



Development of tough ion gel membranes containing CO₂ reactive ionic liquids

Moghadam, Farhad

(Degree)

博士 (学術)

(Date of Degree)

2017-03-25

(Date of Publication)

2018-03-01

(Resource Type)

doctoral thesis

(Report Number)

甲第6910号

(URL)

<https://hdl.handle.net/20.500.14094/D1006910>

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Doctoral Dissertation

**Development of tough ion gel membranes
containing CO₂ reactive ionic liquids**

(CO₂反応性イオン液体含有高強度イオンゲル膜の開発)

January 2017

Graduate School of Engineering

Kobe University

Farhad Moghadam

*This thesis is dedicated to those I love the most, my parents,
my sisters and my brother*

Acknowledgement

First and foremost, I would like to thank my supervisor, Professor Hideto Matsuyama. The experience with professor Matsuyama has been absolutely amazing and I received the best education from him both on a professional and personal level. I have been so lucky to have so many enjoyable interactions with him. His enthusiasm, relentless dedication, and wisdom will continuously inspire me. His influence has been built into my attitude to work, life and the world.

I also would like to express my earnest gratitude to my co-supervisor Dr. Eiji Kamio, who has provided me with the guidance, support, and encouragement over the past three years. His insight and the lessons I have learned from him have been important in both my personal and professional development.

I would like to acknowledge the committee members, Professor Naoto Ohmura and Professor Kenji Ishida, for their time and valuable insights.

All members of gas separation group during the last three years deserve thanks. I have to give special credit to my collaborators Ayumi Yoshizumi, Shohei Kasahara, Tomoki Yasui, Tatsuya Matsuki, and Akihito Otani for all their support. I express my deep gratitude to Dr. Saeid Rajabzadeh for introducing me into Professor Matsuyama group and his countless supports and helps at the beginning of my life in Kobe.

I have always been fortunate to have good Iranian friends who have been present during my good and tough times. I would like to express my endless gratitude to Hamed Karkhanechi, Mahboobeh Vasselbehagh, and Fatemeh Ranjbaran for their great supports and helps.

I am utmost indebted to my parents for their unconditional love and support. They have given constant encouragement in every step I have taken and thereby helped to realize my dreams. I would also like to thank my sisters and my brother for their absolute love and encouragement in every phase of my life.

I would like to greatly appreciate the scholarship received from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) during three and half year. This funding support is the top-class of grant for international students in Japan.

Farhad Moghadam
Kobe University, Japan
January 2017

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Chapter 1

General Introduction

1.1. CO₂ capture and challenges

Fossil fuels are the primary global energy source and account for the largest share of greenhouse gases (GHGs) emissions (Fig. 1.1). In particular, coal-fired post-combustion power plants, as the main source of electricity generation, are the major contributors to carbon dioxide (CO₂) emissions [1]. According to data released in 2014 by the International Energy Agency (IEA), the CO₂ concentration in the atmosphere dramatically increased from 280 to 397 parts per million (ppm) during the last century, which has raised considerable concerns in connection with climate change. Despite the growth of non-fossil fuels, the share of fossil fuels during the last 40 years has remained approximately unchanged. Because of the growing global demand for fossil fuels, it is expected that fuel combustion will be the main source of CO₂ emissions in the next few decades [1-3]. Therefore, development of an economically viable and environmentally friendly technology for separating CO₂ in post-combustion power plants is a pressing need of the industry. CO₂ capture and sequestration (CCS) is one proposed way to mitigate the serious environmental impacts of CO₂ emissions [3]. In this system, CO₂ is captured from post-combustion flue gases and sequestered underground. During the last decades, researchers and industry have focused on developing a highly efficient CO₂ capture technology, with low energy and capital costs, and without serious environmental impacts [3].

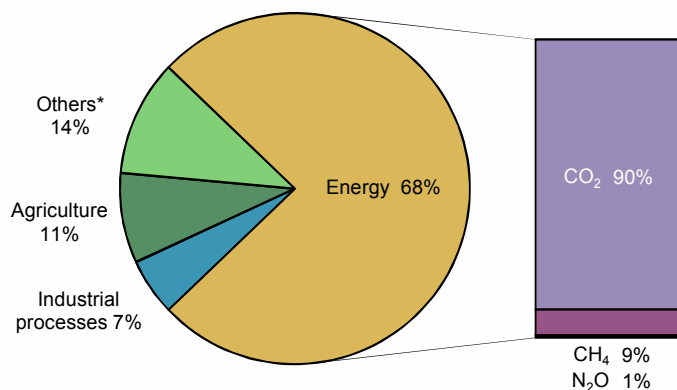


Fig. 1.1 Share of global anthropogenic GHG, 2010 [1]

The currently mature CO₂ capture technology, which has the potential to be applied in CO₂ separation from flue gases, is amine-based absorption [2, 4]. The chemical absorption unit is a conventional and widely used technology for CO₂ separation from natural gas (i.e., natural gas sweetening). However, the low concentration of CO₂ in flue gases (10-15% in volume) and their large volume that should be treated are the two main obstacles in separating CO₂ from post-combustion flue gas by amine-based absorption [3]. The low CO₂ concentration in flue gases means a low driving force for separation and a higher cost for CO₂ capture. It is estimated that adding an amine-based chemical absorption unit into a post-combustion plant implies a 25-40% energy penalty, resulting in a substantial increase in electricity costs. To cope with this, a membrane technology has been proposed as a promising candidate because of its low operating and capital costs, unit simplicity, low energy cost, ease of operation, and environmentally friendly characteristics [4-6].

1.2. Membrane-based CO₂ separation

1.2.1. Polymeric membranes

During the last decades, the major application area of membrane technology (Fig. 1.2) has been in the chemical industry, in processes such as O₂/N₂ separation, natural gas sweetening, ammonia production, etc.

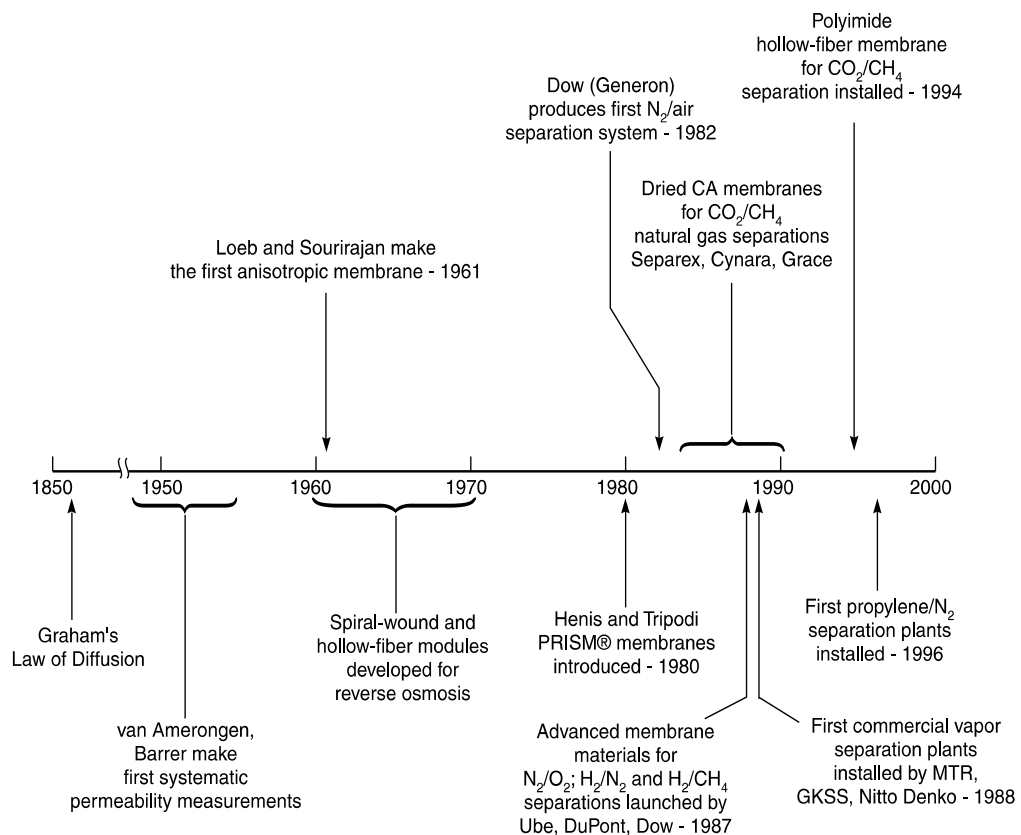


Fig. 1.2 Development of membrane-based gas separation [6]

Because of their low fabrication cost, good film processing, and high mechanical properties, polymeric membranes have been considered an attractive material for separation of gas mixtures. The permeation mechanism in polymeric membranes is based on solution-

diffusion [6-8]. In this mechanism, the permeation of gas species is determined by the gas solubility and diffusion coefficients. Depending on whether the polymeric membranes are rubbery or glassy, the determining step of permeation through the membrane is different [6, 8]. In the glassy polymer, the gas species permeates through the membrane based on the molecular size difference, while in rubbery polymers condensability of the gas species is the controlling parameter. However, both types of polymeric membranes follow a familiar permeability-selectivity trade-off behavior, known as the Robeson upper-bond plot, which means that permeability of the membranes decreases with increasing selectivity and vice versa [9]. In other words, achieving a high CO₂ permeability through polymeric membranes is accompanied by a decline of CO₂/N₂ selectivity and vice versa. Fig. 1.3 shows a Robeson plot for CO₂/N₂ separation. In general, the Robeson plot is a benchmark for evaluating the potential of polymeric membranes in relation to the separation target.

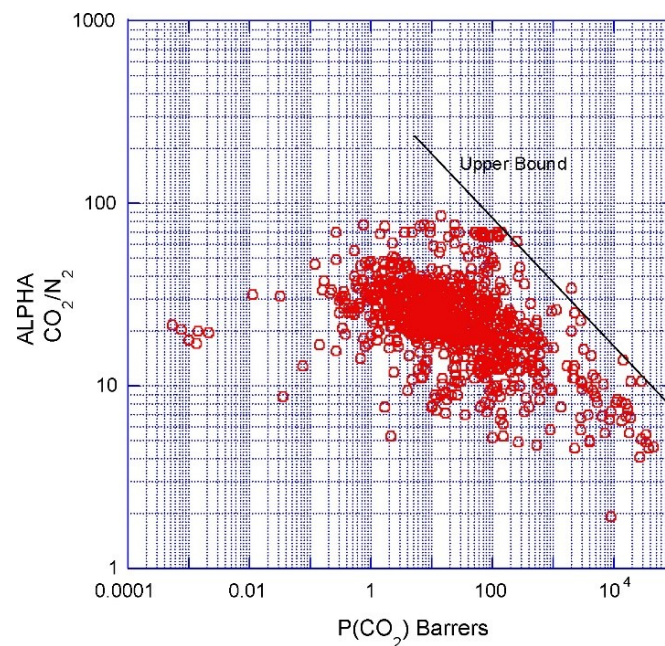


Fig. 1.3 Robeson upper-bond plot for CO₂/N₂ separation [9]

As clearly shown in Fig. 1.3, polymeric membranes have a relatively poor performance for CO₂/N₂ separation. With rubbery polymers, the solubility of gases on the feed side of the membrane determines the selectivity rate. Because, with a low partial pressure, the physical solubility of CO₂ is too low, CO₂/N₂ selectivity is not high enough to be viable in real applications. For glassy polymers, selectivity is controlled by diffusivity selectivity, based on the difference in kinetic diameter of the gas species [6]. For CO₂ and N₂, gases with relatively close kinetic diameters, CO₂/N₂ selectivity is not too high. In summary, the CO₂/N₂ selectivity of both rubbery and glassy polymeric membranes is not high enough for CO₂ separation from post-combustion flue gases.

Because the gas permeation through polymeric membranes, which is based on a solution-diffusion mechanism, is driven by the CO₂ partial pressure difference, the CO₂ permeability is too low for a flue gas with a very low CO₂ concentration. Therefore, the CO₂ permeability and CO₂/N₂ selectivity of polymeric membranes are below the Robeson upper-bond. Several efforts have been made to develop new types of membranes such as the mixed matrix membranes (MMMs) [10], polymers of intrinsic micro-porosity [11], and thermally rearranged (TR) polymers [12] in order to surpass the upper-bond and reach the desired area. However, challenges remain and should be explored.

In this regard, facilitated transport membranes (FTMs) have been considered as a potential alternative for CO₂ capture from a post-combustion flue gas because of their distinctive separation properties compared to other membranes [6, 13]. The selectively chemical reaction of the carrier in FTMs with CO₂ allows for a high CO₂ permeability in

conjunction with CO₂/N₂ selectivity, which is the requirement of a membrane-based separation system for CO₂ capture from gas streams with low CO₂ concentration.

1.2.2. Facilitated transport membranes

1.2.2.1. Conventional facilitated transport membranes

FTMs are functionalized membranes containing chemical compounds, the so-called carriers, which selectively and reversibly react with CO₂. The permeation mechanism of FTMs is based on a reversible complexation reaction of CO₂ with the carrier on the feed side of the membrane and an intra-diffusion of the CO₂-carrier complex through the membrane, in addition to the solution-diffusion mechanism [6, 13, 14]. On the other hand, in the case of a uncomplexed penetrant such as N₂, the facilitated transport mechanism is not accessible and the permeation is then based on the simple solution-diffusion mechanism. Therefore, FTMs display a much higher CO₂ permeability along with CO₂/N₂ selectivity than polymeric membranes and commonly exceed the Robeson upper-bond. The carriers of FTMs are classified into two groups: mobile carrier and fixed carrier. The common FTMs with mobile carriers are supported liquid membranes (SLMs) [15-28], and a solvent swollen polymer [29]. A polymer membrane containing a CO₂-philic functional group is also an example of fixed carrier-based FTMs [30-32]. Polyvinyl amine (PVAm) [30, 31], blends of PVAm and polyvinyl alcohol (PVA) (called PVAm/PVA) [33, 34], polyethylenimine (PEI)/PVA [22], and polyallylamine (PAAm)/PVA [35] are examples of fixed site carrier (FSC)-based FTMs. The permeation of FSC-based FTMs is based on the hopping mechanism, in which CO₂ reacts at one carrier site and then hops to the next carrier site, along the direction of the

concentration gradient (Fig. 1.4(a)). Because the fixed carriers are covalently bonded to the polymer backbone and cannot diffuse freely in the membrane matrix, the CO₂ permeability of FSC-based FTMs is relatively low. To address this issue, the incorporation of mobile carriers into the FSC-based FTMs was considered. The liquid state of the diffusion medium and the freely diffusion of the carrier-CO₂ complex in the mobile carrier-based FTMs (such as SLMs) lead to a higher diffusion coefficient and CO₂ permeability [36, 37]. While their CO₂ transport properties are improved because of the incorporated mobile carriers, the performance of FTMs is not yet high enough. Therefore, the focus is on mobile carrier-based FTMs (Fig. 1.4(b)).

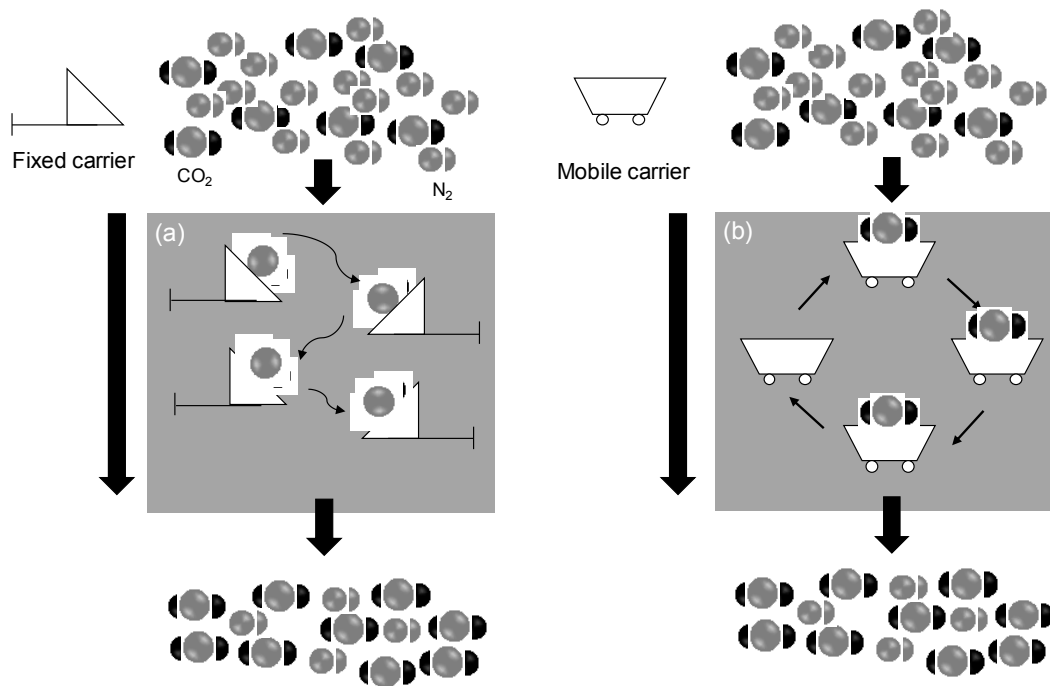


Fig. 1.4. Schematic illustration of facilitated transport membranes (FTMs) (a) fixed site carrier-based and (b) mobile carrier-based [28]

During the last decades, numerous studies have been reported on the fabrication of SLMs-FTMs, demonstrating a remarkable CO₂ separation performance [16-29]. Despite their good CO₂ transport properties, poor stability is still the biggest obstacle for employing this type of FTMs in CO₂ capture applications. The poor stability of mobile carrier-based FTMs is mainly ascribed to the carrier-medium properties. In this type of FTMs, a volatile carrier or a carrier salt dissolved in a solvent (solution-based carrier) have usually been used as carrier media. Hence, loss of carrier or solvent leads to poor stability of SLMs, especially at elevated temperatures. The other issue regarding the mobile carrier-based FTMs is the poor holding property of the carrier in SLMs. The weak capillary force is responsible for retaining the carrier inside the pores of the support. This force is not strong enough to prevent the blowout of the carrier from its porous support, even under low trans-membrane pressures (more than 2 bar).

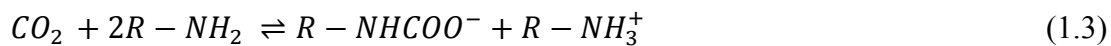
In order to prevent the loss of the volatile carrier, Leblanc et al. [38] used an ion exchange membrane capable of holding it. The carrier used in that study was an ion hold in the membrane network based on electrostatic forces. Other approaches to improve the stability of FTMs used low volatile and hygroscopic liquids, such as polyethylene glycol (PEG) [39] and glycerol [16, 17]. For example, Chen et al. [17] demonstrated the stable performance of an immobilized liquid membrane (ILM) consisting of a carbonate or glycine-Na carrier dissolved in a non-volatile solvent (glycerol) for 25 days under a humid condition. However, the CO₂ separation performance of ILMs strongly depended on the concentration of the carrier in the solvent (i.e., glycerol). At a low carrier concentration, the membrane performance was not high enough, particularly in terms of CO₂ permeance. By increasing the

carrier concentration, the higher viscosity of the carrier solution resulted in a decrease in CO₂ and N₂ permeabilities. In addition to the carrier concentration, the relative humidity (RH) of the feed gas considerably affected the FTMs performance. Because the viscosity of the carrier-glycerol solution strongly depended on the water content, the membrane performance changed markedly at low RHs of the feed gas. The lower water content of glycerol also affected the solubility and therefore the permeance of gases [16, 17].

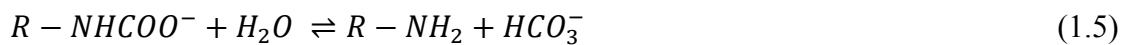
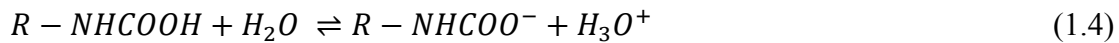
In addition to diffusivity and solubility, the effect of water on the reaction mechanism of CO₂ with an amine-based carrier should be taken into consideration. The proposed reaction mechanism is described as follows [14]:



The overall reaction can be written as follows:



In presence of water, the following reactions can occur to form bicarbonate:



From the viewpoint of the reaction mechanism, the presence of water is not essential for the reaction between CO₂ and an amine-based carrier. However, because amine-based carriers are mostly in solid state, water is indispensable for maintaining a liquid state medium and

facilitating the diffusion of the carrier through the membrane, particularly at elevated temperatures [29, 36].

The main conclusion that can be drawn is that even though the mobile carrier-based FTMs have a high CO₂ separation performance compared with polymeric membranes, several issues affect them. First, the volatility of the carrier is a critical issue leading to the deterioration of FTMs performance. Second, because the mostly amine-based carriers are in a solid state, a non-volatile solvent or water is required to prepare the carrier solution desirable for FTMs. Third, the carrier concentration in the solution is determined by the solubility of the carrier salt in the solvent. Finally, the performance of the FTMs strongly depends on the RH of the feed gas.

Based on above-mentioned critical issues, a set of guidelines can be established for the selection and design of the desirable CO₂ carrier in FTMs, as follows: (1) Liquid state at a wide range of temperatures. (2) Non-volatile at a broad range of temperatures and particularly at elevated temperatures. (3) Containing an amine functional group. (4) With a high concentration of the amine group.

1.2.2.2. Task specific ionic liquids-based facilitated transport membranes

During the last decade, room temperature ionic liquids (RTILs) have drawn considerable attention as a promising material that can be used as a CO₂ separation medium because of their distinctive properties, such as liquid state at ambient temperature, reasonable CO₂ absorption capacity, negligible vapor pressure, high thermal stability, and huge chemical diversity [40-43]. In particular, negligible vapor pressure and the liquid state at ambient

temperature are two unique features of RTILs that make them a desirable CO₂-selective separation medium. Scovazzo et al. [44] were the first to propose a novel type of supported ionic liquid membranes (SILMs), made by immersing a porous support in a RTIL, and demonstrated their excellent CO₂ transport properties and stable performance for more than 100 days. Compared to polymeric membranes, SILMs offered a better performance in terms of CO₂ permeability and CO₂/N₂ selectivity, which is due to the higher diffusion coefficient of gas species in a liquid-state medium. However, as the gas permeation mechanism of RTILs-based membranes is based on the simple solution-diffusion mechanism, their CO₂ separation performance is relatively poor at a low concentration of CO₂. In general, in the solution-diffusion mechanism, the permeability of the target gas is driven by the concentration gradient of the gas species between the feed and permeate sides of the membrane. The gas concentration on the feed side is determined by the gas absorbability of the membrane, while the permeate side concentration is usually kept constant (zero) through a vacuum or sweep system. Therefore, it can be said that the driving force of permeation through the membrane is controlled by the gas absorbability on the feed side of the membrane. The low CO₂ absorbability of the RTILs-based membrane, which is based on the physical dissolution (described by Henry's law), gives rise to lesser amount of absorbed CO₂ on the feed side of the membrane and therefore, a low driving force of separation. Then, the CO₂ permeability and CO₂/N₂ selectivity of RTILs-based membranes would not be high enough for a practical application.

Transcending the conventional amine-based chemical absorption, researchers introduced a novel type of ionic liquids, called task specific ionic liquids (TSILs), which

contain a CO₂-philic functional group capable of a reversible chemical reaction with CO₂. Bate et al. [45] were the first to show the great potential of TSILs as promising materials in CO₂ separation applications. The incorporation of an amine functional group into the structure of TSILs dramatically increased their CO₂ absorption capacity as a result of the chemical complexation of TSIL with CO₂. As displayed in Fig. 1.5, the CO₂ absorption capacity of a TSIL is markedly higher than that of an unreactive RTIL.

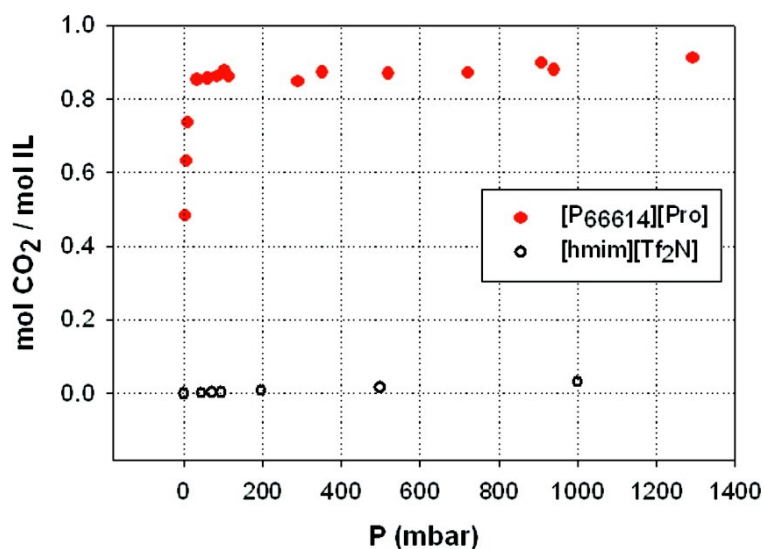
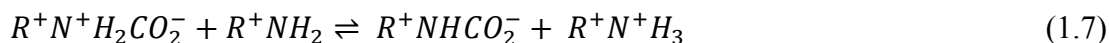


Fig. 1.5 Comparison of CO₂ solubility in terms of the molar ratio of a reactive IL, trihexyltetradecyl phosphonium proline, [P₆₆₆₁₄][Pro], with that of an unreactive IL, 1-hexyl-3-methyl-pyridinium bis(trifluoromethylsulfonyl)imide [hmim][Tf₂N], at 25°C [46]

The amine-based functional group can be tethered to the cation, anion, or both in the TSILs. The cation-tethered TSILs chemically react with CO₂ in accordance with the reaction mechanism proposed as follows [45]:



The CO₂ first reacts with the amine functionality on the IL according to eq. (1.6), followed by a reaction with another amine (on another IL) to form the carbamate. This reaction mechanism leads to one mole of CO₂ captured by two moles of IL (1:2 ratio), which is similar to the ratio observed for amine-based absorption units.

Hanioka et al. [47] for the first time utilized the cation tethered TSILs as the CO₂ separation carrier of a SILM-FTM. The results demonstrated the excellent CO₂ separation performance of *N*-aminopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₃NH₂mim][Tf₂N]- and *N*-aminopropyl-3-methylimidazolium trifluoromethanesulfone [C₃NH₂mim][CF₃SO₃]-based SILMs compared to the unreactive 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₄mim][Tf₂N]-based ones, especially at low CO₂ partial pressures (Fig. 1.6).

Myers et al. [48] also reported that the TSIL-based SILMs showed a higher CO₂/H₂ separation performance under dry conditions compared with the polymeric and RTIL-based membranes, because of the selective and reversible chemical reaction of CO₂ with the amine moiety in TSILs. Even though the CO₂ separation performance of the TSILs-based SILMs was higher than that of unreactive ILs-based membranes, it was still relatively low in order to develop a feasible membrane-based system for industrial applications, such as CO₂ separation from flue gases or H₂. The main reason for the relatively poor performance is the low CO₂ absorption capacity of cation-tethered TSILs.

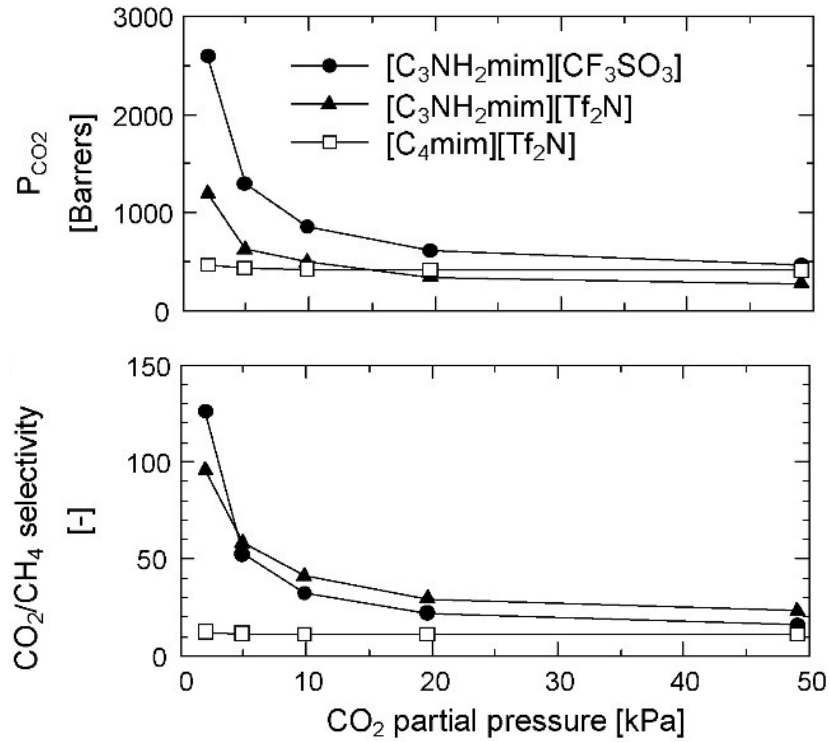
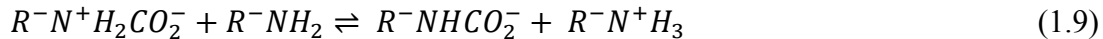


Fig. 1.6. Comparison of the performance of [C₃NH₂mim][Tf₂N]- and [C₃NH₂mim][CF₃SO₃]-based SILMs membranes with [C₄mim][Tf₂N]-based SILMs [47]

In this regard, Ohno et al. [49] developed a novel type of anion tethered TSILs containing amino acid groups, called amino acid ionic liquids (AAILs), which offer an excellent potential to be used as the CO₂ carrier of FTMs because of their high CO₂ absorption capacity (about 1:1 molar ratio). Gurkan et al. [50] experimentally demonstrated that a CO₂:IL molar ratio around 1:1 can be achieved with AAILs such as trihexyl (tetradecyl) phosphonium proline ([P₆₆₆₁₄][Pro]) and methioninate ([P₆₆₆₁₄][Met]). Such a high CO₂ absorption capacity was due to the different reaction mechanism of CO₂ with a TSIL. The proposed mechanism for anion tethered TSILs is as follows [50, 51]:





The theoretical calculations showed that the dianion formed in eq. (1.9) is chemically unstable, and the reaction will be terminated at eq. (1.8) [51]. The experimental results also confirmed that the 1:1 molar ratio is achievable for the anion-tethered TSILs (Fig. 1.7). With such a high CO₂ absorption capacity, it seems logical to expect that the anion tethered TSILs will display a better performance as the carrier of FTMs for CO₂ separation.

