Structural, Thermal, and Gas-Transport Properties of Fe$^{3+}$ Ion-Exchanged Nafion Membranes

Mohsin Mukaddam, Yingge Wang, and Ingo Pinnau

ABSTRACT: The physical and gas-transport properties of Fe$^{3+}$ cross-linked Nafion membranes were examined. Wide-angle X-ray diffraction results revealed a lower crystallinity for Nafion Fe$^{3+}$ but showed essentially no changes in the average chain spacing upon cation exchange of Nafion H$^+$. Raman and Fourier transform infrared spectroscopy techniques qualitatively measured the strength of the ionic bond between the Fe$^{3+}$ cations and sulfonate anions. Thermal gravimetric analysis indicated that the incorporation of Fe$^{3+}$ adversely affected the thermal stability of Nafion due to the catalytic decomposition of perfluoroalkylether side chains. Gas sorption isotherms of Nafion Fe$^{3+}$ measured at 35 °C up to 20 atm exhibited a linear sorption uptake for O$_2$, N$_2$, and CH$_4$ following Henry’s law and slight concave behavior for CO$_2$. Pure-gas permeation results showed reduced gas permeability but higher permselectivities compared to Nafion H$^+$ with $\alpha_{N_2}/CH_4 = 4.0$, $\alpha_{CO_2}/CH_4 = 35$, and $\alpha_{He}/CH_4 = 733$ attributable to the strong physical cross-linking effect of Fe$^{3+}$ that caused chain stiffening with enhanced size-sieving behavior. Gas mixture permeation experiments using 1:1 molar CO$_2$/CH$_4$ feed demonstrated reduced CO$_2$ plasticization for Nafion Fe$^{3+}$. At 10 atm CO$_2$ partial pressure, CO$_2$/CH$_4$ selectivity decreased to 28 from the pure-gas value of 35, which was a significant improvement compared to the performance of a Nafion H$^+$ membrane.

INTRODUCTION

Polymeric membranes are of increasing interest and importance for industrial gas separation applications such as nitrogen production from air, olefin/paraffin separation, hydrogen recovery in petrochemical plants, and carbon dioxide removal from natural gas. The requirements for a preferred membrane material include high permeability, high selectivity, and good thermal and mechanical integrity at the operating conditions. Robeson’s pure-gas permeability/selectivity “upper-bound” curves identified an undesirable tradeoff: polymer membrane materials with high selectivity typically show low permeability and vice versa. In the area of CO$_2$/CH$_4$ separation, removal of CO$_2$ from natural gas or biogas is of particular commercial interest. The strong interaction and resulting high sorption uptake of CO$_2$ in polymer membranes can result in swelling-induced plasticization. Therefore, mixed-gas CO$_2$/CH$_4$ selectivity is often significantly reduced compared to pure-gas values due to the dilution of the polymer matrix, which leads to high CH$_4$ process losses, thus making membrane-based separation less attractive. Therefore, considerable research has been devoted to tailoring the structure/composition of the polymer to achieve improved performance. Ionomers, such as sulfonated polymers comprising strong acidic sulfonate groups, potentially provide a convenient and advantageous approach for tailoring material properties via metal complexations that can cause substantial improvements in gas separation properties.

Ionomers are known for their complex morphology, in which sulfonic groups together with counterions form aggregates that enable physical cross-linking. Consequently, cation exchange in ionomers can induce significant changes in their physical properties including enhancement in glass transition temperature, increase in Young’s modulus, and reduction in chain mobility that play a crucial role in the intrinsic gas separation performance of the material. For example, Park et al. reported pure-gas transport properties of sulfonated polysulfone membranes neutralized with several metal cations and showed that the cation-exchanged membranes improved the CO$_2$/N$_2$ selectivity moderately due to ionic cross-linking. However, the CO$_2$ permeability was reduced by 63% from 5.4 to 2.0 Barrers due to reduction in the CO$_2$ diffusion coefficient. Chen et al. reported the permeabilities for a series of gases including CO$_2$ and CH$_4$ in sulfonated poly(styrene) (PPS) membranes neutralized with Na$^+$ and Mg$^{2+}$ cations. PSS–Mg$^{2+}$ and PSS–Na$^+$ exhibited CO$_2$/CH$_4$ permselectivities of 65 and 49, respectively, which was substantially higher than the value of 18 in the acidic PPS–H$^+$ form. Additionally, it was shown that the CO$_2$ permeability in PSS–Mg$^{2+}$ increased by only 9% between 1 and 7 atm, indicating that the membrane was less prone to CO$_2$ plasticization. Rhim et al. investigated the CO$_2$/CH$_4$ separation properties in sulfonated poly(phenylene oxide) (SPO) membranes cation-exchanged with several mono-, di-, and trivalent cations. The trivalent SPO–Al$^{3+}$
membrane showed the highest enhancement in CO$_2$/CH$_4$ selectivity from 11 in the protonated form to 20 in the cation-exchanged polymer. Similar results were obtained by Khan et al., who reported an increase in the mixed-gas CO$_2$/CH$_4$ selectivity in an Al$^{3+}$-neutralized sulfonated poly(ether ether ketone) membrane by approximately 62% to 19 compared with 11 in the protonated form. The enhanced selectivity was attributed to the strong cross-linking effect of trivalent cations that hindered the diffusivity of the larger-sized CH$_4$ molecule more effectively that CO$_2$.

