

Carbon Dioxide Separation Using a High-toughness Ion Gel with a Tetra-armed Polymer Network

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A high-performance CO₂ separation membrane consisting of an ion gel has been prepared. The tetra-armed poly(ethylene glycol) ion gel contains a large fraction of ionic liquid (94 wt %) and shows excellent CO₂ permselectivity over a wide temperature range, up to 100 °C. We also demonstrate that the ion gel can absorb CO₂ without solvent seeping at a high pressure of 3 MPa.

Room-temperature ionic liquids (ILs) have been widely applied to electrochemical, synthetic, and separation processes as green solvents due to their unique properties such as nonvolatility, nonflammability, good thermal stability, and high ionic conductivity. ILs are recognized as designable solvents, and their structural diversity enables us to control their solvent properties, for example, the miscibility with various chemicals such as metal ions, synthesized and biological polymers, and acidic gases. In the last decade, CO₂ absorption and separation technologies using ILs have attracted much attention, because CO₂ is highly soluble in ILs relative to other neutral gases like N₂, H₂, and CH₄. A large number of investigations have been performed until now to improve the CO₂ absorption properties since the first report on the high solubility of CO₂ in the dialkylimidazolium-based IL.¹ A membrane separation process generally requires smaller operational energy, lower running cost, and smaller equipment footprint compared with an absorption process. The supported IL membranes (SILMs), i.e., polymeric or inorganic porous materials filled with ILs, show comparable or higher permeabilities and selectivities of CO₂ than conventional polymeric membranes.² SILMs have a higher long-term stability than supported membranes with organic solvents, because of nonvolatility and high thermal stability of ILs. However, SILMs cannot hold ILs under pressurized conditions, which is a serious disadvantage for the gas separation membrane. Polymeric ILs, i.e., self-crosslinking ILs were also applied as CO₂ separation membranes.³ However, it was pointed out that their separation performances are inferior to those of the SILMs due to the limited CO₂ diffusion in their rigid polymer matrix. Therefore, ion gels with a low polymer content and/or a high fraction of “free” IL content are more favorable materials for CO₂ separation membrane.

Recently, some research groups reported the CO₂ separation performances of ion gels with relatively low polymer contents.^{2b,4} Lodge et al.^{4a} reported an ion gel containing 15 wt % ABA-type triblock copolymer and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, [C₂mIm⁺][TFSA⁻]. The ion gel possesses a CO₂ permselectivity comparable to that of the [C₂mIm⁺][TFSA⁻]-based SILM, although it melts below

80 °C. They also reported a high-toughness ion gel with 10 wt % triblock copolymer, which was prepared by crosslinking reactions in the IL.⁵ The electrical conductivity is about 2/3 that of the neat IL because the ionic mobility is obstructed by the nonconductive part in their ion gel. Kamio et al.^{4d} reported a CO₂-N₂ separation membrane using poly(vinylpyrrolidone)-based ion gels containing 50–70 wt % amino acid IL, and the ion gel shows a compression breaking stress of 1 MPa at 70 wt % IL content. They demonstrated that both CO₂ permeability and selectivity are significantly improved with increasing IL content. In our recent study, we have proposed high-toughness ion gels with low polymer concentration, i.e., tetra-armed poly(ethylene glycol) (Tetra-PEG) ion gels.⁶ The Tetra-PEG ion gels can be prepared by AB-type cross-end coupling of two symmetrical Tetra-PEGs in typical aprotic ILs. Electrical conductivity measurements for the Tetra-PEG ion gel show that the diffusivity of ionic species in the gel is almost comparable to that in the neat IL. It also shows high mechanical properties even with much lower polymer contents, for example, the maximum breaking strength by compression reaches 18 MPa (83.5% strain) at 6 wt % polymer content. The excellent mechanical properties originate from a homogeneous polymer network structure.⁶ In addition, the Tetra-PEG [C₂mIm⁺][TFSA⁻] gel is thermally stable up to 300 °C. It is thus expected that the Tetra-PEG ion gel is a promising material for CO₂ separation membrane. In this work, we report the CO₂ separation performance of the Tetra-PEG ion gel membrane over wide temperature range, up to 100 °C. Furthermore, we also made a new trial to directly evaluate the CO₂ absorption capacities of the Tetra-PEG ion gel at pressures up to 3 MPa.

