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1-Butyl-3-methylimidazolium tetrafluoroborate/zinc oxide composite membrane for high CO_2 separation performance

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HIGHLIGHTS

- CO_2 separation membranes consisting of ionic liquid $BMIMBF_4$/ZnO nanoparticles composite.
- Abundant free ions of ionic liquid by interaction with surface of ZnO nanoparticles.
- Enhanced solubility of CO_2 molecules by ZnO nanoparticles.

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ABSTRACT

Ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) was utilized for preparation of composite membranes containing ZnO nanoparticles. The separation performance for CO_2 molecules for these composite membranes was investigated. It was found that when ZnO nanoparticles were generated into $BMIMBF_4$, the selectivity of CO_2/N_2 and CO_2 permeance of the composite were significantly enhanced to 42.1 and 101, respectively, compared to the neat $BMIM^+BF_4^-$ membrane that had a CO_2/N_2 selectivity and CO_2 permeance of 5.0 and 17.0, respectively. These enhancement for CO_2 separation was attributable to two factors: (1) the oxide layer of ZnO and (2) free ions of $BMIMBF_4$ to increase the CO_2 solubility. The chemical and physical properties of the membrane were characterized using TEM, SEM, FT-Raman, and TGA.

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1. Introduction

The removal of carbon dioxide from natural gas and flue gas has attracted considerable attention as a means of reducing the greenhouse effect as well as for preventing pipeline corrosion [1]. For this purpose, carbon capture and storage (CCS) technology has been widely used for many years [2–5]. However, CCS technology has many drawbacks such as high operating cost, large scale, energy-intensive operation, etc. [2–5]. Thus, various technologies have been introduced to separate and remove CO_2. Adsorption, absorption, and membrane technologies are novel methods that can replace conventional technologies [6–8]. Among these CO_2 separation methods, membrane technologies have come to the fore due to advantages such as environmental friendliness, energy efficiency, low operating cost, simplicity, and small scale [9–12]. Polymers containing an ether group are especially attractive for polymer-based membranes because of the strong affinity between oxygen atoms of the polymer and CO_2. This strong affinity increases both the solubility of CO_2 and the CO_2/light gas selectivity [13–16]. For example, Liu et al. prepared a poly(ether block amide)/polysulfone (PEBA/Psf) composite hollow fiber membrane [17] that showed a CO_2 permeability of 260 Barrer (1 Barrer = 7.5×10^{-15} m^3(STP) m/m^2 s K Pa) and a CO_2/N_2 selectivity of 40–51.5 [17]. However, poly(ethylene oxide) (PEO), which has a high ether content, suffers from weak mechanical properties and high crystallinity. In contrast, ionic liquids are molten salts at room temperature, and exhibit high viscosities. These promising chemicals have interesting properties such as miscibility with water and organic solvents, high chemical and thermal stability, and negligible vapor pressure [18]. Thus, a variety of membranes based on ionic liquids have been studied for CO_2 separation [19–24]. Imidazolium cations with amine groups can chemically interact with CO_2 and increase the solubility of CO_2. With regard to this ability to affect the solubility of gases in ionic liquids, the Noble group reported that the permeability was sometimes associated with solubility [25–26]. In addition, a carrier which can reversibly interact with CO_2 molecules was introduced to overcome the problem of high viscosity of ionic liquids. For example, a composite membrane composed of positively charged Cu nanoparticles (CuNPs), which

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act as the CO_2 carrier, and 1-hexyl-3-methylimidazolium nitrate ($HmimNO_3$) exhibited CO_2/CH_4 and CO_2/N_2 selectivities of 6.2 and 7.4, respectively [27]. In addition, a CuNPs/1-methyl-3-octyli midazolium tetrafluoroborate ($MoimBF_4$) composite membrane presented a CO_2 permeance of 24.2 GPU and selectivities of 25.2 and 24.3 for CO_2/N_2 and CO_2/CH_4, respectively [28]. Furthermore, when a metal-oxide compound was introduced to ionic liquids, the resultant membranes showed significantly enhanced CO_2 permeance and CO_2/N_2 selectivity. Our group reported that a $BMIMBF_4$/AgO composite membrane showed a CO_2/N_2 selectivity of 28.2 and a CO_2 permeance of 14.1, while the neat $BMIMBF_4$ membrane showed a CO_2/N_2 selectivity of 8.8 and a CO_2 permeance of 5.3 [29]. When strong interactions between the surface of the AgO particles and $BMIMBF_4$ were generated, the AgO particles dissociated to nanoparticles. Consequently, the oxide layer of dissociated AgO enhanced the CO_2 solubility, and free ions in the ionic liquid affected the CO_2 transport. Our group has researched other metal-oxide compounds which can enhance CO_2 solubility to further explore this perspective. In this study, we selected ZnO particles as the metal-oxide compound for enhancing CO_2 solubility, and explored $BMIMBF_4$/ZnO composite membranes. Dissociated ZnO nanoparticles in these membranes have a strong affinity for CO_2 due to the oxide layer originating from ZnO. Thus, we expected that the dissociated ZnO surface would play an important role in increasing the solubility of CO_2. Furthermore, it was found that when ZnO was incorporated in $BMIMBF_4$, free ions in ionic liquid could enhance the CO_2 solubility, resulting in increased CO_2 transport in the $BMIMBF_4$/ZnO membranes.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$) was purchased from Merck KGaA (Darmstadt, Germany), and zinc oxide (ZnO, 99.5%) was purchased from Acros Organics. Ethyl alcohol was purchased from Daejung Chemicals & Metals. All chemicals were used as received.