Taking advantage of this, our group pioneered the development of a novel type of AAILs-based SILM-FTMs with excellent CO₂ permeability and CO₂/N₂ selectivity under dry conditions and elevated temperatures. Kasahara et al. [52] demonstrated that AAILs-based FTMs presented a much higher CO₂ separation performance than that of RTILs-based SILMs under dry conditions, as shown in Fig. 1.8. This excellent CO₂ separation performance was mainly due to the higher CO₂ absorbability of AAILs, based on chemical absorption. The comparison of the CO₂ permeability of AAILs-based FTMs with that of cation-tethered TSILs (Fig. 1.6) also confirmed the better performance of anion-tethered FTMs.

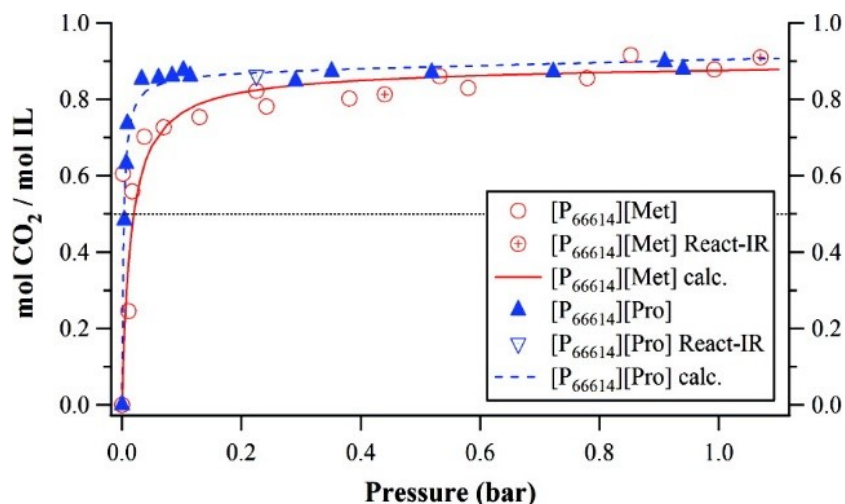


Fig. 1.7. CO₂ absorption of anion tethered TSIL [P₆₆₆₁₄][Pro] and [P₆₆₆₁₄][Met] at 22 °C [50]

In addition to their excellent CO₂ separation performance, the distinctive feature of AAILs-based FTMs was their excellent CO₂ permeability under a dry condition [52]. It was shown that the CO₂ separation properties of AAILs-based FTMs did not have a strong dependency on RH, while those of conventional FTMs severely deteriorated with a decreasing water vapor partial pressure in the feed gas. The promising CO₂ separation behavior of AAILs-based FTMs under low RH or dry conditions resulted from the liquid state of the carrier (i.e., AAILs). In fact, the intrinsically liquid state of AAILs at a dry condition and their wide range of temperatures eliminated the need for water presence in the system. In contrast, for conventional FTMs, water plays the crucial role of keeping the carrier in a liquid state. Therefore, it can be claimed that by developing the AAILs-based FTMs, the issues related to low stability (loss of the carrier or the solvent in a carrier-based solution) and poor CO₂ separation performance of conventional FTMs at low RH were addressed.

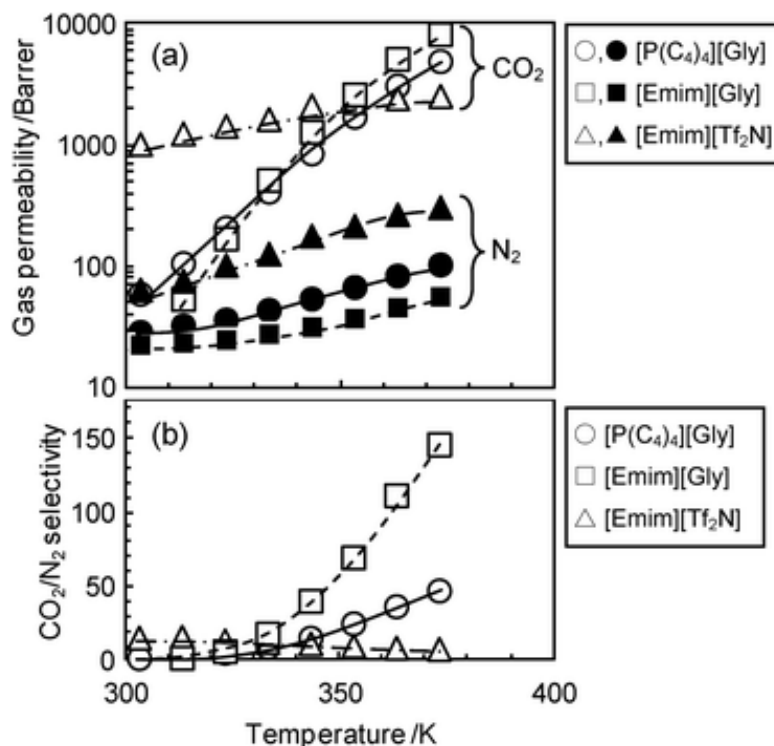


Fig. 1.8. (a) CO₂ and N₂ permeabilities and (b) CO₂/N₂ selectivity of [P(C₄)₄][Gly]-FTM, [Emim][Gly]-FTM and [Emim][Tf₂N]-SILM (CO₂/N₂ = 10/90 mol/mol, feed-side pressure (P_F) = sweep-side pressure (P_S) = 101.3 kPa, humidity = 0%) [52]

As can be seen in Fig. 1.8, in spite of the high temperatures, the CO₂ separation performance of AAILs-based FTMs is lower than that of RTILs-based SILMs at low temperatures. This low performance results from the higher viscosity of AAILs at low temperatures. In general, the viscosity of TSILs significantly increases upon reacting with CO₂ and forming the chemically CO₂-TSILs complex [51, 53]. It has already been demonstrated that the formation of a hydrogen-bonding network is the main reason for the drastic increase in viscosity [54]. Therefore, it can be said that the high CO₂ permeability of AAILs-based FTMs is more pronounced at an elevated temperature. Kasahara et al. [55] demonstrated the design of a novel TSIL such as tetrabutylphosphonium 2-cyanopyrrolide

([P₄₄₄₄][2-CNpyr]) with no proton donor that is mainly responsible for the viscosity increase of AAILs upon reaction with CO₂ by formation of a hydrogen bond network. This showed the feasibility of fabricating TSILs-based FTMs with a CO₂ separation performance higher than that of RTILs-based SILMs, even at low temperatures.

The potential of a membrane-based separation system for industrial applications is evaluated for two intrinsic parameters: permeability and selectivity. A membrane with high permeability and selectivity means a membrane with a more compact size and lower capital and operating costs. Therefore, the improvement in the performance of TSILs-based FTMs raises the possibility of using them for CO₂/N₂ separation. For this purpose, Kasahara et al. [56-58], our group, proposed some useful guidelines to improve the CO₂/N₂ separation performance of TSILs-based FTMs. They have demonstrated that the CO₂/N₂ selectivity of TSILs-FTMs can be controlled by choosing TSILs with low cation size [56]. In other words, the N₂ barrier property and therefore, the CO₂/N₂ selectivity of FTMs could be improved using TSILs with low molar volume, which is achievable with low cation size TSILs. It was also found that the CO₂ absorption amount and CO₂ permeability of FTMs can be improved by using dual amine functionalized TSILs as the carrier [58]. For example, under a humid condition, low CO₂ partial pressure (1 kPa), and elevated temperature (373 K), the CO₂ permeability of 1,1,1-trimethylhydrazinium glycinate ([aN₁₁₁][Gly]) was 50% and 400% higher than tetrabutylammonium glycinate ([N₄₄₄₄][Gly]) and tetramethylammonium glycinate ([N₁₁₁₁][Gly]), respectively, which contain one amine functional group in their chemical structure. This leads to a higher permeance of AAILs-based FTMs and therefore, to a smaller membrane area required for separation.

In summary, the promising physiochemical properties of TSILs such as low vapor pressure, intrinsically liquid state at ambient temperature and high CO₂ absorbability offer the possibility of fabricating TSILs-based FTMs with high CO₂/N₂ separation performance under various experimental conditions, such as elevated temperatures and dry condition, without the loss of carrier and decline in performance. In addition, by taking the advantage of tuning the chemical structure of TSILs, the separation performance of FTMs can be easily improved.

1.3. Stability of SILMs under high pressures

As it was mentioned in the previous section, the challenge associated with the loss of carrier or solvent in SLMs was addressed by utilizing ILs as CO₂-selective separation. Scovazzo et al. [44] confirmed the stable performance of RTILs-based SILMs for 100 days and Hanioka et al. [47] also demonstrated the good stability of TSILs-based FTMs without any loss of performance for more than 250 days. However, the performance of most of the ILs-based SILMs was evaluated under low trans-membrane pressure differences (< 2 atm). If the trans-membrane pressure difference exceeds the weak capillary forces, which are responsible for holding the IL inside the pores of the support, the ILs will leak out and the performance of SILM would be deteriorated. Therefore, the poor stability of SILMs at even moderate pressures is one of the critical issues that limit their potential for industrial applications.

1.4. ILs-based gel membranes

To overcome the drawback of poor stability of SILMs under high trans-membrane pressure differences, several researchers have been making great efforts to develop novel ILs-based membranes with good stability, such as polymerized RTILs, called poly(RTIL) [59], poly(ionic liquids)-copolymer membranes [60], poly(RTIL)/RTIL composite membranes [61-63], polymer-ILs gels [64], and ion-gels [65, 66]. One of the proposed approaches was the preparation of poly(RTIL) via polymerization of IL-based monomers [59]. The poly(RTIL)-based membranes showed a CO₂ separation performance similar to or slightly better than that of conventional polymeric membranes. Although the new platform of ILs-based membranes (i.e., poly(RTIL)) showed a great stability under high pressure conditions, the CO₂ separation performance was one order of magnitude lower than that of analogous SILMs. This was largely associated with the cross-linked and dense network structure of the poly(RTIL), which leads to a remarkable decrease in diffusion coefficients. In subsequent works, considerable efforts were made to improve the CO₂/light-gases separation performance via changing the structure of the poly(RTIL) backbone through modifications such as changing the chain length of the monomer cation [67] or using polar, oligo(ethylene glycol) appendages in the monomer structure [68]. While successes were achieved via tuning the structure of ILs-based monomers, the CO₂ permeabilities were still far lesser than those obtained with SILMs. In a different work, a series of phenolate-containing polyelectrolytes-based gel membranes were prepared via the post-polymerization treatment of poly(4-vinylphenol) with ILs [60]. The poly(RTIL)-copolymer membrane showed a CO₂ permeability of around 1200 barrer with a CO₂/N₂ selectivity of 68 at 288 K,

which exceeds the Robeson upper bound. However, CO₂/N₂ selectivity significantly decreased with increasing temperature.

Bara et al. fabricated a novel type of poly (RTI)/RTIL composite membranes with poly(RTIL) as the polymer network impregnated with non-reactive, free RTIL. The free RTILs incorporated into the poly(RTIL) matrix brought larger diffusivity coefficients compared to the solid poly(RTIL) network. Thus, diffusivity enhancement was the dominating factor for increasing CO₂ permeability and CO₂/N₂ selectivity. For example, the CO₂ permeability of a poly(styrene-based) membrane was increased from 16 to 60 barrer via incorporation of 20 wt% 1-ethyl-3-methylimidazolium bis(trifluoromethane)-sulfonimide [C₂mim][Tf₂N] [61]. However, the amount of free RTILs incorporated into the poly(RTIL) network was limited because of the observed trade-off between CO₂ permeability and mechanical strength. This means that by increasing the free RTIL content in a poly(RTIL)/RTIL membrane, its CO₂ permeability was increased at the expense of a deteriorated mechanical strength and vice versa. A similar trade-off behavior was reported for PVDF-HFP-based polymer-IL gel membranes [64]. As shown in Fig. 1.9, the Young's modulus of polymer-IL blend membrane was markedly diminished by increasing the IL content.

The fabrication of ion-gel membranes with a high CO₂ separation performance by mixing a small amount (2-5 wt%) of a low-molecular weight organic gelator (LMOG) with ILs, called ion-gel, was another proposed approach [66]. In this platform, the IL played the role of the solvent and the membrane network was formed via cross-linking of LMOG at an elevated temperature. This ion-gel membrane could retain a larger amount of IL (50-90 wt%)

and gave CO₂ permeability and CO₂/N₂ selectivity of 650 barrer and 22, respectively. In the same way, ion-gel membranes showed a trade-off behavior between CO₂ permeability and mechanical strength as a function of LMOG loading. The higher gelator content brought about an enhancement in mechanical strength and a decrease in CO₂ permeability, and vice versa.

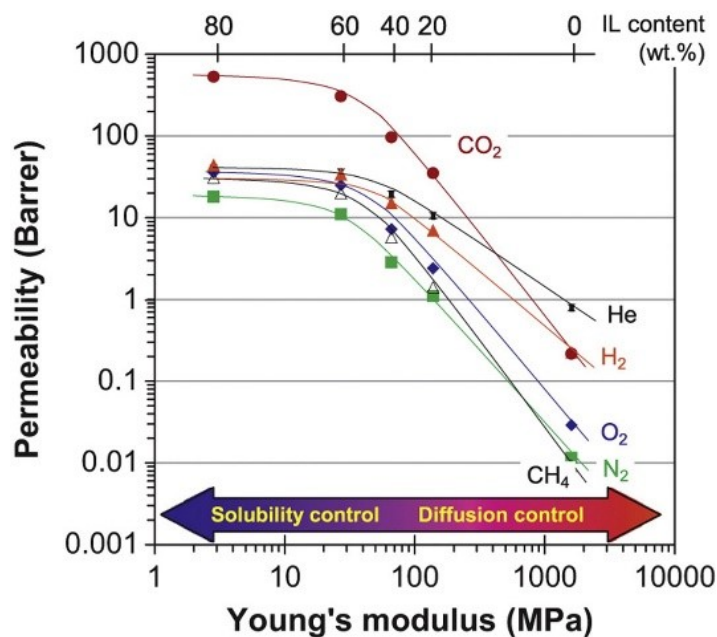


Fig. 1.9. Correlation between gas permeabilities and Young's modulus of PVDF-HFP-based polymer-IL gel membranes [64]

Based on the above-presented literature review, it can be said that the ion-gel concept seems to be the most promising and effective approach to address the poor mechanical stability of SILMs. However, several issues should be solved. First, the use of a gel network normally is accompanied by a permeability decline because of the higher diffusivity resistance. Thus, an ILs-based gel membrane should contain a larger amount of IL, lower polymer content, and lower degree of cross-linking. Second, the mechanical strength of ion-

gel membranes containing a large amount of ILs is too low and the fabrication of a thin ion-gel membrane with a weak gel network would be an obstacle. Finally, most of the proposed ion-gel membranes were composed of unreactive RTILs and their CO₂ separation performance is not attractive because of their low CO₂ absorbability, particularly at low CO₂ concentrations.

According to the above-mentioned issues, a desirable ion-gel membrane for CO₂ separation at low CO₂ partial pressures should possess the following features: (1) High CO₂ permeability and CO₂/N₂ selectivity, (2) High mechanical strength, (3) Large content of ILs, and (4) Feasibility of fabrication with a small thickness. Using AAILs as the solvent of a gel network with good mechanical strength appears to be an appropriate way to meet these requirements. With the advantage of high CO₂ absorbability, AAILs can improve the CO₂ separation performance of ion-gel membranes. The incorporation of AAILs into a tough gel network can fulfill the requirements for achieving ion-gel membranes with high performance and good stability. There are few reports on the preparation of AAILs-based ion-gels. Kagimoto et al. [69] reported a novel type of AAILs-based ion-gel by simple mixing AAILs with RTILs in order to make a gel network applicable to electronic devices. The same group also prepared a thermotropic gel via adding a phosphonium-type zwitterion to AAILs [70]. However, the reported ion-gels were not appropriate for gas separation membranes because of the low mechanical strength. Our group was the first to develop a new type of polymeric ion-gel membranes containing AAILs with good CO₂ permeability and CO₂/N₂ selectivity [71]. The AAILs were used as the solvent of ion-gel membranes and the carrier for AAIL-based FTMs. Dimethylacrylamide (DMAAm) or vinylpyrrolidone (VP) were used as

monomers to form the polymer network of the ion-gel membrane via free-radical polymerization. For example, a PVP-[P₄₄₄₄][Pro] ion-gel membrane with a thickness of 300 μm and consisting of 70 wt% of [P₄₄₄₄][Pro] displayed a CO₂ permeability and CO₂/N₂ selectivity of 6700 barrer and 180, respectively, far better than the unreactive ILs-based ones [71]. Only focusing on their CO₂ separation performance, there is no doubt that AAILs-based ion-gel membranes have higher potential for CO₂/N₂ separation applications. However, the developed ion-gel membrane also showed a trade-off between CO₂ permeability and mechanical strength. In addition, because amine groups existing in AAILs limited the polymerization degree of monomers, higher loadings of cross-linker were used to form a gel network appropriate for membrane preparation. This higher loading of cross-linker induced a brittle-rigid ion-gel network that poses a challenge to the fabrication of the thin ion-gel membrane. Therefore, it is required the preparation of an AAILs-based ion-gel membrane with an appropriate network structure that not only has a high CO₂ permeability but also possesses good mechanical strength.

1.5. Development of tough and high AAIL content ion-gels with excellent CO₂ separation performance

As mentioned above, all fabricated ILs-based ion-gel membranes, containing RTILs or AAILs as solvent, suffered from low mechanical strength at higher loadings of ILs. In this study, a novel type of AAILs-based ion-gel membrane with extraordinary mechanical strength and excellent CO₂ separation properties was proposed based on a new concept.

To date, all proposed ion-gel membranes contain a single polymer network and an IL as solvent. The typical trade-off between ILs content (CO_2 permeability) and mechanical strength observed for all categories of ion-gels implies that fabrication of an ion-gel with a distinctive network structure without showing that trade-off behavior is the current challenge. In the last decade, several types of hydrogels such as tetra-PEG hydrogels [72], nanocomposite hydrogels [73, 74], sliding gels [75] and double network (DN) hydrogels [76, 77] with excellent mechanical properties have been developed and become attractive in wide range of applications, such as medicine and tissue engineering [78, 79]. The unique feature of these hydrogels, with around 90 wt% water as solvent, is their excellent mechanical strength. Beyond the tough hydrogels, it is possible to extend these concepts to the fabrication of ion-gel membranes with a large amount of AAIL and great mechanical strength.

Tetra-PEG (TPEG) gels are synthesized by combining two well defined symmetrical tetrahedron-like macro monomers with tetra-arm poly(ethylene glycol) (tetra-PEG) units that have tetra amine (TAPEG) and activated ester (TNPEG) terminal groups. These TPEG gels showed an excellent mechanical strength behavior (with a fracture compressive stress over 2 MPa) while containing a large amount of water. TPEG hydrogels are neutral and do not change to a highly swollen state when immersed in water [72].

Nanocomposite (NC) hydrogels contain an inorganic phase (such as clay) and an organic phase, which consists of water soluble amide-based monomers such as N-isopropyl acrylamide, (NIPA), N,N-dimethylacrylamide (DMAA), and acrylamide (AAm). An amide-based monomer has adequate interaction with a clay surface. It was demonstrated that NC

hydrogels with a large content of water presented excellent mechanical, optical, and swelling/deswelling properties [73, 74].

Sliding gels are another class of hydrogels with a good mechanical strength proposed by Okumura et al. [75]. In this type of network, the crosslink points are not fixed but sliding. The polymer chains in the polyrotaxane gel can pass through cross-links to equalize the tensions cooperatively and prevent stress localization, resulting in a high mechanical strength.

Double network hydrogels have an interpenetrating polymer network (IPN) structure, containing an electrolyte, a rigid and highly cross-linked first network, and a soft, ductile, and loose second network [76, 77, 79]. At the optimized condition of preparation, DN hydrogels with more than 90 wt% water as the solvent, exhibited an extraordinary tensile fracture stress of more than 1 MPa and a compressive fracture stress over 15 MPa (Fig. 1.10). The cross-linking degree of the first network and the molar ratio of the second to first networks are the two parameters determining the toughness of hydrogels [76].

Among the above-presented tough gels, the DN hydrogel concept is the most promising and attractive approach for the preparation of tough and high AAIL content ion-gel membranes. Because the AAILs as a solvent restricts the polymerization degree, using the tetra-PEG gel concept for the fabrication of the ion-gel is a challenge. In the case of NC hydrogels, the compatibility of an AAILs consisting of cation and anion with inorganic phase (such as clay) is also the major obstacle. A DN gel seems a suitable choice for the preparation of tough AAILs-based ion-gel membranes because of the following reasons. First, because the first network of DN hydrogels was prepared from electrolyte-based monomers, it can be expected that a possible ionic interaction between the first network and the AAILs might lead

to a better holding property of AAILs in the ion-gel network. Second, in accordance with the previous study carried out by Kasahara et al. [71], amide-based monomers, generally utilized as the second network monomers of a DN hydrogel, have shown good compatibility with AAILs. Therefore, a good combination of an electrolyte network (providing a better AAIL holding property) and a ductile amide-based network (bringing good compatibility of the gel network with AAIL) raises the possibility of preparing tough ion-gel membranes. Third, DN hydrogels showed the highest tensile and compressive fracture stresses among all the proposed tough gel networks. Therefore, the DN concept was applied for the fabrication of tough and high-CO₂ performance AAILs-based ion-gel membranes, with good stability under the pressurized condition.

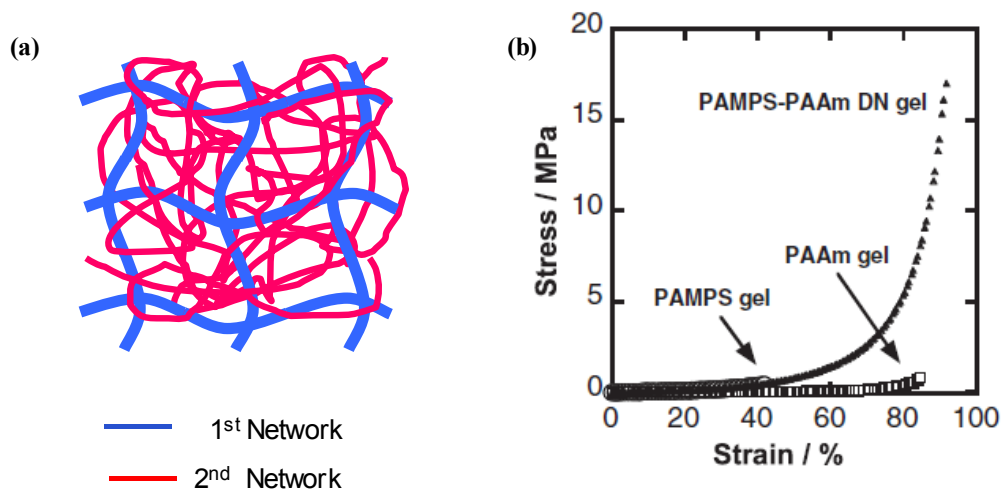


Fig. 1.10. (a) Schematic illustration of a DN hydrogel and (b) stress-strain curves of first network gel, second network gel, and DN gel [76]

The toughening mechanism of a DN hydrogel is explained based on the sacrificial bond concept [77-79]. The brittle and highly cross-linked first network breaks into small clusters under the applied stress, which efficiently disperses the stress around the crack tip

into the surrounding zone. This irreversible deformation, known as the necking phenomenon, can be observed during uniaxial loading (Fig. 1.11). Thus, the fragmented first network serves as sacrificial bonds to toughen the DN hydrogel. The role of the second network is also crucial for the toughening mechanism of DN gels. A second network with a low cross-linking degree and a high molar ratio compared to the first network is required in order to bring a network with flexible chains and good fluidity, which prevent the crack growing from microscopic to macroscopic level through an effective relaxation of the applied stress and dissipation of the crack energy. According to the above-mentioned reasons, there are several parameters to be optimized, such as the first and the second network selection, the cross-linker loading of networks, and the ratio of second to first network. Most importantly, the compatibility of AAILs with the gel networks plays a crucial role. The selection and combination of the appropriate first and second networks based on the DN concept raise the possibility of fabricating tough and high performance ion-gel membranes.

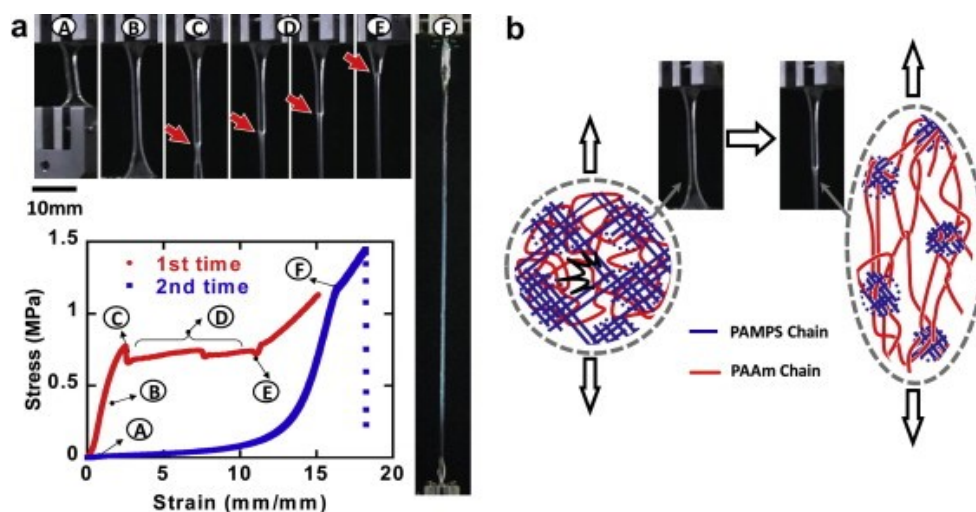


Fig. 1.11. (a) Loading curves of a PAMPS/PAAm double network (DN) gel under uniaxial elongation (necking behavior) and (b) Illustration of the network structure of a DN gel before and after necking [78]

1.6. Objective of this study

As explained in the previous section, the overall objective of this study is the development of a novel type of TSILs-based facilitated transport ion-gel membranes with high CO₂ separation performance, high mechanical strength, and good stability under pressurized conditions, in order to overcome the stability issues related to TSILs- or RTILs-based SILMs. Because of the unique structure and extraordinary mechanical properties of DN hydrogels, the TSILs-based ion-gel membranes were developed based on the DN concept. To date, there has not been any report on the utilization of the DN concept for fabricating ion-gel membranes. The overall objective of this research has been divided into three sub-objectives.

Objective 1: *To development a novel type of AAILs-based ion-gel membranes with excellent CO₂ separation performance, good mechanical properties, and good stability under a pressurized condition.*

The first objective of this study was to develop a novel ion-gel network that meets all the above-mentioned requirements based on the DN concept. Thorough experimental investigations were conducted and the parameters determining the CO₂ separation performance and mechanical properties of ion-gel membranes were identified. Based on the achieved results, an AAIL-based ion-gel membrane was fabricated at optimized conditions. Its stability under pressurized conditions and its long-term stability were studied.

Objective 2: *To demonstrate the great potential of the developed AAILs-based DN ion-gel membrane for air capturing applications.*

The CO₂ separation performance of the fabricated DN facilitated transport ion-gel membrane was evaluated for air capturing applications under very low CO₂ partial pressures (500-1000 ppm) and a wide range of temperatures and relative humidities. The developed ion-gel membrane demonstrated a CO₂ permeability of one order of magnitude higher than that of conventional FTMs. The effect of parameters such as CO₂ partial pressure, RH, and temperature on the performance of a ion-gel membrane were investigated.

Objective 3: *To propose a new approach for the fabrication of TSILs-based DN ion-gel membrane via a casting method.*

The developed DN ion-gel membrane, as described in previous sections, was prepared with a mold-injection method, in which the thickness of the ion-gel membrane was adjusted via a PTFE spacer placed between sandwiched glass plates. This approach was not applicable to a thin ion-gel membrane preparation. In this part of the study, a new approach based on casting was proposed to fabricate the DN ion-gel membrane. This was the first report on the preparation of DN hydrogel and DN ion-gel membranes via a casting method. This approach raises the possibility of fabricating very thin DN ion-gel membranes.

1.7. Dissertation organization

This dissertation is divided into 5 chapters and is organized in the following way:

Chapter 1 presents an overview of the essential background relevant to the CO₂ capture challenges and the previous works on membrane-based CO₂ separation. The research issues and challenges, objective, strategies, and the scope of this dissertation are provided.

Chapter 2 describes the fabrication of AAILs-based DN ion-gel membranes. Thorough and fundamental studies have been undertaken to understand the CO₂ permeation

mechanism through the membrane and the effect of AAIL content on CO₂ transport properties. The mechanical strength of ion-gel bulks and films with different content of AAILs was also measured. The relationship between ion-gel thickness and CO₂ permeance was also investigated. Finally, the CO₂ separation performance of the DN ion-gel membrane under different trans-membrane pressure differences and long-term stability at high pressures were evaluated.

Chapter 3 demonstrates the advantages of the developed AAIL-based DN ion-gel membranes over the conventional FTMs for air capturing applications and the CO₂ separation from gas streams containing very low concentration of CO₂ (500-1000 ppm), under humid condition and different temperatures. The DN facilitated transport ion-gel membrane showed a CO₂ permeability of one order of magnitude higher than conventional FTMs.

Chapter 4 describes the new approach proposed for the fabrication of a TSILs-based DN ion-gel membrane via a novel casting method. The effect of different parameters on the CO₂ separation performance of the ion-gel were studied, such as TSIL content, CO₂ partial pressure, and cross-linker loading of the first network. The relationship between the ion-gel thickness, the CO₂ permeance, and the pressure stability of a high TSIL-content ion-gel membrane were investigated. The effect of the cross-linker content of the first network on the structure of an ion-gel network was assessed through cyclic loading tests.

Chapter 5 presents a summary of the findings of this thesis.

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Chapter 2

Fabrication of AAILs-based facilitated transport DN ion-gel membranes for CO₂ separation

2.1. Introduction

DN hydrogels have attracted considerable attentions due to their great mechanical properties. It was reported that DN hydrogels containing more than 90 wt% water as the solvent showed tensile and compressive fracture stress of more than 1 and 15 MPa, respectively [1, 2]. Therefore, by extending the DN concept for fabrication of ion-gel membranes containing AAILs, it is possible to address the “CO₂ permeability-mechanical strength” trade-off of ion-gels consisting of a large amount of the IL. Here, I fabricated a novel type of AAILs-based DN ion-gel membranes demonstrating excellent CO₂ separation performance, high mechanical strength and outstanding stability under the pressurized conditions.