Interestingly, only a few studies reported the gas separation performance of cation-exchanged Nafion membranes. For example, Sakai et al. investigated gas transport properties of a K$^+$ cation-exchanged Nafion membrane and showed that O$_2$/N$_2$ selectivity increased from 2.2 to 7.4. Mohamed et al. investigated the free volume and gas permeation properties of Nafion Na$^+$ and K$^+$ cation-exchanged membranes. Their study demonstrated an increase in free volume coupled with a decrease in O$_2$ permeability for the cation-exchanged Nafion membranes compared to the H$^+$ form. This behavior was different from the general free volume concept, where polymers with higher free volume typically exhibit higher gas permeability. More recently, Fan et al. studied Nafion H$^+$ neutralized with monovalent (Li$^+$, Na$^+$, K$^+$) and divalent (Ca$^{2+}$) cations to investigate the effect of ionic interaction on the gas-transport properties. Their study showed a higher gas permeability for cation-exchanged membranes compared to Nafion H$^+$ and suggested that the high gas solubility of metal-ion-functionalized Nafion dominated gas permeation. Our group recently reported the effect of CO$_2$ plasticization on CO$_2$/CH$_4$ separation performance in Nafion H$^+$. Despite low CO$_2$ solubility in Nafion H$^+$ compared to conventional hydrocarbon polymers, binary mixed-gas experiments revealed that the strong affinity of CO$_2$ to the sulfonate groups caused a large increase in segmental mobility, resulting in 40% reduction in the CO$_2$/CH$_4$ selectivity from 26 to 15 by increasing the CO$_2$ partial pressure from 2 to 15 atm.

This study investigated the physical modification of Nafion by exchanging the H$^+$ ions with trivalent Fe$^{3+}$ cations. It was anticipated that the cross-linking effect of Fe$^{3+}$ could reduce the intersegmental mobility of Nafion, leading to improved resistance toward undesirable penetrant-induced plasticization effects under demanding CO$_2$/CH$_4$ gas mixture test conditions. The Fe$^{3+}$ cation-exchanged membrane was characterized by wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), Raman spectroscopy, and Fourier transform infrared spectroscopy (FT-IR). Pure-gas sorption, diffusion, and permeation properties of Nafion Fe$^{3+}$, as well as pressure-dependent mixture performance using a 1:1 molar CO$_2$/CH$_4$ feed, are reported.

### RESULTS AND DISCUSSION

**Structural Properties of Fe$^{3+}$ Ion-Exchanged Nafion.** Nafion H$^+$ films (NRE 211) with thickness of 25 µm and equivalent weight of 1100 g equiv$^{-1}$ were purchased from Ion Power, Inc. Ion exchange was performed by soaking Nafion H$^+$ films in an aqueous 0.05 molar Fe(NO$_3$)$_3$ solution, as described in more detail in Experimental Section. The structures of Nafion H$^+$ and Fe$^{3+}$ ion-exchanged Nafion are shown in Figure 1.

The effect of cation exchange on the microstructure of Nafion Fe$^{3+}$ was qualitatively assessed using the wide-angle X-ray diffraction (WAXD) as illustrated in Figure 2. Similar to

Figure 2. Microstructure of Nafion Fe$^{3+}$. The diffraction spectrum was corrected for background scattering and the crystalline and amorphous peaks were obtained by applying the Pearson VII distribution function.
This weight loss has been attributed to the degradation of between 350 and 450 °C. The absence of the desulfonation process for NaFe³⁺, which was calculated by applying the Pearson VII distribution function. Such a change in crystallinity upon cation exchange has been previously reported and influences the gas-transport properties as the crystallites act as impermeable regions in the polymer. The TGA profiles of NaH⁺ and NaFe³⁺ membranes are presented in Figure 3a,b as percentage weight loss and first-order derivatives, respectively.