As reported in our previous work,^{6a} the Tetra-PEG ion gel can be prepared by mixing two Tetra-PEG prepolymers, i.e., tetraamine-terminated and tetra-*N*-hydroxysuccinimide-terminated PEGs (Tetra-PEG-NH₂ and Tetra-PEG-NHS), in aprotic [C₂mIm⁺][TFSA⁻] IL. The gelation time in [C₂mIm⁺][TFSA⁻] was less than 60 s, which was too short to prepare an ion gel membrane by a conventional method described in Figure S1. Here, note that the gelation time of the Tetra-PEG gel system strongly depends on the pH or concentration of H⁺ in the solutions.⁷ In the hydrogel system, it has been established that (1) Tetra-PEG gelation follows simple second-order reaction kinetics ($-d[-NH_2]/dt = k_{\text{gel}}[-NH_2]^{-2}$), k_{gel} : reaction rate constant) and (2) the gelation time is directly related to the acid–base reaction of the reactive NH₂ end group within Tetra-PEG-NH₂ (Tetra-PEG-NH₂ + H⁺ ⇌ Tetra-PEG-NH₃⁺).^{7a,7b} Thus, the concentration of the NH₂ end group, [-NH₂] decreases with a lower pH (= higher [H⁺]), resulting in a longer gelation time. In an aprotic IL system, the addition of H⁺ sources is required

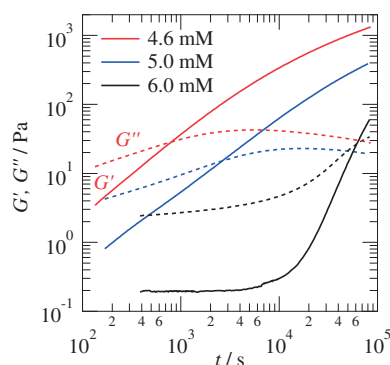


Figure 1. Dynamic moduli, G' (solid line) and G'' (broken line), for the gelation of Tetra-PEG in $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ with varying the concentration of protic IL, $[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$.

for gelation control, because there is no dissociative H^+ within either the cation or the anion in typical aprotic ILs. Therefore, we focused on protic ILs as “nonvolatile” H^+ sources. In this work, 1-ethylimidazolium bis(trifluoromethanesulfonyl)amide ($[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$), an analogous protic IL of aprotic $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$, was added into Tetra-PEG- $\text{NH}_2/[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ and Tetra-PEG-NHS/ $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ solutions with 6 wt% prepolymer content. The molecular weight was 20000 for both prepolymers. After mixing them, the gelation reaction was investigated by rheological measurements to estimate the gelation time. Figure 1 shows typical results of the storage (G') and loss (G'') moduli for the Tetra-PEG gelation in $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ with varying $[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$ concentration. Both G' and G'' gradually increased with reaction time for all the systems, and the intersection of the G' and G'' profiles, corresponding to the gelation point, was clearly observed. The gelation times were 775, 2660, and 62375 s for 4.6, 5.0, and 6.0 mM $[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$ solutions, respectively. Figure S2 shows the gelation time plotted against the concentration of $[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$. It was deduced from this figure that we can successfully control the gelation time as a function of protic IL concentration, enabling easy preparation of gas separation membranes containing a large amount (94 wt%) of IL. We point out here that acid–base reactions of the terminal NH_2 group within Tetra-PEG in aprotic $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ significantly affect the gelation time, which has been investigated by potentiometric titration in our recent work.⁸ The mechanical properties of the Tetra-PEG ion gel obtained in this work were evaluated by a stretching test, which is shown in Figure S3 (stretching stress–elongation curve). The maximum breaking elongation, λ_{max} was over 4.0, which is larger than that of the high-toughness ion gels reported recently.^{5,6a} The breaking stress was 24 kPa at $\lambda = 4.0$, and the elastic modulus was estimated to be 3.6 kPa.