As it is the first report on the DN ion-gel membranes, fundamental studies were carried out for a better understanding of the properties of developed membranes. The effect of the AAIL content on the CO₂ separation performance and mechanical strength (tensile and compressive fracture stress) of DN ion-gel membranes were investigated. In addition, the network structure of the ion-gel membrane was elucidated by direct observation of the loading-unloading behavior of ion-gel membranes through mechanical properties measurements. It was experimentally indicated that DN ion-gel membranes possess extraordinary mechanical strength. The permeation mechanism of CO₂ and N₂ was also

confirmed through gas permeation test at different CO₂ partial pressures. The excellent stability of DN ion-gel membrane with best CO₂ permeation properties was demonstrated under pressurized conditions. Finally, the rate-controlling step of permeation through the ion-gel membrane was also determined by measuring the permeance of DN ion-gel membranes with different thicknesses.

For this study, 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) and dimethylacrylamide (DMAAm) were chosen as the monomers for the first and second networks, respectively. For the fabrication of AAIL-based DN gels, the most important parameter is the compatibility between AAILs and the polymer networks. In the previous report, I found that polyvinylpyrrolidone (PVP) and polydimethylacrylamide (PDMAAm) exhibited good compatibility with several phosphonium based AAILs [3]. As PVP and PDMAAm are neutral polymers, I 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 a high osmotic pressure inside the gel during immersion in water. The large osmotic pressure between inside and outside of the gel leads to full swelling of the gel and also the incorporation of a large amount of AAILs into the gel matrix.

Proline-type AAILs with different cation sizes were selected as carriers of DN ion-gel FTMs because of following reasons. First, it was previously reported that proline-based AAILs have better CO₂ separation performance [4]. Second, compatibility of proline-based AAILs with DMAAm for fabrication of ion-gel membrane was confirmed. By choosing the

AAILs with different sizes of cation, it was also possible to control and improve the CO₂/N₂ separation factor of DN ion-gel membranes [5].

2.2. Experimental

2.2.1. Materials

Tetrabutylphosphonium hydroxide ([P₄₄₄₄][OH], 40 wt.% in water) and proline (>99%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and Tokyo Chemical Industry Co. (Tokyo, Japan), respectively. These were used to synthesize [P₄₄₄₄][Pro] according to a previously reported method. The chemical structure of the resulting [P₄₄₄₄][Pro] was confirmed by ¹H NMR (Bruker Avance 500, Bruker Bio Spin) and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics) spectroscopy. Of the reagents for AAIL-based tough gel preparation, 2-acrylamido-2-methylpropanesulfonic acid (AMPS, >99.8%), N,N-dimethylacrylamide (DMAAm, >99.5%), and 2-oxoglutaric acid (OA, >99%) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan), while N,N'-methylenebisacrylamide (MBAA) was supplied by Wako Pure Chemicals Industry Ltd. (Osaka, Japan). All reagents were used without further purification.

2.2.2. Preparation of AAILs

A 100 mL of triethylphosphine (1 M in THF) was mixed with 15 g of 1-bromopentane and stirred for 6 h at 353 K. Subsequently, 200 mL of hexane was added to prepared solution and stirred for at least 12 h. Finally, the solution was evaporated at 313 K in vacuum for 3 h and [P₂₂₂₅][Br] was obtained (the chemical structure was confirmed by ¹H NMR spectroscopy (Bruker Advance 500, Bruker BioSpin)). [P₂₂₂₅][Br] (40.0 g) was dissolved in water (40.0 g), and the resulting solution was treated with a basic anion exchange resin (142.0 g) to form

[P₂₂₂₅][OH].

[P₄₄₄₄][Pro] and [P₂₂₂₅][Pro] were synthesized by a neutralization procedure written in elsewhere [6, 7]. An aqueous solution of [P_{xy}][OH] (x, y: carbon number of the alkyl groups, x = 4 or 2, y = 4 or 5) was added to an aqueous solution dissolving an equimolar proline to prepare the [P_{xy}][Pro] salts, with water formed as a byproduct. The product was dried in vacuum for more than 8 h at 313 K.

2.2.3. Preparation of DN ion-gel membrane

For the preparation of AAILs-impregnated DN ion-gel membranes, a DN hydrogel with a suitable combination of first and second networks was fabricated via multi-step UV polymerization procedure, schematically shown in Fig.2.1. The thickness of hydrogel film was adjusted by PTFE spacer used between two quartz plates. 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) and dimethylacrylamide (DMAAm) were chosen as the monomers for the first and second networks, respectively. In the first step, AMPS gel film was prepared via UV-light initiated polymerization of aqueous solution containing AMPS (1 M, with respect to solvent), N,N'-methylenebisacrylamide (MBAA) as a crosslinker (4 mol%, with respect to monomer), and 2-oxoglutaric acid (OA) (0.1 mol%, with respect to monomer) as an initiator. The compositions of solutions of the first and second networks are summarized in Table 2.1. The weak hydrogel film was immersed in a pre-DN solution consisting of DMAAm (4 M, with respect to solvent), OA (0.1 mol%) and NaCl (0.08 M) for at least 24 h. Here, NaCl was added to the pre-DN solution in order to control the swelling ratio of PAMPS network for easy manipulation of the hydrogel film [8]. Subsequently, the swelled hydrogel film was put under UV for 8 h to fabricate a pre-reinforced DN hydrogel film. Because the

mechanical strength of the pre-reinforced DN hydrogel was improved by partially introducing of DMAAm chain into the first network, the pre-reinforced DN hydrogel film can be easily manipulated by hands. In the next step, the pre-reinforced DN hydrogel film was immersed in distilled water for at least 24 h in order to remove NaCl. The washed hydrogel film was immersed in an aqueous solution dissolving DMAAm (2 M) and OA (0.1 mol%) for 24 h, and finally put under UV for 8 h to prepare a tough complete double network hydrogel film. The DN hydrogel films were washed by distilled water for more than 4 days before using them for the AAIL-based DN ion-gel films.

Table 2.1. Composition of the first and second networks used for DN hydrogel preparation

	Reagent	Amount
1 st Network	AMPS	1.4506 g
	MBAA	0.0432 g (4 mol %)
	OA	0.0010 g (0.1 mol %)
	water	7 ml
Pre-reinforced Network	DMAAm	39.65 g (4 M)
	OA	0.0544 g (0.1 mol %)
	NaCl	0.4675 g
	Water	100 ml
2 nd Network	DMAAm	19.83 g
	OA	0.0292 g
	Water	100 ml

mol.% = (mole of /mole of monomer), M = (mmole of monomer/mL of solvent)

To prepare the AAIL-based ion-gel films, the DN hydrogel film was immersed in an aqueous solution of AAIL for 24 h. Impregnation of AAILs in DN hydrogel matrix was confirmed by measuring the AAIL content in the DN gel. The obtained DN gel film containing AAIL/water mixture was dried at room temperature for 24 h and finally, put into the vacuum oven at 373 K under for 10 h to remove water and any possible non-reacted monomers

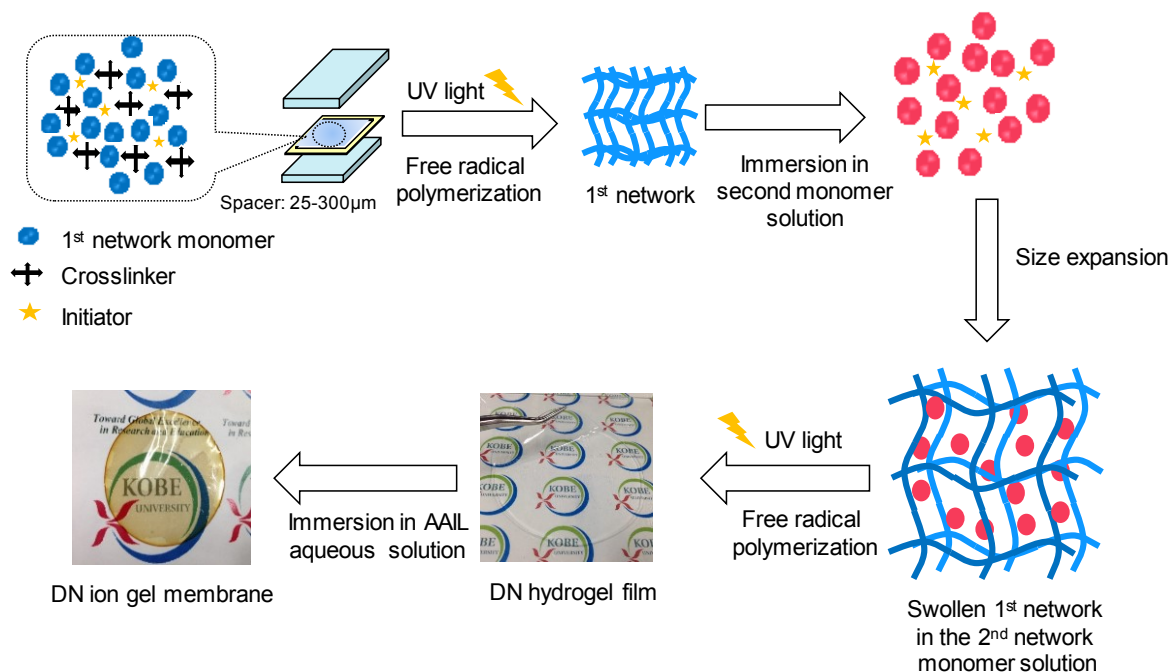


Fig.2.1. Schematic illustration of DN ion-gel membrane preparation via multi-step polymerization.

2.2.4. Measurement of AAIL content in DN ion-gels

The AAIL content in the fabricated DN gel films was measured by the following procedure. Firstly, the AAIL-based DN ion-gel samples with different AAIL content were prepared. Small pieces of DN hydrogel were immersed in aqueous solutions containing 10, 30, 40, 50, 60, 70, and 80 wt% of AAIL for 24 h. Then, the DN gel sample containing AAIL/water mixture was taken out and the equilibrium concentration of AAIL in the aqueous solution was measured for every sample. The removed DN gel samples were dried at room temperature for at least 10 h followed by complete drying in a vacuum oven at 373 K for 5 h. The weight of the prepared samples, m_1 , were immediately measured. Subsequently, the AAIL in the samples were completely extracted to obtain the only polymer-based skeleton of PAMPS/PDMAAm double-network. The DN ion-gel samples were immersed in a large

amount of distilled water (500 cm³) for 48 h in order to remove the AAILs. The distilled water was changed with fresh water every 10 h to make sure all AAIL being removed from the gel. After complete AAIL extraction, the obtained DN hydrogels were put into the vacuum oven at 373 K for 5 h in order to evaporate all water, and finally, the weights of the dried DN skeleton, m_2 , were measured. The AAIL content in each sample was calculated by the following equation.

$$\text{AAIL content (wt\%)} = \frac{m_1 - m_2}{m_1} \times 100 \quad (2.1)$$

The relationship between the AAIL content and the equilibrium AAIL concentration in the AAIL aqueous solution used for the preparation ion-gel samples are presented in Fig. 2.2.

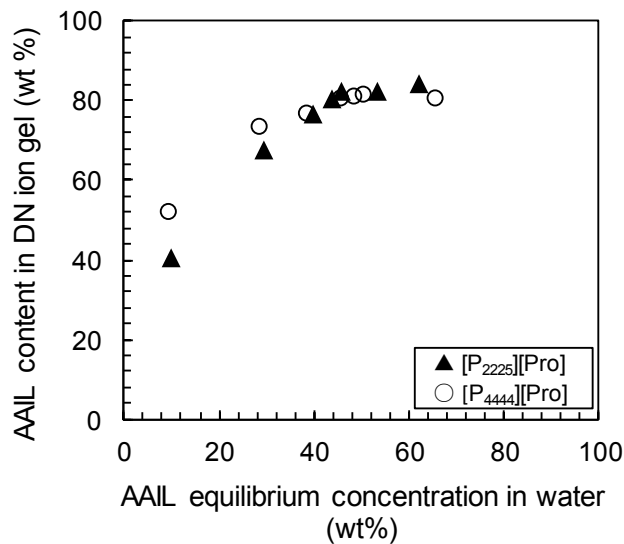


Fig. 2.2. Relationship between AAIL content and equilibrium AAIL concentration in the AAIL/water mixture used for DN ion-gel preparation.

2.2.5. Gas permeation measurement

CO₂ and N₂ gases with 99.9% purity were used for gas permeation tests. A schematic of the experimental set-up is shown in Fig. 2.3(a). The gas transport properties of the ion-gel membrane were measured by using a flat-type permeation cell (Fig. 2.3(b)) that was placed in a thermostat oven (YAMATO Scientific Co. Ltd., Japan) adjusted to the desired temperature. The permeation cell (GTR TEC Co., Japan) is made of stainless steel with an effective permeation area of 9.51 cm². A model feed gas was prepared by mixing CO₂ and N₂ under dry condition. The flow rates of CO₂ and N₂ were controlled by mass flow controllers (Hemmi Slide Rule Co. Ltd., Japan) to adjust the mole fraction of each gas. The total flow rate of the feed gas was adjusted to 200 mL/min at 298 K, and 101.3 kPa. The flow rates of the feed streams were measured by soap-film flow meters (HORIBA STEC Ltd., Japan). The feed gas was pre-heated by a coiled heat exchanger and introduced into the cell. The permeability tests were carried out at 373 K. The feed side pressure was maintained at atmospheric pressure. Helium was supplied to the permeate side of the cell as a sweep gas through a coiled heat exchanger at the flow rate of 2.98×10^{-5} mol/s at 298 K, 101.3 kPa. The flow rate of the sweep gas was also measured by a soap-film flow meter (HORIBA STEC Ltd.). The pressure on the sweep side was also maintained at almost atmospheric pressure. The sweep gas containing the permeated CO₂ and N₂ through the AAIL-gel films was introduced to a gas chromatograph (Shimadzu GC-8A, column: activated carbon, 1 m) to determine the composition of permeate.

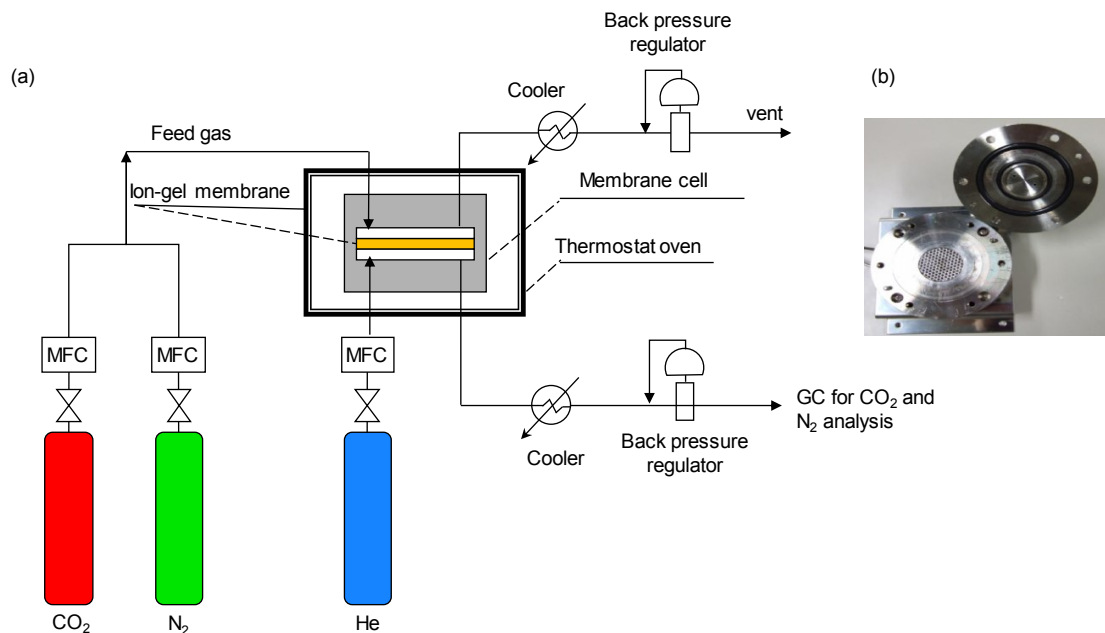


Fig. 2.3. (a) Schematic diagram of gas permeation setup used in this study and (b) flat-type permeation cell (MFC refers to mass flow controller).

2.2.6. Mechanical strength measurement

Compressive and tensile stress-strain measurements were performed using an automatic recording universal testing instrument (Autograph AGS-X, Shimadzu Co.). A cylindrical sample of diameter 4.7 mm and height ca. 2.5 mm was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 10%/min. Tensile tests were performed using a dumbbell specimen of width, height, and thickness 4.0, 30.0, and 0.5-0.7 mm, respectively. The specimen was held on the instrument between clamps and the tensile stress was loaded at a strain rate of 100%/min. The tensile stress was calculated as the force normalized by the cross-section area of each sample. For cyclic loading tests, the tensile stress was measured at different loading intervals with similar strain rate until the sample fractured.

2.3. Results and discussion

2.3.1. Mechanical strength

In order to demonstrate the excellent mechanical strength of fabricated ion-gel films and bulks, tensile and compressive fracture stresses were measured. For this purpose, I compared the compressive fracture stress of the bulk of single network (SN) PVP ion-gel containing 70 wt% of [P₄₄₄₄][Pro], reported in the previous work done by Kasahara et al. [3], with the PAMPS/PDMAAm-based DN ion-gel containing 80 wt% of similar AAIL. As can be clearly observed from Fig. 2.4(a) and Fig. 2.4(b), the developed PAMPS/PDMAAm DN ion-gel is extraordinary tough and not broken under compressive stress more than 20 MPa, while the SN PVP ion-gel fractured at stress less than 1 MPa. The stress-strain curves of compression test shown in Fig. 2.5(a) also revealed that DN ion-gel bulk containing 80 wt% of [P₄₄₄₄][Pro] is remarkably tougher than the SN PVP ion-gel (25 times). This result point out that DN structure gave rise to a remarkable improvement of the mechanical strength of the ion-gels while retaining the large amount of AAIL (more than 80 wt%).

In the next step, the tensile fracture stress of PAMPS/PDMAAm DN ion-gel film containing 80 wt% of [P₄₄₄₄][Pro] was measured. Fig. 2.4(d) illustrates the outstanding mechanical strength of the ion-gel film. The corresponding stress-strain curve is also presented in Fig. 2.5(b). To our knowledge, this is the highest value of the tensile fracture stress reported for ion-gel films containing such a large amount of AAIL.

I also considered the effect of AAIL content on the tensile fracture stress of DN ion-gels containing [P₂₂₂₅][Pro] and [P₄₄₄₄][Pro]. The results are displayed in Fig. 2.5(c) and 2.5(d), respectively. The tensile fracture stress of both DN ion-gels was increased with decreasing

the content of AAIL. This trend seems logical because the density of polymer network in ion-gel films with the lower loading of AAILs would be higher and therefore, the mechanical strength was increased. The most important point is that DN ion-gel films containing both types of AAILs possessed tensile fracture stress more than 0.6 MPa for the AAIL contents of higher than 70 wt%.

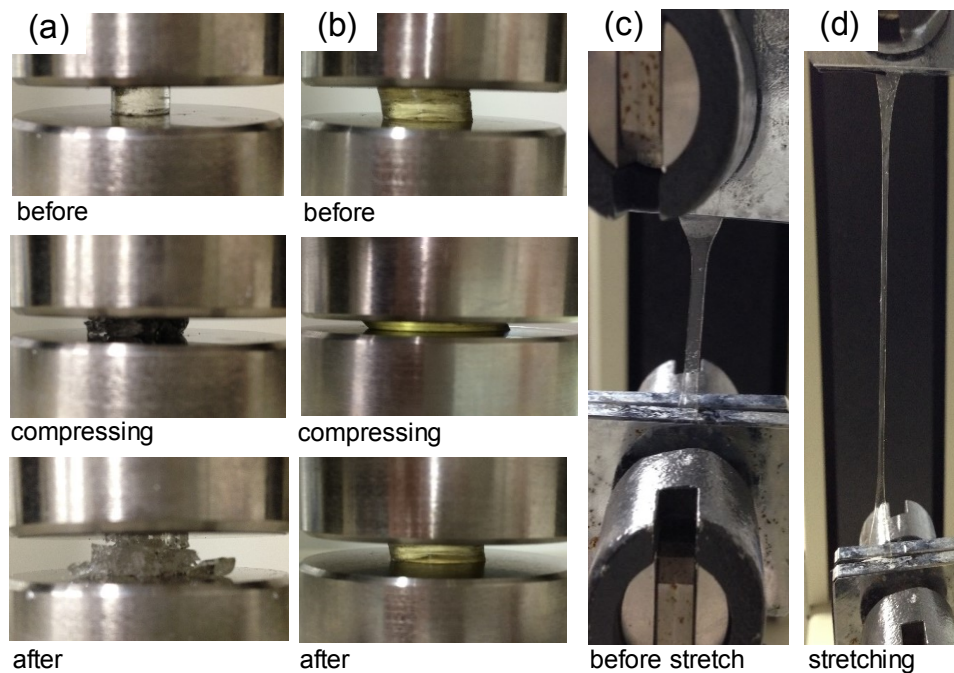


Fig. 2.4. Photo of (a) SN PVP-based ion-gel before (top), under (middle), and after(bottom) compression (b) PAMPS/PDMAAm-based DN ion-gel before, before (top), under (middle), and after(bottom) (c) DN ion-gel film before, and (d) under stretching.

This extraordinary mechanical strength of developed DN ion-gel membranes can be explained based on the toughening mechanism of DN gels proposed by Gong et al. [1, 2, 9]. In the fracture process of the DN gels, the applied stress initially causes an internal fracture of the brittle first network around the crack tip that efficiently dissipates energy and therefore, enhances the fracture propagation resistance. The brittle first PAMPS network is fragmented

into small clusters that function as the sacrificial bonds to dissipate the energy upon crack propagation. Thus, breaking up of highly cross-linked/brittle first network into small clusters, known as sacrificial bond concept, is mainly responsible for the toughening behavior of DN gels. A ductile and loosely cross-linked second network with flexible chains (in this study PDMAAm), which is entangled with the fractured PAMPS clusters and other PDMAAm chains, extends extensively under stress to keep large deformation. In fact, the second network effectively absorbs the crack energy by deforming the network conformation and isotropically dissipates the mechanical stress [1, 2, 9, 10]. As a conclusion, the attractive mechanical strength of DN ion-gels is mainly attributed to an appropriate combination of two networks with the different structures that effectively dissipate the applied stress.

In order to elucidate the network structure of the developed ion-gels, a more detailed insight into the structure is given by the cyclic loading-unloading test. Fig. 2.6 shows the successive loading-unloading test of DN ion-gel membranes containing 80 wt% of [P₄₄₄][Pro] or [P₂₂₂₅][Pro]. Both ion-gel membranes showed a softening behavior during the loading-unloading stress-strain test. This prominent softening phenomenon is a characteristic feature of gels with the DN structure [2, 10]. It was already reported that this softening behavior is largely associated with the irreversible structural change because of the fragmentation of the brittle first network chains during deformation. The main conclusion that can be drawn from above results is as follows: First, the excellent mechanical strength of ion-gel membranes with a large amount of AAILs was confirmed. Second, the network structure of developed ion-gels was verified as well. This excellent mechanical strength of ion-gel membranes raises the possibility of the fabrication of thin ion-gel membranes with

good mechanical strength along with high CO₂/N₂ separation performance. In the next sections, a comprehensive investigation will be carried out on CO₂ permeation properties of DN ion-gel membranes.

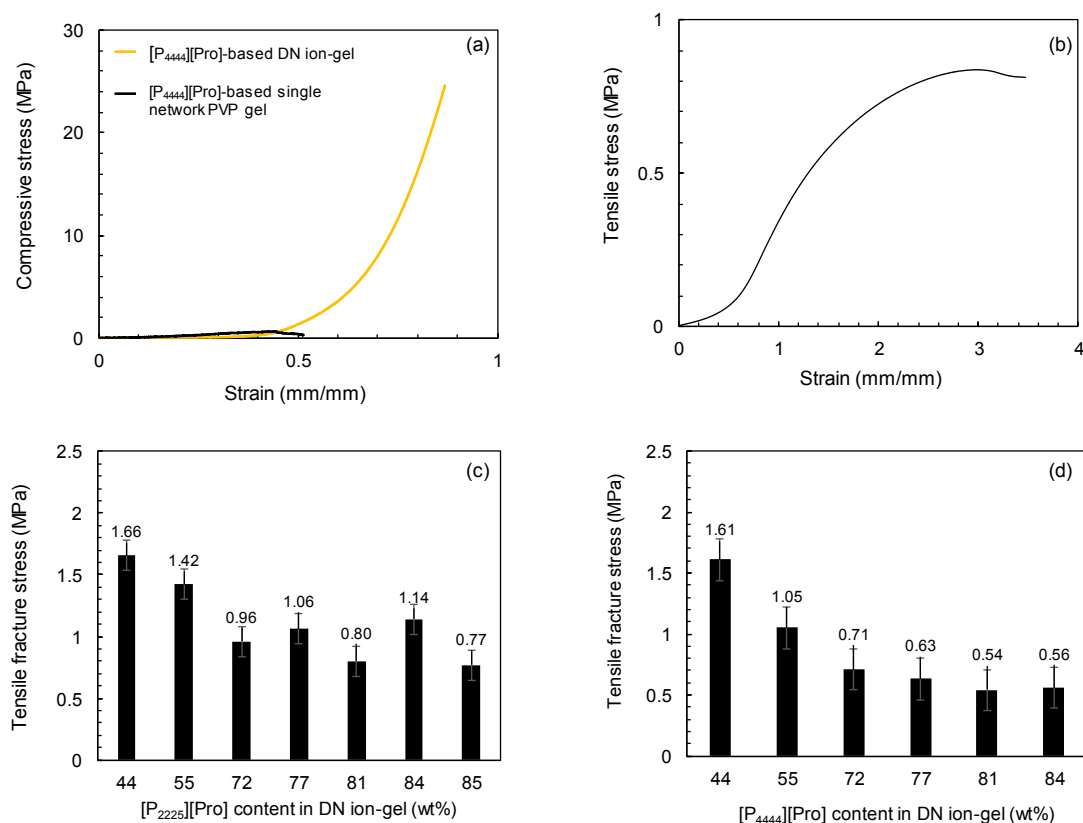


Fig. 2.5. (a) Compressive stress-strain curves of (a) SN PVP-based ion-gel and PAMPS/PDMAAm-based DN ion-gel containing 70 wt% [P₄₄₄₄][Pro], respectively. (b) Tensile stress-strain curve of PAMPS/PDMAAm-based DN ion-gel with 80 wt% [P₄₄₄₄][Pro]. (c,d) Summary of tensile fracture stress data of PAMPS/PDMAAm-based DN ion-gel at different loadings of (c) [P₂₂₂₅][Pro] and (d) [P₄₄₄₄][Pro]. The values in figures indicate the averages.

2.3.2. Effect of AAIL content on CO₂/N₂ separation performance of DN ion-gel membranes

As it was shown in section 2.2.4, the AAIL content of DN ion-gel membranes can be controlled via immersion of DN hydrogels in AAIL aqueous solution with different

concentrations. It seems reasonable to expect that the AAIL content in DN ion-gel affects the CO_2/N_2 permeation properties based on our previous study [3]. Therefore, in this study, CO_2 permeability and CO_2/N_2 selectivity of PAMPS/PDMAAm DN ion-gel membranes containing different loadings of $[\text{P}_{4444}][\text{Pro}]$ or $[\text{P}_{2225}][\text{Pro}]$ were measured at 373 K and CO_2 partial pressure of 2.5 kPa. The results are presented in Fig. 2.6.

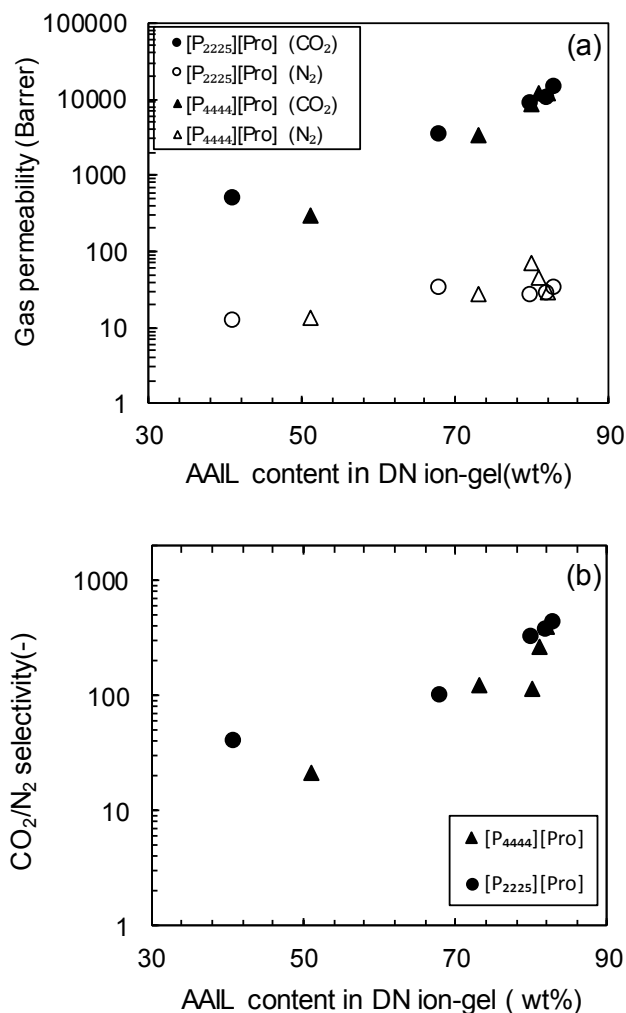


Fig. 2.6. Effect of AAIL content on the (a) gas permeabilities and (b) CO_2/N_2 selectivity of PAMPS/PDMAAm DN ion-gel membranes containing $[\text{P}_{4444}][\text{Pro}]$ or $[\text{P}_{2225}][\text{Pro}]$ (Experimental conditions: $\text{CO}_2/\text{N}_2 = 2.5/97.5$ mol/mol, $T = 373$ K, feed-side pressure (P_F) = sweep-side pressure (P_S) = 101.3 kPa, RH = 0%, Thickness = 500–600 μm).