Both Naion types exhibited four decomposition stages between 100 and 600 °C. The first stage weight loss occurred between 100 and 280 °C. The gases evolved during this temperature range were mostly water with trace amounts of SO₂ and CO₂ as identified using FT-IR. The second stage weight loss occurred between 280 and 350 °C and according to Wilkie et al. was primarily due to the release of SO₂ and CO₂ gases with minimal amount of water. SO₂ evolved due to the cleavage of C=S bonds, forming CF₂, SO₂, and OH radicals. Interestingly, the weight reduction (excluding water loss) observed in Naion H⁺ was ∼7%, whereas the weight loss in the cation-exchanged Naion Fe³⁺ was only 1%, indicating that the stronger interaction between Fe³⁺ cations and the sulfonate anions prevented the cleavage of the C=S bonds. The absence of the desulfonation process for Naion cation-exchanged membranes has been previously reported. The third stage weight loss occurred between 350 and 410 °C in Naion Fe³⁺, with a sharp decomposition temperature peak at 400 °C, whereas in Naion H⁺, the weight loss occurred between 350 and 450 °C, with the peak maxima at 423 °C. This weight loss has been attributed to the degradation of perfluoroalkylether side-chain groups of Naion. The shift toward a lower degradation temperature in the Fe³⁺ ion-exchanged membrane corresponded to a decrease in thermal stability. A similar trend was observed for an Al³⁺ ion-exchanged Naion membrane in which the decrease in the thermal stability was attributed to the breaking of the perfluoroalkylether bonds catalyzed by aluminum oxides that act as Lewis acids. Above ∼400 °C, the final decomposi-

| Naion type | d₁ (Å) | d₂ (Å) | d₃ (Å) | crystallinity (%) |
|------------|--------|--------|--------|------------------|
| H⁺         | 5.0    | 5.25   | 2.3    | 11.4             |
| Fe³⁺       | 5.0    | 5.30   | 2.3    | 6.3              |

Table 1. Interchain Spacing and Percentage of Crystallinity for Naion H⁺ and Fe³⁺ Ion-Exchanged Naion Obtained from WAXD

The Raman and FT-IR spectra in Naion H⁺ and Naion Fe³⁺ membranes are presented in Figure 5a,b, respectively. The spectra provide information on the changes in the membrane microstructure (chain packing, ordering, bond strength) by measuring the shift and broadening of the spectra maxima. The maxima observed at 1057 (FT-IR) and 1062 (Raman) for Naion H⁺ corresponded to the symmetric S=O stretching vibrations of the sulfonate group. The assignment of this band has been reported in previous work. As shown, the maxima shifted toward a higher frequency when the protons were exchanged with Fe³⁺ cations. The shift in frequency is a qualitative indication of the bond strength between the cation and the sulfonate anion. The strength of the ionic interactions influences the flexibility of the polymer chains, which has a significant effect on the gas transport properties, as discussed below.

**Pure-Gas-Transport Properties of Naion Fe³⁺ Membrane.** The permeabilities of pure gas He, H₂, N₂, O₂, CH₄, and CO₂ and gas-pair selectivities of Naion Fe³⁺ membranes are summarized in Table 2. The permeabilities of Naion H⁺ membranes were determined in our previous study under the same conditions and are reported here for comparison.

The permeabilities of the Fe³⁺ ion-exchanged membrane followed the order He > H₂ > CO₂ > O₂ > N₂ > CH₄, indicative of its strong size-dependent permeation properties, qualitatively similar to the permeability behavior of Naion H⁺. The Fe³⁺ ion-exchanged membrane demonstrated a

Figure 3. TGA profile presented as (a) percentage weight loss and (b) first-order derivative of Naion H⁺ (black) and Naion Fe³⁺ (red) operated under N₂ atmosphere at a heating rate of 3 °C min⁻¹.
reduced permeability for all the gases compared to the H\(^+\) type. Increased chain stiffness due to interchain cross-linking could be a plausible cause to explain the reduced permeability in the Fe\(^{3+}\) ion-exchanged membrane. The significant 45% drop in CH\(_4\) permeability enhanced the N\(_2\)/CH\(_4\) selectivity from 2.9 to 4.0, CO\(_2\)/CH\(_4\) selectivity from 28 to 35, and He/CH\(_4\) selectivity from 446 to 733. The higher selectivity can be attributed to the strong cross-linking effect by the trivalent Fe\(^{3+}\) cations that stiffened the amorphous phase in Na\(_{x}\)ion and, thereby, hindered the diffusivity of the larger-sized CH\(_4\) molecule more effectively than that of the other gases.