The Tetra-PEG ion gel membrane used for the CO_2 separation test in this work was prepared as illustrated in Figure S1. The 6 wt% Tetra-PEG- NH_2 and Tetra-PEG-NHS in $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ solutions were mixed and stirred for minutes to obtain a homogeneous mixture. The concentration of $[\text{C}_2\text{ImH}^+][\text{TFSA}^-]$ in each solution was 6.0 mM. The mixture was cast on a Teflon plate with 1 mm-thick silicon spacers, and then it was pressed by another Teflon plate at room temperature for 24 h in a N_2 atmosphere. The gas permeability of the 6 wt%

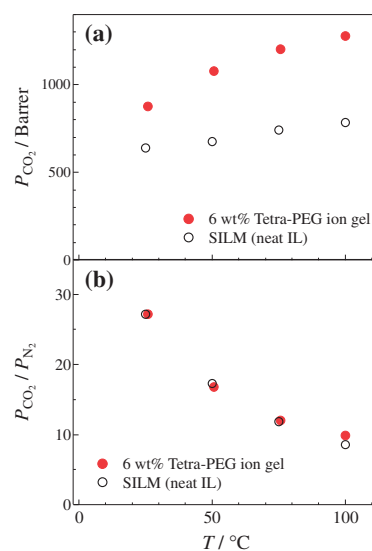


Figure 2. Temperature dependences of (a) the CO_2 permeability, P_{CO_2} , and (b) the CO_2 – N_2 selectivity, $P_{\text{CO}_2}/P_{\text{N}_2}$, for the 6 wt% Tetra-PEG+ $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$ ion gel, together with those for the corresponding SILM.

Tetra-PEG ion gel (94 wt% IL) was investigated in the temperature range from 25 to 100 °C. Details of the gas separation measurement are described in the Supporting Information (SI). Figure 2a shows the CO_2 permeability, P_{CO_2} , for the ion gel membrane with varying temperature, together with those for the SILM of porous hydrophilic Teflon film filled with $[\text{C}_2\text{mIm}^+][\text{TFSA}^-]$. The CO_2 permeability for the Tetra-PEG ion gel was 877 barrer at 25 °C, and the value is ca. 1.4 times larger than that for the SILM. This might be ascribed to the difference in the cross-sectional area where gas molecules come into contact with the IL or a change in the thickness of the ion gel during the measurement. The CO_2 permeability monotonically increased with rising temperature, indicating the increase in the CO_2 diffusion in the IL medium. Figure 2b shows the CO_2 – N_2 selectivity estimated from the permeabilities of CO_2 and N_2 , $P_{\text{CO}_2}/P_{\text{N}_2}$. The selectivity for the Tetra-PEG ion gel decreased with increasing temperature, and the values at each temperature were almost similar to those for the SILM. According to a solution-diffusion transport mechanism, the ideal selectivity between two different gases (i, j) mainly depends on solubilities (S) and diffusion coefficients (D), i.e., $P_i/P_j = (S_i/S_j)(D_i/D_j)$. The result obtained here implies that both solubilities and diffusion coefficients of CO_2 and N_2 in the Tetra-PEG ion gel are almost the same as those in the neat IL. We thus concluded that the supporting polymer, Tetra-PEG, does not hinder the gas separation performance at the temperatures examined because of the same selectivity in both the ion gel and SILM systems.

In order to obtain deeper insight into the CO_2 – N_2 permselectivity of the Tetra-PEG ion gel mentioned above, we extended our study to CO_2 absorption properties under high-pressure conditions. As far as we know, this is the first report on the gas absorption for ion gel under high pressures. First, we carried out volume expansion measurements for the Tetra-PEG ion gel prepared in a capillary (1.4 mm ϕ) by using an optical microscope. The details are described in the SI. The volume

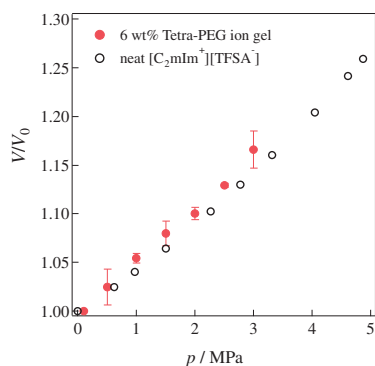


Figure 3. Volume expansion V/V_0 plotted against pressure p for the 6 wt% Tetra-PEG ion gel + CO_2 (filled circles) and the corresponding neat IL + CO_2 (open circles)⁹ systems.