The CO₂ and N₂ permeabilities of DN ion-gel membranes containing [P₄₄₄₄][Pro] and [P₂₂₂₅][Pro] exhibited an increasing trend over the AAIL content range. For example, the permeability of DN ion-gel membranes containing [P₂₂₂₅][Pro] was increased from 500 to 14000 barrer for CO₂ and from 12 to 32 for N₂ with increasing the AAIL content from 40 to 85 wt%. However, the rate of permeability increase is obviously different for gases. The enhancement of the N₂ permeability is mainly due to the diffusivity coefficients increase because of the larger AAIL content in the matrix of the DN ion-gel membrane. In other words, the higher AAIL content in ion-gel network can be translated to lower polymer content and therefore, less diffusion resistant in the gel network [3, 11]. As it is displayed in Fig. 2.6(a), CO₂ permeability was enhanced markedly with increasing the AAILs content, which is more pronounced increment than that of N₂. To clarify the difference in the rate of permeability enhancement with the AAIL content, the permeation mechanism of the CO₂ and N₂ should be taken into account. N₂ permeation mechanism through AAILs-based FTMs is generally based on the simple solution-diffusion [5, 12]. In this mechanism, N₂ permeability is described based on the product of solubility (physical absorption) and diffusivity coefficient. Since N₂ solubility on the feed side of the membrane is too small because of its low absorbability at low pressures, the driving force for diffusion through the ion-gel membrane would be too small and therefore, the N₂ permeability is low. Therefore, increasing the AAIL content resulted in the moderately enhancement of diffusivity coefficient and thus, N₂ permeability. On the other hand, CO₂ follows a facilitated transport mechanism for permeation in AAILs-based FTMs, as confirmed by Kasahara et al. [3, 4, 6, 12]. Therefore, the remarkably higher CO₂ permeability of DN ion-gel membranes is

attributed to the facilitated transport mechanism. Thus, it seems reasonable to say that increasing the AAIL content in the ion-gel membranes not only led to CO₂ diffusivity coefficients but also provided more available carriers in the ion-gel membrane that chemically and selectively react with CO₂. In conclusion, the enhancement of N₂ permeability with the AAIL content is a consequence of diffusivity coefficient increase while in the case of CO₂ this increasing trend is the combined effect of more available carriers in membrane matrix and increase of CO₂ diffusivity coefficient.

The CO₂/N₂ selectivity also followed a trend similar to CO₂ permeability. According to obtained results, with increasing [P₂₂₂₅][Pro] content from 40 to 85 wt%, CO₂/N₂ selectivity was enhanced from 40 to 440. A similar trend was observed for DN ion-gel membrane composed of [P₄₄₄₄][Pro]. In general, the CO₂/light gases selectivity of ILs-based is a solubility-dependent parameter. This means the CO₂/N₂ selectivity of AAILs-based DN ion-gel membranes is determined by the CO₂ absorbability of AAILs. An ion-gel membrane with a larger amount of AAIL provides more carriers chemically reacting with CO₂, compared with high polymer content ion-gel, and has the higher CO₂/N₂ selectivity. As it was explained in detail in chapter 1, the main advantage of AAILs over RTILs is their high CO₂ absorbability, which is based on chemical absorption. Hence, the AAILs-based FTMs show much higher CO₂/N₂ selectivity than RTILs-based membranes. This higher CO₂/N₂ selectivity demonstrated the great potential of developed DN ion-gel membranes for CO₂ capture application, particularly at very low CO₂ concentration.

In summary, the developed DN ion-gel membrane containing the large amount of AAILs ($\approx$ 80 wt%) exhibited not only excellent mechanical strength (as it was shown in the

previous section) but also have extraordinary CO₂/N₂ separation performance. In the next step, the effect of CO₂ partial pressure on the performance of [P₄₄₄₄][Pro]- and [P₂₂₂₅][Pro]- based DN ion-gel membranes containing different AAIL contents will be investigated.

2.3.3. Effect of CO₂ partial pressure on CO₂/N₂ separation performance of DN ion-gel membranes

The CO₂ permeation properties of the [P₄₄₄₄][Pro]- and [P₂₂₂₅][Pro]- based DN ion-gel membranes containing different contents of AAILs were investigated at wide range of partial pressures of CO₂ and temperature of 373 K. The experimental conditions are summarized in Table 2.2. The CO₂ permeation results are presented in Fig. 2.7 and Fig. 2.8 for [P₄₄₄₄][Pro]- and [P₂₂₂₅][Pro]- based DN ion-gel membranes, respectively. It was found that, at CO partial pressure of 10 kPa, DN ion-gel membranes with 80 wt% of AAILs exhibited CO₂ permeability of 6500 and 5300 barrer and CO₂/N₂ selectivity of 170 and 210 for [P₂₂₂₅][Pro] and [P₄₄₄₄][Pro], respectively. These results demonstrate the great potential of developed ion-gel membranes for CO₂ capture from post-combustion flue gas. As it was shown in Fig. 2.7(a) and Fig. 2.8(a), CO₂ permeabilities of both types of ion-gel membranes followed a decreasing trend with increasing the CO₂ partial pressures. This trend was observed over the whole range of AAILs content. Decrease in CO₂ permeability with increasing the CO₂ partial pressure is a well-known behavior of facilitated transport membranes as a result of saturation of carriers. Therefore, it can be concluded that for all samples of DN ion-gel membranes with different contents of AAIL the facilitated transport is the dominant mechanism of CO₂ permeation. Despite CO₂ permeability, which was significantly changed with varying CO₂ partial pressure, N₂ permeability remained constant

over the whole range of CO₂ partial pressure. This is an expected and familiar trend for ILs-based membranes, in which solution-diffusion is the dominant permeation mechanism.

Table 2.2. Experimental condition of CO₂ partial pressure dependency test

Temperature		373	K
Pressure	Feed	100	kPa
	Sweep	100	kPa
Partial pressure difference	CO ₂	2.5, 5, 10, 25, 50, 75	kPa
Pressure difference		0	kPa
Gas flow rate (dry base)			
Feed	Total	200	ml/min
	CO ₂	5, 10, 20, 50, 100, 150	ml/min
	N ₂	Balance	ml/min
Sweep	He	40	ml/min
Relative humidity		0%	

As it was mentioned in the introduction part, two types of AAILs with a similar anion, i.e., proline, and different sizes of cation, i.e., [P₂₂₂₅] and [P₄₄₄₄], were chosen in this study with the purpose of controlling the CO₂/N₂ separation factor. The achieved results indicate that DN ion-gel membranes containing AAIL with smaller size cation, i.e., [P₂₂₂₅][Pro], have better CO₂/N₂ selectivity than that with larger molecular size AAIL, i.e., [P₄₄₄₄][Pro]. This finding is consistent with the previous work reported by Kasahara et al. [5]. They have pointed out that AAILs with low cation size exhibited better N₂ barrier properties, due to lower molar volume, and therefore, higher CO₂/N₂ selectivity. Regarding outstanding mechanical strength of DN ion-gel membranes with the large amount of AAIL, it was expected that DN ion-gel membranes show good stability under pressurized conditions. Therefore, in the next step, I will experimentally demonstrate the excellent stability of developed ion-gel membranes.

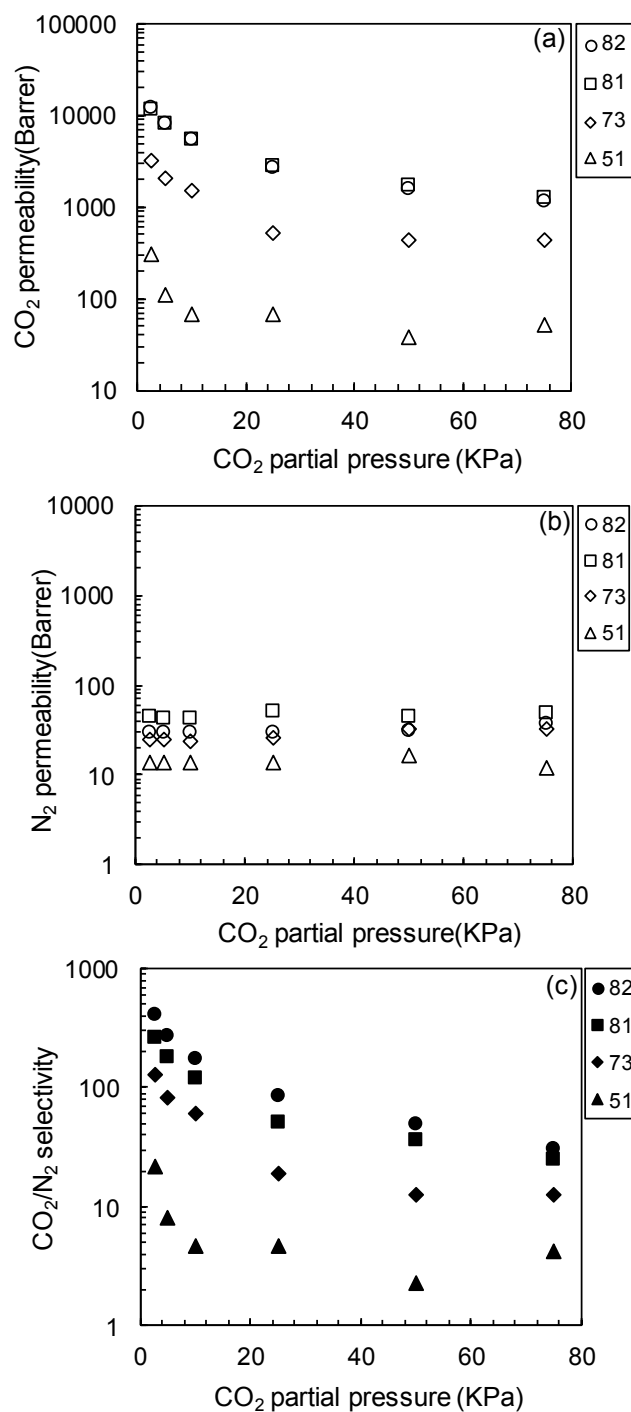


Fig. 2.7. Effect of CO₂ partial pressure on (a) CO₂ permeability, (b) N₂ permeability, and (c) CO₂/N₂ selectivity of PAMPS/PDMAAm DN ion-gel membranes containing [P₄₄₄₄][Pro] (Experimental conditions: T=373 K, feed-side pressure (P_F)= sweep-side pressure (P_S)= 101.3 kPa, RH=0%, Thickness= 500-600 μ m).

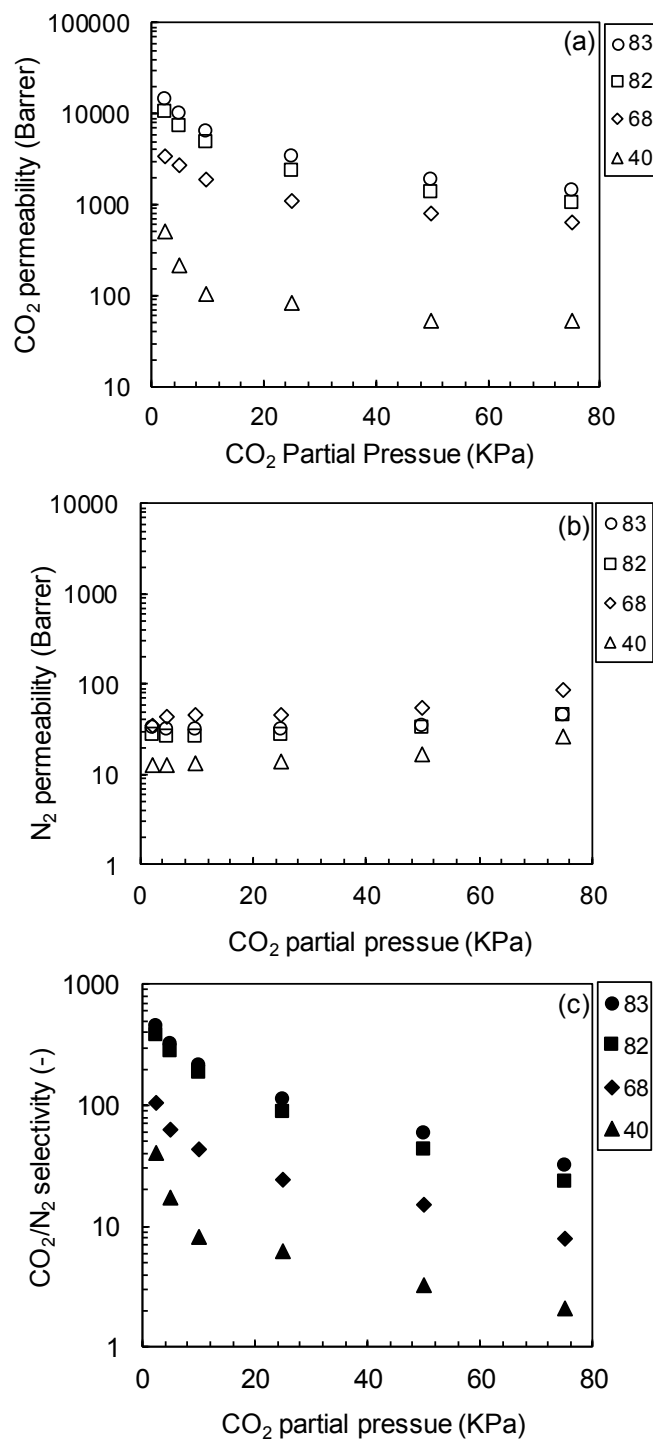


Fig. 2.8. Effect of CO₂ partial pressure on (a) CO₂ permeability, (b) N₂ permeability, and (c) CO₂/N₂ selectivity of PAMPS/PDMAAm DN ion-gel membranes containing [P₂₂₂₅][Pro] (Experimental conditions: T=373 K, feed-side pressure (P_F)= sweep-side pressure (P_s)= 101.3 kPa, RH=0%, Thickness= 500-600 μ m).

2.3.4. Pressure stability of DN ion-gel membranes

As discussed in chapter 1, the motivation behind the fabrication of AAILs-based DN ion-gel membranes was the addressing the poor stability and weak ILs holding properties of SILMs under pressurized conditions. It was experimentally revealed in previous sections (2.3.1 and 2.3.3) that developed ion-gel membranes have excellent CO₂ separation performance and mechanical strength. Evaluation of CO₂ permeation properties under pressurized conditions seems an appropriate way to demonstrate the good stability of DN ion-gel membranes. For this purpose, in this investigation, the CO₂/N₂ separation performance of PAMPS/PDMAAm DN ion-gel membranes were assessed under different trans-membrane pressure differences (from 0 to 400 kPa). In this experiment, the sweep side pressure was held constant at 100 kPa and the feed side pressure was changed from 100 to 500 kPa, with 100 kPa intervals. The AAIL content of ion-gel membranes was kept at 80 wt% for this examination. The experimental conditions are summarized in Table 2.3. The CO₂ partial pressure of feed gas was kept constant (10 kPa) in this investigation. Results of CO₂/N₂ permeation measurements are displayed in Fig. 2.9.

Table 2.3. Experimental conditions of pressure stability test

Temperature		373	K
Pressure	Feed	100-500(100 intervals)	kPa
	Sweep	100	kPa
Partial pressure difference	CO ₂	10	kPa
Pressure difference		0 - 400 (100 intervals)	kPa
Gas flow rate (dry base)			
Feed	Total	200	ml/min
	CO ₂	20, 10, 6.67, 5, 4	ml/min
	N ₂	Balance	ml/min
Sweep	He	40	ml/min
Relative humidity		0%	

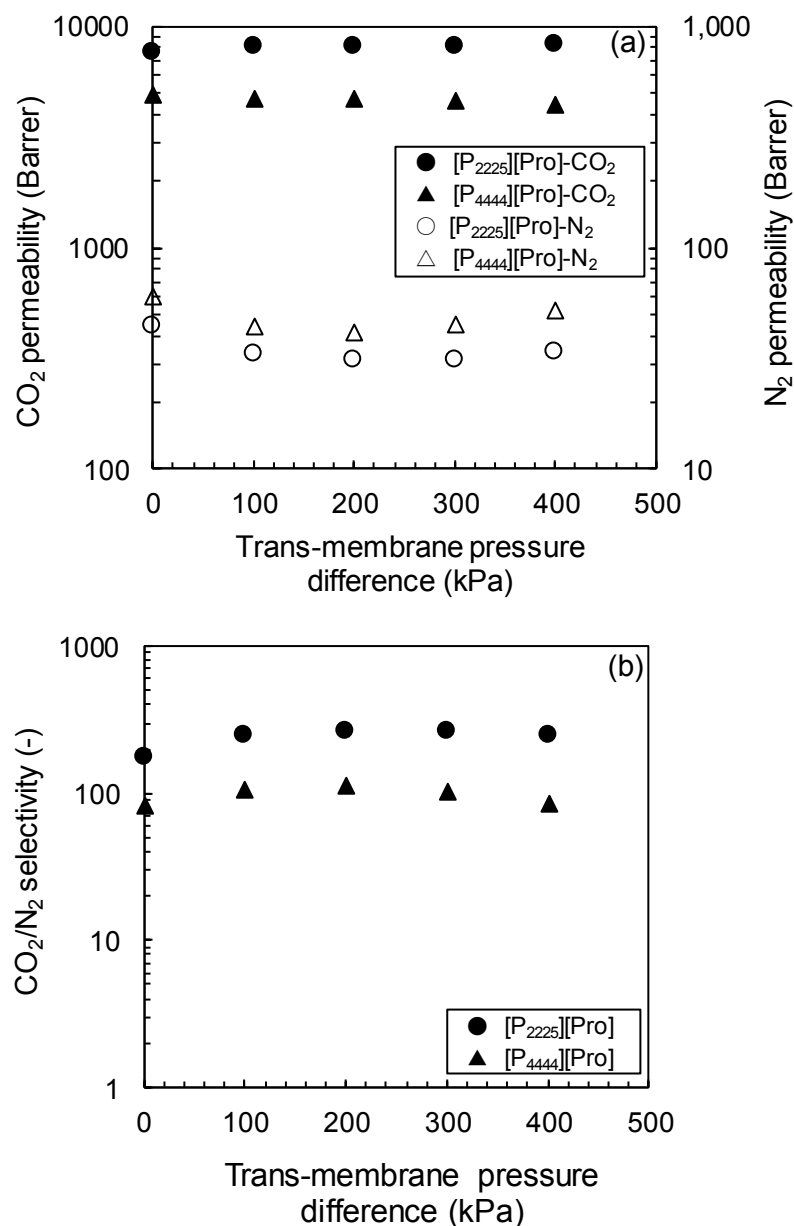


Fig. 2.9. Pressure stability of the AAIL-based DN gel membranes at different trans-membrane pressure differences (Experimental conditions: $T = 373$ K, P_s = atmospheric pressure, $P_{\text{CO}_2, \text{feed}} = 10$ kPa, and $\text{RH} = 0\%$).

The CO₂ permeabilities of DN ion-gel membranes containing [P₂₂₂₅][Pro] and [P₄₄₄₄][Pro] demonstrated the outstanding stability and good AAILs holding property. As it was shown in Fig. 2.7 and Fig. 2.8, CO₂ permeability of DN ion-gel membranes strongly

depended on the AAIL content. Therefore, it seems logical to assume that any possible leakage of AAILs from DN ion-gel membranes leads to deterioration of CO₂ permeability. However, the stable performance of DN ion-gel membranes under pressurized condition (Fig. 2.9) clearly emphasized that there was no any possible leakage of DN ion-gel membranes.

In order to give further reliable evidence concerning the stable performance of PAMPS/PDMAAm DN ion-gel membranes, the long-term stability of ion-gel membranes at the highest feed pressure (up to 500 kPa) was examined for 5 days, as shown in Fig. 2.10. There was not any performance decline in terms of CO₂ permeability and CO₂/N₂ selectivity for both DN ion-gel membranes. Therefore, according to the stable performance of ion-gel membranes at pressure of 500 kPa, there is no doubt that DN ion-gel matrix can retain the AAIL without any leakage.

In addition, it should be mentioned that the DN ion-gel membrane containing [P₂₂₂₅][Pro] showed better CO₂/N₂ separation performance that is mainly associated with the following parameters. First, low molecular size AAILs (i.e., [P₂₂₂₅][Pro]) provides more available carriers in the unit of volume of ion-gel network. Therefore, CO₂ molecules have more access to the carriers on the feed side of DN ion-gel membrane. The second is that low cation size AAILs offer more N₂ barrier property, as displayed in Fig. 2.10(a). As consequence, the CO₂/N₂ selectivity of [P₂₂₂₅][Pro]-based DN ion-gel membrane was twice of [P₄₄₄₄][Pro]-based ion-gel.

As a summary of this investigation, it can be claimed that the issue corresponding to the poor stability and poor IL holding property of ILs-based membranes was addressed by

developing a novel type of ion-gel membrane, prepared from a combination of two polymer networks with the unique structure.

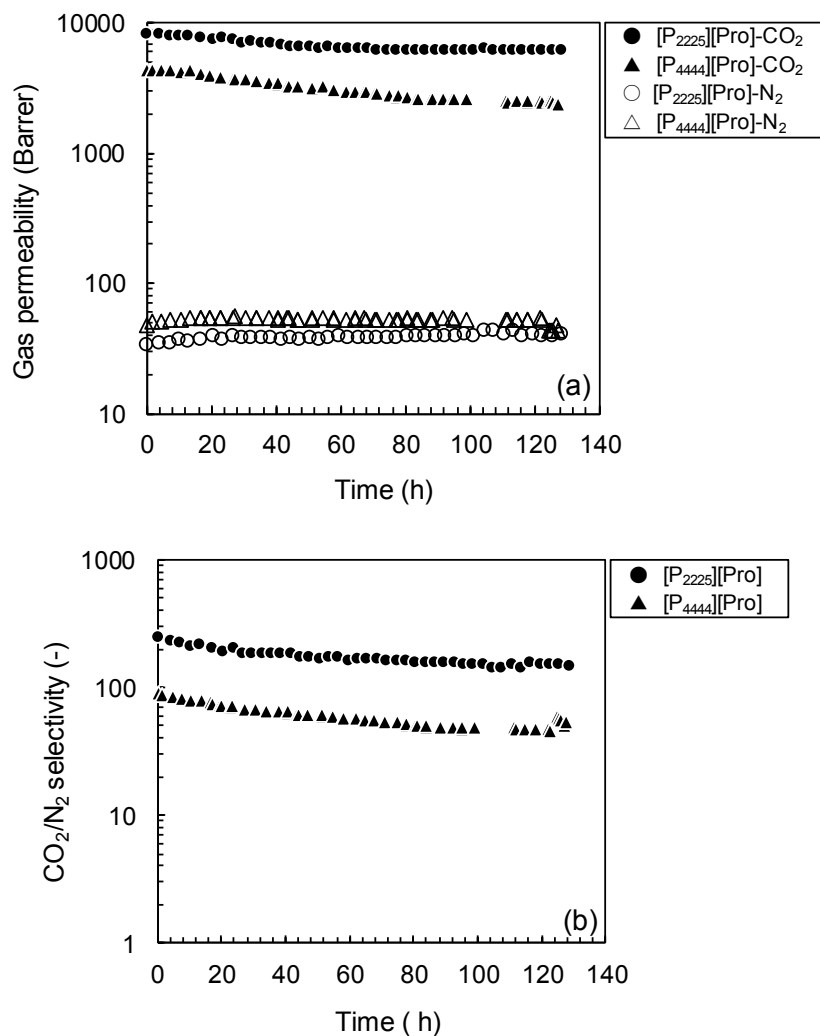


Fig. 2.10. Time course of (a) CO₂ and N₂ permeabilities and (b) CO₂/N₂ selectivity of AAIL-based DN ion-gel films containing [P₂₂₂₅][Pro] and [P₄₄₄₄][Pro] (Experimental conditions: $T = 373$ K, $P_F = 500$ kPa, $P_S =$ atmospheric pressure, $P_{CO_2, feed} = 10$ kPa, and relative humidity = 0%).

2.3.5. Fabrication of thin DN ion-gel membrane with high CO₂ permeance

From the industrial application point of view, in addition to the high CO₂ permeability and CO₂/N₂ selectivity, an economically viable membrane-based system should possess high

CO₂ permeance, in order to reduce the capital and operating costs of membrane unit [13]. It was reported that a membrane suitable for CO₂ capture from flue gas should have a CO₂ permeance more than 1000 GPU (1 GPU= 10⁻⁶ cm³(STP)/cm².s.cmHg) [14].

Permeance of membrane generally is defined as follows [13, 15].

$$Permeance = \frac{permeability}{thickness} = \frac{P}{L} \quad (2.2)$$

According to equation 2.2, the permeance of a membrane could be improved by increasing the permeability or decreasing the thickness. In general, the permeability of a membrane is a parameter depending on the material property. This means that it is possible to improve the permeability by tuning the property of materials used for membrane preparation. In our study, I have tried to fabricate the ion-gel membranes with very high CO₂ permeation properties. The achieved values for CO₂ permeability and CO₂/N₂ selectivity of ion-gel membranes, at optimized conditions of preparation, significantly traversed the upper bound proposed by Robeson. However, the CO₂ permeance of the DN ion-gel membrane containing 80 wt% [P₂₂₂₅][Pro] with the CO₂ permeability of 14000 barrer is about 24 GPU. This value is far lower than the requirement for the real application. The low permeance of our developed ion-gel membrane comes from its higher thickness, which was about 600 μm. Therefore, to achieve the higher values of CO₂ permeance, it is needed to reduce the thickness of developed ion-gel membranes.

As explained before, the thickness of DN ion-gel membrane was adjusted by the PTFE spacer used for the first network hydrogel preparation. In order to make a thinner ion-gel membrane, a 25 μm PTFE spacer was utilized and a procedure similar to that was used for 600 μm DN hydrogel sample was followed. The measured thickness of the prepared DN

ion-gel was 58 μm . Fig. 2.11 showed the CO_2 permeance and CO_2/N_2 selectivity of a $[\text{P}_{4444}][\text{Pro}]$ -based SILM and DN ion-gel membrane containing 80 wt% of $[\text{P}_{4444}][\text{Pro}]$ with thickness of 58 μm and 600 μm .

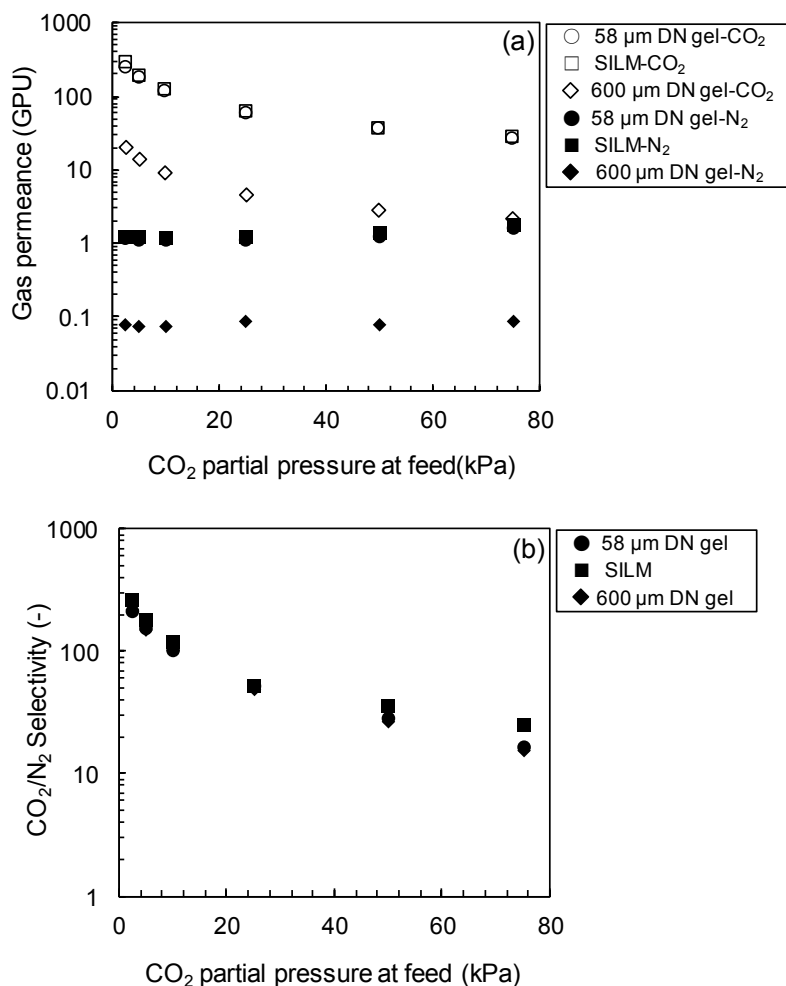


Fig. 2.11. CO_2 partial pressure dependency of the thin AAIL-based DN ion-gel film containing $[\text{P}_{4444}][\text{Pro}]$ as the CO_2 separation medium (Experimental conditions: $T=373$, $P_F=P_S=100$ kPa, AAIL content in DN ion-gel membrane was ca. 80 wt%, $\text{RH}=0\%$).

According to the obtained results, at CO_2 partial pressure of 2.5 kPa, the CO_2 permeance of 250 GPU was obtained for the thinner DN ion-gel membrane with 58 μm thickness. This value is almost one order of magnitude higher than that of 600 μm . Most

importantly, the CO₂ permeance of the thinner DN ion-gel membrane is akin to that of the SILM. Therefore, it can be claimed that a thinner DN ion-gel membrane was fabricated that not only showed CO₂ permeance similar to SILM but also indicated great mechanical strength and good IL holding property.

CO₂/N₂ selectivity data pointed out that both DN ion-gel membranes have similar performance. Thus, it can be concluded that the separation performance of DN ion-gel membranes will not be changed with lessening the thickness of the membrane.

To gain more insight into the understanding rate-determining step of the permeation, I have prepared DN ion-gel membranes with four different thicknesses 58, 93, 189, and 600 μm . The CO₂ and N₂ permeances of DN ion-gel membranes at different CO₂ partial pressures were evaluated (Fig. 2.12). It can be seen that CO₂ permeance showed a linear relationship with the inverse thickness of the ion-gel membranes. In other words, CO₂ permeance proportionally increased with decreasing the ion-gel membrane thickness. Therefore, it can be concluded that intra-membrane diffusion is the rate-determining step of permeation. This raises the possibility of achieving the higher CO₂ permeance through further reducing of the thickness of ion-gel membranes. According to the obtained results and by a rough calculation, it can be estimated that CO₂ permeance of 6000 GPU can be realized for an ion-gel membrane with 1 μm thickness, at CO₂ partial pressure of 10 kPa. Therefore, one of the next challenges of our research could be the preparation of thinner ion-gel membrane.

N₂ permeances of DN ion-gel membranes exhibited the similar trend at different thicknesses, as shown in Fig. 2.11(b). The constant slope of N₂ permeance versus inverse

thickness implying that N_2 permeability of ion-gel membranes will not change with further decreasing of thickness.