To better understand the effect of cation exchange on the gas-transport properties of Na\(_{x}\)ion, the diffusivity and solubility data of the Fe\(^{3+}\) ion-exchanged film are compared with the previously measured values of the Na\(_{x}\)ion H\(^+\) membrane in Table 3.\(^{42}\) The gas solubility coefficients in the Na\(_{x}\)ion Fe\(^{3+}\) membrane were measured using the gravimetric technique and the diffusivity coefficients were then deduced from the relationship \(D = \frac{P}{S}\). The gas solubilities followed the order of increasing condensability: N\(_2\) < O\(_2\) < CH\(_4\) < CO\(_2\). The Na\(_{x}\)ion Fe\(^{3+}\) ion-exchanged membrane demonstrated a \(\sim 2\)–3-fold higher gas solubility values compared to the Na\(_{x}\)ion H\(^+\) membrane. Similar solubility enhancements have been

![Figure 4. Thermogravimetric analysis (TGA) profile for (a) Na\(_{x}\)ion H\(^+\) and (b) Na\(_{x}\)ion Fe\(^{3+}\) films comparing the amount of water lost as a function of time upon drying at 80 °C under inert N\(_2\) gas.](image)

![Figure 5. (a) Raman spectra and (b) FT-IR spectra of Na\(_{x}\)ion H\(^+\) and Na\(_{x}\)ion Fe\(^{3+}\) films. The black dotted line is drawn through the center of Na\(_{x}\)ion H\(^+\) maxima for visualizing the relative frequency shift.](image)

### Table 2. Pure-Gas Permeability and Ideal Selectivity in Na\(_{x}\)ion H\(^+\) and Na\(_{x}\)ion Fe\(^{3+}\) Membranes at 2 atm and 35 °C

| Na\(_{x}\)ion type | permeability (Barrer\(^{b}\)) | selectivity | N\(_2\)/CH\(_4\) | CO\(_2\)/CH\(_4\) | O\(_2\)/CH\(_4\) | CH\(_4\)/He |
|------------------|-----------------------------|-------------|----------------|----------------|----------------|------------|
| H\(^+\)          | 37                          | 7.2         | 2.3            | 1.0            | 0.24           | 0.083      |
| Fe\(^{3+}\)      | 33                          | 6.2         | 1.6            | 0.78           | 0.18           | 0.045      |

\(^{a}\)Previous work,\(^{42}\) \(^{b}\)1 Barrer = \(10^{-10}\) cm\(^3\) (STP) cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\).

### Table 3. Summary of Gas Diffusion and Solubility Coefficients in Na\(_{x}\)ion H\(^+\) and Na\(_{x}\)ion Fe\(^{3+}\) Membranes Determined at 2 atm and 35 °C

| Na\(_{x}\)ion type | diffusion coefficient \((10^{-5} \text{ cm}\(^2\) \text{s}^{-1})\) | solubility coefficient \((10^{-2} \text{ cm}^3 \text{ (STP)} \text{cm}^{-3} \text{cmHg}^{-1})\) |
|-------------------|-------------------------------------------------|-------------------------------------------------|
| H\(^+\)           | 5.88 1.85 2.64 0.44 0.17 0.13 0.87 0.19 | O\(_2\) N\(_2\) CO\(_2\) CH\(_4\) O\(_2\) N\(_2\) CO\(_2\) CH\(_4\) |
| Fe\(^{3+}\)       | 2.00 0.56 0.70 0.08 0.39 0.32 2.30 0.57 | 5.88 1.85 2.64 0.44 0.17 0.13 0.87 0.19 |

\(^{a}\)Solubility \((S)\) values were obtained barometrically from a previous study.\(^{42}\) The corresponding diffusion \((D)\) values were determined using \(D = \frac{P}{S}\).
reported for Nafton \textsuperscript{37,40} and other ionomers upon cation exchange.\textsuperscript{20,21} Fan et al. suggested that the high gas sorption in the cation-exchanged Nafton membranes resulted from the large cation size that acted as a spacer causing polymer chain expansion.\textsuperscript{40} Furthermore, the reduction in crystallinity in Nafton Fe\textsuperscript{3+} could have contributed to the enhanced gas solubility.