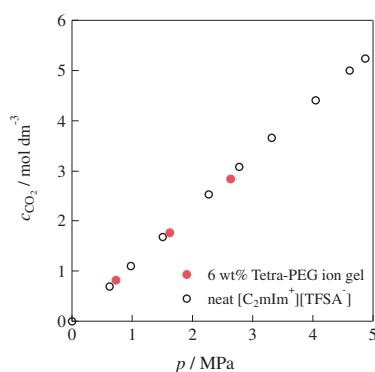


Figure 4. CO_2 solubilities c_{CO_2} plotted against pressure p for the 6 wt% Tetra-PEG ion gel + CO_2 (filled circles) and the corresponding neat IL + CO_2 (open circles)⁹ systems.

expansion, V/V_0 , was defined as a change in diameter between the ion gels absorbing CO_2 (d) and without CO_2 (d_0), that is, $V/V_0 = (d/d_0)^3$. We assumed that the ion gel isotropically expands with the absorption of CO_2 . Figure 3 shows the V/V_0 as a function of CO_2 pressure at 298 K for the 6 wt% Tetra-PEG ion gel. It was found that the Tetra-PEG ion gel expands without solvent seeping out of the gel even under the high pressures examined. The V/V_0 for the ion gel linearly increased with increasing pressure (the amount of CO_2 absorbed), and it is practically equal to that for the neat $[C_2mIm^+][TFSA^-]$ reported in ref 9. Figure 4 shows the pressure dependence of the CO_2 solubility (molarity scale) at 298.15 K. The experimental apparatus and procedure are described elsewhere.¹⁰ The Tetra-PEG ion gel can absorb CO_2 physically as much as the corresponding neat IL.⁹ These results suggest the following: (1) Liquid-like CO_2 absorption occurs in the solid-state ion gel containing 94 wt% $[C_2mIm^+][TFSA^-]$; (2) Tetra-PEG as a support network does not interfere with CO_2 absorption due to its low content in the ion gel. We thus propose that the Tetra-PEG ion gel shows the maximum CO_2 physical absorption among polymer–IL composite materials, because IL physical absorbents without polymers absorb the largest amount of CO_2 . A similar behavior was observed for the ionic conductivity in our previous work; that is, the conductivity of the Tetra-PEG ion gel with low polymer contents was nearly equal to that of the neat IL.^{6a}

In conclusion, a high-toughness Tetra-PEG ion gel was prepared by controlling gelation time with the addition of a protic IL to afford an ion gel membrane with an amount of IL (94 wt%) larger than any other polymer–IL membrane reported in literature. We demonstrated that the Tetra-PEG ion gel membrane shows a CO_2 – N_2 permselectivity comparable to that of the corresponding SILM even in the high-temperature range without any degradation. This excellent performance is derived from the good CO_2 absorption and diffusion properties, which are almost the same as those for the neat IL. The Tetra-PEG ion gel absorbs CO_2 without solvent seeping under pressure conditions up to 3 MPa. Again, Tetra-PEG allows one to prepare a high-toughness and thermally stable ion gel membrane even with very low polymer concentrations. A low polymer content in ion gels is the key to maximize the potential of IL membranes. The present study may open up new possibilities for gas separation membrane under a wide range of temperatures and pressures. For practical use, however, membranes much thinner than the present one are required. Such trial to prepare thinner and tougher Tetra-PEG ion gels is in progress by optimizing the condition of the acid–base reaction in ILs.

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Supporting Information is available electronically on J-STAGE.

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