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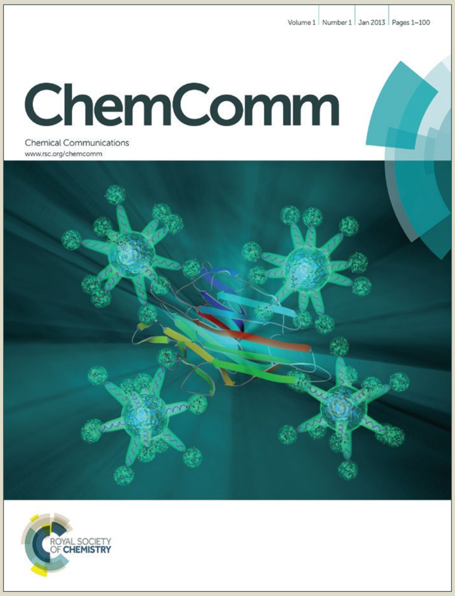

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Amino Acid Ionic Liquid-based Tough Ion Gel Membrane for CO_2 Capture

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A tough and thin double-network gel membrane containing amino acid ionic liquids as a CO_2 carrier exhibited superior CO_2 permeability and stability under pressurized conditions.

Concerns on CO_2 emissions from coal-fired power plants are rapidly increasing owing to their major contribution to global warming and climate change. Hence, the development of an economically viable and environmental friendly CO_2 capture technology is inevitable. From an engineering point of view, the low partial pressure of CO_2 and huge volume of emitted flue gas are two serious challenges to increasing plant size and minimizing the cost of CO_2 capture. During the last two decades, membrane technology has drawn considerable interest owing to the potential for a CO_2 capture process with low energy consumption and low capital and operating costs. A feasible and desirable CO_2 separation membrane with high CO_2 flux that does not sacrifice CO_2/N_2 selectivity should be developed to fulfill practical requirements.

In this context, room temperature ionic liquids (RTILs) have been proposed as attractive CO_2 permeation media for supported ionic liquids membranes (SILMs)[1] owing to their distinct properties such as high CO_2 absorption capacity, negligible vapor pressure, huge chemical diversity, and high thermal stability. However, "blow-out" of the ILs through the pores of the support membranes, which is the inherent problem of SILMs due to the weak capillary force for the holding of ILs in the porous support and becomes serious under pressurized conditions, limits the application of SILMs to low trans-membrane pressure systems.[2] Therefore, development of a material which overcomes blow-out of ILs had been desired for IL-based CO_2 separation membranes. Incorporation of non-polymerizable ionic liquids (free ILs) into the matrix of functional cross-linkable ILs, called poly(RTIL)/RTIL composite membranes, has been considered a promising strategy to overcome the blow-out issue of SILMs.[3] However, despite blow-out improvement, the poly(RTIL)/RTIL composite membranes suffer from low CO_2 permeability due to the low CO_2 absorbability of RTILs.[4] Recently, the use of amine-functionalized task-specific ILs (TSILs) for CO_2 capture, which have at least a CO_2-reactive amino moiety in the molecule, have been considered as an attractive approach to overcome the poor CO_2 absorbability.[4b,5] The amine-functionalized TSILs can chemically and reversibly react with CO_2 to form CO_2 complexes (carbamic acid and/or carbamate)[6] and increase the trans-membrane concentration gradient of the CO_2 complexes, which realizes the fast and selective CO_2 permeation.

By taking advantage of selective reactions between CO_2 and TSILs, we recently reported a new class of SILMs containing amino acid ILs (AAILs).[7] The AAIL-based SILMs demonstrate remarkably fast and selective CO_2 permeation based on a facilitated transport mechanism. The advantages of AAILs over widely used conventional non-IL-type CO_2 carriers make them a promising candidate as CO_2 carriers and as a diffusion medium for facilitated transport membranes. However, similar to conventional SILMs, the AAIL-based SILMs cannot be used under pressurized conditions because the AAILs are held in a porous support system with weak interactions and easily leak from the support.

To resolve the aforementioned issue related to the pressure stability of AAIL-based SILMs, we proposed a straightforward approach to fabricate polymer gel membranes containing AAILs (AAIL-gel membranes).[8] The developed AAIL-based membrane with 70 wt% of AAIL content prevented the blow-out of AAILs under pressurized condition up to 1 MPa because the strong interaction between the polymer network and the AAIL yielded large osmotic pressure of the AAIL-gels. In addition, the AAIL-gel membranes exhibited acceptable CO_2 separation potential, nearly analogous to that of AAIL-based SILMs. However, to achieve desirable CO_2 separation

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† Electronic Supplementary Information (ESI) available: Materials and general procedures for the preparation of AAIL-based DN ion gel membranes, measurement of AAIL content, effects of AAIL content, CO_2 partial pressure, and membrane thickness of the DN ion gel membranes on gas permeabilities, fracture stress data of the DN ion gels, and a durability test of the DN ion gel membranes. See DOI: 10.1039/c000000x/

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performance, a large amount of AAILs must be incorporated into the AAIL-gel membrane, and this is associated with a decrease in mechanical strength as well as pressure resistance of the AAIL-gel membranes. That is, the trade-off between mechanical strength and CO_2 separation ability still remains a challenge. Moreover, the low mechanical strength of the gel membrane hinders the preparation of thin gel membranes with high CO_2 flux for practical applications.

