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# Novel tough ion-gel-based CO<sub>2</sub> separation membrane with interpenetrating polymer network composed of semi-crystalline and cross-linkable polymers

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ABSTRACT: A tough ion gel constructed from an interpenetrating polymer network (IPN) and high ionic liquid (IL) content was developed using a one-pot/one-step method. The IPN structure was composed of the physically cross-linked poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) network and the chemically cross-linked poly(*N,N*-dimethylacrylamide-*co-N*-succinimidyl acrylate) (poly(DMAAm-*co*-NSA)) network, which respectively contributed to the high mechanical strength and good IL holding property of the IPN ion gel. The IPN ion gel containing 80 wt% of IL, 10 wt% of PVDF–HFP network, and 10 wt% of poly(DMAAm-*co*-NSA) network prepared at 50 °C displayed high tensile fracture energy (758 kJ/m<sup>3</sup>) and good IL holding property under compression at 1.16 MPa (weight loss of the ion gel: 0.79 wt%). An IPN ion gel membrane with a high IL content of 91.3 wt% was successfully fabricated and showed high CO<sub>2</sub> permeability of 1421 barrer and CO<sub>2</sub>/N<sub>2</sub> permselectivity of 27.

## INTRODUCTION

Ionic liquids (ILs) are innovative materials with attractive properties, such as non-volatility, good stability, high and selective CO<sub>2</sub> solubility, making them a preferred medium for gas separation.<sup>1-4</sup> An IL-based gel (ion gel) is a kind of composite material which typically consist of IL and polymer networks. Ion gels are a promising form of high-performance CO<sub>2</sub> separation membranes because it can accommodate a large amount of IL in solid form while maintaining the excellent physicochemical properties of ILs. Owing to the high and selective CO<sub>2</sub> solubility of ILs relative to other light gases, ion gel membranes showed good CO<sub>2</sub> separation performance.<sup>5</sup> Moreover, it was reported that higher IL content can result in higher gas permeability of ion gel membranes.<sup>6,7</sup> For example, Kamio *et al.* found that when the IL content was increased from 51 wt% to 95.2 wt%, the CO<sub>2</sub> permeability of an inorganic/organic double-network ion gel membrane exponentially increased from 146 to 1380 barrer.<sup>7</sup>

Increasing the IL content of the ion gel is therefore an effective and straightforward strategy for developing ion gel membranes with high CO<sub>2</sub> permeation performance. However, most ion gels are weak materials, especially when their IL content is high. As the IL content in ion gels increases, the mechanical strength of the ion gel severely declines to the detriment of the ion gel membrane application stability<sup>7-9</sup>. The development of ion-gel-based membranes with not only a large IL content but also high mechanical strength is crucial for the practical application of ion-gel-based membranes.

Several strategies have been applied to develop tough ion gels. For example, Fujii *et al.* fabricated an ion gel by incorporating a tetra-arm poly(ethylene glycol) (tetra-PEG) cross-

linking network into an IL. The homogeneous Tetra-PEG network led to the successful fabrication of an ion gel with 96.8 wt% of the IL, and the Tetra-PEG ion gel membrane containing 94 wt% IL displayed a high CO<sub>2</sub> permeability of 877 barrer.<sup>6, 10</sup> Lodge *et al.* prepared a tough ion gel by introducing a self-assembled triblock copolymer network.<sup>11, 12</sup> The fabricated ion gels exhibited good performance when applied as conductive materials and CO<sub>2</sub> separation membranes.<sup>13-16</sup> Some other tough ion gels were developed based on the double-network (DN) principle,<sup>17, 18</sup> such as inorganic/organic DN ion gels,<sup>19-23</sup> and organic/organic DN ion gels.<sup>9, 24-29</sup> The inorganic/organic DN ion gel membrane, prepared using cross-linkable polymer, SiO<sub>2</sub> nanoparticles, and 80 wt% of an IL exhibited high CO<sub>2</sub> permeability of 920 barrer and good durability and stability for CO<sub>2</sub>/N<sub>2</sub> separation.<sup>23</sup> Tough ion gels have proven to be an excellent membrane material for gas separation.

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), a semi-crystalline polymer, is a material which has attracted extensive attention due to its high chemical and thermal stabilities.<sup>30-32</sup> The PVDF-HFP could be physically cross-linked by the crystallization of the VDF segments, and it was widely utilized as the network material for tough ion gel preparation.<sup>8, 33-39</sup> It was reported that PVDF-HFP single-network (SN) ion gels had excellent mechanical strength.<sup>8, 40</sup> For example, a tough ion gel composed of 80 wt% of an IL and 20 wt% of the PVDF-HFP network fabricated by Jansen *et al.* showed high Young's modulus of 3 MPa and high break strength of 2 MPa.<sup>8</sup> However, PVDF-HFP SN ion gels had poor IL holding properties because of their sponge-like network structure,<sup>24</sup> leading to IL leakage from the ion gel membrane. On the other hand, Lan *et al.* developed a tough ion gel with a dual-network composed of poly(methyl methacrylate-*co*-

butylmethacrylate) (poly(MMA-*co*-BMA) network and the PVDF-HFP network.<sup>9</sup> Because poly(MMA-*co*-BMA) has good compatibility with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Emim][Tf<sub>2</sub>N]), the developed ion gel with 70 wt% of [Emim][Tf<sub>2</sub>N] showed a good IL holding property and high mechanical strength. However, when the content of the IL in the ion gel was increased to 80 wt%, the IL leakage occurred.

Introducing a polymer network with high compatibility with the IL could be a promising way to enhance the IL holding property of the PVDF-HFP based tough ion gel. It can be expected that the IL holding property will be improved by an adequate choice of the second network polymer and the design of the IPN network composition. Regarding the second polymer for the PVDF-HFP based IPN, in this study, we selected poly(*N,N*-dimethylacrylamide-*co-N*-succinimidyl acrylate) (poly(DMAAm-*co*-NSA)) because of the high compatibility with an imidazolium type ILs. The polymer network compositions and preparation temperatures of the IPN ion gels were investigated to optimize their mechanical properties and IL holding properties. Using the optimized preparation conditions, IPN ion gels with IL contents over 90 wt% were successfully fabricated. The most promising of these IPN ion gels showed high mechanical strength and good IL holding properties and was used as a gas separation membrane. The CO<sub>2</sub> permeabilities and CO<sub>2</sub>/N<sub>2</sub> permselectivities of IPN ion gel membranes prepared with different polymer network compositions, different preparation temperatures, and different IL contents were measured to investigate the gas separation performance of the IPN ion gel membranes.

