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Accelerated CO₂ transport on surface of AgO nanoparticles in ionic liquid BMIMBF₄

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The AgO nanoparticles were utilized for a CO₂ separation membrane. The AgO nanoparticles were successfully generated in ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIMBF₄) by favorable interaction between the surface of particles and the counteranion of BMIMBF₄. The generated AgO nanoparticles were confirmed by TEM, and the average size was 20 nm. Coordinative interactions of dissociated AgO particles with BMIM⁺BF₄[−] were investigated by FT-Raman spectroscopy. When the ionic liquid BMIMBF₄ containing AgO nanoparticles was utilized as a CO₂ separation membrane, the separation performance was largely enhanced.

Reducing the emission of carbon dioxide is a recent major concern for global environmental issues, especially climate change. Carbon dioxide results from the continuous use of fossil fuels from coal-fired power plants^{1–5}. To control the CO₂ concentration in the atmosphere, conventional methods, such as amine scrubbing, have been proposed for CO₂ capture in post-combustion^{6–8}. However, this conventional method has drawbacks such as high cost and inefficiency because of the degradation of the absorbent at high temperature, as well as toxic and harmful effects^{9,10}. Thus, imidazolium-based ionic liquids have been suggested for the replacement of volatile organic solvents due to low vapor pressure, thermal stability and chemical stability. Furthermore, imidazolium cations with amine group can also chemically capture CO₂ and increase the solubility of CO₂^{11,12}.

Regarding the ability to affect the solubility of gases in ionic liquids, Noble group reported that permeability is often related to solubility. Thus, ionic liquids should be properly selected for use in gas separation, suggesting trends in the solubility of CO₂ according to the regular solution theory^{12–17}.

Unfortunately, the viscosities of ionic liquids are much greater than those of traditional organic solvents. Furthermore, ionic liquid-based membranes for gas separation have shown a relatively thick selective layer. Because of these characteristics, ionic liquids limit the diffusivity and solubility of gases, resulting in low permeance¹⁸.

Therefore, to enhance the CO₂ solubility and gas separation performance in ionic liquids, a carrier that can be reversibly complexed with CO₂ has been introduced^{19–21}. For example, separation performance was reported for 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIM⁺BF₄[−])/copper nanoparticles (Cu NPs). Imidazolium cations with an amine group and the surface of Cu NPs partially polarized by BF₄[−] anions cause an increase in copper–CO₂ complexation, enhancing the solubility of CO₂. This improved separation performance resulted in a CO₂ permeance of 25 GPU (1 GPU = 1 × 10^{−6} cm³ (STP)/(cm²·s·cm Hg)) and the ideal selectivity of 11 for CO₂/N₂²².

In the present study, carbon dioxide dissociated in ionic liquids was investigated to increase the solubility. Dissociated silver(II) oxide particles have a strong affinity for CO₂ because of the oxide layer. As a result, silver(II) oxide as a carrier could be used to selectively remove CO₂. Imidazolium ions with the amine moiety covalently coupled in BMIM⁺BF₄[−] also plays an important role in the increased solubility of carbon dioxide. Thus, when silver(II) oxides are added, ‘free’ ionic liquids are expected to reversibly

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Figure 1. TGA curves of $\text{BMIM}^+\text{BF}_4^-$ and $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$.

Figure 2. Transmission electron micrographs of (a) the dissociated AgO particles by the ionic liquid and (b) enlarged image. Weight ratio of $\text{BMIM}^+\text{BF}_4^-/\text{AgO} = 1/0.001$.

interact with CO_2 molecules, increasing the solubility of CO_2 and resulting in an increase in the separation performance.

Results and Discussion

The decomposition characteristics of the $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ composite were assessed by TGA and are shown in Fig. 1. The weight loss of $\text{BMIM}^+\text{BF}_4^-$ occurred at 315–470 °C. The prepared $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ composite was stable up to 345 °C and decomposed at 345–495 °C. The increase of decomposition temperature could be explained by the state of AgO particles in ionic liquid. If the aggregation of AgO particles proceeded in ionic liquid, the decomposition temperature would remain constant. Thus, this phenomenon suggested that the AgO particles were well dispersed in $\text{BMIM}^+\text{BF}_4^-$, and the interaction between $\text{BMIM}^+\text{BF}_4^-$ and the AgO surface increased the thermal stability of $\text{BMIM}^+\text{BF}_4^-$.