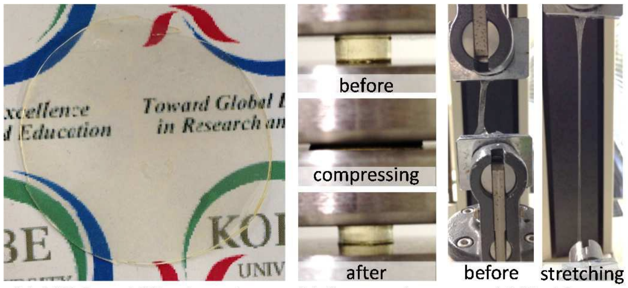
Here, we propose a novel, tough AAIL-gel membrane with excellent mechanical strength based on a specific double-network (DN) gel matrix[9] that improves the pressure resistance of the gel membrane containing a large amount of AAIL and also enables fabrication of a thin membrane with high CO_2 permeance. To the best of our knowledge, this is the first report on the fabrication of AAIL-based polymeric gel membranes exhibiting excellent CO_2 permeability and CO_2/N_2 selectivity as well as outstanding stability under pressurized conditions.

The DN gel concept was applied to develop tough AAIL-based gel membranes in this study. These DN gels were first proposed to prepare tough, high-water-content hydrogels for use as alternatives to natural tissues of the human body.[9] DN hydrogels contain two asymmetric polymer networks: the first is a rigid, brittle, and tightly cross-linked polyelectrolyte and the second is a soft, ductile, and loosely cross-linked polymer. This unique structure offers many polymer network options for the DN gels. For the fabrication of AAIL-based DN gels, the most important parameter is the compatibility between AAILs and the polymer networks. In a previous report,[8] we found that polyvinylpyrrolidone (PVP) and polydimethylacrylamide (PDMAAm) have good compatibility with several phosphonium-based AAILs. Because PVP and PDMAAm are neutral polymers, we adopted them as the second network of the AAIL-based DN ion gels. As the first network of the DN gel, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), which is a rigid polyelectrolyte, was used because it provides high osmotic pressure inside the gel during immersion in water. The large osmotic pressure between the inside and outside of the gel led to full swelling and the incorporation of a large amount of AAILs into the gel matrix. Additionally, it could contribute to the enhancement of the holding ability of AAILs in the gel networks due to the increase of the osmotic pressure of the AAIL-based DN gel owing to the counter-ions of PAMPS. Based on the excellent CO_2 permeation properties of prolinate-based AAILs,[10] we selected tetrabutylphosphonium prolinate ($[P_{4444}]$[Pro]) and triethyl(pentyl)phosphonium prolinate ($[P_{2225}]$[Pro]) as the AAIL. Although poor retention of low-viscosity $[P_{2225}]$[Pro] inside the porous support makes it difficult to fabricate SILMs, the synthesized DN could strongly hold all AAILs, up to 80 wt%.

AAIL-based DN ion gel membranes were prepared via a multi-step preparation method as follows: (1) DN hydrogel preparation, (2) impregnation of an AAIL/water mixture into the DN matrix, and (3) removal of water from the gel by evaporation. First, DN hydrogel films consisting of PAMPS and either PVP or PDMAAm, were prepared according to the procedure explained in the supplementary information (ESI†). Although the hydrogel with PAMPS/PVP was weak, the hydrogel composed of PAMPS/PDMAAm exhibited extraordinary toughness. The PAMPS/PDMAAm DN hydrogel was immersed in the aqueous solution of AAILs for 24 h to incorporate AAILs into the gel network. After drying at 373 K in a vacuum oven for at least 8 h to remove any possible water, AAIL-based DN ion gel membranes were successfully prepared.