## EXPERIMENTAL SECTION

**Materials.** PVDF–HFP purchased from Sigma-Aldrich ( $M_w \sim 400000$  g/mol,  $M_n \sim 130000$  g/mol, pellets) was used as received. Poly(DMAAm-*co*-NSA) with an NSA molar ratio of 2.91 mol%, a molecular weight of approximately 121 kg/mol and purity of 91.13 wt% was synthesized following the method described in our previous works.<sup>19, 23</sup> Diethylene glycol bis(3-aminopropyl) ether (DGBE) and [Emim][Tf<sub>2</sub>N] were purchased from Tokyo Chemical Industry Co., Ltd. DGBE was used as the cross-linker of poly(DMAAm-*co*-NSA). In this study, we selected [Emim][Tf<sub>2</sub>N] because of the following reasons; (1) [Emim][Tf<sub>2</sub>N] could be gelled by PVDF-HFP, and the gel had high mechanical strength,<sup>9, 38, 41, 42</sup> and (2) [Emim][Tf<sub>2</sub>N] is one of the widely used ILs for the CO<sub>2</sub> separation membrane.<sup>2</sup> All ion gels, in this study, were fabricated using [Emim][Tf<sub>2</sub>N] as the IL. Acetone (99.5 wt%, FUJIFILM Wako Pure Chemical Co.) was used as the diluent of the IPN ion gel precursor solution. The chemical structures of the [Emim][Tf<sub>2</sub>N] and network precursors used for the IPN ion gel preparation are shown in Figure S1(a).

**Ion gel preparation.** The preparation procedure for the PVDF–HFP/poly(DMAAm-*co*-NSA) IPN ion gel is shown in Figure S1(b). A certain amount of PVDF–HFP was first added into 9.24 g of acetone and stirred for 3 h until completely dissolved. Then, a certain amount of poly(DMAAm-*co*-NSA) was added to the PVDF–HFP solution and stirred for 1 h to completely dissolve the poly(DMAAm-*co*-NSA). For the preparation of the IPN ion gel with 80 wt% IL content, the total weight of the polymer networks was fixed at 1.28 g, and each polymer weight was determined by the PVDF–HFP/poly(DMAAm-*co*-NSA) network weight ratio. Subsequently, 5.12 g of IL was added and stirred for 30 min. Finally, the cross-

linker solution, which was composed of DGBE and acetone (1.0 g), was added to the mixture. After stirring for 3 min, the IPN ion gel precursor solution was prepared. As shown in Figure S2, PVDF-HFP and poly(DMAAm-*co*-NSA) could be dissolved in the precursor solution and formed a transparent and homogeneous solution, which indicates the good miscibility of these two polymers in the solution. Therefore, PVDF-HFP and poly(DMAAm-*co*-NSA) polymer chains could be easily entangled in the precursor solution. In the precursor solution, the DGBE/NSA molar ratio was fixed at 0.5 mol/mol. By one minute of sonication, the air bubbles in the precursor solution were removed and the bubble-free solution was poured into a mold. The acetone in the precursor solution was evaporated in an oven for 24 h at a temperature described hereafter as the “evaporation temperature”. During this heating process, an amide crosslinking reaction between *N*-hydroxysuccinimide (NHS) ester from the poly(DMAAm-*co*-NSA) and a primary amine from DGBE took place (Figure S1(c)). The obtained ion gel was completely dried by a hot plate at 70 °C for 24 h.

The single-network (SN) ion gel with the poly(DMAAm-*co*-NSA) network was prepared in the same way as IPN ion gels, except for the use of PVDF–HFP. In 9.24 g of acetone, 1.24 g of poly(DMAAm-*co*-NSA) and 5.12 g of IL were dissolved sequentially as described above. Acetone DGBE solution (0.04 g of DGBE dissolved in 1.0 g of acetone) was then added into the solution and stirred for 3 min to prepare the precursor solution. For the SN ion gel with PVDF–HFP network, 1.28 g of PVDF–HFP was dissolved in 10.24 g of acetone; then, 5.12 g of IL was added, and the solution was stirred for 30 min to form the precursor solution. Both precursor solutions of the SN ion gels were degassed by ultrasonication for 1 min, poured into a mold, and heated in an oven at evaporation temperature for 24 h. The obtained



SN ion gels (poly(DMAAm-*co*-NSA) SN ion gel and PVDF–HFP SN ion gel) were completely dried on a hot plate at 70 °C for 24 h.

In this study, IPN ion gels with different polymer network compositions were fabricated at 50 °C by changing the PVDF–HFP weight ratios in the IPN (0, 0.25, 0.5, 0.75, and 1 g/g) so that a PVDF–HFP/IPN ratio of 0.25 g/g indicates that the IPN structure is composed of 25 wt% of the PVDF–HFP network and 75 wt% of the poly(DMAAm-*co*-NSA) network. Therefore, the ion gel with the PVDF–HFP/IPN weight ratio of 0 g/g corresponds to the poly(DMAAm-*co*-NSA) SN ion gel, while the PVDF–HFP/IPN weight ratio of 1.0 g/g corresponds to the PVDF–HFP SN ion gel. The IL contents of the IPN and SN ion gels were fixed at 80 wt%.

To evaluate the effect of evaporation temperature on the mechanical strength of the IPN and PVDF–HFP SN ion gels, the IPN ion gels with PVDF–HFP/IPN weight ratios of 0.5 g/g and PVDF–HFP SN ion gels were prepared at different evaporation temperatures (30, 50, 70, 90, and 110 °C).

To explore the effect of the IL content on the mechanical properties and gas separation performance of the IPN ion gel membranes, IPN ion gel membranes containing different contents of the IL were fabricated. The PVDF–HFP/IPN weight ratio of the IPN ion gel was fixed at 0.5 g/g, and the DGBE/NSA molar ratio was fixed at 0.5 mol/mol. The weight ratio of acetone to the mixture of IL and polymer networks was fixed at 1.6 g/g.

**Mechanical property test.** The ion gels were made into dumbbell-shaped samples for mechanical property measurement using a universal testing instrument (EZ-LX, Shimadzu Co., Japan). The sample thickness was measured using a digital microscope system (Leica

DMS300). For the uniaxial tensile test, the tensile strain rate was 100 mm/min. The loading–unloading cyclic tensile test was conducted with the tensile strain increased by 50% after each cycle.