As shown in Figures 6a–c, the sorption isotherms in Nafton Fe\textsuperscript{3+} were linear up to 20 atm, following Henry’s law. Both Nafton types showed similar qualitative solubility trends; however, the solubilities in Nafton Fe\textsuperscript{3+} were significantly higher than those in Nafton H\textsuperscript{+} across the entire pressure range. Interestingly, the isotherm for CO\textsubscript{2} in Nafton Fe\textsuperscript{3+}, as shown in Figure 6d, was slightly concave to the pressure axis, contrary to the linear CO\textsubscript{2} isotherm for Nafton H\textsuperscript{+}.\textsuperscript{42} Cross-linking in Nafton induced by trivalent Fe\textsuperscript{3+} ions effectively reduced the segmental mobility in the vicinity of ionic aggregations and possibly created rigid regions consisting of fixed holes similar to glassy polymers that provide additional sites for gas sorption. The observed increase in glass transition temperature reported in Nafton\textsuperscript{28−30,34,35} and other ionomers\textsuperscript{32,33} upon cation-exchange supports this hypothesis.

Multivalent cations are known to physically cross-link the Nafton matrix by coordinating with sulfonate anions, resulting in enhanced chain rigidity and, therefore, improved size-sieving properties.\textsuperscript{21,22} The higher N\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/CH\textsubscript{4} selectivity in Nafton Fe\textsuperscript{3+} was primarily due to its enhanced diffusivity selectivity, as shown in Table 4.

| Nafton type | N\textsubscript{2}/CH\textsubscript{4} | CO\textsubscript{2}/CH\textsubscript{4} | N\textsubscript{2}/CH\textsubscript{4} | CO\textsubscript{2}/CH\textsubscript{4} |
|------------|-----------------|-----------------|-----------------|-----------------|
| H\textsuperscript{+} | 4.2 | 6.0 | 0.68 | 4.6 |
| Fe\textsuperscript{3+} | 7.0 | 8.8 | 0.56 | 4.0 |

Pressure-Dependant Pure- and Mixed-Gas Permeation Properties. Pure-gas permeabilities of CO\textsubscript{2} and CH\textsubscript{4} in Nafton H\textsuperscript{+} and Fe\textsuperscript{3+} membranes are compared in Figure 7 as a function of pressure at 35 °C. Across the entire pressure range investigated, Nafton Fe\textsuperscript{3+} demonstrated lower CO\textsubscript{2} and CH\textsubscript{4} permeabilities compared to Nafton H\textsuperscript{+}.

Figure 7a shows that the pure CO\textsubscript{2} permeability increased with pressure for both Nafton types, which can be attributed to increased diffusivity. Presumably, quadrupolar CO\textsubscript{2} molecules interacted favorably with the polar sulfonate groups of Nafton to increase its segmental chain mobility, causing membrane plasticization.\textsuperscript{27,41,53,54} The Fe\textsuperscript{3+} ion-exchanged membrane was less affected by CO\textsubscript{2} plasticization, as indicated by the smaller relative increase in CO\textsubscript{2} permeability compared to the Nafton H\textsuperscript{+} membrane. Our previous work showed that pure CH\textsubscript{4}...
permeability of Nafion H\textsuperscript{+} decreased with increasing feed pressure, which was caused by a decrease in gas diffusivity most likely due to chain compression of the relatively flexible protonated ionomer.\textsuperscript{41} On the other hand, CH\textsubscript{4} permeability of Nafion Fe\textsuperscript{3+} remained essentially constant over the pressure range of 2 to 15 atm (Figure 7b), which can be ascribed to its enhanced chain rigidity due to cross-linking. The pure-gas CO\textsubscript{2} and CH\textsubscript{4} permeation properties of both Nafion types indicated that CO\textsubscript{2}/CH\textsubscript{4} selectivity increases with feed pressure. However, the opposite trend was observed when the polymers were tested under mixed-gas conditions, as discussed below.