Taking the effect of AAIL content into consideration, DN gel membranes with different AAIL contents were prepared using aqueous solutions with different concentrations of AAILs. The AAIL content in the prepared gel membranes reached up to 80 wt% and became constant as the AAIL concentration in the aqueous solution increased (Fig. S1, ESI†). It is worth pointing out that even DN gel membranes containing up to 80 wt% AAIL are mechanically strong enough to be easily manipulated by hand and their gas transport properties can be evaluated under pressurized conditions. The prepared AAIL-based DN ion gel membrane is shown in Fig. 1(a). Typical photographs demonstrating the extraordinary mechanical strength of the AAIL-based DN ion gels are also shown in Fig. 1(b, c). The effect of AAIL content on CO_2 and N_2 permeation properties are presented in Fig. S3 (ESI†). As shown in Fig. S3, the CO_2 and N_2 permeabilities depended on the AAIL content, *i.e.*, the permeabilities increased as the AAIL content increased. The increase in N_2 permeability likely resulted from the decrease in the diffusion resistance (which is a function of the polymer content and gel network density). Regarding the CO_2 permeability, which was more significantly affected by the AAIL content than N_2, the strong dependency is the combined effect of the decrease in diffusion resistance and the increase in the CO_2 absorption amount (resulting from the increase in available AAILs (carriers) in the DN gel network). That is, the CO_2 permeation through the AAIL-based DN ion gel membranes was based on a facilitated transport mechanism. The facilitated CO_2 transport was also confirmed based on the CO_2 partial pressure dependency of CO_2 permeabilities for the $[P_{4444}]$[Pro]-based and $[P_{2225}]$[Pro]-based DN ion gel membranes with various AAIL contents (See ESI† (5) and Figs. S4 and S5).

One of the most outstanding features of the AAIL-based DN gels is the extraordinary mechanical strength. We measured the fracture stress of the DN ion gels consisting of



(a) AAIL-based DN gel membrane (b) Compression (c) Stretch

Fig. 1 (a) Typical AAIL-based DN ion gel membrane, (b) AAIL-based DN ion gel before compression (top), during compression (middle), and after compression (bottom), and (c) the AAIL-based DN ion gel membrane before stretching (left) and under stretching (right). AAILs: amino acid ionic liquids

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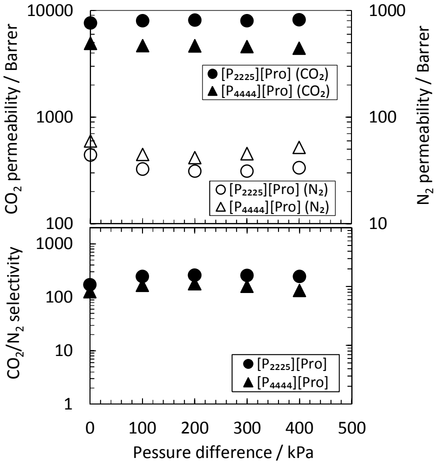

Fig. 2 Pressure resistance of the AAIL-based DN gel membranes (Experimental conditions: T = 373 K, P_{sweep} = atmospheric pressure, $P_{\text{CO2,feed}}$ = 10 kPa, and relative humidity = 0%, membrane properties: thickness was 600 μm and AAIL content was *ca*. 80 wt%).

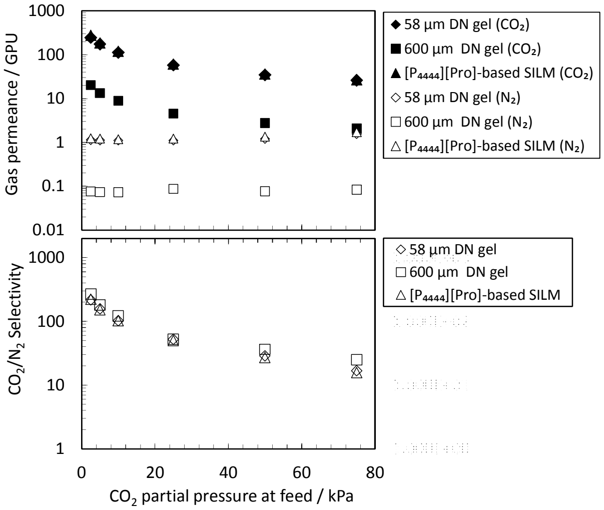

Fig. 3 CO$_2$ partial pressure dependency of the thin AAIL-based DN ion gel membrane containing *ca*. 80 wt% of [P$_{4444}$][Pro] as the CO$_2$ separation medium (Experimental conditions: T = 373 K, P_{feed} = P_{sweep} = atmospheric pressure, and relative humidity = 0%).