**IL holding property test.** The IL holding property was examined by checking the IL leakage from the ion gel under compression using a universal testing instrument (EZ-LX, Shimadzu Co., Japan). The ion gel was compressed under the initial pressure of 1.16 MPa and kept at the constant compression strain for 2 min. After compression, the ion gel was removed from the apparatus, and the surface of the ion gel sample was wiped to remove the leaked IL. The weights of the ion gel before and after compression were measured to determine the leaked IL weight. The IL leakage was calculated using Eq. 1.

$$\text{IL leakage} = (m_0 - m_1)/m_0 \times 100\% \quad (1)$$

where  $m_0$  and  $m_1$  are the weights of the ion gel samples before and after compression, respectively.

**X-ray diffraction.** Using an X-ray diffractometer (D2 PHASER Specifications, BRUKER), the X-ray diffraction (XRD) patterns of the ion gels in the  $2\theta$  range from  $10^\circ$  to  $40^\circ$  were detected. The measurement was conducted at 30 kV and 10 mA using a Cu  $K\alpha$  radiation with  $\lambda$  of 1.54 Å.

**Gas separation performance evaluation.** The sweep method was adopted in this study to evaluate the gas separation performance of the membranes. The thicknesses of the IPN ion gel membranes, which were detected via a digital microscope (Leica DMS300, Leica Microsystems Inc.), were approximately 400 ~ 500  $\mu\text{m}$ . The gas permeation apparatus and the membrane cell were the same as those used in our previously reported work.<sup>7, 23</sup> A mixed

gas composed of 50/50 mol/mol of CO<sub>2</sub> and N<sub>2</sub>, of which the total flow rate was 200 mL/min, was used as the feed gas. The sweep gas was pure helium with the flow rate of 40 mL/min. For gas flow rate controlling, mass flow controllers (Hemmi Slide Rule Co., Ltd., Japan) were used. The absolute pressures at the feed and sweep sides were set as the atmospheric pressure. The gas permeation tests were conducted at 30 °C.

The compositions of the permeated CO<sub>2</sub> and N<sub>2</sub> were measured using a gas chromatograph (GC-8A, Shimadzu Co., Japan) to calculate the permeances of CO<sub>2</sub> and N<sub>2</sub>. The steady-state of the gas permeation test was confirmed from the GC peak area difference, and steady data was obtained when the difference in the adjacent peak areas was less than 1%.

## RESULTS AND DISCUSSION

**Mechanical properties and IL holding property of the IPN ion gel.** The ion gel composed of the PVDF–HFP/poly(DMAAm-*co*-NSA) IPN and a high content of the IL [Emim][Tf<sub>2</sub>N] was successfully fabricated. The IPN was formed by the physically crosslinked PVDF-HFP network and the chemically crosslinked poly(DMAAm-*co*-NSA) network. First, the mechanical properties and IL holding property of the IPN ion gel were optimized by varying the polymer network ratios and evaporation temperatures.

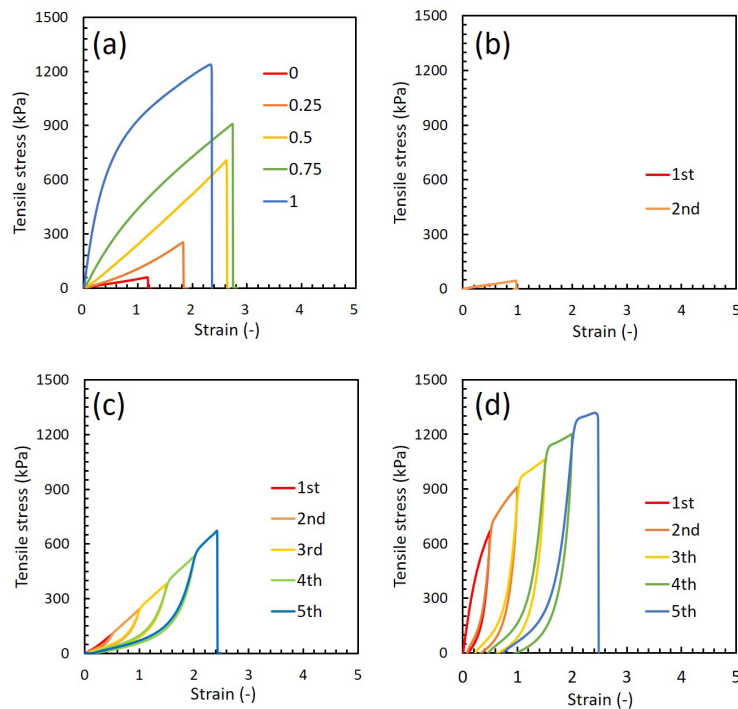
First, to confirm the formation of IPN structure in the ion gel, crosslinking of each PVDF-HFP and poly(DMAAm-*co*-NSA) network was evaluated. Regarding the crosslinking of the PVDF-HFP network, it was reported that PVDF–HFP formed a semi-crystalline structure in an IL.<sup>8,9</sup> To confirm the formation of the semi-crystalline structure in the developed ion gel, we measured the XRD patterns of the ion gels with different PVDF–HFP/IPN weight ratios.

The results are shown in Figure S3(a). The PVDF–HFP SN ion gel and IPN ion gel showed a peak at  $2\theta = 20.0^\circ$ , which corresponds to the (110) reflection of the  $\alpha$  crystal phase in PVDF.<sup>8, 35</sup> The ion gels also showed another peak at  $2\theta = 12.5^\circ$ , which corresponds to the structured [Emim][Tf<sub>2</sub>N]. From the peak at  $2\theta = 20.0^\circ$ , the physical crosslinking structure formation of the PVDF–HFP network by the formation of the PVDF crystalline part in the ion gel was evidenced. On the other hand, regarding the crosslinking of the poly(DMAAm-*co*-NSA) network, the extent of the crosslinking reaction of the poly(DMAAm-*co*-NSA) network was determined by <sup>1</sup>H-NMR measurement as described in the *Supporting Information*. The extents of the crosslinking reaction in the ion gels with different PVDF–HFP/IPN weight ratios are shown in Figure S4(a). The results indicated the formation of the chemically crosslinked poly(DMAAm-*co*-NSA) network in the ion gel. Because the PVDF–HFP and poly(DMAAm-*co*-NSA) showed good miscibility (Figure S2), these polymers could be entangled with each other in the precursor solution. The entangled structure could be kept in the ion gel. In addition, the entangled each network was crosslinked separately. Therefore, it can be considered that the IPN structure was formed in the ion gel.