Figure 8 compares the permeabilities of CO\textsubscript{2} and CH\textsubscript{4} in Nafion H\textsuperscript{+} and Nafion Fe\textsuperscript{3+} membranes tested with a 1:1 molar feed gas mixture as a function of pressure at 35 °C. These mixture experiments are important to assess the membrane material performance as CO\textsubscript{2} tends to introduce nonideal effects such as plasticization and competitive sorption, typically resulting in different permeation behavior compared to pure-gas permeabilities. In comparison to Nafion H\textsuperscript{+}, CO\textsubscript{2} mixture permeabilities in Nafion Fe\textsuperscript{3+} were lower at all pressure points, as shown in Figure 8a. It is important to note that mixed-gas CO\textsubscript{2} permeabilities in Nafion Fe\textsuperscript{3+} were lower than their pure-
gas values most likely due to competitive sorption effects. As pressure increased from 2 to 15 atm, mixed-gas CO₂ permeability was only marginally affected for Nafton H⁺ and Nafton Fe³⁺.

Mixed-gas CH₄ permeabilities in Nafton Fe³⁺ were lower than their pure-gas values across the investigated pressure range. As discussed above, competitive sorption and polymer chain compression can explain this decrease. In comparison to Nafton H⁺, mixture CH₄ permeabilities in Nafton Fe³⁺ were lower at all pressure points, as shown in Figure 8b. As the pressure increased from 2 to 15 atm, the mixed-gas CH₄ permeability in Nafton Fe³⁺ increased by ~30%, whereas that in Nafton H⁺ increased by 56%. The strong cross-linking in Nafton Fe³⁺ suppressed the CO₂-induced increase in segmental mobility more effectively compared to Nafton H⁺, and consequently reduced plasticization.

Figure 9 compares pure- and mixed-gas (1:1 molar feed ratio) CO₂/CH₄ selectivities in Nafton H⁺ and Nafton Fe³⁺ membranes. In the pure-gas experiment, Nafton Fe³⁺ showed a higher CO₂/CH₄ selectivity with increased feed pressure, similar to the trend previously observed for Nafton H⁺, as shown in Figure 9a.⁴¹ The increased pure-gas selectivity resulted from two effects: (i) increased CO₂ permeability due to plasticization and (ii) reduction in CH₄ permeability to chain compression.⁴¹ However, when tested under mixed-gas conditions, the dominant increase in CH₄ permeability due to CO₂-induced plasticization caused the mixed-gas CO₂/CH₄ selectivities to decrease for both Nafton types. In comparison, Nafton Fe³⁺ exhibited a higher selectivity than Nafton H⁺ over the entire pressure range. The mixture CO₂/CH₄ selectivity of Nafton Fe³⁺ dropped by only 19% from 32 at 2 atm to 26 at 15 atm CO₂ partial pressure. At typical natural gas operating conditions (~10 atm CO₂ partial pressure), Nafton Fe³⁺ exhibited the mixed-gas CO₂/CH₄ selectivity of 28, which was 48% higher than the value of 19 obtained for Nafton H⁺. When compared to the most commonly used membrane material for natural gas treatment, cellulose triacetate, Nafton Fe³⁺ had a slightly higher CO₂/CH₄ selectivity (28 vs 25) but a lower CO₂ permeability (1.1 vs 8 Barrer), which may limit its commercial potential for CO₂/CH₄ separations.

CONCLUSIONS

The physical and gas-transport properties of Nafton complexes with trivalent Fe³⁺ cations were investigated. The physical cross-linking in Nafton Fe³⁺ resulted in high pure-gas N₂/CH₄ and CO₂/CH₄ permeeselectivities of 4.0 and 35, respectively, compared to the values of 2.9 and 28 in Nafton H⁺. This was attributed to the strong ionic interactions between Fe³⁺ cations and sulfonate anions that caused chain stiffening leading to enhanced diffusivity selectivities. High-pressure gas solubility measurements showed linear solubility isotherms for N₂, O₂, and CH₄ and a slightly concave isotherm for CO₂, potentially indicative of the existence of microvoids that created additional sorption sites. Consequently, the gas solubilities in Nafton Fe³⁺ were higher than those in Nafton H⁺. Binary mixed-gas experiments demonstrated that physical cross-linking via trivalent Fe³⁺ cations was an effective approach to reduce the high-solubility CO₂-induced plasticization of Nafton. At a typical natural gas feed CO₂ partial pressure of 10 atm, Nafton Fe³⁺ exhibited a CO₂/CH₄ selectivity of 28 compared to 19 in Nafton H⁺.

