 (Branson Ultrasonics Corporation, Danbury CT, USA) with a standard tip.

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**Author contributions**

S.W.K. led the project, conducted the data analysis and reviewed the manuscript. H.Y.K. performed the experiments, collected the data and wrote the paper.
Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to S.W.K.

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