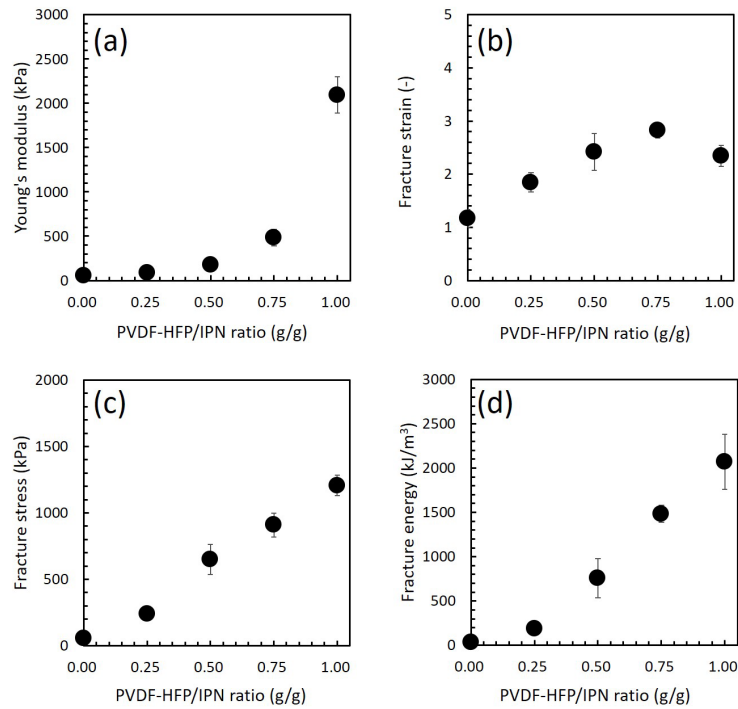
Subsequently, to investigate the effect of the PVDF–HFP/poly(DMAAm-*co*-NSA) network compositions on the IPN ion gel mechanical properties, ion gels with different PVDF–HFP/IPN ratios were prepared. The PVDF–HFP ratio in the PVDF–HFP/poly(DMAAm-*co*-NSA) IPN varied from 0 to 1 g/g. The IPN and IL contents of the IPN ion gels were fixed at 20 wt% and 80 wt%, respectively.

The ion gel mechanical properties were evaluated using uniaxial tensile tests. The obtained tensile stress–strain curves are shown in Figure 1(a). The mechanical strength of the ion gels

dramatically increased with increasing PVDF–HFP weight ratio in the IPN. The mechanical properties of the ion gels, such as Young’s modulus, fracture stress, fracture strain, and fracture energy, were determined from the stress–strain curves. These are summarized in Figure 2. From the results, it was found that the mechanical properties tended to increase with increasing the PVDF–HFP ratio. The mechanical properties of the ion gels fabricated with PVDF–HFP/IPN weight ratios of 1.0, 0.75, 0.5 and 0.25 g/g were also investigated by dynamic mechanical analysis (DMA). The ion gel with PVDF–HFP/IPN weight ratio of 0 g/g was too weak to be measured by DMA. The results are shown in Figure S5. The storage modulus  $G'$  shows a decreasing trend with decreasing PVDF–HFP/IPN weight ratios, which is in good agreement with the mechanical properties measured by the uniaxial tensile test. These results indicate that the PVDF–HFP network greatly enhances the mechanical strength of the IPN ion gel.



**Figure 1.** (a) Stress–strain curves measured by the uniaxial tensile test of the ion gels fabricated with different PVDF–HFP/IPN weight ratios. (b–d) Stress–strain curves measured by the cyclic tensile test of ion gels with PVDF–HFP/IPN ratios of (b) 0 g/g (poly(DMAAm-*co*-NSA) SN ion gel); (c) 0.5 g/g (IPN ion gel); and (d) 1 g/g (PVDF–HFP SN ion gel). The ion gels were formed at an evaporation temperature of 50 °C.



**Figure 2.** (a) Young's modulus; (b) fracture strain; (c) fracture stress; and (d) fracture energy of the ion gels fabricated with different PVDF–HFP/IPN weight ratios. The ion gels were prepared at the evaporation temperature of 50 °C.

Furthermore, to clarify the effect of the PVDF–HFP network on the high mechanical strength, the results of the cyclic tensile test of the ion gels with PVDF–HFP/IPN ratios of 0, 0.5, and 1.0 g/g were measured as shown in Figure 1(b), (c), and (d), respectively. The cyclic tensile stress–strain curves of the ion gels with PVDF–HFP/IPN ratio of 0.5 g/g (IPN ion gel) and 1 g/g (PVDF–HFP SN ion gel) showed clear hysteresis, while that of the poly(DMAAm-*co*-NSA) SN ion gel showed no hysteresis. These results indicate that the PVDF–HFP network dissipated the energy loaded to the ion gels.

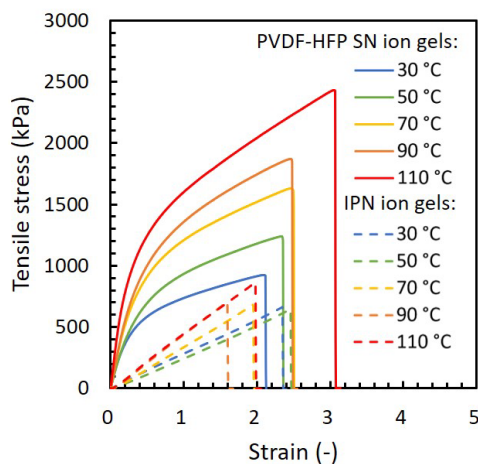
To compare the amounts of crystalline PVDF in the IPN ion gels, the XRD patterns were normalized using the structured [Emim][Tf<sub>2</sub>N] peak. The normalized IPN ion gel XRD patterns are shown in Figure S3(b). As shown in this figure, the crystalline part of PVDF in the IPN ion gels increased with the increase in the PVDF–HFP/IPN weight ratio. Regarding the mechanical properties, as mentioned above, the ion gels with the PVDF–HFP network dissipated the loaded energy. As indicated in Figures 1(c) and (d), the dissipated energy, which corresponds to the area of the hysteresis loop, became large with increasing the PVDF–HFP/IPN ratio in the ion gel. From these results of the amount of the PVDF crystalline part and the mechanical property of the IPN ion gel, it was considered that the destruction of the PVDF crystalline region in PVDF–HFP network dissipated the loaded energy during the stretching process.