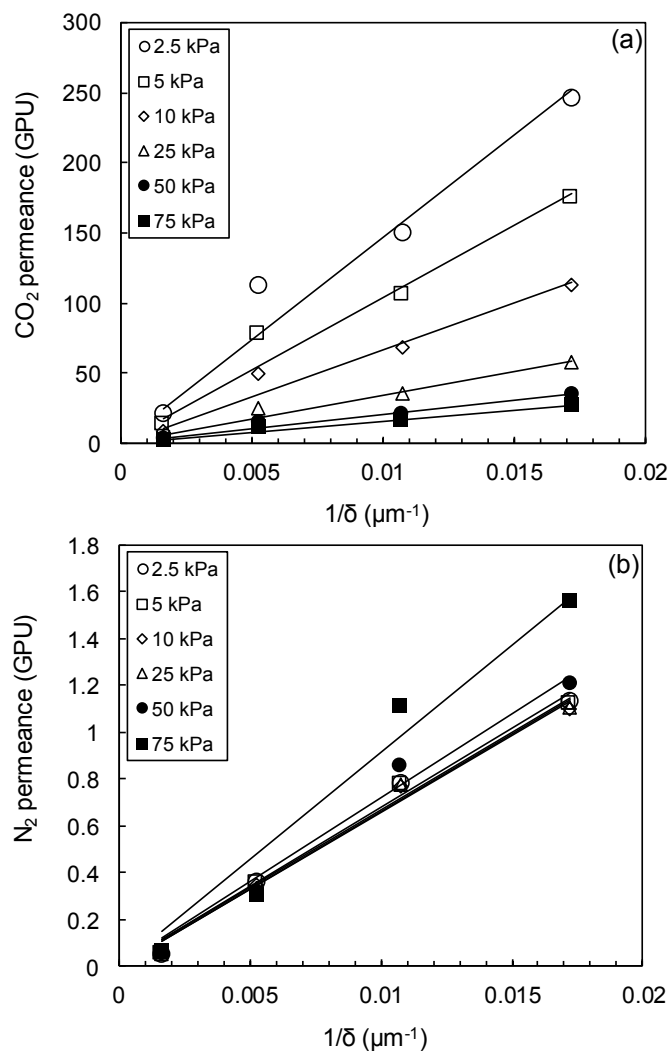


Fig. 2.12. relationship between CO_2 permeances measured under different CO_2 partial pressure conditions and inverted thickness of the DN gel membranes containing ca. 80 wt% of $[\text{P}_{4444}][\text{Pro}]$ (Experimental conditions: $T = 373$ K, $P_F = P_S =$ atmospheric pressure, and $\text{RH} = 0\%$)

2.4. Conclusion

A novel type of PAMPS/PDMAAm DN ion-gel membranes containing AAILs with excellent CO₂/N₂ separation performance, outstanding mechanical strength and good stability under pressurized conditions were fabricated. The DN ion-gel membrane composed of more than 80 wt% of AAILs showed tensile and compressive fracture stress of more than 0.6 and 25 MPa, respectively. The gas permeation properties of ion-gel membranes at different CO₂ partial pressures also demonstrated that permeation mechanism of CO₂ and N₂ through the membrane are facilitated transport and solution-diffusion, respectively.

The CO₂ permeability and CO₂/N₂ selectivity of ion-gel membranes with different AAIL contents were also measured. The CO₂ permeability 14000 and CO₂/N₂ selectivity of 440 were obtained for [P₂₂₂₅][Pro]-based PAMPS/PDMAAm DN ion-gel membrane at CO₂ partial pressure of 2.5 kPa. The DN ion-gel membranes with highest AAIL content were examined under pressurized condition up to 500 kPa and no deterioration of performance was found. In addition, long-term stability of ion-gel membranes at the feed pressure of 500 kPa for more than 5 days showed that there is no any leakage of AAILs from the DN ion-gel network. The measurement of CO₂ permeances of DN ion-gel membranes with various thicknesses elucidated that intra-membrane diffusion is the rate-determining step of permeation. Surprisingly, comparing CO₂ permeance of 58 μm DN ion-gel membrane with [P₄₄₄₄][Pro]-based SILM disclosed the similar CO₂ separation performance. Therefore, it can be claimed the DN concept provided the opportunity of developing novel ion gel membranes with excellent stability and outstanding CO₂ separation performance similar to AAILs-based SILMs.

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Chapter 3

High CO₂ separation performance of amino acid ionic liquid-based double network ion-gel membranes in low CO₂ concentration gas mixtures under humid conditions

3.1. Introduction

Recently, removing CO₂ from atmospheres with very low concentrations of CO₂ has attracted a great deal of attention. For example, the removal of CO₂ from ambient air, a process called “air capture,” has been proposed as a methodology for direct reduction of the amount of CO₂ in the atmosphere [1]. Continuous separation and removal of CO₂ resulting from human breathing in enclosed spaces can help to reduce the amount and energy cost of ventilation required. Furthermore, development of technologies for CO₂ separation from gases containing very low partial pressures of CO₂, e.g., venting devices for spacewalking and spaceship applications for upcoming space exploitation, is desired [2-5]. In this context, several studies have been carried out on the use of FMTs for CO₂ separation from gases with low concentrations of CO₂. For example, Sirkar *et al.* [4, 6] prepared FMTs by immobilizing carrier solutions of carbonate-glycerol and glycine-Na-glycerol and evaluated their CO₂ permeation performances in low CO₂ concentration gases (0.6-81 kPa) under humid conditions (RH = 40-100%). It was reported that a glycine-Na-glycerol FTM containing 2.5 M glycine-Na as the carrier exhibited high CO₂ permeability (ca. 10000 barrer) and CO₂/N₂ selectivity (ca. 4000) under highly humid conditions. However, the CO₂ permeability of the FTM was strongly dependent on the RH of the feed stream and markedly declined with

decreasing RH. This drastic drop in CO₂ permeation performance has also been reported in other FTMs [7, 8].

In this chapter, I have demonstrated the great potential and advantage of the developed AAIL-based PAMPS/PDMAAm DN ion-gel membranes for CO₂ separation from gas mixtures containing very low concentration of CO₂ (500-1000 ppm) at low temperature. By taking the advantages of DN ion-gel membranes (i.e., good stability and holding the large amounts of AAIL) and the liquid state of AAIL-based carrier under the dry condition, I have shown that CO₂ permeability of DN ion-gel membranes is remarkably higher (one order of magnitude) than that of the conventional FTMs.

In this study, the effects of key operating parameters including CO₂ partial pressure, RH, and temperature on the CO₂ separation performance of DN ion-gel membranes were examined. To demonstrate the advantage of our developed ion-gel membranes over conventional FTMs, I have fabricated an amine-based gel membrane and its CO₂ permeation properties were evaluated and compared with the DN ion-gel FTM.

3.2. Experimental

3.2.1. Materials

Regarding the great CO₂ separation performance of DN ion-gel membranes containing proline-type AAILs, I have chosen [P₄₄₄₄][Pro] as carrier of ion-gel FTMs. AMPS and DMAAm were chosen as the first and second networks of DN ion-gel, respectively.

Tetrabutylphosphonium hydroxide ([P₄₄₄₄][OH], 40 wt.% in water) and proline (>99%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and Tokyo Chemical Industry

Co. (Tokyo, Japan), respectively. These were used to synthesize $[P_{4444}][Pro]$ according to a previously reported method [9]. The chemical structure of the resulting $[P_{4444}][Pro]$ was confirmed by 1H NMR (Bruker Avance 500, Bruker Bio Spin) and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics) spectroscopy. Of the reagents for AAIL-based tough gel preparation, 2-acrylamido-2-methylpropanesulfonic acid (AMPS, >99.8%), N,N-dimethylacrylamide (DMAAm, >99.5%), and 2-oxoglutaric acid (OA, >99%) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan), while N,N'-methylenebisacrylamide (MBAA) was purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). All reagents were used without further purification.

DL-2,3-diaminopropionic acid hydrochloride (DAPA-HCl), used as the CO_2 carrier in conventional FTMs, was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Cesium hydroxide monohydrate ($CsOH \cdot H_2O$), purchased from Sigma Aldrich (St. Louis, MO, USA), was used to deprotonate the amino group of DAPA [10]. A poly(vinyl alcohol)/poly(acrylic acid) copolymer (PVA/PAA copolymer) was supplied by Sumitomo Seika Chemicals Co., Ltd., (Osaka, Japan) and was used as the gel matrix for the DAPA-based FTM. All chemicals were used without further purification. A hydrophilic polytetrafluoroethylene (PTFE) microporous membrane (pore size: 0.2 μm , thickness: 55 μm , purchased from Sumitomo Electric Industries Ltd. (Osaka, Japan)) and a hydrophobic PTFE microporous membrane (pore size: 0.1 μm , thickness: 81 μm ; purchased from Advantec Toyo Kaisha Ltd. (Tokyo, Japan)) were used as the supports for the DAPA-based FTM.

3.2.2. Membrane preparation

A DN ion-gel was fabricated according to a procedure reported in the previous chapter. First, a DN hydrogel was prepared via a multi-step UV polymerization. An aqueous solution containing AMPS as the first network monomer, MBAA as a cross-linker, and OA as an initiator was prepared and stirred for 20 min. The solution was injected between two quartz plates and placed under UV light (365 nm) for 3 h. The thickness of the first network hydrogel was adjusted using a PTFE spacer. The brittle as-prepared first network hydrogel was immersed in an aqueous solution of the second network solution, which contained DMAAm, OA, and NaCl, for 3 h. The swollen hydrogel film was then put under UV illumination for 4 h to yield a PAMPS/PDMAAm DN hydrogel film. The compositions of the first and second network solutions are listed in Table 3.1.

Table 3.1. Composition of first and second networks used for double network hydrogel preparation

	Reagent	Amount
1st Network	AMPS	1.4506 g
	MBAA	0.0432 g (4 mol %)
	OA	0.0010 g (0.1 mol %)
	Water	7 cm ³
2nd Network	DMAAm	39.65 g
	OA	0.0544 g (0.1 mol %)
	NaCl	0.4675 g
	Water	100 cm ³

$$\text{mol \%} = (\text{mol} / \text{mol of monomer}) \times 100$$

In the next step, the as-prepared PAMPS/PDMAAm DN hydrogel was immersed in an aqueous solution of [P₄₄₄₄][Pro]/water (80/20 wt.%) for 3 h, then dried in a vacuum oven at 373 K for 8 h to remove water and any non-reacted monomers, after which a PAMPS/PDMAAm DN ion-gel membrane containing [P₄₄₄₄][Pro] was obtained. The

average thickness and [P₄₄₄₄][Pro] content of the DN ion-gel membranes were 150 μm and 80 wt.%, respectively.

The DAPA-based FTM was fabricated according to a previously reported procedure [8, 10]. PVA/PAA copolymer, DAPA, and CsOH were dissolved in water and stirred at room temperature for 24 h. The molar ratio of CsOH to DAPA was adjusted to 2:1. The solution was centrifuged at 5000 rpm for 30 min to remove air bubbles and cast onto a hydrophilic PTFE support using a casting knife (casting thickness was 500 μm). The membrane was dried at room temperature overnight and then put into a thermostat oven at 393 K for 2 h to ensure complete removal of water. The average thickness of the gel layer was 14 μm . In order to protect the gel layer, it was covered with a hydrophobic microporous PTFE membrane for the gas permeation experiment.

3.2.3. Measurement of physiochemical properties of [P₄₄₄₄][Pro]

The hygroscopicity and water-holding ability of [P₄₄₄₄][Pro] under humid conditions were measured at 303 K using a thermogravimetry-differential thermal analyzer with a humidity generator (TG-DTA/HUM, Rigaku Co.). First, the desired amount of [P₄₄₄₄][Pro] was placed in a cell. The cell was heated to 423 K at 0.0167 K/s and held at this temperature for 10 h to remove any remaining water from the [P₄₄₄₄][Pro]. Subsequently, the cell temperature was decreased to 303 K at 0.033 K/s and kept at this temperature for 1 h to allow an equilibrium to be reached. Next, nitrogen with a RH of 30% was introduced to the cell for 5.5 h while the weight of the [P₄₄₄₄][Pro] sample was continuously monitored to confirm equilibration. The water content of the sample at equilibrium was calculated from the weight

difference before and after water vapor absorption. The RH was changed from 30 to 70% at 303 K to measure the amount of water absorbed by $[P_{4444}][Pro]$ at different RHs.

The viscosity of $[P_{4444}][Pro]$ was measured using an electromagnetically spinning sphere (EMS) viscometer (EMS-1000 W, Kyoto Electronics Manufacturing Co., Ltd.). Fig. 3.1 shows a schematic diagram of the viscosity measurement system under humid conditions. First, $[P_{4444}][Pro]$ was dried for 24 h under a nitrogen atmosphere to remove any free water. After this, a feed gas with the desired CO_2/N_2 /water vapor composition was introduced to a sample vessel containing $[P_{4444}][Pro]$ stirred by a metallic sphere at a constant rotation speed of 1000 rpm. The RH of the feed gas was adjusted using a humidifier. Viscosity measurements were carried out at 303 K and atmospheric pressure for gases with $P_{CO_2} = 0.5$ kPa and without CO_2 ($P_{CO_2} = 0$ kPa) at RHs between 30 and 70%.

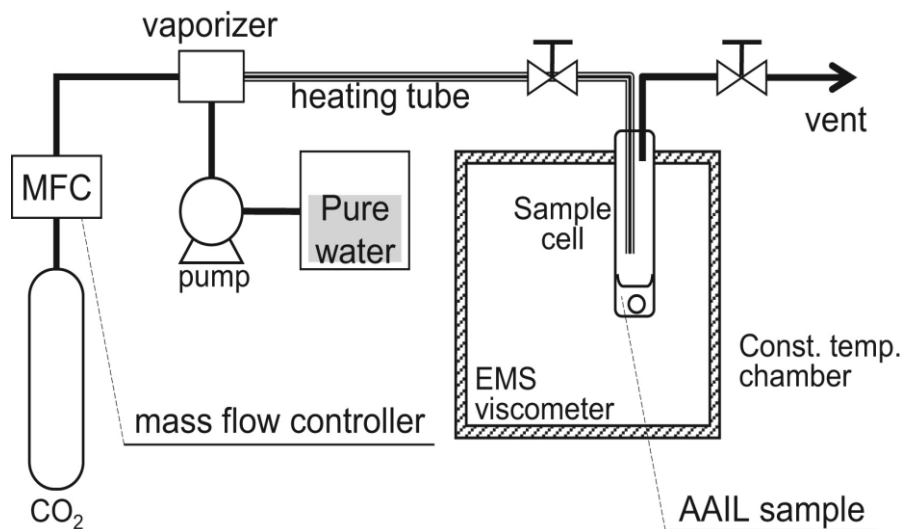


Fig. 3.1. Schematic diagram of the viscosity measurement system.

3.2.4. Gas permeability measurement

A schematic diagram of the mixed gas permeation system under humid conditions is shown in Fig. 3.2. A stainless steel flat-type permeation cell with an effective permeation area of 9.5 cm^2 was placed in a thermostat oven (YAMATO Scientific Co., Ltd.) and adjusted to the desired temperature. The feed and sweep gas flow rates were held at 200 and 40 cm^3/min , respectively. The flow rates of CO_2 and N_2 in the feed gas were controlled using mass flow controllers (Hemmi Slide Rule Co., Ltd.) and the water vapor flow rate in the feed was adjusted to the desired RH using a humidifier (Micro Equipment Inc.). The humid feed gas was passed through a heating tube before introduction to the permeation cell. The feed and sweep side pressures were held at atmospheric pressure. The water vapor in the streams from both feed and permeate sides of the permeation cell was measured using a humidity detector. After condensation of the permeated water vapor in the sweep gas by passing it through a condenser, the dried sweep gas was introduced to a gas chromatograph (GC-8A, Shimadzu Co., column: activated carbon, 1 m) to determine the composition of the permeated CO_2 and N_2 . Each test was conducted for at least 3 h, until the difference between sequential CO_2 and N_2 peak areas as measured by GC became less than 1%, in order to check the steady state.

In the case of air capturing process, a vacuum pump should be used to drive the pressure gradient. However, it was hard to measure the concentration of permeate side continuously by connecting a line from vacuum pump outlet (discharge) to the GC. From membrane performance standpoint, since the sweep system keeps the permeation driving force constant, similar to the vacuum system, it seems reasonable to assume that the CO_2 capture

performance of ion-gel membrane at current system would be similar to the vacuum-driven system.

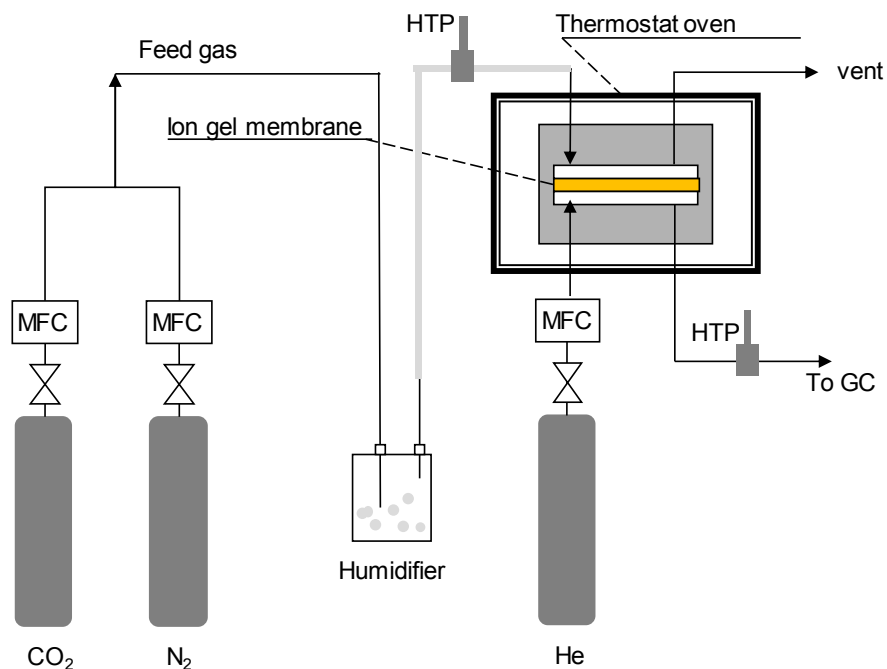


Fig. 3.2. Schematic diagram of gas permeation measurement set-up used. MFC and HTP refer to a mass-flow controller and a humidity-temperature detector, respectively.

3.3. Results and discussion

3.3.1. Water absorbability and viscosity of [P₄₄₄₄][Pro]

In general, AAILs are inherently hygroscopic and absorb large amounts of water even at low RH. Kasahara et al. [11] reported that AAILs strongly absorbed water under humid conditions at elevated temperatures. In particular, proline-type AAILs showed higher water absorption capacity than other AAILs. It was reported that existed water in AAILs results in drastically decrease in the viscosity [12], which remained low under humid conditions even after contact with CO₂. In general, it is well known that the viscosities of AAILs drastically

increase upon contacting with CO₂ under dry conditions due to the formation of an intermolecular hydrogen-bonding network between the AAIL-CO₂ complexes [13, 14]. In contrast, it was found the viscosity of AAIL after exposure to CO₂ under humid conditions did not increase significantly due to the intercalation of water molecules between the AAIL-CO₂ complexes, which could destroy the intermolecular hydrogen-bonding network [15]. Therefore, if an AAIL can absorb a considerable amount of water vapor at around room temperature, the viscosity of the AAIL after exposure to CO₂ under humid conditions would be low.

The moisture absorption isotherm of [P₄₄₄₄][Pro] as measured at 303 K is shown in Fig. 3.3. The amount of water absorbed increased linearly as RH increased from 30-70%. From this result, it was expected that the viscosity of [P₄₄₄₄][Pro] around room temperature would significantly decrease under humid conditions. Fig. 3.4 shows the viscosity of [P₄₄₄₄][Pro] at different relative humidities (RH = 30-70%) before and after CO₂ absorption at 303 K. With increasing RH (or water vapor partial pressure), the viscosity of neat [P₄₄₄₄][Pro] displayed a significant drop. For example, the viscosity of neat [P₄₄₄₄][Pro] at RH = 30% (91 mPa. s) reduced to 16 mPa. at RH = 70%. This behavior is in good agreement with previously reported results [12, 15]. The reduction in viscosity at higher RHs can mainly be ascribed to the larger amount of water absorbed by AAIL, as shown in Fig. 3.3. A similar trend was also observed in the viscosity of [P₄₄₄₄][Pro] after exposure to a CO₂/N₂/water vapor mixture with a CO₂ partial pressure of 0.5 kPa across a wide RH range. As shown in Fig. 3.4, although the viscosity of the AAIL after contact with the CO₂/N₂/water vapor mixture was higher than that of neat AAIL, the viscosity showed declining trend with increasing RH. The considerable

decrease in the viscosity of $[P_{4444}][Pro]$ can likely be attributed to the intercalation of water molecules between the $[P_{4444}][Pro]$ -CO₂ complexes. It was reported that the viscosity of AAILs significantly affects the diffusivity of gases and the resultant gas permeation properties of AAIL-based FTMs [16]. Therefore, the high water vapor absorbability and the low viscosity of $[P_{4444}][Pro]$ under humid conditions could have a positive impact on the CO₂ permeability of $[P_{4444}][Pro]$ -based FTMs.

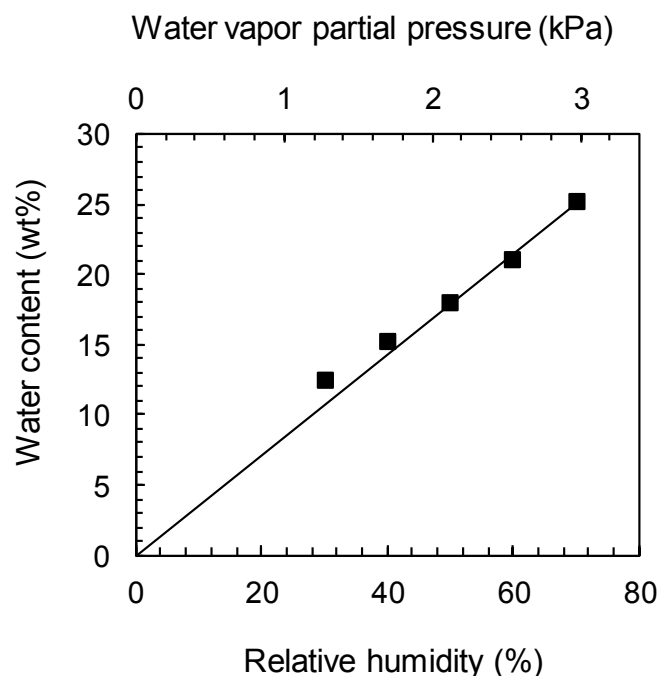


Fig. 3.3. Relationship between water content of $[P_{4444}][Pro]$ and relative humidity at 303 K.

3.3.2. Gas permeation results

3.3.2.1. Effect of CO₂ partial pressure on CO₂/N₂ separation performance

The CO₂ permeation properties of the $[P_{4444}][Pro]$ -based DN ion-gel membrane and DAPA-based FTM (PVA/PAA gel membrane containing DAPA), which is a typical example of a conventional amino acid-based FTM, were investigated at 303 K for gas mixtures with

RHs of 70% and partial pressures of CO₂ of 0.05-0.1 kPa. The experimental conditions are summarized in Table 3.2. Fig. 3.5(a)-(c) show the CO₂, water vapor, N₂ permeabilities and the CO₂/N₂ selectivities of the membranes.

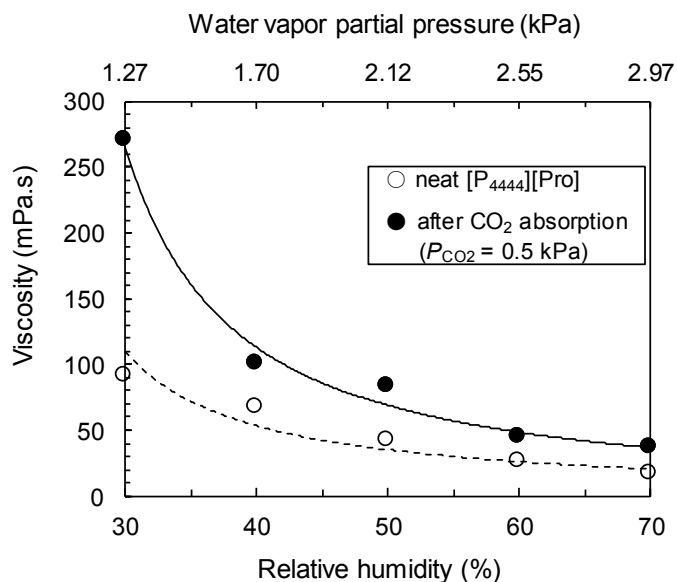


Fig. 3.4. Effect of relative humidity on the viscosity of [P₄₄₄₄][Pro] exposed to a N₂/water vapor mixture (neat AAIL) and a CO₂/N₂/water vapor mixture (P_{CO₂} = 0.5 kPa) at 303 K.

The DN ion-gel membrane exhibited a remarkable CO₂ permeability of over 50000 barrer and a CO₂/N₂ selectivity of more than 8000. The excellent CO₂ permeability was due to the facilitated transport mechanism of the [P₄₄₄₄][Pro]-based DN ion-gel membrane. In general, carriers in FTMs would be saturated with CO₂ under relatively high CO₂ partial pressure conditions because of their strong CO₂ absorbability. However, at very low CO₂ concentrations, which was the focus of this study, carriers were not saturated and driving force of trans-membrane for the diffusion of CO₂-carrier complex become maximum. Therefore, higher CO₂ permeability was achieved under lower CO₂ concentrations. On the other hand, the N₂ permeability of the [P₄₄₄₄][Pro]-based DN ion-gel membrane was very low

because N₂ permeation was based on a solution-diffusion mechanism. From this excellent CO₂ separation performance, it can be said that the [P₄₄₄₄][Pro]-based DN ion-gel membrane has great potential for CO₂ separation from gases containing low concentrations of CO₂.

Table 3.2. Experimental conditions for CO₂ partial pressure dependency test

Temperature		303 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
	CO ₂	0.05 - 0.1 kPa
Partial pressure difference		
Pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm ³ /min
	CO ₂	0.1-0.2 cm ³ /min
	N ₂	Balance
Sweep	He	40 cm ³ /min
Relative humidity in Feed		70%

In order to compare the CO₂ separation performance of DN ion-gel membrane with the conventional FTMs, CO₂ transport properties of the DAPA-based FTM were investigated. The CO₂ permeability of the DAPA-based FTM was lower than that of the [P₄₄₄₄][Pro]-based DN ion-gel membrane, which also resulted in a lower CO₂/N₂ selectivity. The lower CO₂ permeability was due to the nature of DAPA in the FTM, the details of which are considered in the next section. The DAPA-based FTM also showed low N₂ permeability, which was similar to that of the [P₄₄₄₄][Pro]-based DN ion-gel membrane. This similarity was arisen from the N₂ permeation being based on a solution-diffusion mechanism for both membranes.

The water vapor pressure gradient, between the humidified feed gas and dry sweep gas, produced a driving force for permeation of the water vapor across the membrane. As it was displayed schematically in Fig. 3.2, the RH of feed side and permeated side were

continuously measured during gas permeation tests and water vapor permeabilities of membranes were calculated based on RH values. According to the Fig. 3.5(a), [P₄₄₄₄][Pro]- and DAPA-based FTMs showed the higher water vapor permeabilities than those of CO₂. In particular, in the case of AAIL-based FTM, the high water vapor permeability can be explained based on high water absorbability of intrinsically hygroscopic [P₄₄₄₄][Pro] (shown in Fig. 3.3) and fast diffusion of water vapor across the membrane due to the low viscosity of AAIL under humid conditions. As it was shown in Fig. 3.3, [P₄₄₄₄][Pro] absorbed the large amount of water that produced a large water vapor driving force across the membrane. This large driving force led to the fast diffusion of water vapor through the membrane and therefore, high water vapor permeability. The obtained value of water permeability for [P₄₄₄₄][Pro]-based DN ion-gel membrane is comparable/or higher than that of RTILs-based SILMs [17, 18] or facilitated transport membranes [19] reported in the literature.

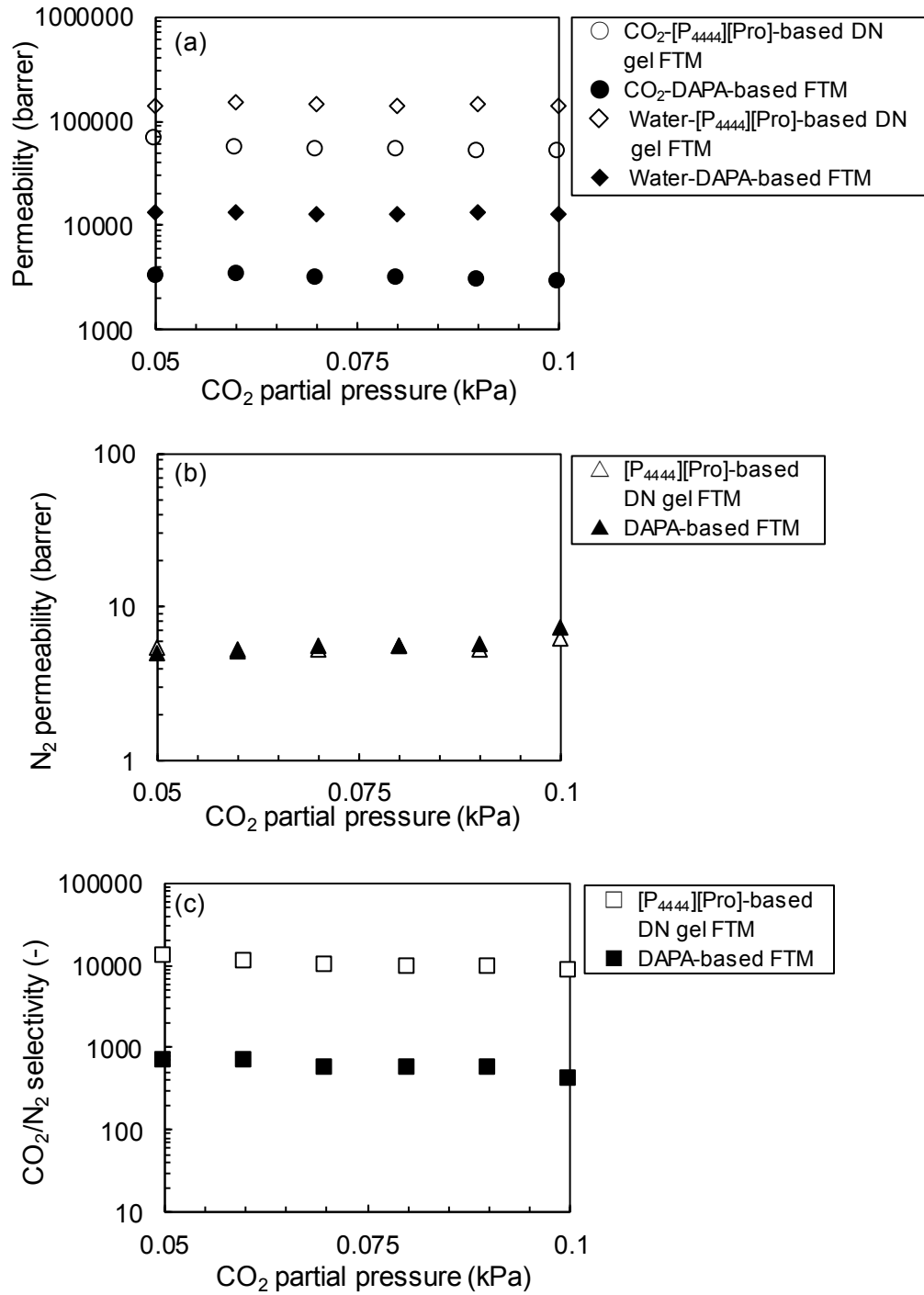


Fig. 3.5. Effect of CO₂ partial pressure on (a) CO₂ and water vapor permeabilities, (b) N₂ permeability, and (c) CO₂/N₂ selectivity of the [P₄₄₄₄][Pro]-based DN ion-gel membrane and the DAPA-based membrane ($T = 303$ K, $RH = 70\%$, $P_F = P_S = 100$ kPa).