TEM images were used to investigate the size and dispersity of the dissociated silver oxide particles, as shown in Fig. 2. Most of the AgO particles were aggregated. However, after sonication, AgO particles were mostly observed as relatively small particles as average 20 nm. It could be expected that these dissociated AgO particles were beneficial for increasing the solubility of CO_2 .

Coordinative interactions of dissociated AgO particles with $\text{BMIM}^+\text{BF}_4^-$ were investigated by FT-Raman spectroscopy. The Raman spectra in the regions of the BF_4^- stretching bands for the $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ (1/0.001) are shown in Fig. 3. The BF_4^- bands at 765, 770 and 774 cm^{-1} were assigned to free ions, ion pairs and ion aggregates, respectively. Compared to neat $\text{BMIM}^+\text{BF}_4^-$, the symmetric stretch modes at 765 cm^{-1} in free BF_4^- anions increased upon addition of AgO particles. These results could be explained by the weakened interaction between BF_4^- and BMIM^+ . Consequently, the

Figure 3. FT-Raman spectra of neat $\text{BMIM}^+\text{BF}_4^-$ and $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ in the BF_4^- stretching region.

Figure 4. SEM cross-sectional image of the polysulfone support.

	Permeance (GPU)		Selectivity
	N_2	CO_2	CO_2/N_2
Neat $\text{BMIM}^+\text{BF}_4^-$ ²²	3.4	17	5.0
$\text{BMIM}^+\text{BF}_4^-/\text{Cu}^{22}$	2.3	25	11
Neat $\text{BMIM}^+\text{BF}_4^-$	0.6 ± 0.02	5.3 ± 0.2	8.8
$\text{BMIM}^+\text{BF}_4^-/\text{AgO}$	0.5 ± 0.02	14.1 ± 0.2	28.2

Table 1. Permeance and selectivity of neat $\text{BMIM}^+\text{BF}_4^-$ and $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ (1/0.001, weight ratio).

numbers of ion pairs and aggregates decreased. The change in Raman spectra was thought to be due to well-dissociated AgO particles mutually interacting with ionic liquid $\text{BMIM}^+\text{BF}_4^-$.

The gas permeation properties were different depending on the support. The cross-section structures of the support were investigated by SEM images. A polysulfone support with a structure with a finger-like cross-section was used in our previous reports. However, in the present study, a sponge-like structure was used, as shown in Fig. 4. Compared to the previous finger-like support, the gas permeation performance of the sponge-like structure was relatively low because of conformational differences. The flux of N_2 was dramatically reduced.

The dissociated AgO particles in the ionic liquid $\text{BMIM}^+\text{BF}_4^-$ were applied to CO_2 separation. The measurements were done 5 times and the separation performance for CO_2 permeance and selectivity (CO_2/N_2) is shown in Table 1. Neat $\text{BMIM}^+\text{BF}_4^-$ and $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ composite membranes were investigated. Previous study showed that the selectivity of CO_2/N_2 and CO_2 permeance for neat $\text{BMIM}^+\text{BF}_4^-$ were 5.0 and 17 GPU²². The difference for separation performance was attributable to the different polymer support. Previous study was investigated with polysulfone support to have finger-like structure while this research was done on sponge-like structure. Thus, since the ionic liquid could be easily penetrated into polymer support, the possibility of defect between support and liquid was high. Therefore, the relatively selectivity was lower and permeance was higher for than finger-like than sponge-like structure. When AgO was dissociated into the ionic liquid $\text{BMIM}^+\text{BF}_4^-$, the separation performance was significantly enhanced. These enhanced values could be compared with previous membranes consisting of $\text{BMIM}^+\text{BF}_4^-/\text{Cu}$ nanoparticles²². $\text{BMIM}^+\text{BF}_4^-/\text{Cu}$ nanoparticles composite membranes showed the selectivity of 11 and 25 GPU for CO_2 ²². The enhanced selectivity of $\text{BMIM}^+\text{BF}_4^-/\text{AgO}$ than $\text{BMIM}^+\text{BF}_4^-/$

Figure 5. BMIM⁺BF₄⁻/AgO membrane coated on the polysulfone support (sponge-like structure) for CO₂ separation.