To further confirm the effect of the PVDF crystalline part on the enhancement of the mechanical strength of the IPN ion gels, the mechanical properties of the IPN ion gels with different crystallinity of the PVDF network were measured. In general, the temperature is a vital factor that affects the crystallization process.<sup>43, 44</sup> The crystallinity of the PVDF networks in this study was found to be controlled by the evaporation temperature, defined as the temperature of the acetone removal process during the ion gel preparation. The uniaxial tensile stress–strain curves of ion gels prepared at different evaporation temperatures are shown in Figure 3. The ion gel mechanical properties determined from the stress–strain curves are summarized in Figure S6. As can be seen in these figures, the mechanical properties of the PVDF–HFP SN ion gels were strongly dependent on the evaporation temperature. As shown in Figure S7, the dissipated energy of the PVDF–HFP SN ion gels



increased with increasing evaporation temperature. Furthermore, the SN ion gel XRD patterns normalized by the structured [Emim][Tf<sub>2</sub>N] peak ( $2\theta = 12.5^\circ$ ) are shown in Figure S8(a); the intensity of the XRD peak at  $2\theta = 20.0^\circ$ , which results from the PVDF crystalline structure in the PVDF–HFP SN ion gel, increased with increasing evaporation temperature. These results further suggest that energy dissipation was caused by the destruction of the crystalline part of the PVDF segment.

On the other hand, as shown in Figures 3 and S6, the mechanical properties of the IPN ion gels changed only slightly with increasing evaporation temperatures. As shown in Figure S4(b), the crosslinking reaction extent of the poly(DMAAm-*co*-NSA) network was decreased with increasing evaporation temperatures. This might be because the time for solvent evaporation was dramatically shortened and resulting a rapid increase of the viscosity of the precursor solution. However, it is considered that the mechanical properties were mainly dominated by the PVDF–HFP network. Therefore, the decrease of the crosslinking reaction extent did not strongly contribute to the mechanical properties. As shown in Figure S9, the evaporation temperature scarcely affected the dissipated energy of the IPN ion gels. The crystallinity of the PVDF segment in the IPN ion gel was hardly dependent on the evaporation temperature, as shown in Figure S8(b). This might be because the chemically cross-linked poly(DMAAm-*co*-NSA) network interpenetrated with the PVDF–HFP network and inhibited the crystallization of PVDF segments. These relationships among the mechanical properties, dissipated energy, and crystallinity of the PVDF segment of the IPN ion gels also suggest that the IPN ion gel mechanical properties were dominated by the PVDF crystalline portion, which dissipated the loaded energy like a sacrificial bond.

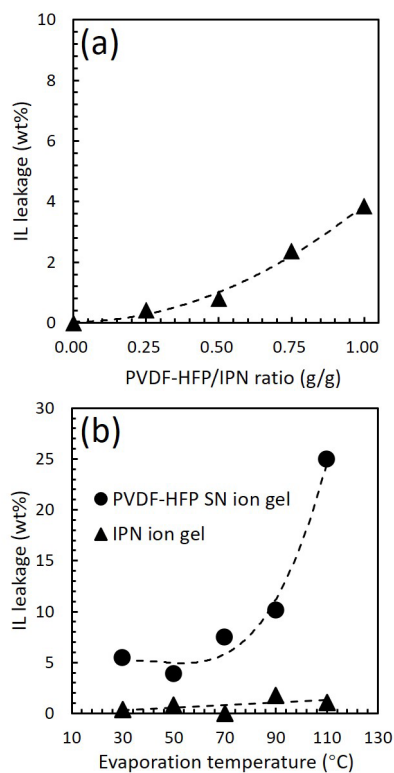


**Figure 3.** Stress–strain curves measured by the uniaxial tensile test of the PVDF–HFP SN ion gels and the IPN ion gels fabricated at different evaporation temperatures. The PVDF–HFP/IPN ratio of the IPN ion gels is fixed at 0.5 g/g. The IL content of the ion gels was fixed at 80 wt%.

To the best of our knowledge, the PVDF–HFP SN ion gel fabricated at the evaporation temperature of 110 °C has the highest fracture energy (4396 kJ/m<sup>3</sup>) (Figure S6(d)) in comparison to the reported ion gels with the same IL content of 80 wt%. However, as shown in Figure 4, the PVDF–HFP SN ion gel (PVDF–HFP/IPN ratio of 1 g/g) exhibited poor IL holding property. This is a serious problem for the practical application of ion gels. By contrast, the IL was hardly leaked from the poly(DMAAm-*co*-NSA) ion gel (PVDF–HFP/IPN ratio of 0 g/g) as shown in Figure 4(a). This was because of the good compatibility between poly(*N,N*-dimethylacrylamide) and [Emim][Tf<sub>2</sub>N].<sup>45</sup> Thus, as shown in Figure 4(a), for the IPN ion gels, the IL leakage monotonically decreased with the increase in the ratio of

poly(DMAAm-*co*-NSA) in the IPN. This result indicated that poly(DMAAm-*co*-NSA) effectively improved the IL holding property of the IPN ion gels. However, as shown in Figures 2 and 4(a), the mechanical strength and IL holding property of the IPN ion gel are in a trade-off relationship, i.e. when the PVDF-HFP network ratio increases, the mechanical strength increases but the IL holding property decreases. Therefore, in this study, a PVDF-HFP/IPN ratio of 0.5 g/g was chosen as the optimal composition for the IPN.

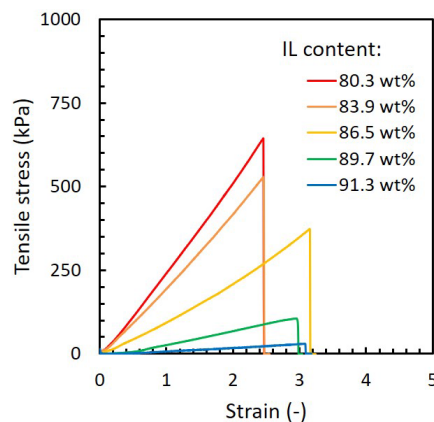
The effect of the evaporation temperature on the ion gel IL holding property is shown in Figure 4(b). The PVDF-HFP SN ion gel fabricated at elevated evaporation temperatures showed a dramatically reduced IL holding property. By contrast, the IPN ion gels fabricated under different evaporation temperatures showed excellent IL holding properties, as evidenced by their remarkably low IL leakage of the ion gel after compression. This might be attributed to the IPN structure formed in the ion gels. As discussed in previous sections, the crystalline structure formation in PVDF-HFP SN ion gels was facilitated by increasing the evaporation temperature, while the crystallinity was not dependent on the evaporation temperature for IPN ion gel preparation. Therefore, it was considered that the IL holding property decreased with the increase in the amount of the crystalline structure of the PVDF segments. In addition, the results in Figures 3 and 4(b) indicate that the mechanical properties and IL holding property of the IPN ion gel were independent of the evaporation temperature. This means that IPN ion gels with good mechanical and IL holding properties could be prepared over a wide evaporation temperature range. The preparation of IPN ion gels at elevated temperatures could effectively shorten the preparation time, which has implications for large-scale manufacturing.