3.3.2.2. Effect of RH on CO₂/N₂ separation performance

The CO₂ permeation properties of the [P₄₄₄₄][Pro]-based DN ion-gel membrane and the DAPA-based membrane were investigated at CO₂ partial pressure of 0.1 kPa, temperature of 303 K and RHs from 30 to 70%. The experimental conditions are summarized in Table 3.3. Fig. 3.6(a)-(c) show the effect of RH on the CO₂ and N₂ permeabilities and the CO₂/N₂ selectivities. Comparing the CO₂ separation performances of the [P₄₄₄₄][Pro]-based DN ion-gel membrane and the DAPA-based FTM, it was found that the DN ion-gel membrane has the substantially higher CO₂ permeability across the whole investigated RH range. A more significant difference between CO₂ permeabilities was observed at low RH because of the severe RH dependence of the DAPA-based FTM. This remarkable difference of CO₂ permeation performance can be explained based on the two determining parameters of the permeation, i.e., (1) CO₂ absorption amount and (2) fluidity of carrier medium. The both parameters strongly depend on the nature of the carrier medium. In the [P₄₄₄₄][Pro]-based DN ion-gel membrane, the outstanding CO₂ separation performance is mainly due to the following factors. First, the CO₂ carrier, i.e., [P₄₄₄₄][Pro], existed in the liquid state in the gel and acted as a carrier even without presence of water. Therefore, the DN ion-gel membrane did not show strong dependence on RH. Second, the DN ion-gel contained a large amount of [P₄₄₄₄][Pro] (80 wt.%). In other words, the gel network composition in the DN ion-gel membrane was low, bringing about the lower diffusion resistance for the [P₄₄₄₄][Pro]-CO₂ complex. Third, as shown in Fig. 3.4, even when only a small amount of water vapor was present in the atmosphere, [P₄₄₄₄][Pro] kept a relatively low viscosity around room temperature, leading to the CO₂ complex having a high diffusivity in the DN ion-gel

membrane. Forth, because AAILs can react with CO₂ regardless of the presence of water vapor [16], a larger amount of the [P₄₄₄₄][Pro]-CO₂ complex could be formed and the concentration gradient across the gel membrane would be large. As a result, CO₂ permeation through the [P₄₄₄₄][Pro]-based DN ion-gel membrane would be high across a wide RH range.

Table 3.3. Experimental conditions for RH dependency test

Temperature		303 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO ₂	0.1 kPa
Pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm ³ /min
	CO ₂	0.2 cm ³ /min
	N ₂	Balance
Sweep	He	40 cm ³ /min
Relative humidity in Feed		30 - 70%

In contrast, the CO₂ separation performance of the DAPA-based PVA/PAA membrane severely declined with decreasing RH of the feed stream, as is clearly shown in Fig. 3.6(a). The strong RH dependency of the DAPA-based membrane is in consistent with the findings regarding amino acid based-FTMs reported by Chen *et al.* [4, 6]. They attributed the sever drop of CO₂ permeability of glycine-based FTMs with decreasing RH to two main factors. First, the viscosity enhancement of the carrier solution and the decrease in the solubility of CO₂ in immobilized liquid membrane. A similar behavior was observed in our DAPA-based PVA/PAA FTM. Since the DAPA carrier could not exist in the liquid state in the PVA/PAA network at low RH, the diffusivity of the DAPA-CO₂ complex in the PVA/PAA network was considerably diminished. Moreover, the CO₂ solubility in DAPA-

based membrane also dropped with decreasing RH. In addition, as reported by Caplowz [20] and Danckwerts [21], the reaction of an amino acid salt carrier with CO₂ requires water, with CO₂ first reacting with an amine group to form a zwitterion. The intermediate zwitterion is then deprotonated by amine or water to form a carbamate salt. Due to low stability, the carbamate ion of the amine may undergo hydrolysis, forming bicarbonate. CO₂ transport can be facilitated in the forms of carbamate/or bicarbonate. Therefore, water plays a key role in facilitating the reaction of CO₂ with amine-based carriers, and a water-swollen PVA/PAA network is crucial for facilitating transport of CO₂ through DAPA-based FTMs [22]. According to above results, it can be said that the poor CO₂ permeability of conventional FTMs at low RH is a serious disadvantage for their application to separation of low concentrations of CO₂ from gases.

The water vapor permeability of FTMs at a wide range of RH showed a trend similar to that observed in the previous section. Regarding higher water vapor absorption amount and lower viscosity of AAILs at higher RHs, it was expected that water permeability increased at higher RHs. However, it was observed that water vapor permeability remained constant at the wide range of RH. Similar trend was reported for RTILs-based SILMs [17, 18].

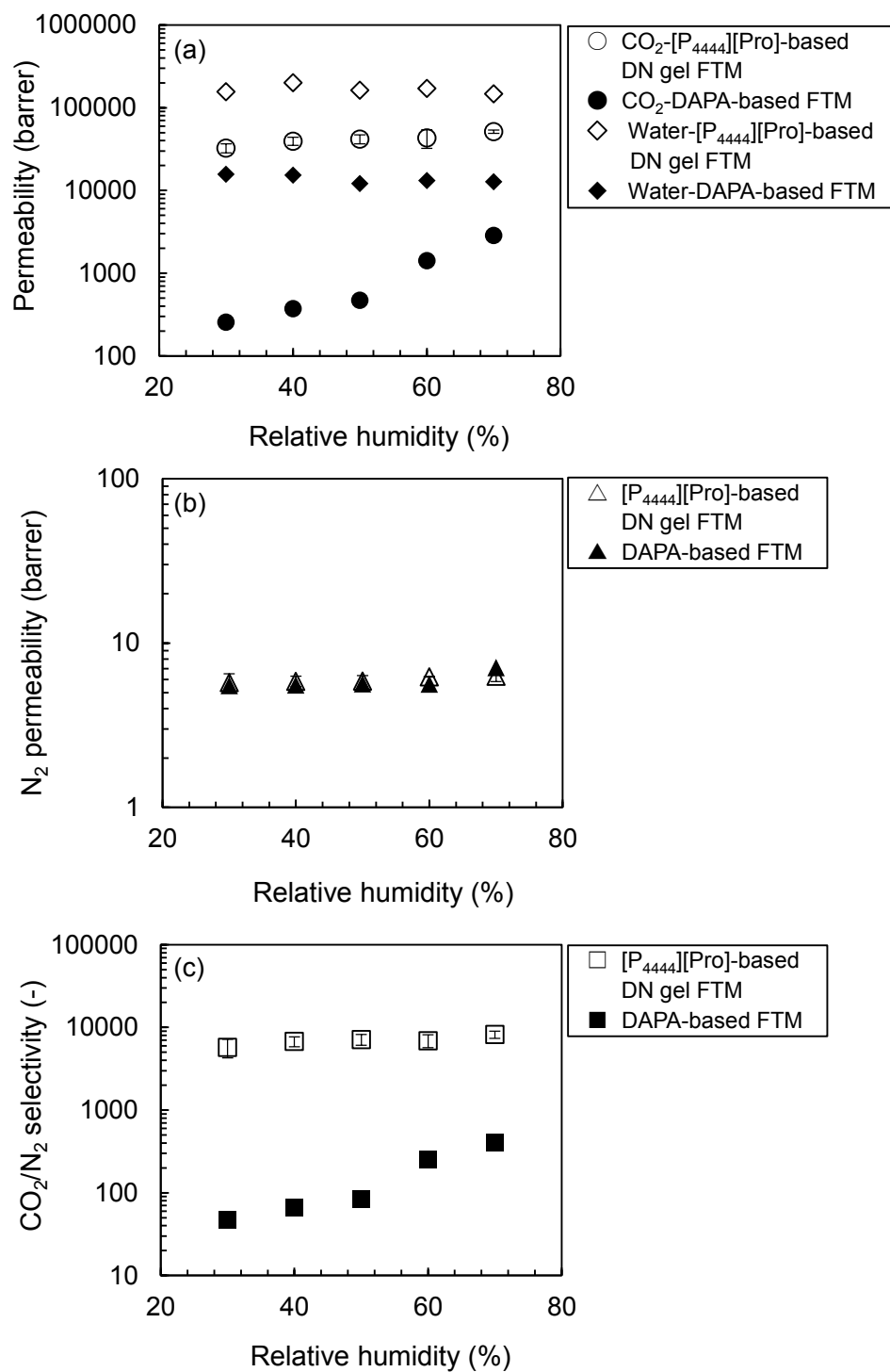


Fig. 3.6 Effect of RH on (a) CO₂ and water vapor permeabilities (b) N₂ permeability and (c) CO₂/N₂ selectivities of DN ion-gel and DAPA-based membranes ($T = 303\text{ K}$, $P_{\text{CO}_2} = 0.1\text{ kPa}$, and $P_{\text{F}} = P_{\text{S}} = 100\text{ kPa}$).

3.3.2.3. Effect of temperature on CO₂/N₂ permeability and selectivity

The gas permeation properties of the [P₄₄₄₄][Pro]-based DN ion-gel were investigated at different temperatures and a constant CO₂ partial pressure of 0.1 kPa and RH = 70%. The experimental conditions and results are shown in Table 3.4 and Fig. 3.7, respectively. As can be seen from Fig. 3.7, with increasing temperature from 303 K to 323 K, the CO₂ and N₂ permeabilities of the DN ion-gel membrane were increased from 52000 to 99000 barrer and 5.8 to 12.7 barrer, respectively, while the CO₂/N₂ selectivity remained approximately constant. Kasahara et al. [16] studied the effect of temperature on the CO₂ transport properties of AAILs-based FTMs under dry conditions and concluded that the enhancement of CO₂ permeability was higher than that of N₂ and that the CO₂/N₂ selectivity increased with rising temperature. The difference between the temperature dependence of the CO₂ permeabilities in two studies can be ascribed to the experimental conditions, in particular RH. Because the hydrogen bonding network formation increased at lower temperatures, the viscosity of AAIL in the FTMs reported by Kasahara et al. [16] radically increased with decreasing temperature under dry condition. On the other hand, our results showed that CO₂ permeability did not have strong dependency on temperature under humid condition, meaning the viscosity of [P₄₄₄₄][Pro] in the gel was determined entirely by the effects of temperature and water intercalation between the CO₂ complexes. At elevated temperatures, the hydrogen-bonding network easily decomposed, as was the case in Kasahara's investigation. However, at around room temperature in our work, the absorbed water molecules in the [P₄₄₄₄][Pro] strongly affected the hydrogen-bonding network deformation, implying that across the temperature range studied the change in the viscosity of [P₄₄₄₄][Pro] in the gel membrane was less

significant. As the result, the temperature dependence of the CO₂ permeability shown in Fig. 3.7(a) was less than that reported by Kasahara.

Table 3.4. Experimental conditions for temperature dependency test

Temperature		303 - 323 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO ₂	0.1 kPa
Pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm ³ /min
	CO ₂	0.2 cm ³ /min
	N ₂	Balance
Sweep	He	40 cm ³ /min
Relative humidity in Feed		70%

Although the temperature dependence of the CO₂ permeability of the [P₄₄₄₄][Pro]-based DN ion-gel membrane was small, it was clear that the CO₂ permeability increased with increasing temperature. As reported by Kasahara et al.[16], the amount of CO₂ absorption would not be significantly changed across the temperature range investigated. Therefore, CO₂ permeability was mainly determined by the viscosity of the [P₄₄₄₄][Pro] in the gel membrane. It was suggested that the viscosity of [P₄₄₄₄][Pro] in the gel membrane would be slightly decreased at higher temperatures. The decrease of viscosity also caused the N₂ permeability of the ion-gel membrane to increase slightly at higher temperatures (Fig. 7(b)). Thus, the CO₂/N₂ selectivity of the ion-gel membrane remained constant across the entire temperature range investigated in this study (Fig. 3.7(c)). The water vapor permeability of [P₄₄₄₄][Pro]-based ion-gel membrane showed a constant trend with increasing the feed temperature (Fig. 3.7(a)). This behavior is similar to that observed at the wide range of RH and CO₂ partial pressure.

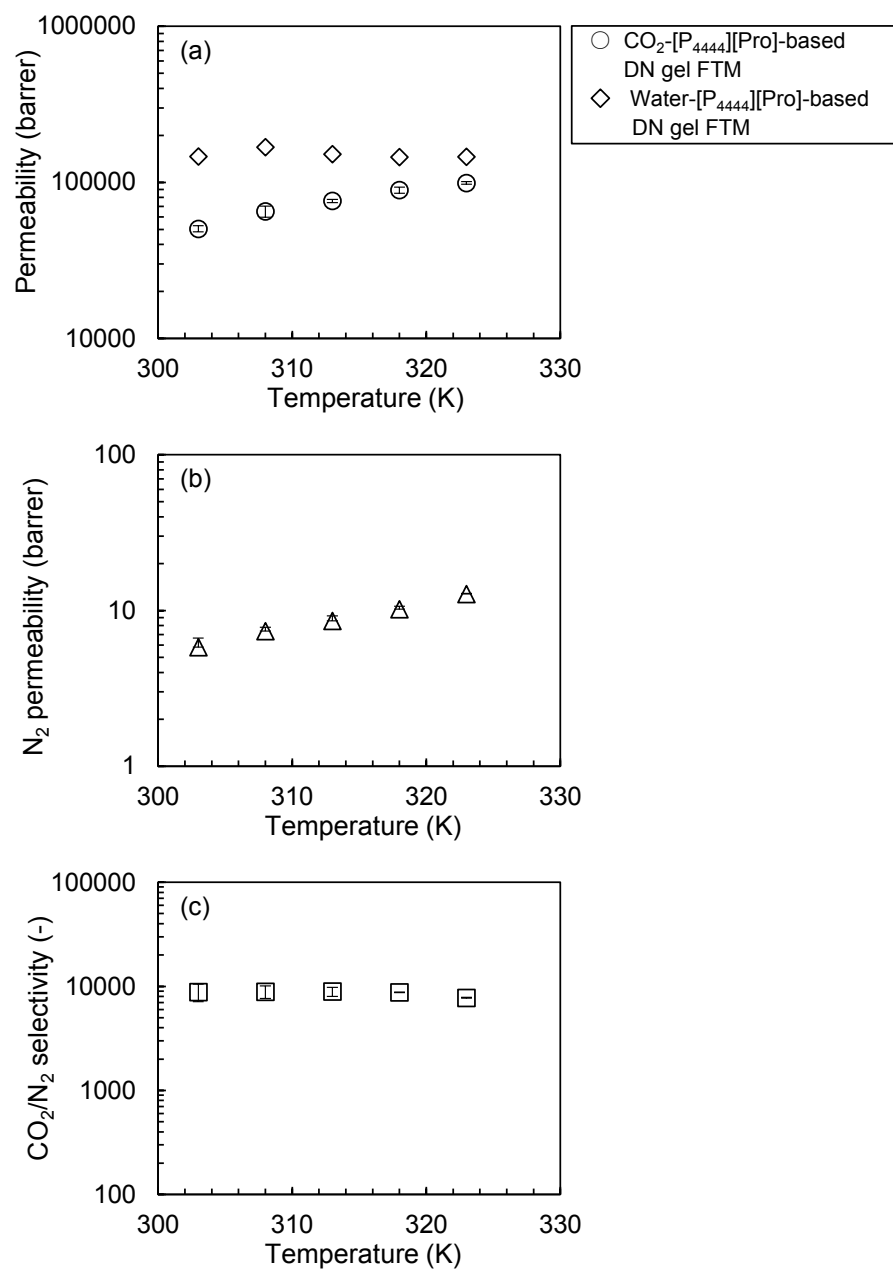


Fig. 3.7. Effect of temperature on (a) CO_2 and water vapor permeabilities, (b) N_2 permeability, and (c) CO_2/N_2 selectivity of $[P_{444}][Pro]$ -based DN ion-gel membrane ($P_{CO_2} = 0.1$ kPa, RH = 70%, and $P_F = P_S = 100$ kPa).

3.3.2.4. Durability of DN ion-gel membrane

In the previous chapter, I showed the high pressure resistance of a DN ion-gel membrane containing 80 wt.% [P₄₄₄₄][Pro] at the elevated temperature of 373 K under dry conditions. However, in practical operation most gases including atmospheric air contain water vapor. As both the DN network (PAMPS/PDMAAm) and [P₄₄₄₄][Pro] are strongly hydrophilic, a large amount of water vapor was absorbed by the DN ion-gel membrane under humid conditions, as shown in Fig. 3.3. As the water content in the DN ion-gel increased, the viscosity of the [P₄₄₄₄][Pro] was declined, as shown in Fig. 3.4. This decrease in the viscosity of [P₄₄₄₄][Pro] could result in serious leakage of [P₄₄₄₄][Pro] from the DN ion-gel membrane, and so it is important to investigate the durability of the [P₄₄₄₄][Pro]-based DN ion-gel membrane under humid conditions. As such, the durability of the [P₄₄₄₄][Pro]-based DN ion-gel membrane at 303 K in the presence of humid gas with a CO₂ partial pressure of 0.1 kPa was examined. The feed and sweep pressures were held constant at 100 kPa and the RH of the feed gas was adjusted to 70% during the test. The thickness and [P₄₄₄₄][Pro] content of the DN ion-gel membrane were 150 μm and 80 wt.%, respectively. As shown in Fig. 3.8(a)-(c), the DN ion-gel membrane maintained an outstanding performance even under humid conditions, with average CO₂ and N₂ permeabilities of 57000 and 7.2 barrer, respectively, and CO₂/N₂ selectivity of 7900. The durability of the DN ion-gel membrane was a result of the high osmotic pressure of the gel, which was generated by the sulfonic acid groups of PAMPS. From this examination, it is suggested that [P₄₄₄₄][Pro]-based DN ion-gel membranes could be used under highly humid conditions.

The water vapor permeability data of ion-gel membrane are shown in Fig. 3.8(a). Similar to CO_2 , the water vapor permeability displayed a constant and stable trend for about 100 h.

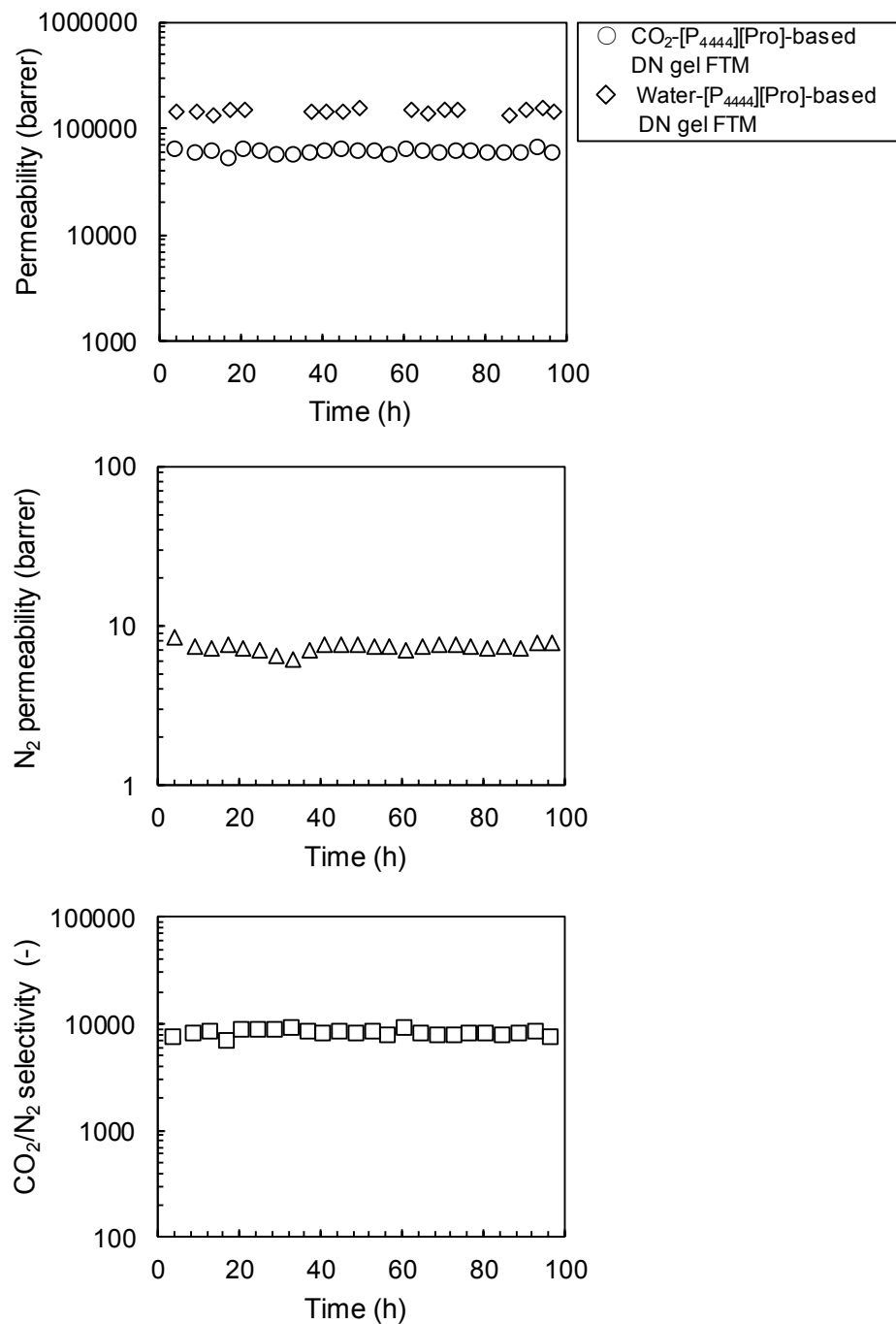


Fig. 3.8. Durability of $[\text{P}_{4444}][\text{Pro}]$ -based DN ion-gel membrane at 303 K and RH = 70% ($P_{\text{CO}_2} = 0.1$ kPa, $P_{\text{F}} = P_{\text{S}} = 100$ kPa).

3.4. Conclusions

Separation of CO₂ from CO₂/N₂ mixtures with very low CO₂ concentrations (500–1000 ppm) under humid conditions around room temperature using [P₄₄₄₄][Pro]-based DN ion-gel membranes was investigated, and its performance was compared with that of a conventional DAPA-based PVA/PAA FTM. The DN ion-gel membrane showed excellent CO₂ permeability (52000 barrer) and CO₂/N₂ selectivity (8100) at RH = 70%, much higher than those of the DAPA-based FTM. The outstanding CO₂ separation performance of the DN ion-gel membrane was attributed to the facilitated CO₂ transport mechanism, aided by several factors: (1) the high [P₄₄₄₄][Pro] content of the DN ion-gel membrane (>80 wt.%), (2) the high CO₂ absorbability and CO₂ absorption capacity of [P₄₄₄₄][Pro], (3) the high water absorbability of [P₄₄₄₄][Pro], and (4) the low viscosity and liquidity of [P₄₄₄₄][Pro] across a wide RH range. The DN ion-gel membrane showed excellent CO₂ separation performance across a wide range of RHs and temperatures. In addition, the DN ion-gel membrane presented stable performance for more than 100 h under humid conditions. From these investigations, it was demonstrated that [P₄₄₄₄][Pro]-based DN ion-gel membranes have strong potential for practical CO₂ separation applications including “air capture”.

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Chapter 4

New approach for the fabrication of double-network ion-gel membranes with high CO₂/N₂ separation performance based on facilitated transport

4.1. Introduction

As it was demonstrated in chapter 2 and 3, AAILs-based DN ion-gel membranes have a great potential for CO₂ separation from post-combustion flue gas and air stream with very low concentration of CO₂ about 500-1000 ppm (called “air capturing”). To our knowledge, the achieved CO₂ permeability and CO₂/N₂ selectivity for both application targets were the highest values reported until today. Most importantly, the DN ion-gel membrane showed a stable performance under high pressure or high RH feed streams, confirming the good durability of this novel type of ion-gel membranes. However, the developed DN ion-gel membranes suffer from some problems in terms of the thin ion-gel membrane preparation. The thickness of the first network hydrogel was adjusted by a polytetrafluoroethylene (PTFE) spacer placed between two quartz plates. Such thickness adjustment for a gel film is not possible for the preparation of a thin ion-gel membrane. In general, the most common techniques for the preparation of thin membranes are casting and coating. Therefore, the method used to prepare the first network hydrogel by mold injection is not a facile one and needs to be modified. In this regard, two main obstacles need to be overcome to make the first network gel via casting. One is the volatility of the electrolyte-based monomer that makes it impossible to fabricate the first network hydrogel by conventional casting. Another issue is associated with the solvent used for the dissolution of the first network monomer.

Typically, water is used for this purpose in the DN hydrogel fabrication. Therefore, when the first network solution is cast on a glass plate and irradiated by UV light to induce free-radical polymerization, water easily evaporates, making it impossible to prepare a smooth and defect-free film of the first network hydrogel.

In this study, a novel approach is proposed for the fabrication of TSIL-based DN ion-gel membranes, based on the casting method. An IL-based monomer was selected for the preparation of the first network. This monomer possesses two distinctive features required for DN ion-gel formation. First, it is an electrolyte (consisting of cations and anions) that can be swollen and impregnated with the second network monomer to form the DN ion-gel. Second, it is non-volatile and can be cast on glass plates without evaporation and monomer loss. In addition, instead of a volatile water solvent, hydrophilic ionic liquid was chosen as a solvent for the first network. Hence, it is possible to prepare the first network of ion-gel membrane via casting method. An aprotic heterocyclic anion (AHA) type TSIL was used as the carrier of DN ion-gel membranes. The reason behind of this selection was that AHA type TSIL has low viscosity desirable to be used as the carrier of TSILs-based FTMs [1].

In this chapter, for the first time, I have proposed a novel approach for preparation of DN ion-gel membrane based on casting method. The effect of the cross-linkage density of the first network gel on the mechanical strength and network structure of DN hydrogels and ion-gels was investigated. In addition, the effect of cross-linker loading of the first network, TSIL content and membrane thickness on the gas permeation properties of ion-gel membranes was assessed. The stability of ion-gel membranes was also evaluated for different trans-membrane pressures.

4.2. Experimental

4.2.1. Materials

[3-(Methacryloylamino) propyl] trimethylammonium chloride solution (MAPTAC, 50 wt.% in H₂O, Sigma-Aldrich) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄], ≥ 98% (HPLC), Sigma-Aldrich) were used as the monomer and solvent for the first network ion-gel, respectively. *N,N'*-methylenebis(acrylamide) (MBAA) and 2-oxoglutaric acid (OA, > 99%) were supplied by Tokyo Chemical Industry Co. and were used as a cross-linker and initiator for the first network, respectively. *N,N*-dimethylacrylamide (DMAAm, > 99%, Tokyo Chemical Industry Co.) was used as the second network monomer. Triethylphosphine (1.0 M in THF, Sigma-Aldrich), bromomethyl methyl ether (> 95.0%, Tokyo Chemical Industry Co.), and indazole (99.0%, Tokyo Chemical Industry Co.) were used for the preparation of TSILs. Poly(vinyl alcohol) (PVA, M_w = 89000~98000) and poly(4-vinylphenol) (PVP, M_w = 11000) were purchased from Sigma-Aldrich. All materials were used without any further purification. The chemical structures of MAPTAC, DMAAm, and MBAA are shown in Fig. 4.1(a–c).

4.2.2. Synthesis of ionic liquid

[P₂₂₂₍₁₀₁₎][Inda] was synthesized by a neutralization reaction between [P₂₂₂₍₁₀₁₎][OH] and indazole. The precursor of [P₂₂₂₍₁₀₁₎][OH], [P₂₂₂₍₁₀₁₎][Br] was synthesized according to a previously described procedure [1]. A 1.0 M solution of triethylphosphine in THF (50 mL, 0.05 mol) was poured into a necked round-bottom flask equipped with a reflux condenser at 353 K under nitrogen atmosphere. An equimolar amount of bromomethoxymethyl ether (6.3 g, 0.05 mol) was gradually added, and the solution was stirred for 6 h. Subsequently, the

solution was cooled at room temperature for 30 min, and hexane (300 mL) was added. The mixture was stirred overnight, and $[P_{222(101)}][Br]$ was obtained as a white solid after solvent evaporation at 313 K. The synthesized $[P_{222(101)}][Br]$ (24.3 g) was dissolved in Milli-Q water (100 mL), and the solution was treated with an OH-type anion exchange resin (80 g) for 1 h to form $[P_{222(101)}][OH]$.

$[P_{222(101)}][Inda]$ was synthesized via a previously reported neutralization reaction between $[P_{222(101)}][OH]$ and indazole [2, 3]. An equimolar amount of indazole (5.97 g, 0.05 mol) was dissolved in ethanol, and the solution was stirred for 30 minutes. The obtained solution was added to $[P_{222(101)}][OH]$, and the reaction mixture was stirred overnight. Finally, the reaction mixture was evaporated at 333 K to remove the solvent and produced water. The chemical structure of the synthesized IL is shown in Fig. 4.1(d).

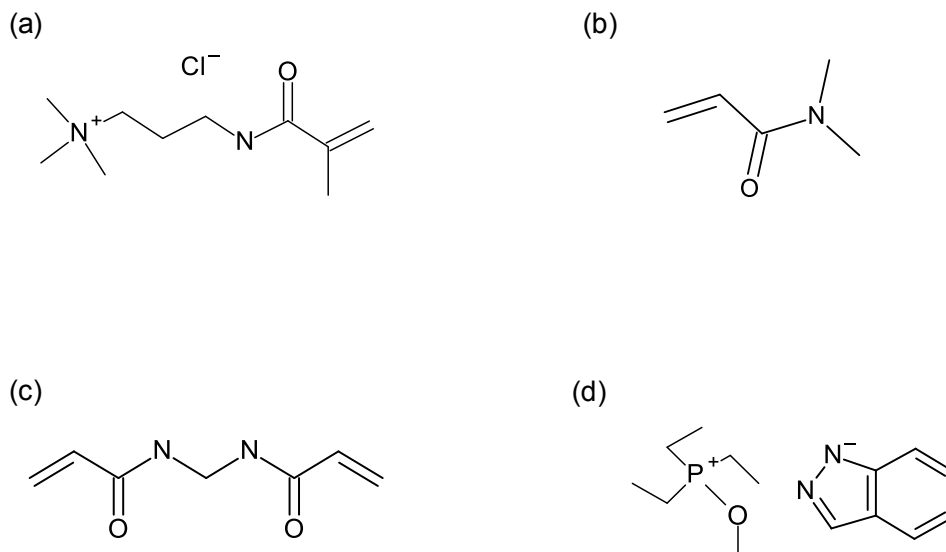


Fig. 4.1. Chemical structure of (a) MAPTAC (first network monomer), (b) DMAAm (second network monomer), (c) MBAA cross-linker, and (d) $[P_{222(101)}][Inda]$ (carrier).