[P$_{4444}$][Pro] and [P$_{2225}$][Pro] with different contents. It is worth mentioning that even the DN ion gels with *ca*. 80 wt% AAIL contents did not break under compression stress of more than 25 MPa (Fig. S6(a), ESI†), which is more than 25 times higher than those previously reported for [P$_{4444}$][Pro]-based ion gels consisting of PVP and PDMAAm single networks prepared by our group[8]. During compression, no AAIL leakage from the gel network was observed as a consequence of good compatibility between PDMAAm and the AAILs. Regarding the tensile strength, the AAIL-based DN ion gel membranes exhibited high tensile fracture stress of more than 0.5 MPa (Fig. S6(b-d), ESI†). We also confirmed the hysteresis of the stress-strain curves and softening behavior of the AAIL-based DN gel membrane during cyclic stretching tests (Fig. S7, ESI†), which is a specific property of DN gels.[11] In general, it is hard to confirm the DN structure directly. However, the specific softening behavior and hysteresis are the strong evidence of the roles of the brittle 1st network as "sacrificial bonds" and the ductile 2nd network as "hidden length" in the gel.[12] That is, the toughening mechanism of the AAIL-based DN gels was attributed to the DN concept.

Based on the excellent mechanical strength observed, it was expected that the fabricated AAIL-based DN ion gel membranes could be used under pressurized conditions. Figure 2 demonstrates the pressure resistance of the AAIL-based DN gel membranes. The AAIL contents of the DN ion gel membranes used in this investigation were *ca*. 80 wt%. The pressure resistance was evaluated at an elevated temperature of 373 K and a constant permeate side pressure (atmospheric pressure) through changing the feed side pressure from 100 to 500 kPa. As clearly indicated in Fig. 2, the CO$_2$ permeability, the N$_2$ barrier property, and CO$_2$/N$_2$ selectivity for both AAILs remained constant at a high level for the whole range of trans-membrane pressure differences investigated in this study. In particular, the observed CO$_2$ permeability and CO$_2$/N$_2$ selectivities were more than 4000 Barrer and 100 at high pressure difference conditions, respectively. These results indicated that the AAIL-based DN ion gel membranes withstood pressurized conditions due to their tough DN structure. In addition, the AAIL-based DN ion gel membranes showed stable CO$_2$ and N$_2$ permeation for 5 days at elevated temperatures under pressurized conditions (Fig. S8, ESI†). The high and selective CO$_2$ permeability, the superior pressure resistance, and the long term stability of the fabricated AAIL-based DN ion gel membranes make them an attractive option for a broad range of CO$_2$ capture applications.

A reduction in the thickness of the fabricated DN gel membranes still remained a challenge. In practical applications, a high flux and CO$_2$-selective membrane is required to reduce the size and cost of the CO$_2$ separation unit. The CO$_2$ flux basically depends on the membrane thickness when the CO$_2$ permeation is limited by intra-membrane diffusion of CO$_2$. In other words, fast CO$_2$ permeation can be achieved through maintaining CO$_2$ permselectivity by reducing membrane thickness. The tough AAIL-based DN ion gel has the potential to be fabricated in a thinner form with high CO$_2$ permselectivity because the rate-controlling step of CO$_2$ permeation through the AAIL-based membranes would be controlled by intra-membrane diffusion of the CO$_2$ complex.[7b] Therefore, we fabricated thinner AAIL-based DN ion gel membranes and measured the CO$_2$ and N$_2$ fluxes. In this investigation, [P$_{4444}$][Pro]-based DN ion gel membranes were used to compare the performances with that of the AAIL-SILM. The CO$_2$ partial pressure dependency of CO$_2$ and N$_2$ permeances (GPU) for the thinnest AAIL-based ion gel membrane (58 μm) prepared in this study are shown in Fig. 3 along with those for the thick AAIL-based DN ion gel membrane (600 μm) and the AAIL-SILM (37 μm). The CO$_2$ permeance of the thinner AAIL-based DN ion gel membrane was almost identical to that of the AAIL-SILM, although the ion gel membrane was thicker than the AAIL-SILM. This result

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indicates that the diffusion resistance in the DN ion gel network is smaller than that of the porous support used for AAIL-SILMs owing to the low polymer content in the DN ion gel membrane. Furthermore, based on the relationship between the CO_2 permeance and inverted thickness of the membrane, $1/\delta$, shown in Fig. S9 (ESI†), the CO_2 permeance increased linearly with the decrease of $1/\delta$, which indicates that the CO_2 permeation through the thinner DN ion gel membrane was still controlled by intra-membrane diffusion. This raises the possibility that faster CO_2 permeation can be achieved through further reductions in membrane thickness.

In this study, we demonstrated the advanced properties of AAIL-based DN ion gel membranes with respect to CO_2 separation. The prepared membranes were tough and had high pressure resistance as well as high CO_2 permeability and CO_2/N_2 selectivity. This is the first report to utilize a DN gel network for ion gels. Many opportunities to improve the mechanical strength as well as to reduce the polymer content for higher CO_2 permeability still remain. Optimization of the AAIL-based DN ion gel membranes would provide feasible and desirable CO_2 separation membranes for various practical CO_2 separation processes.

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