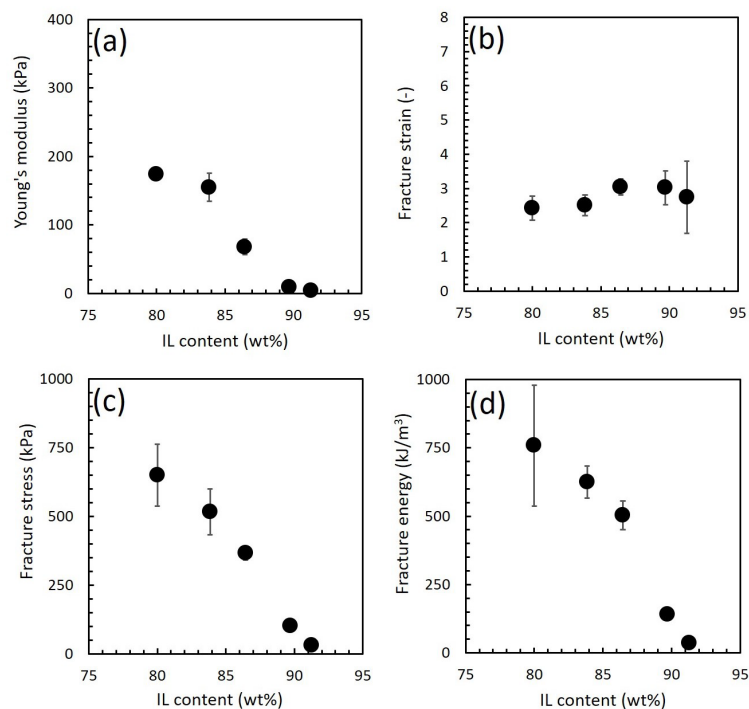
**Figure 4.** IL leakage of the ion gels after compression at the stress of 1.16 MPa: (a) Effect of PVDF–HFP/IPN weight ratios; the ion gels were fabricated at the evaporation temperature of 50 °C. (b) Effect of evaporation temperatures; the ion gels were fabricated with PVDF–HFP/IPN ratio of 0.5 g/g.

An important goal of toughening an ion gel is the fabrication of an ion gel membrane with a high IL content and manipulable mechanical strength. Hence, IPN ion gels with different IL contents were fabricated and investigated. The IL content of the ion gels was measured as described in the *Supporting Information*. The IPN ion gels with the IL contents from 80 wt%

to 91.3 wt% were prepared. The extents of the crosslinking reaction of the poly(DMAAm-*co*-NSA) network kept the same level even when the IL content in the IPN ion gel increased up to 91.3 wt% (Figure S4(c)). The uniaxial tensile stress–strain curves of these IPN ion gels (Figure 5) show that the mechanical strength of the IPN ion gels is highly dependent on their IL content. The detailed mechanical properties are summarized in Figure 6. As shown in Figures 6(a), (c), and (d), because of the decreasing content of the IPN, Young's modulus, fracture stress, and fracture energy of the IPN ion gels decreased with increasing IL content. The fracture strain of the IPN ion gel was maintained at a constant level with increasing IL content, as shown in Figure 6(b).



**Figure 5.** Stress–strain curves measured by the uniaxial tensile test of the IPN ion gels with different IL contents. The IPN ion gels were prepared with the PVDF–HFP/IPN ratio of 0.5 g/g at the evaporation temperature of 50 °C.



**Figure 6.** (a) Young's modulus, (b) fracture strain, (c) fracture stress, and (d) fracture energy of IPN ion gels with different IL contents. The IPN ion gels were prepared with the PVDF–HFP/IPN ratio of 0.5 g/g under the evaporation temperature of 50 °C.

Cyclic stress loading–unloading tensile tests were also performed on the IPN ion gel with an IL content of 91.3 wt%, as shown in Figure S10. The clear hysteresis indicated that the PVDF crystalline part was also formed in the IPN ion gel even when the ion gel has high IL content. To evaluate the IL holding property of an IPN ion gel with high IL content, the IL leakage of the IPN ion gel having 91.3 wt% of the IL was measured after compression. The IL leakage of the IPN ion gel was only 0.81 wt%, similar to the leakage amount of the IPN

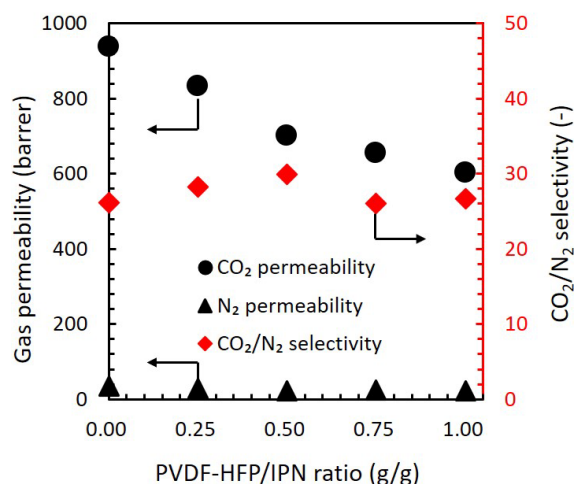
ion gel with 80 wt% of the IL (0.79 wt%). This result confirmed the good IL holding property of this IPN ion gel even with a high IL content.

**Gas separation performance of the IPN ion gel membrane.** The investigations above show that IPN ion gels can achieve both excellent IL holding property and high mechanical strength. The IL content of the IPN ion gel could be increased to more than 90 wt% while maintaining a manipulatable toughness. These remarkable properties indicate that IPN ion gels have great potential as gas separation membrane materials. To evaluate the gas separation performance of IPN ion gel membranes, we investigated the CO<sub>2</sub> and N<sub>2</sub> permeabilities and CO<sub>2</sub>/N<sub>2</sub> permselectivities of IPN ion gel membranes fabricated under different conditions.

First, the gas separation performance of IPN ion gel membranes with different PVDF–HFP/IPN weight ratios was evaluated. The results are shown in Figure 7. The permeabilities of CO<sub>2</sub> and N<sub>2</sub> decreased as the PVDF–HFP ratio in the IPN increased, while the permselectivities were maintained at approximately 27. In general, gas permeation through an ion gel membrane is governed by the solution-diffusion mechanism.<sup>4, 46</sup> When the PVDF–HFP/IPN ratio increased, the crystalline regions in the IPN ion gel membrane increased. The crystalline region is resistant to the diffusion of dissolved gas molecules, resulting in a decrease in the gas permeability of the IPN ion gel membrane. In other words, increasing the poly(DMAAm-co-NSA) network ratio in the IPN can improve the gas permeability of the IPN ion gel membranes.