Cu nanoparticles composite membranes was attributable to the interaction between the oxide layer of the dissociated AgO particles and CO₂. As another example, poly(ethylene oxide) (PEO) containing a polar ether group was reported to increase the solubility of CO₂ due to an affinity for CO₂^{23–27}. Thus, CO₂ is better able to penetrate through PEO than is N₂. Therefore, the oxide layer of the dissociated AgO affects the increase in CO₂ solubility. Furthermore, free imidazolium cations in ionic liquids interact with AgO to play a role as CO₂ carriers for facilitated transport, resulting in enhanced solubility and diffusivity of CO₂. As a result, BMIM⁺BF₄⁻/AgO composite membranes were significantly improved compared with neat BMIM⁺BF₄⁻, as shown in Fig. 5. The ideal selectivity for CO₂/N₂ was 28.2 with a CO₂ permeance of 14.1, while the neat BMIMBF₄ membrane showed a selectivity of 8.8 and a CO₂ permeance of 5.3.

In conclusion, the ionic liquid BMIMBF₄/AgO composite membrane was successfully prepared for CO₂ separation. When the AgO nanoparticles were generated in ionic liquid BMIMBF₄ by strong interaction between the surface of the particles and counteranion of the ionic liquid, the selectivity of CO₂/N₂ and CO₂ permeance were largely enhanced to 28.2 and 14.1, respectively, while the neat BMIMBF₄ membrane showed a selectivity of 8.8 and CO₂ permeance of 5.3. These enhancements in both selectivity and permeance were attributed to a synergy effect: (1) the oxide layer of the dissociated AgO affects the increase in CO₂ solubility, and (2) free imidazolium cations in ionic liquids interact with AgO to play a role as CO₂ carriers for facilitated transport.

Methods

Materials. 1-Butyl-3-methyl imidazolium tetrafluoroborate (BMIM⁺BF₄⁻) was purchased from Merck KGaA (Darmstadt, Germany). 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.

Fabrication process. The membranes were prepared using BMIM⁺BF₄⁻, silver(II) oxide and ethanol. First, silver(II) oxide was sonicated to disperse in ethanol for 5 min. Then, BMIM⁺BF₄⁻ was added to the mixtures of silver(II) oxide and ethanol. The solution was heated at 70 °C under constant stirring to evaporate the ethanol. Since the BMIM⁺BF₄⁻ was liquid state, the porous polymer support was utilized. Thus, the final solution was coated onto a macroporous polysulfone support to have average 0.1 μm pore (Toray Chemical Korea Inc.) and then cast using a RK control coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). The best performance of BMIM⁺BF₄⁻/silver(II) oxide was observed at 1/0.001 (weight ratio). Gas permeance values were measured with a bubble flow meter at upstream 2 kgf·cm⁻² and atmospheric downstream pressure. Gas permeance is expressed as units of GPU (1 GPU = 1 × 10⁻⁶ cm³ (STP)/(cm² s cmHg)).

Characterization. A sonifier (Branson 450, Branson Ultrasonics Corporation, Danbury CT, USA) with a standard tip was used. Thermogravimetric analysis (TGA) was obtained using a Universal V4.5A TA. The TEM images were obtained using a JEOL JEM-3000 operating at 300 kV. Raman spectra were obtained using a Horiba Jobin-Yvon/LabRAM ARAMIS instrument at 785 nm (diode laser). The structural morphology was observed by scanning electron microscopy (SEM, JEOL JSM-5600LV, Japan).

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Author Contributions

S.W.K. and Y.S.K. led the project, conducted the data analysis and reviewed the manuscript. D.J. performed the experiments, collected the data and wrote the paper.

Additional Information

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