4.2.3. Selection of the first network monomer for casting

To determine the appropriate monomer and solvent for the preparation of the first network gel by casting, preliminary experiments were carried out. The first network monomer should fulfill two important criteria: (1) a non-volatile electrolyte suitable for preparation of the ion-gel by casting and (2) good compatibility with the second network to form the DN network. For this purpose, bulk gels of the first network were initially prepared to determine the proportions of the IL-based monomer and solvent required for the ion-gel fabrication. Tributyl(4-vinylbenzyl)phosphonium chloride ([TVBP][Cl]), MAPTAC, and 1-vinyl-3-ethylimidazolium bromide ([veim][Br]) were selected as IL monomers. Four RTILs, namely 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), [emim][BF₄], and 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO₄]) were chosen as solvents for the IL monomers. The results of preliminary experiments are summarized in Table 4.1, showing that [emim][BF₄] is a good solvent for forming an ion-gel with [TVBP][Cl] and MAPTAC. In the second step, the compatibility of prepared ion-gels with the second network monomer (i.e., dimethylacrylamide (DMAAm), which exhibits good compatibility with TSILs) was investigated. In the compatibility test, the pre-fabricated first network ion-gel was immersed in an aqueous solution of DMAAm. Since this ion-gel is a polyelectrolyte, it swelled as a result of impregnation with the DMAAm solution. Finally, the swollen hydrogel was irradiated by UV-light to achieve the second network. The poly(TVBPC)/poly(DMAAm) and poly(MAPTAC)/poly(DMAAm) hydrogels were evaluated in terms of their mechanical

strength, with high tensile fracture stress observed for the second one. Therefore, the MAPTAC monomer (Fig. 4.1 (a)) was selected to fabricate the DN ion-gel by casting.

Table 4.1. Gel formation test of IL-based monomer with different solvents

	[emim][Tf ₂ N]	[emim][BF ₄]	[bmim][BF ₄]	[emim][EtSO ₄]
MAPTAC	×	○	×	×
TVBP-Cl	×	○	×	×
[Veim][Br]	×	×	×	×

4.2.4. Fabrication of PMAPTAC/PDMAAm DN ion-gel membrane

To prepare the DN ion-gel membrane containing [P₂₂₂₍₁₀₁₎][Inda], a DN hydrogel was prepared by a two-step free radical polymerization. The preparation of the PMAPTAC/PDMAAm hydrogel is schematically shown in Fig. 4.2. First, the PMAPTAC ion-gel was prepared using the casting method described below. The desired amount of MAPTAC (50 wt.% solution in H₂O) was dissolved in [emim][BF₄], and the solution was stirred for 10 minutes. The obtained solution was dried in a vacuum oven at 373 K for 3 h to evaporate the water present therein. Subsequently, certain amounts of MBAA (4 mol.%) and OA (0.2 mol.%) were added to the solution, and the mixture was stirred for 20 minutes. The composition of the first network solution is summarized in Table 4.2. Prior to casting the first network solution, a sacrificial PVP-containing layer was coated on the glass plate [4] using an ethanol/PVP solution (20 mg mL⁻¹). This layer enables the smooth and fracture-free detachment of the PMAPTAC ion-gel film from the glass plate. Due to the hydrophobic nature of PVP, another thin PVA sacrificial layer was coated on top of the PVP layer to provide a basement for the casting of the hydrophilic PMAPTAC/[emim][BF₄] solution. The

PVA layer was prepared from an aqueous solution of PVA (5 mg mL^{-1}), and the coated layer thickness was adjusted to $50 \text{ }\mu\text{m}$.

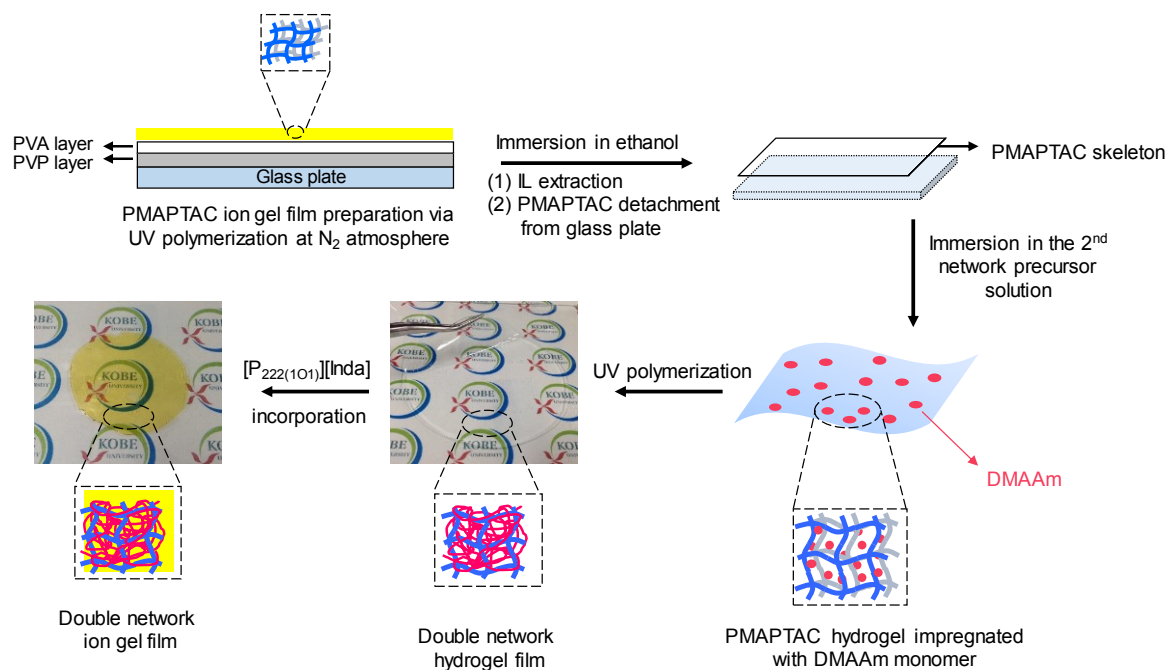


Fig. 4.2. Schematic illustration of DN ion-gel membrane preparation via a casting method

Table 4. 2. Composition of the first and second networks used for DN hydrogel preparation

	Reagent	Amount
1 st Network	MAPTAC	2.0470 g (3M)
	MBAA	0.0572 g (4 mol %)
	OA	0.0027 g (0.2 mol %)
	[Emim][BF ₄]	4 g
2 nd Network	DMAAm	39.65 g (4M)
	OA	0.05844 g (0.1 mol %)
	NaCl	2.922 g
	Water	100 ml

mol.% = (mole of /mole of monomer), M = (mmole of monomer/mL of solvent)

After coating of the PVP and PVA layers, the PMAPTAC/[emim][BF₄] solution was cast on the PVA layer and irradiated by UV light under N₂ atmosphere for 6 h to afford the PMAPTAC ion-gel film. To detach the obtained film from the glass plate, it was subsequently

immersed in ethanol, which dissolved the PVP layer and detach the PVA layer from ion-gel film as well. At the same time, the solvent of the ion-gel film, i.e., [emim][BF₄], was extracted into ethanol, producing a PMAPTAC film with a rigid structure. The PMAPTAC film was then immersed in the second network solution (with composition listed in Table 4.2) for 12 h. The large osmotic pressure difference between the inside and the outside of the PMAPTAC network induced full swelling of the gel and impregnation with the DMAAm monomer. The swelling ratio of the PMAPTAC film could be easily controlled via addition of NaCl to the second network solution. The PMAPTAC hydrogel impregnated with DMAAm was sandwiched between two quartz plates, followed by UV-light-induced free radical polymerization for 3 h to afford the PMAPTAC/PDMAAm DN hydrogel.

In the final step, the DN hydrogel was immersed in ethanol to exchange the water solvent in the gel. The DN gel was then immersed in an ethanolic solution of [P₂₂₂(101)][Inda] for 6 h to incorporate the IL into the gel network. The solution concentration was measured every 1 h to ensure equilibration. Finally, the PMAPTAC/PDMAAm DN gel impregnated with [P₂₂₂(101)][Inda] was dried in a vacuum oven at 373 K for 5 h to remove ethanol and any remaining non-reacted monomers in the gel network. The dried DN ion-gel containing [P₂₂₂(101)][Inda] could now be used in the gas permeation test. The IL content of the fabricated DN ion-gel was controlled by adjusting the concentration of the ethanol/ [P₂₂₂(101)][Inda] solution. Figure 4.3 shows the results of IL content measurement for DN ion-gels prepared using ethanol/[P₂₂₂(101)][Inda] solutions with different concentrations. The IL content of the ion-gel was measured according to a procedure provided in Chapter 2 (section 2.2.4). As can be clearly seen from Fig. 4.3, the [P₂₂₂(101)][Inda] content of the DN ion-gel membrane

increased with increasing $[P_{222(101)}][Inda]$ concentration in the solution, finally reaching a constant value (~ 80 wt.%).

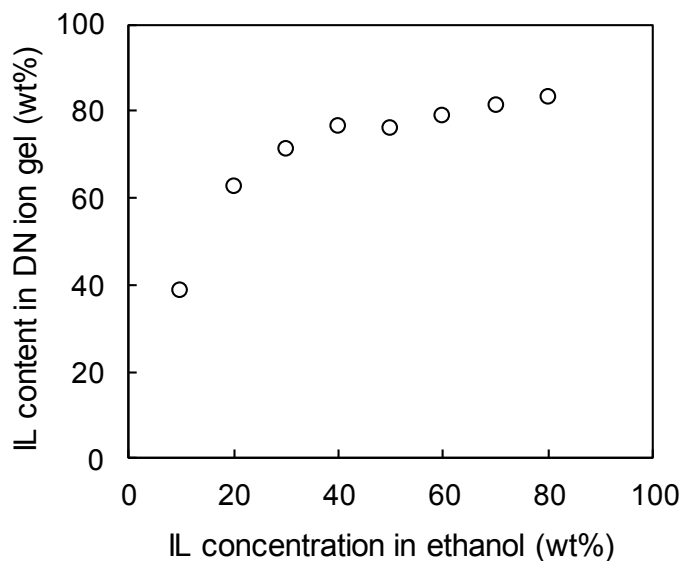


Fig. 4.3. Relationship between the IL content in the DN ion-gel and the equilibrium IL concentration in the IL/ethanol mixture used for DN ion-gel preparation.

4.2.5. Gas permeability measurement

Gas permeability measurement of DN ion-gel membranes were carried out according to the procedure explained in Chapter 2 (section 2.2.5).

4.2.6. Mechanical strength measurement

Cyclic loading-unloading tensile stress-strain curves of DN hydrogels and DN ion-gel films were obtained according to the procedure explained in Chapter 2 (section 2.2.6).

4.3. Results and discussion

4.3.1. Effect of cross-linker loading

4.3.1.1. Effect of cross-linker loading on gel structure

To investigate the effect of the cross-linker loading of the PMAPTAC network on the structure of PMAPTAC/PDMAAm hydrogels, samples containing 0.5, 1, 2, 3, 4, and 6 mol.% of MBAA were fabricated, and their mechanical strength was examined. The polymer network and water (as a solvent) contents in the PMAPTAC/PDMAAm hydrogels were measured for all samples, according to the following procedure. The weight of hydrogel samples was initially measured (m_1), and the samples were dried in a vacuum oven at 373 K for 5 h to completely remove water. Subsequently, the weight of the obtained polymer skeleton was re-measured (m_2), and the polymer network content ($\text{wt.\%} = (m_2/m_1) \times 100\%$) was calculated for all samples. The polymer and water (as solvent) contents of all hydrogel samples were ca. 10 and 90 wt.%, respectively. The tensile fracture stress and strain data of hydrogels are displayed in Fig. 4.4, which demonstrates that increasing the MBAA loading from 0.5 to 3 mol.% resulted in an enhancement of tensile fracture stress. Upon further increasing the MBAA loading, the mechanical properties of the hydrogels deteriorated. To elucidate the dependence of mechanical properties on the cross-linker loading of the MAPTAC network, cyclic loading tests at different loading intervals were performed, with the stress-strain curves shown in Fig. 4.5. Decreasing the MBAA loading had a significant effect on the structural changes of the PMAPTAC/PDMAAm hydrogel network. The irreversible softening during loading-unloading, observed for samples with MBAA loadings below 3 mol.%, demonstrated the double-network structure of the hydrogels. This softening

behavior is the identifying characteristic of DN gels and is attributed to the irreversible network structure changes during the deformation [5].

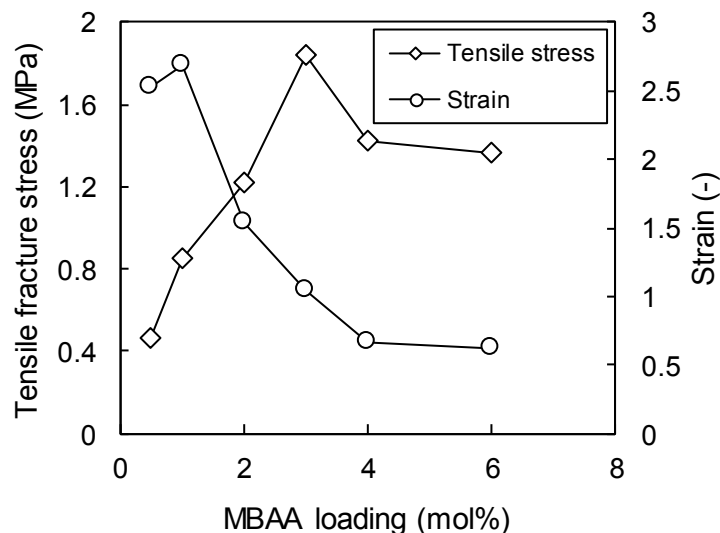
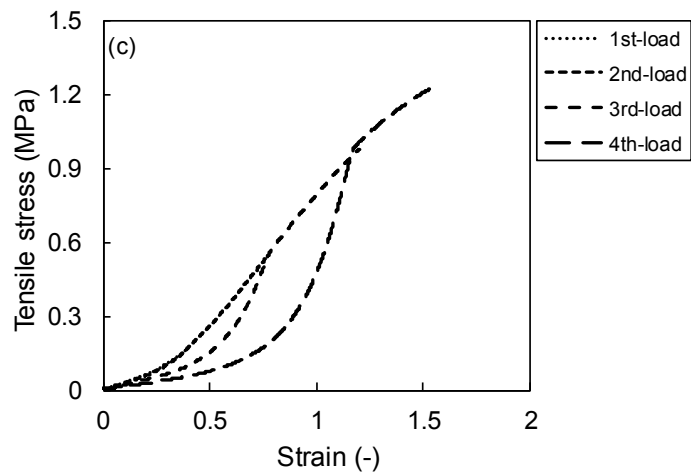
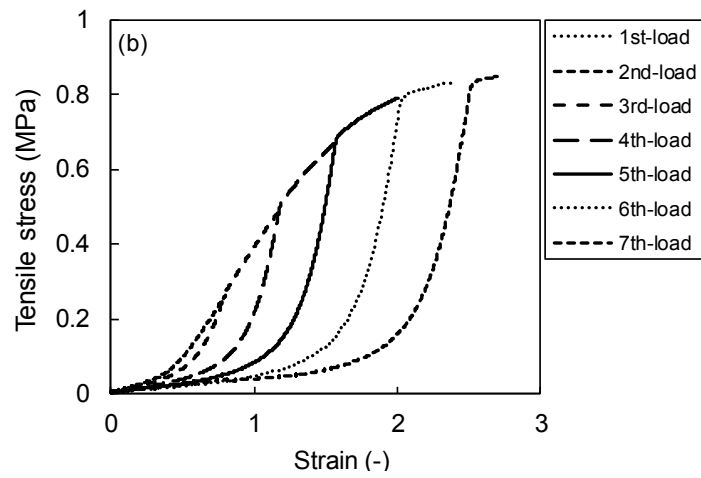
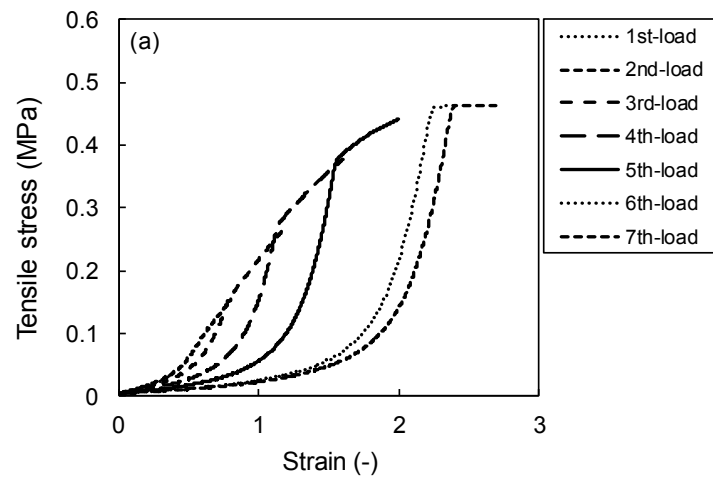


Fig. 4.4. Effect of MBAA loading on the tensile fracture stress and strain of PMAPTAC/PDMAAm hydrogels (MAPTAC = 3 M, hydrogel thickness = 0.2–0.3 mm, water content = 90 wt.%).

Generally, from the point of view of network structure, the cross-linker density of the first network and the molar ratio of the second network to the first network are the two important parameters mainly contributing to the toughening of DN hydrogels [5-8]. The effect of the former is described based on the sacrificial bond concept. The fragile first network breaks into small chains (clusters) that dissipate energy under the applied stress. These sacrificial bonds also act as cross-linkers of the long and flexible chains of the second network. The loosely cross-linked second network also plays a crucial role to propagate the micro-cracks in the brittle first network, transfer the stress to a wide region of the DN network, and prevent the crack growth from a microscopic to a macroscopic level [5, 6]. Thus, a higher molar ratio of the second monomer is needed to provide enough fluidity to the network structure for effective dissipation of energy through the hydrogel matrix. Therefore,

these two parameters need to be optimized to prepare a hydrogel with good mechanical strength.

According to the cyclic loading curves (Fig. 4.5), the PMAPTAC/PDMAAm hydrogels containing 0.5 to 3 mol.% of MBAA exhibited softening during the loading-unloading test, while the hydrogels with higher MBAA loadings (4 and 6 mol.%) exhibited a different structural behavior. The irreversible hydrogel softening at low MBAA loadings is mainly attributed to the higher swelling degree of the PMAPTAC network. This resulted in the incorporation of a larger amount of the second network monomer into the hydrogel network, which is crucial for the DN structure formation. At higher MBAA loadings, the limited swelling of the highly cross-linked PMAPTAC network led to the partially incorporation of the second network. Therefore, the PMAPTAC/PDMAAm hydrogels did not show any softening behavior. In addition to the network structure, as can be seen in Fig. 4.4, the tensile fracture stress of hydrogels was significantly affected by changes in MBAA loading. For example, when the MBAA loading was increased from 0.5 to 3 mol.%, the hydrogel tensile fracture stress was markedly enhanced from 0.46 to 1.84 MPa. I attributed this sharp rise of tensile fracture stress to the highly cross-linked first network that substantially influences the toughening behavior of hydrogels based on the sacrificial bond concept. However, a further MBAA loading increase to 4 and 6 mol.% was accompanied by a decrease in tensile fracture stress. It seems reasonable to attribute this behavior to the lower swelling ratio of the PMAPTAC hydrogel network at higher MBAA loadings. Hence, it can be concluded that at higher MBAA loadings (> 3 mol.%) the swelling ratio of the first network and incorporation of the second network are the determining parameters for the toughening of hydrogels.



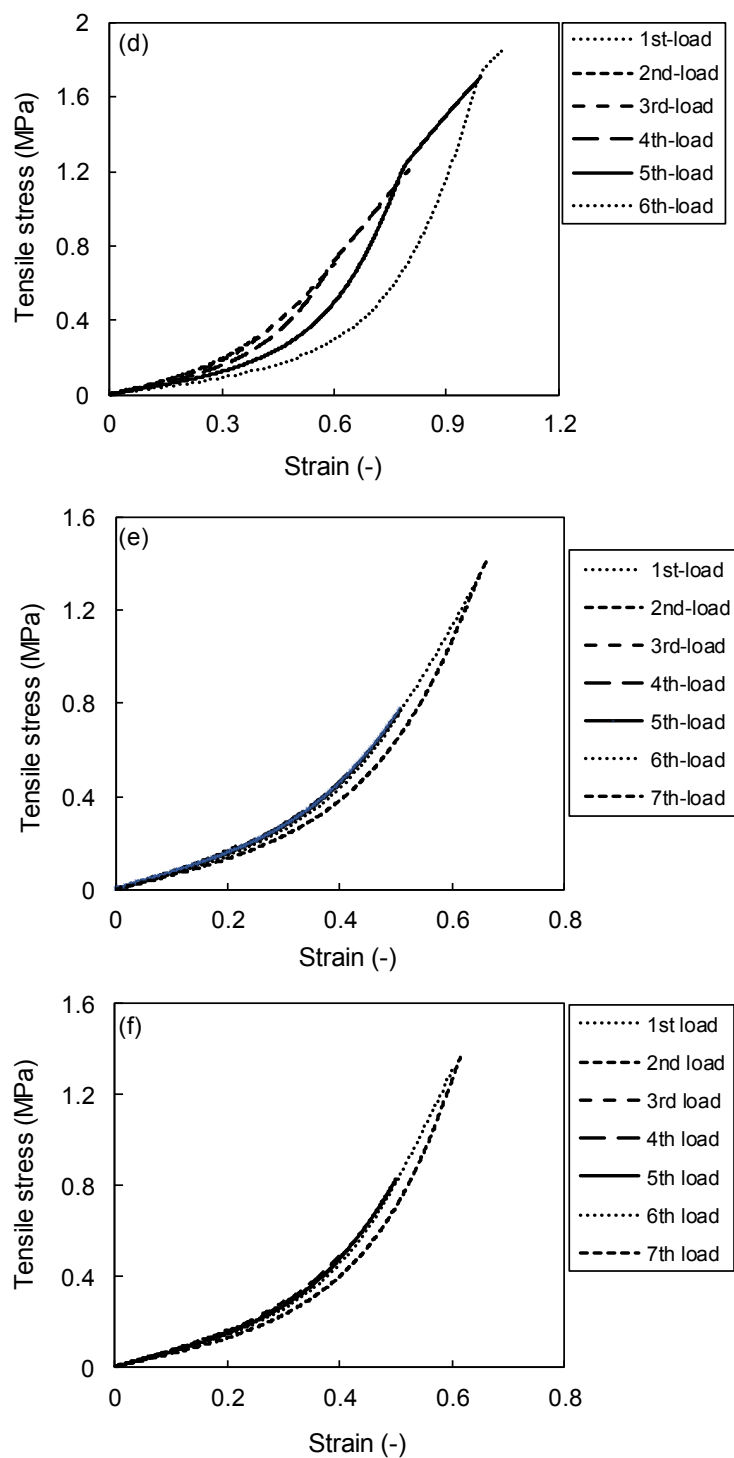


Fig. 4.5. Cyclic loading measurement of PMAPTAC/PDMAAm hydrogels with different MBAA cross-linker loadings: (a) 0.5 mol.%, (b) 1 mol.%, (c) 2 mol.%, (d) 3 mol.%, (e) 4 mol.%, and (f) 6 mol.%.

In the next step, the cyclic tensile stress loading of the PMAPTAC/PDMAAm ion-gel containing 80 wt.% [P₂₂₂₍₁₀₁₎][Inda] (as solvent) with MBAA cross-linker loadings of 0.5, 2, and 6 mol.% was evaluated. As shown in Fig. 4.6, the ion-gel films exhibited similar changes in their network structure, as was observed for hydrogels, with increasing MBAA loading. This means that the network structure of the PMAPTAC/PDMAAm hydrogel remained unchanged after impregnation with [P₂₂₂₍₁₀₁₎][Inda]. It is important to note that the tensile fracture stress of the PMAPTAC/PDMAAm ion-gel is higher than that of analogous PMAPTAC/PDMAAm hydrogels, which is mainly due to the higher polymer network content (ca. 20 wt.%) of the ion-gel compared to hydrogels (ca. 10 wt.%). A tensile fracture stress of more than 1 MPa for the PMAPTAC/PDMAAm ion-gel containing 80 wt.% of IL indicates that the developed ion-gel membranes possess good mechanical strength and can be used for gas separation. Surprisingly, the novel ion-gel membranes prepared via casting showed better mechanical strength than those fabricated based on mold-injection method, exhibiting tensile fracture stress values of 0.7 MPa for DN ion-gel membranes with 80 wt.% AAIL.

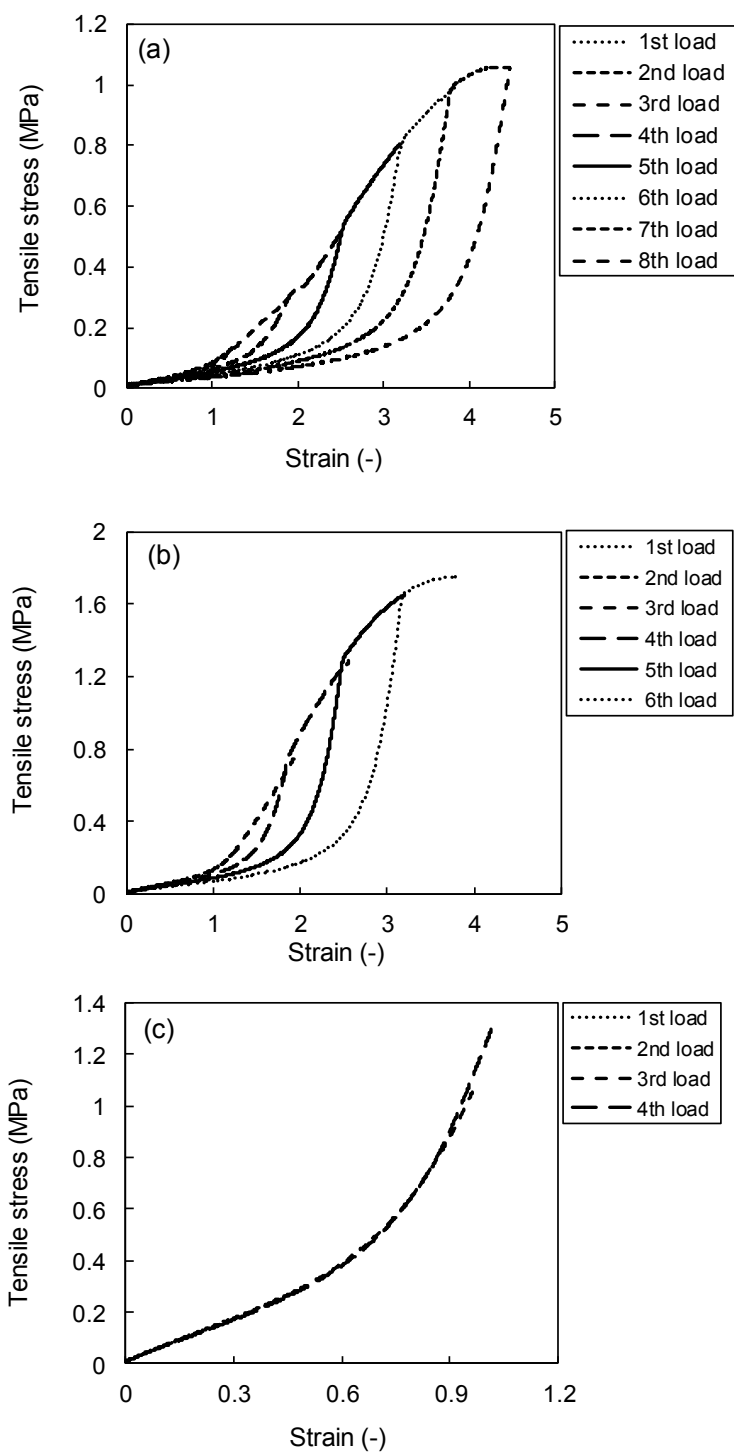


Fig. 4.6. Cyclic tensile stress loading test of a PMAPTAC/PDMAAm ion-gel membrane containing [P₂₂₂(101)][Inda] (a) MBAA = 0.5 mol.%, (b) MBAA = 2 mol.%, (c) MBAA = 6 mol.% (MAPTAC = 3 M, IL content = 80 wt.%).

4.3.1.2. Effect of cross-linker loading on CO₂/N₂ separation performance

When trans-membrane diffusion is the rate-determining step of CO₂ permeation through a membrane, the corresponding CO₂ flux can be described by a product of the concentration gradient of CO₂ dissolved in the membrane and the diffusion coefficient. In the case of TSIL-based FTMs, this flux is expressed by the product of the concentration gradient and diffusion coefficient of the CO₂-TSIL complex due to its high viscosity [9]. The polymer network density is also expected to affect the diffusivity of the CO₂-TSIL complex in TSIL-based DN ion-gel membranes.

As shown in the previous section, the network structure of the ion-gel membrane depended on the cross-linker loading of the PMAPTAC network. The change of network structure is expected to affect the gas transport properties of ion-gel membranes. Hence, the CO₂/N₂ separation performance of PMAPTAC/PDMAAm ion-gel membranes with different MBAA loadings of 0.5, 1, 2, and 4 mol.% was evaluated at 373 K (Fig. 4.7), with experimental conditions summarized in Table 4.3. The [P₂₂₂(101)][Inda] content of ion-gel membranes was adjusted to 80 wt.%. As shown in Fig. 4.7, the change in MBAA loading was found to have a considerable impact on the CO₂ permeability. The permeability of ion-gel membranes exhibited the following order (based on the MBAA loading of the PMAPTAC network): 0.5 mol.% > 1 mol.% > 2 mol.% > 4 mol.%. For example, at a constant CO₂ partial pressure of 2.5 kPa, the CO₂ permeability of ion-gel membranes markedly increased from 6450 to 20000 Barrer as the MBAA loading was reduced from 4 mol.% to 0.5 mol.%. A similar trend was also observed for a broad range of CO₂ partial pressures. Since the polymer content of ion-gel membranes is constant, the dramatic increase in CO₂ permeability with

reducing MBAA loading is mainly associated with their network structure. As shown in the previous section, ion-gel membranes with higher MBAA loadings possess a stiff and rigid network structure. From the standpoint of gas permeation properties, it is reasonable to assume that a PMAPTAC/PDMAAm ion-gel membrane containing highly cross-linked PMAPTAC affords a network structure with higher diffusion resistance to CO₂ permeation. Therefore, the cross-linker loading of the PMAPTAC network strongly influences the network structure and CO₂ permeation properties of ion-gel membranes. The N₂ permeability data of ion-gel membranes (Fig. 4.7(b)) are also in good agreement with the trend observed for CO₂ permeability. The ion-gel membranes containing 0.5 and 1 mol.% of MBAA presented higher N₂ permeabilities than the highly cross-linked ones (MBAA loading of 2 and 4 mol.%). Similarly, this trend is largely related to the high diffusion resistance of ion-gel membranes induced by the highly cross-linked PMAPTAC network.