By contrast, the permselectivities were dominated by the solubility selectivity of the gas pair in the IL and hardly affected by the PVDF–HFP ratio. Therefore, from the gas

permeation performance point of view, it can be said that the IPN ion gel membrane with a higher poly(DMAAm-*co*-NSA) ratio was preferable.



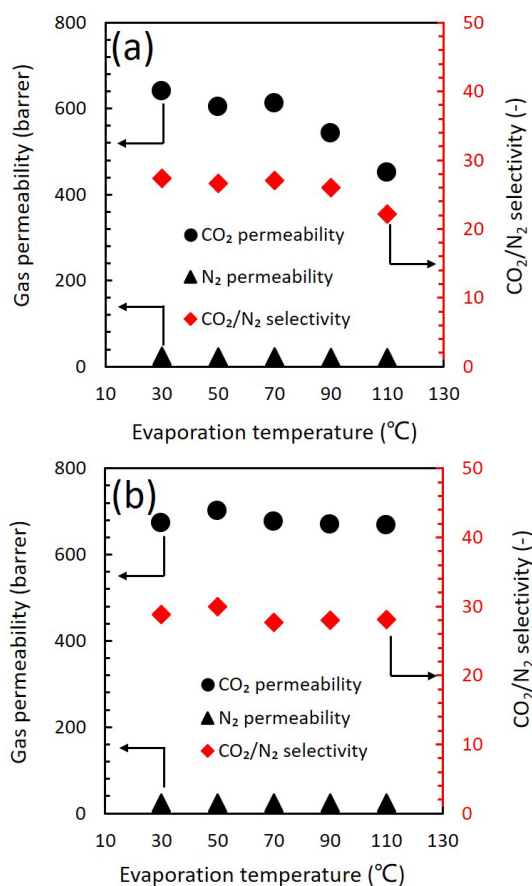
**Figure 7.** Permeabilities of CO<sub>2</sub> and N<sub>2</sub>, and CO<sub>2</sub>/N<sub>2</sub> permselectivities of the IPN ion gel membranes fabricated with different PVDF–HFP/IPN weight ratios. The ion gel membranes were fabricated with an IL content of 80 wt% at the evaporation temperature of 50 °C. The gas permeabilities were evaluated using 50/50 mol/mol CO<sub>2</sub>/N<sub>2</sub> mixed gas at 30 °C under dry and atmospheric pressure conditions.

The gas separation performances of the IPN ion gel membranes and PVDF–HFP SN ion gel membranes fabricated at different evaporation temperatures were also investigated. As shown in Figure 8, the CO<sub>2</sub> permeability of the PVDF–HFP SN ion gel membrane decreased with increasing evaporation temperature. This was because when the PVDF–HFP SN ion gel was prepared at a high evaporation temperature, the PVDF segment crystallinity increased,



resulting in higher resistance to gas transport. In addition, the CO<sub>2</sub>/N<sub>2</sub> permselectivity significantly decreased to 21 when the evaporation temperature was 110 °C. This might be because the structure of the IL in the PVDF–HFP SN ion gel membrane changed when the ion gel was prepared at high evaporation temperatures, and the CO<sub>2</sub>/N<sub>2</sub> solubility selectivity in the IL decreased. As shown in Figure S8(c), comparing the XRD patterns of the SN ion gels, the intensity of the peak at  $2\theta = 12.5^\circ$ , attributed to the structured IL, dramatically decreased when the evaporation temperature was 110 °C.

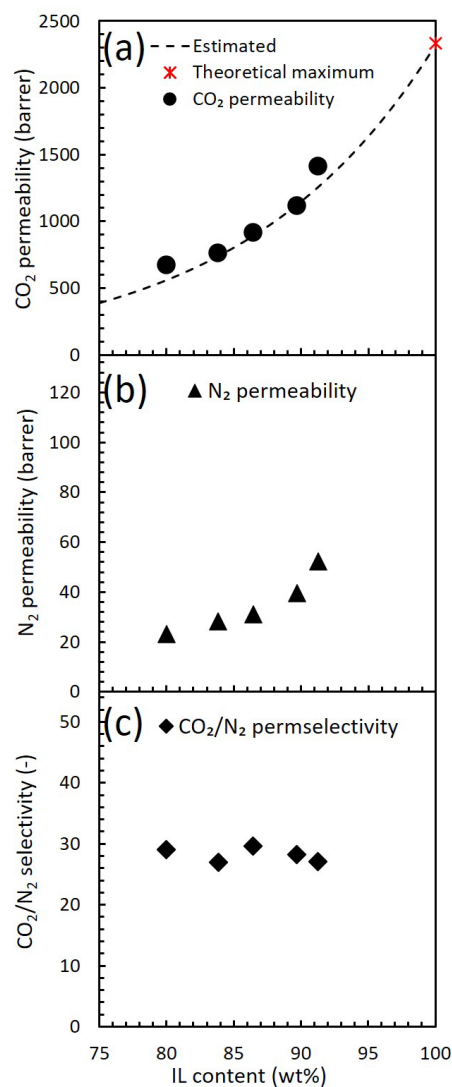
For the IPN ion gel membranes, as shown in Figure 8(b), the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> permselectivity were independent of the evaporation temperature. As shown in Figure S8(d), the XRD peak at  $2\theta = 12.5^\circ$ , attributed to the structured IL, was almost unaffected by evaporation temperature changes. As discussed in the mechanical properties section, the interpenetration of the poly(DMAAm-*co*-NSA) network with the PVDF–HFP network could inhibit the change in the PVDF crystalline structure along with the change in the evaporation temperature. Hence, the CO<sub>2</sub> and N<sub>2</sub> permeabilities did not change because of the uniform structures of not only the PDVF crystalline part but also the IL in the IPN ion gel membranes prepared at different temperatures. From this result, it can be said that the IPN ion gel membrane with high CO<sub>2</sub> permeation performance can be prepared over a wide evaporation temperature range.



**Figure 8.** Permeabilities of CO<sub>2</sub> and N<sub>2</sub>, and CO<sub>2</sub>/N<sub>2</sub> permselectivities of the (a) PVDF–HFP SN ion gel membranes, and (b) IPN ion gel membranes fabricated at different evaporation temperatures. The PVDF–HFP/IPN ratio of the IPN ion gels was 0.5 g/g. The IL contents of both the SN and IPN ion gel membranes were 80 wt%. The gas permeability was evaluated using 50/50 mol/mol CO<sub>2</sub>/N<sub>2</sub> mixed gas at 30 °C under dry and atmospheric pressure conditions.