2.2. Preparation of membranes

The composite membranes consisting of a $BMIM^+BF_4^-$/ZnO layer were prepared by a simple method. To disperse the ZnO nanoparticles, the ZnO powder was introduced into an ethanol solution and sonicated by using a sonicator (Sonifier 450, Branson) for more than 10 min. Then, the $BMIM^+BF_4^-$ was mixed with the dispersed ZnO solution. The mixed solution was continuously heated to evaporate the remaining ethanol solution over a period of one day.

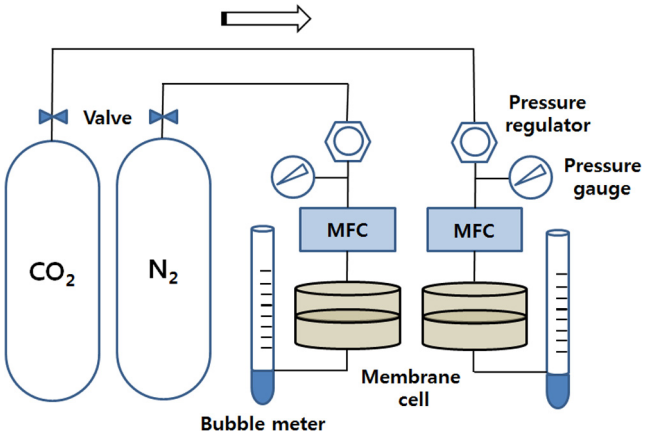
Then, the solution was coated onto polysulfone microporous membrane supports (Toray Chemical Inc, Korea) using an RK Control Coater (Model K202, Control Coater RK Print-Coat Instruments Ltd, UK). The resultant $BMIM^+BF_4^-$/ZnO composite membrane was immediately used for gas permeance tests.

2.3. Gas separation experiments

The experimental set-up for gas permeation test was shown in Scheme 1. The permeances of single gases such as CO_2 and N_2 were measured by a gas bubble meter. Permeance was expressed using gas permeance units (GPU), where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cm Hg).

2.4. Characterization

To establish the chemical and physical properties of the $BMIM^+BF_4^-$/ZnO composite membrane, various characterization were performed. The thickness of the selective layer was measured by scanning electron microscopy (SEM, JEOL JSM-5600LV). The morphology of the ZnO nanoparticles in $BMIM^+BF_4^-$ was observed using transmission electron microscopy (TEM, JEOL JEM-2010), operating at an accelerating voltage of 200 kV. Weight loss was confirmed using thermogravimetric analysis (TGA, TGA Q50, TA Instrument) of the $BMIM^+BF_4^-$/ZnO nanoparticle solution in flowing N_2. The Raman measurements were performed on a LabRam ARAMIS spectrometer equipped with a 785 nm diode laser where 64 scans were signal averaged at a resolution of 4 cm^{-1}.



Scheme 1. Experimental set-up for the gas permeation test.

3. Results and discussion

3.1. Transmission electron microscopy (TEM) images of ZnO

The TEM images of the ZnO nanoparticles in $BMIM^+BF_4^-$ are presented in Fig. 1(a) and (b). Fig. 1(a) shows small, agglomerated oxide particles. However, most ZnO particles in $BMIM^+BF_4^-$ were well dispersed, as shown in Fig. 1(b). The dispersed particle diameter is 20–200 nm. We expect that these ZnO nanoparticles will play a role in increasing the solubility of CO_2 in the $BMIM^+BF_4^-$/ZnO composite membrane.

3.2. Scanning electron microscopy (SEM) images of the membrane

SEM images were obtained to measure the thickness of the solution coated on the polysulfone microporous membrane supports, as shown in Fig. 2. The structure of the polysulfone support was finger-like. The void spaces of polysulfone are beneficial for the penetration of single gases such as CO_2 and N_2. The average thickness of the coated $BMIM^+BF_4^-$/ZnO layer on polysulfone was about 6 μm, as shown in Fig. 2.

3.3. Separation performance

To determine the gas separation performance, the dissociated ZnO particle-incorporated-$BMIM^+BF_4^-$ ionic liquids were used to separate CO_2/N_2. Membranes with increasing weight ratios of ZnO were tested at room temperature using single gases (CO_2 and N_2). These measurements were repeated more than 3 times, and the single gas permeance values measured for CO_2 and N_2 are shown in Fig. 3(a). As the ZnO weight ratio increased, the CO_2 permeance increased significantly until a weight ratio of 0.01. After a weight ratio of 0.015, the CO_2 permeance shows a tendency to decrease sharply. These results are attributable to the interactions between the oxide layer formed by the dissociated ZnO

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