Increasing the CO₂ partial pressure was also found to cause a steady reduction in CO₂ permeability for all ion-gel membranes (Fig. 4.7(a)). This permeability drop is mainly due to the carrier saturation upon further increase of CO₂ partial pressure, which is an identifying characteristic of FTMs [2, 3, 9-11]. Thus, this result implied that facilitated transport is the dominant permeation mechanism for CO₂. The relatively constant N₂ permeability of ion-gel membranes with increasing CO₂ partial pressure also pointed out that N₂ permeation follows the solution-diffusion mechanism [2, 3, 9-11]. It is worth mentioning that the fabricated ion-gel membranes showed excellent N₂ barrier properties even at high IL contents. As can be seen from Fig. 4.7(b), the N₂ permeability values of ion-gel membranes containing 80 wt.% IL changed from 16 to 45 Barrer. Fundamental studies on TSIL-based FTMs [9] indicated

that the size of the IL cation is a tunable parameter substantially impacting the CO₂/N₂ selectivity. The N₂ absorption capacity and thus N₂ permeability of ILs could be controlled and decreased by choosing small cations, which is desirable for improving the separation factor [3]. Making use of this advantage, the small-cation [P₂₂₂(101)][Inda] was used as a carrier of these ion-gel membranes, with the obtained results demonstrating good N₂ barrier properties and high CO₂/N₂ selectivity. As shown in Fig. 4.7(c), the ion-gel membranes displayed great CO₂/N₂ selectivity, particularly at low CO₂ partial pressures. For example, at 2.5 kPa CO₂ partial pressure, the ion-gel membranes displayed CO₂/N₂ selectivities in the range of 400–900. The CO₂/N₂ selectivity of IL-based ion-gel membranes is controlled by IL absorbability. In the case of TSIL-based ion-gel membranes, the high CO₂/N₂ selectivity resulted from the high CO₂ absorption capacity, which is based on chemical absorption.

Table 4.3. Experimental conditions of gas permeation test.

Conditions		Value	Unit
Temperature		373	K
Pressure	Feed	100	kPa
	Sweep	100	kPa
Partial pressure difference	CO ₂	2.5, 5, 10, 25, 50, 75	kPa
Pressure difference		0	kPa
Gas flow rate (dry base)			
Feed	Total	200	cm ³ /min
	CO ₂	5, 10, 20, 50, 100, 150	cm ³ /min
	N ₂	Balance	cm ³ /min
Sweep	He	40	cm ³ /min
Relative humidity		0%	

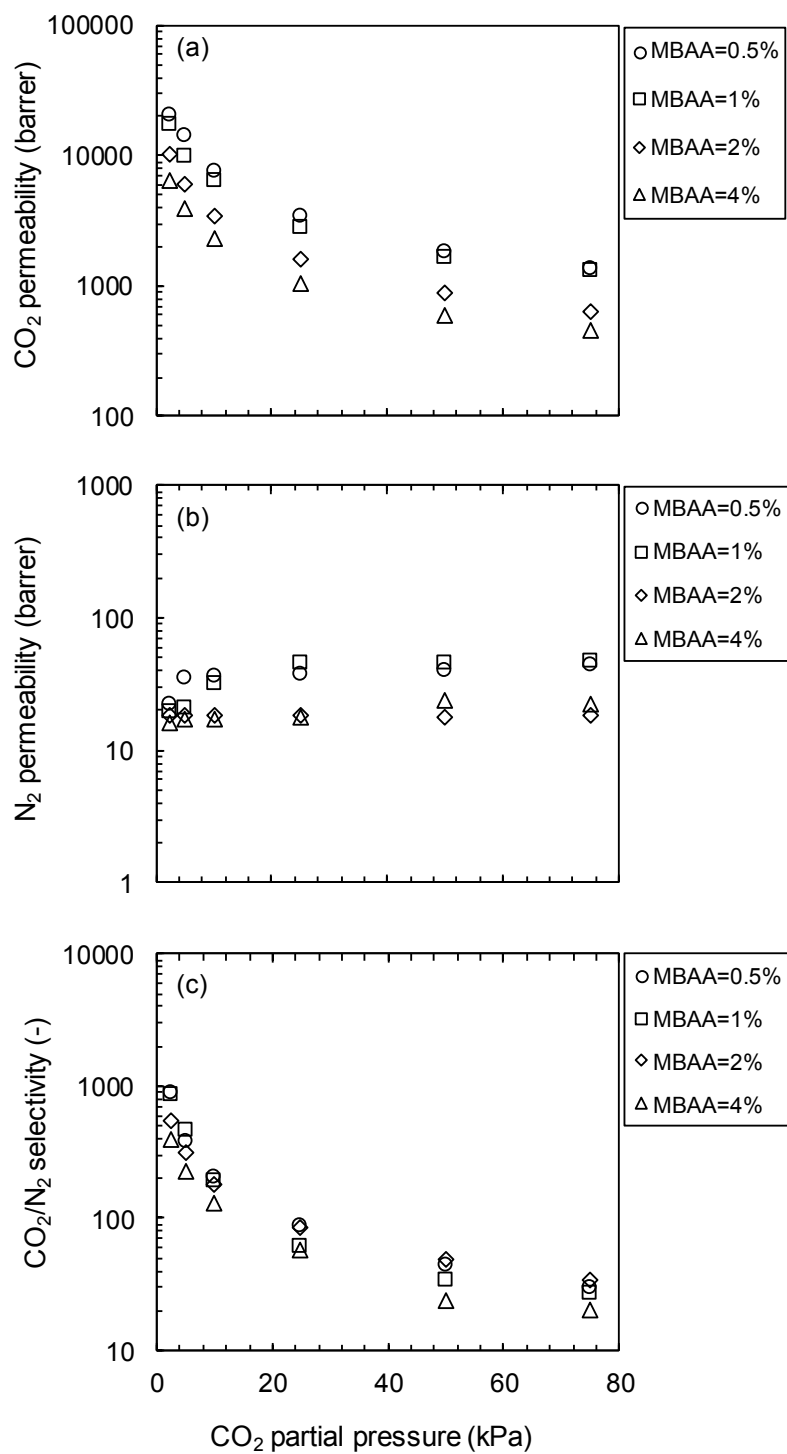


Fig. 4.7. Effect of cross-linker loading on (a) CO₂ permeability, (b) N₂ permeability, and (c) CO₂/N₂ selectivity of a PMAPTAC/PDMAAm ion-gel membrane containing [P₂₂₂₍₁₀₁₎][Inda] ($T = 373$ K, $P_F = P_S = 100$ kPa, MAPTAC = 3 M, IL content = 80 wt.%, membrane thickness = 80–200 μ m).

4.3.1.3. Effect of IL content on CO₂/N₂ separation performance

As shown in Fig. 4.3, the IL content of ion-gel membranes can be controlled by immersion of the hydrogel in an ethanol/IL solution of different concentrations. To investigate the effect of IL content, DN ion-gel membranes containing 55, 62, 74, and 83 wt.% [P₂₂₂₍₁₀₁₎][Inda] were prepared, and their CO₂/N₂ separation performance was assessed (Fig. 4.8). In view of the high CO₂ separation performance of the PMAPTAC/PDMAAm ion-gel membrane with a low cross-linker content, the MBAA loading of the PMAPTAC network in this investigation was adjusted to 0.5 mol.%. The CO₂ permeability of DN ion-gel membranes was enhanced with increasing IL content. For example, as the content of [P₂₂₂₍₁₀₁₎][Inda] was increased from 55 to 74 wt.%, the CO₂ permeability was increased from 3350 to 5450 Barrer. A further increase of the [P₂₂₂₍₁₀₁₎][Inda] content to 83 wt.% resulted in a CO₂ permeability enhancement to 7600 Barrer. To better understand the effect of IL content, two parameters should be taken into consideration: (1) the carrier content in the ion-gel network and (2) the polymer network density. Ion-gel membranes with high IL contents offer more CO₂-selective carriers in the network that chemically and reversibly react with CO₂. The enhancement of CO₂ permeability with increasing IL amount confirmed the role of carrier content. In addition, the increased IL content of the ion-gel membrane network is accompanied by a lower polymer network density. This is expected to cause a permeability rise due to the decreased diffusion resistance of the ion-gel network. However, the N₂ permeability change (i.e., relatively constant trend) with increasing IL content revealed that the polymer network density did not play a significant role in the permeation behavior of ion-gel membranes.

According to Fig. 4.8(a), all DN ion-gel membranes with different $[P_{222(101)}][Inda]$ contents showed enhanced CO_2 permeability with decreasing CO_2 partial pressure. This suggests that facilitated transport is the dominant CO_2 permeation mechanism for all DN ion-gel membranes, as described above. Fig. 4.8(b) shows that DN ion-gel membranes also showed excellent N_2 barrier properties. For example, the N_2 permeability of the DN ion-gel membrane containing 83 wt.% IL was ca. 20–30 Barrer. The constant N_2 permeability in a broad range of CO_2 partial pressures also demonstrated that N_2 permeation through the ion-gel membranes is based on the solution-diffusion mechanism. As the IL content was increased, the CO_2/N_2 selectivity followed a trend similar to the one observed for CO_2 permeability (see Fig. 4.8(c)). This means that a considerable increase in CO_2/N_2 selectivity was observed with increasing IL content. As mentioned above, the CO_2/N_2 selectivity of DN ion-gel membranes is controlled by absorption selectivity. Ion-gel membranes with high $[P_{222(101)}][Inda]$ contents possess a larger number of available carriers capable of chemically absorbing the CO_2 molecules on the feed side of the membrane, resulting in a larger driving force across the membrane and, therefore, higher CO_2 permeability. On the other hand, the effect of $[P_{222(101)}][Inda]$ content on the absorption capacity of N_2 is insignificant, since nitrogen absorption is based on physical dissolution. Hence, one can say that the increase of CO_2 absorption is the main contributor to the enhancement of CO_2/N_2 selectivity.

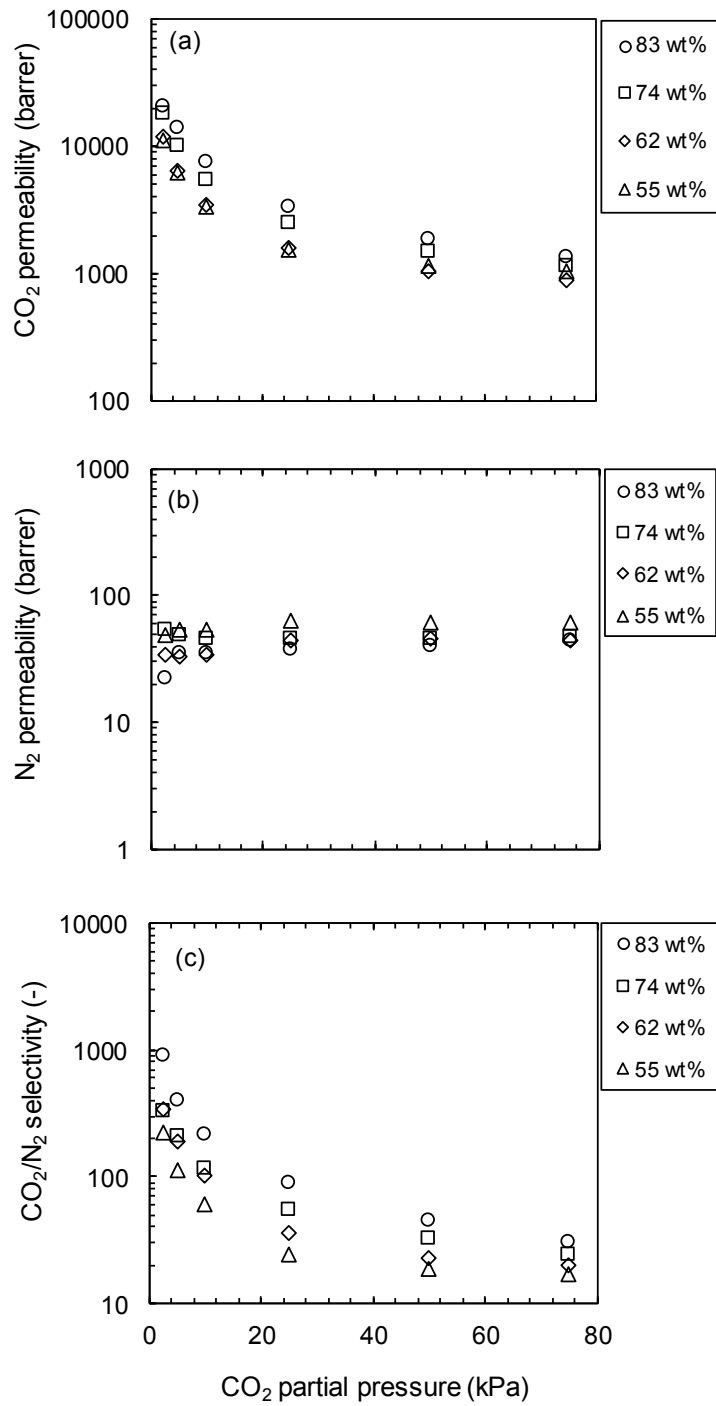


Fig. 4.8. Effect of [P₂₂₂₍₁₀₁₎][Inda] content on (a) CO₂ permeability, (b) N₂ permeability, and (c) CO₂/N₂ selectivity of a PMAPTAC/PDMAAm ion-gel membrane ($T = 373$ K, $P_F = P_S = 100$ kPa, MAPTAC = 3 M, MBAA = 0.5 mol.%, membrane thickness = 80–200 μ m).

4.3.1.4. Dependence of CO₂ permeance on membrane thickness

In this study, an ion-gel membrane containing a PMAPTAC network with 0.5 mol.% of loaded MBAA cross-linker and 80 wt.% of [P₂₂₂(101)][Inda] was prepared, and the effect of DN ion-gel membrane thickness on CO₂ permeance was investigated. DN ion-gel membranes with 80, 150, and 250- μ m thicknesses were prepared, and their CO₂ permeances at different CO₂ partial pressures were measured at 373 K (Fig. 4.9). The DN ion-gel membrane with an 80- μ m thickness exhibited the highest CO₂ permeance at different CO₂ partial pressures. For example, a CO₂ permeance of 250 GPU (1 GPU = 10⁻⁶ cm³/(cm²·s·cm Hg)) was obtained for the above DN ion-gel membrane at 2.5 kPa CO₂ partial pressure. The rate of CO₂ permeation through the TSIL-based membranes is controlled by CO₂ absorption on the feed side of the membrane, diffusion of the CO₂-TSIL complex across the membrane, or complex deformation on the permeate surface of the membrane. As seen in Fig. 4.9, CO₂ permeance is inversely proportional to the thickness (δ) of ion-gel membranes. This trend clearly implies that the rate-determining step of CO₂ permeation is the diffusion of the CO₂-TSIL complex across the ion-gel matrix.

The permeance of a membrane is defined as permeability divided by membrane thickness. Increasing the CO₂ permeability or reducing the membrane thickness are two possible ways to improve the CO₂ permeance. In this study, DN ion-gel membranes were fabricated under optimized conditions (i.e., low MBAA cross-linking degree and high IL content) to attain high CO₂ permeability. Therefore, further improvement of CO₂ permeance can be achieved by fabrication of very thin DN ion-gel membranes. Based on a rough calculation, a DN ion-gel membrane with 1- μ m thickness is expected to have a permeance

of 8000 GPU at a CO₂ partial pressure of 10 kPa, analogous to the CO₂ concentration in post-combustion flue gas. Therefore, fabrication of thinner DN ion-gel membranes is our next challenge.

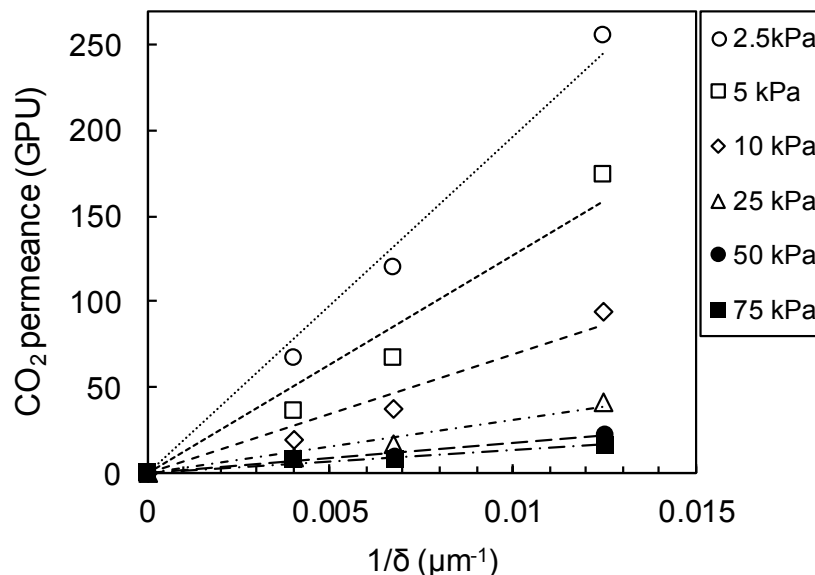


Fig. 4.9. Relationship between CO₂ permeance measured at different CO₂ partial pressures and the reciprocal thickness of DN ion-gel membranes containing [P₂₂₂₍₁₀₁₎][Inda] ($T = 373$ K, $P_F = P_S = 100$ kPa, MAPTAC = 3 M, MBAA = 0.5 mol.%, IL content = 80 wt.%).

4.3.1.5. Ion-gel membrane performance under pressurized conditions

To assess the IL holding capability and performance stability of PMAPTAC/PDMAAm DN ion-gel membranes under pressurized conditions, the CO₂ transport properties of the thin ion-gel membrane (80 μm) were evaluated at different trans-membrane pressure differences (0 to 500 kPa) and constant CO₂ partial pressure (10 kPa). For this purpose, the sweep side pressure was held constant at 100 kPa, and the feed pressure was changed from 100 to 600 kPa. The experimental conditions are summarized in Table 4.4. The gas permeation results are shown in Fig. 4.10. The DN ion-gel membrane displayed

a stable gas separation performance under the experimental conditions, exhibiting excellent N₂ barrier properties (N₂ permeability ~35 Barrer) and a CO₂/N₂ selectivity of ca. 150, along with excellent CO₂ permeability for a broad range of feed pressures. To the best of our knowledge, this is the first report on ion-gel membranes with high IL content prepared via casting that displayed good stability at high pressures and excellent CO₂ separation performance. The design of a DN gel composed of two networks with distinctive features makes it is possible to prepare a new type of ion-gel membranes displaying outstanding mechanical strength (tensile stress > 1 MPa) and exceptional CO₂ permeation properties. Importantly, the issues corresponding to CO₂ permeability/mechanical strength trade-off and poor IL holding retention were addressed by this novel type of DN ion-gel membranes.

Table 4.4. Experimental conditions of pressure stability test

Conditions		Value	Unit
Temperature		373	K
Pressure	Feed	100-600	kPa
	Sweep	100	kPa
Partial pressure difference	CO ₂	10	kPa
Pressure difference		0 - 500 (100 intervals)	kPa
Gas flow rate (dry base)			
Feed	Total	200	cm ³ /min
	CO ₂	20, 10, 6.67, 5, 4, 3.34	cm ³ /min
	N ₂	Balance	cm ³ /min
Sweep	He	40	cm ³ /min
Relative humidity		0%	

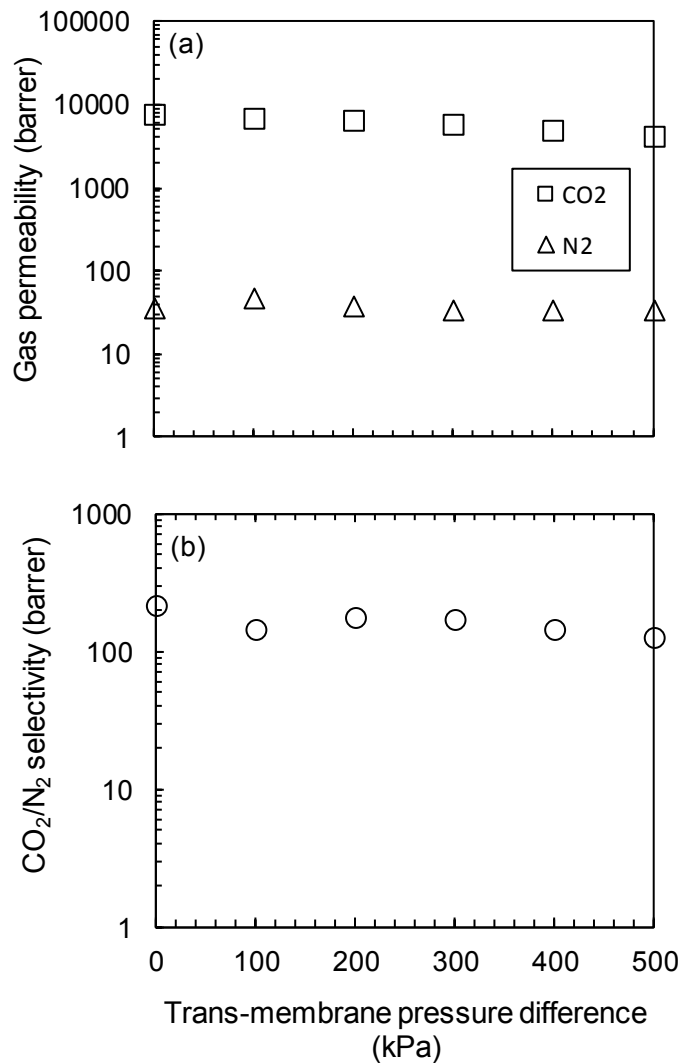


Fig. 4.10. Pressure stability test of DN ion-gel membranes ($T = 373$ K, $P_{\text{CO}_2, \text{feed}} = 10$ kPa, $P_s = 100$ kPa, MAPTAC = 3 M, MBAA = 0.5 mol.%, IL content = 80 wt.%, membrane thickness = 80 μm).

4.4. Conclusion

This study reports the first-time application of a casting method to fabricate TSIL-based PMAPTAC/PDMAAm DN ion-gel membranes for CO₂/N₂ separation. The mechanical properties and network structure of ion-gel membranes were investigated by measuring their cyclic loading behavior and tensile fracture stress. The effect of the cross-

linker loading of the PMAPTAC network on the CO₂/N₂ separation performance was also assessed for ion-gel membranes containing 80 wt.% of [P₂₂₂₍₁₀₁₎][Inda]. The effect of IL loading on CO₂ permeability and CO₂/N₂ selectivity was also investigated for DN ion-gel membranes with 0.5 mol.% of the MBAA cross-linker.

Compared with ion-gel membranes prepared via mold-injection mold, the fabricated ion-gel membranes possessed higher mechanical strength. For example, a DN ion-gel membrane containing 80 wt.% [P₂₂₂₍₁₀₁₎][Inda] exhibited a fracture tensile stress and strain of 1 MPa and 2.50, respectively. The network structure and mechanical properties of ion gels strongly depended on the cross-linker loading of the PMAPTAC network. A reduction in the loading of the MBAA cross-linker produced a soft PMAPTAC/PDMAAm ion gel with DN structure, with a higher MBAA loading resulting in an ion gel with a different network structure. The soft network structure of the PMAPTAC/PDMAAm ion gel induced by decreased MBAA loading caused a drastic enhancement of CO₂ permeability. I suspect that this sharp increase in CO₂ permeability of ion-gel membranes was mainly associated with enhanced diffusivity coefficients of CO₂-carrier complexes. The IL content of DN ion-gel membranes was also found to have a substantial impact on CO₂ permeability and CO₂/N₂ selectivity. For example, as the IL loading was increased from 55 to 83 wt.% at a CO₂ partial pressure of 10 kPa, the CO₂ permeability and CO₂/N₂ selectivity increased from 3300 to 7600 Barrer and 60 to 210, respectively. The inverse proportionality of CO₂ permeance to the thickness of the ion-gel membrane demonstrated that intra-membrane diffusion was the rate-determining step of CO₂ permeation. This implies that a further improvement of permeance can be achieved by decreasing the membrane thickness. Since the ion-gel membrane

containing 80 wt.% IL and having an 80- μm thickness showed good mechanical strength, excellent IL holding properties, and pressure stability, the fabrication of a thin ion-gel layer by a modification of the current casting method is our next challenge.

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Chapter 5

Conclusions

The primary goal of this study was to fabricate the TSILs-based ion-gel FTMs with not only high CO₂/N₂ separation performance but also good holding property of TSILs and great stability under pressurized conditions, in order to address the poor stability issue of TSILs-based SILMs. For this purpose, I developed a novel type of ion-gel FTMs prepared based on the double network concept. The combination of two networks with different properties gave rise to ion-gel membranes containing a large amount of TSILs with excellent mechanical strength. Fundamental studies were carried out to understand the permeation mechanism of gases, elucidate the structure of ion-gel membranes and find out the effect of various parameters on permeation properties and mechanical strength of ion-gel membranes. The great potential of DN ion-gel FTMs was not limited to the capturing CO₂ from high CO₂ concentration gas streams. It was demonstrated that ion-gel membrane has the extraordinary performance for CO₂ separation from gas mixtures containing the very low concentration of CO₂. Moreover, a facile and new approach was also proposed for the fabrication of DN ion-gel FTMs based on casting method. The ion-gel membrane fabricated by this method showed great mechanical strength as well as CO₂/N₂ separation performance. This new approach raises the possibility of preparation of thin ion-gel membranes. The conclusions of this study are summarized as follows:

I. Development of AAILs-based DN ion-gel FTMs with high CO₂/N₂ separation performance and outstanding pressure stability

Novel ion-gel membranes containing a large amount of AAILs were fabricated based on DN concept. The mechanical strength measurement of DN ion-gels containing more than 80 wt% AAIL gave the tensile fracture stress of 0.6 MPa and compressive fracture stress of 25 MPa, 25 times higher than that of single network AAIL-based ion-gels.

Investigating the CO₂/N₂ permeation properties of DN ion-gel membranes with different AAILs contents revealed that the CO₂ permeability and CO₂/N₂ selectivity of DN ion-gel FTMs are considerably affected by the AAIL content. Surprisingly, the DN ion-gel membrane with lowest thickness (58 μ m) and highest AAIL content (ca. 80 wt%) showed the CO₂ permeance and CO₂/N₂ selectivity similar to the AAILs-based SILM. In addition, the stable CO₂ separation performance under pressurized conditions (up to 500 kPa) was observed for DN ion-gel membranes, demonstrating their excellent and good AAIL holding property of gel network. From above results, it can be said that by developing the DN ion-gel membranes, the issue related to the poor stability of ILs-based membranes was solved. The linear relationship between CO₂ permeance and inverse thickness of ion-gel membranes raises the possibility of preparation of thin ion-gel membranes through modification of current method.

II. Demonstrating the exceptional performance of AAIL-based DN ion-gel membrane for CO₂ capture from gas mixtures with low CO₂ concentration (500-1000 ppm)

It showed the great performance (i.e., CO₂ permeability 30000-52000 barrer and CO₂/N₂ selectivity of 4000-8000) of developed DN ion-gel membranes for CO₂ capture from

ambient air with the very low concentration of CO₂ in the range of 500 – 1000 ppm. The comparison of the performance of DN ion-gel FTM with a fabricated conventional amine-based polymer gel FTM revealed that the novel ion-gel membrane had the CO₂ permeability of one order of magnitude higher than conventional FTM. Most importantly, it was found that despite conventional FTM, DN ion-gel membrane kept its great CO₂ separation performance even at low relative humidity conditions, mainly due to the liquid state of the AAIL-based carrier. The long-term stability of the DN ion-gel membrane at room temperature and high RH demonstrated the stable performance and good AAIL holding property of the gel network. The great separation performance of ion-gel membrane was largely due to its unique features, i.e., holding the large amount of AAILs by the gel network and good stability, along with liquid state of carrier even at dry condition. It can be claimed that a DN ion-gel membrane with low thickness has great potential for real applications such as air capturing and venting devices in spaceships.

III. A facile and new approach for fabrication of TSILs-based DN ion-gel membranes based on casting method

A novel approach was proposed for fabrication of TSIL-based DN ion-gel membranes, which was based on using the IL-based monomer and solvent for the first network preparation. Utilizing the ILs-based monomer and solvent provided the opportunity of ion-gel preparation via more common membrane fabrication method, i.e., casting. Through comprehensive studies on parameters affecting the structure of the ion-gel network, it was found that the cross-linker loading of the first network of DN ion-gel membrane is the determining parameter of network structure and mechanical strength. The gas permeation

results also indicated that cross-linker loading of the first network and TSIL content of ion-gel membrane had a significant impact on the separation performance. The optimized conditions of preparation, based on mechanical strength and CO₂ permeation properties, were obtained in this investigation (cross-linker loading: 0.5-1 mol% and TSIL content: 80 wt%). DN ion-gel membranes prepared at optimized conditions showed better CO₂ separation performance, pressure stability, and mechanical strength compared with those fabricated using mold-injection method. Through modification of the current method and further decrease of the thickness of ion-gel membranes, it is possible to achieve the high CO₂ permeance required for real applications.

List of publications

Chapter II:

Farhad Moghadam, Eiji Kamio, Ayumi Yoshizumi, Hideto Matsuyama, An amino acid ionic liquid-based tough ion gel membrane for CO₂ capture, Chemical Communication, 2015, 51, 13658-13661.

Chapter III:

Farhad Moghadam, Eiji Kamio, Hideto Matsuyama, High CO₂ separation performance of amino acid ionic liquid-based double network ion gel membranes in low CO₂ concentration gas mixtures under humid conditions, Journal of Membrane Science, 2017, 525, 290-297.

Chapter IV:

Farhad Moghadam, Eiji Kamio, Tomohisa Yoshioka, Hideto Matsuyama, New approach for the fabrication of double-network ion-gel membranes with high CO₂/N₂ separation performance based on facilitated transport, Journal of Membrane Science, under revision.

Doctoral Dissertation, Kobe University

“Development of tough ion gel membranes containing CO₂ reactive ionic liquids”, 128 pages

Submitted on 01, 18, 2017

The date of publication is printed in cover of repository version published in Kobe University Repository Kernel.

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