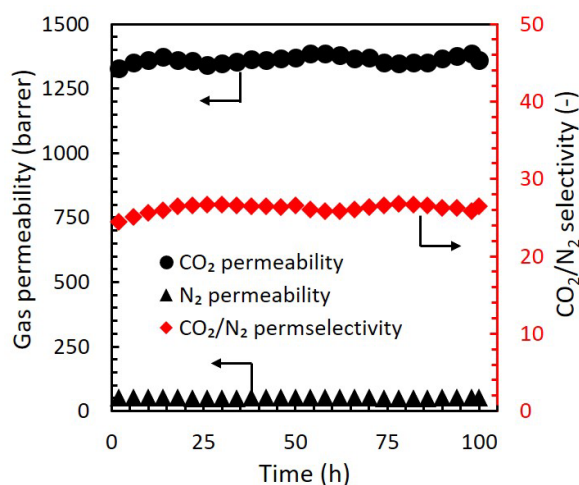
Increasing the IL content of an ion gel is an effective way to increase the gas permeance of ion-gel-based membranes.<sup>7</sup> The CO<sub>2</sub> and N<sub>2</sub> permeabilities of IPN ion gel membranes with

different IL contents are shown in Figures 9(a) and (b). The CO<sub>2</sub> permeability exponentially increased with the increasing IL content of the IPN ion gel membrane. The experimental results correlated well with the estimated CO<sub>2</sub> permeability dotted curve, which was calculated from the solubility coefficient and the diffusion coefficient of CO<sub>2</sub> in the ion gel according to a previously reported method,<sup>7</sup> the calculation was also described in the *Supporting Information* of this work. The IPN ion gel membrane with the IL content of 91.3 wt% displayed excellent CO<sub>2</sub> permeability of 1421 barrer, much higher than that of the IPN ion gel with the IL content of 80 wt% (670 barrer). By contrast, the CO<sub>2</sub>/N<sub>2</sub> permselectivity of the IPN ion gel membranes was constant at approximately 27 and was independent of the IL content, as shown in Figure 9(c). The constant permselectivity indicated that the IPN ion gel membranes with high IL contents were defect-free, which was also confirmed by the good surface morphology as shown in Figure S11.



**Figure 9.** Gas separation performance of IPN ion gel membranes with different IL contents: (a) CO<sub>2</sub> permeability; (b) N<sub>2</sub> permeability; (c) CO<sub>2</sub>/N<sub>2</sub> permselectivity. The IPN ion gel membranes were fabricated with the PVDF–HFP/IPN ratio of 0.5 g/g at the evaporation temperature of 50 °C. The gas permeability of the IPN ion gel membrane was evaluated using 50/50 mol/mol CO<sub>2</sub>/N<sub>2</sub> mixed gas at 30 °C under dry and atmospheric pressure conditions. The calculation of the estimated curve and the theoretical maximum CO<sub>2</sub> permeability of the [Emim][Tf<sub>2</sub>N]-based ion gel membrane was described in the *Supporting Information*.

The ion gel membrane with an IL content of 91.3 wt% was continuously operated for more than 100 h. Constant gas permeabilities and permselectivities (Figure 10) indicate good long-term stability of the IPN ion gel membrane. The stable gas separation performance indicated that no IL leaked from the IPN ion gel membrane during the long-time gas permeation test. From this result, it could be confirmed that the IPN ion gel membrane with 91.3 wt% IL had excellent CO<sub>2</sub> permeability, good CO<sub>2</sub>/N<sub>2</sub> permselectivity, and good IL holding property. Thus, it can be said that the developed IPN ion gel is a promising material for high-performance CO<sub>2</sub> separation membranes to be used in practical CO<sub>2</sub> separation applications.



**Figure 10.** Long-term stability during the gas permeation process of the IPN ion gel membrane with the IL content of 91.3 wt%. The IPN ion gel membranes were fabricated with a PVDF–HFP/IPN ratio of 0.5 g/g at the evaporation temperature of 50 °C. The IPN ion gel membrane gas permeability was evaluated using 50/50 mol/mol CO<sub>2</sub>/N<sub>2</sub> mixed gas at 30 °C under dry and atmospheric pressure conditions.

## CONCLUSION

A novel tough ion-gel-based CO<sub>2</sub> separation membrane with an IPN structure and high IL content was designed and developed. The IPN structure was fabricated by introducing a chemically cross-linked poly(DMAAm-*co*-NSA) network into a physically cross-linked PVDF–HFP network. With increased PVDF–HFP content in the polymer networks, the mechanical strength of the IPN ion gel membrane increased, while the IL holding property and gas permeability decreased. The IPN ion gel membrane (80 wt% of IL) with PVDF-HFP/IPN ratio of 0.5 g/g prepared at the evaporation temperature of 50 °C displayed high fracture energy of 758 kJ/m<sup>3</sup>, low IL leakage (0.79 wt%) after compression, high CO<sub>2</sub> permeability of 670 barrer and CO<sub>2</sub>/N<sub>2</sub> permselectivity of 27. In addition, the IPN ion gel membrane with a high IL content of 91.3 wt% showed not only excellent CO<sub>2</sub> permeability of 1421 barrer and CO<sub>2</sub>/N<sub>2</sub> permselectivity of 27 but also good IL holding property. The high mechanical strength, good IL holding property, high CO<sub>2</sub> permeability, and high CO<sub>2</sub>/N<sub>2</sub> permselectivity indicate that the IPN ion gel has good application prospects as a gas separation membrane material.

## ASSOCIATED CONTENT

### **Supporting Information**

Illustrations of IPN ion gel preparation; miscibility between PVDF–HFP and poly(DMAAm-*co*-NSA); X-ray diffraction patterns of ion gels fabricated with different PVDF–HFP/IPN weight ratios; extent of the crosslinking reaction; DMA measurement of

IPN ion gels; mechanical properties of ion gels fabricated under different evaporation temperatures; cyclic tensile stress–strain curves and dissipated energy of PVDF–HFP SN ion gels; X-ray diffraction patterns of ion gels prepared at different evaporation temperatures; cyclic tensile stress–strain curves and dissipated energy of IPN ion gels; IL content measurement of the ion gels; cyclic tensile stress–strain curve of IPN ion gel with high IL content; surface morphology of the IPN ion gel; estimation of gas separation performance of the ion gel with different IL contents (PDF).

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## Notes

The authors declare no competing financial interest.

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