EXPERIMENTAL SECTION

Materials. Nafton NRE 211 films with the thickness of 25 μm and the equivalent weight of 1100 g equiv⁻¹ were purchased from Ion Power, Inc., in the H⁺ form. Before the Fe³⁺ exchange, the as-received Nafton H⁺ membranes were first washed with distilled water to remove any surface impurities. Next, the films were immersed in an aqueous Fe(NO₃)₃ solution of 0.05 molar concentration. The exchange process was monitored using a pH meter until the pH value stabilized. To ensure complete ion exchange, the films were then stored in the solution for at least 10 days. The wet films were gently wiped with soft tissue paper to remove any excess solution from the surface. The films were air dried for 12 h by sandwiching between two filter papers and then dried under high vacuum at 80 °C for 2 days before testing. The film density of Nafton Fe³⁺ was 2.14 g cm⁻³ ± 1% using a mass-volumetric technique by accurately measuring the weight, area, and thickness of dry samples.

Polymer Characterization and Methods. Wide-angle X-ray diffraction (WAXD) measurements were conducted on a Bruker D8 Advance diffractometer.⁴² The thermal stability of Nafton H⁺ and Fe³⁺ samples was investigated on a TA instrument 2950 thermogravimetric analyzer (TGA) in a nitrogen atmosphere. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained with a Varian 670-IR spectrometer. Raman spectra of Nafton H⁺ and Nafton Fe³⁺ were collected on a LabRAM ARAMIS (Horiba Jobin Yvon, Inc.) instrument.

Pure-Gas Solubility and Permeation Tests. The gas solubility of Nafton Fe³⁺ was measured using a Hiden Intelligent Gravimetric Analyzer (IGA-003, Hiden Isochema, U.K.) as previously described.⁴¹ Pure-gas permeabilities at 35 °C were determined with a custom-designed constant volume/variable pressure test system.⁴²

Mixed-Gas Permeation Tests. The mixed-gas permeation experiments were performed at 35 °C with a feed gas containing 50 vol % CH₄/50 vol % CO₂ at total pressures ranging from 4 to 30 atm following a method described by O’Brien et al.⁵² and applied in our previous work.⁴¹

AUTHOR INFORMATION

Corresponding Author
*E-mail: Ingo.Pinnau@kaust.edu.sa.

ORCID
Ingo Pinnau: 0000-0003-3040-9088

References

1. Baker, R. W.; Lokhandwala, K. Natural Gas Processing with Membranes: an Overview. Ind. Eng. Chem. Res. 2008, 47, 2109–2121.
2. Bernardo, P.; Drioli, E. Membrane Gas Separation Progresses for Process Intensification Strategy in the Petrochemical Industry. Pet. Chem. 2010, 50, 271–282.
3. Yampolskii, Y. Polymeric Gas Separation Membranes. Macromolecules 2012, 45, 3298–3311.
4. Baker, R. W.; Low, B. T. Gas Separation Membrane Materials: a Perspective. Macromolecules 2014, 47, 6999–7013.
(50) Heitner-Wirguin, C. Infra-Red Spectra of Perfluorinated Cation-Exchanged Membranes. *Polymer* 1979, 20, 371–374.
(51) Gruger, A.; Régis, A.; Schmatko, T.; Colomban, P. Nanostructure of Nafion Membranes at Different States of Hydration: an IR and Raman Study. *Vib. Spectrosc.* 2001, 26, 215–225.
(52) Laporta, M.; Pegoraro, M.; Zanderighi, L. Perfluorosulfonated Membrane (Nafion): FT-IR Study of the State of Water with Increasing Humidity. *Phys. Chem. Chem. Phys.* 1999, 1, 4619–4628.
(53) Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. The Effects of Crosslinking Chemistry on CO₂, Plasticization of Polyimide Gas Separation Membranes. *Ind. Eng. Chem. Res.* 2002, 41, 6139–6148.
(54) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. Specific Intermolecular Interaction of Carbon Dioxide with Polymers. *J. Am. Chem. Soc.* 1996, 118, 1729–1736.
(55) Bhide, B. D.; Stern, S. A. Membrane Processes for the Removal of Acid Gases from Natural Gas. II. Effects of Operating Conditions, Economic Parameters, and Membrane Properties. *J. Membr. Sci.* 1993, 81, 239–252.
(56) Baker, R. W. Future Directions of Membrane Gas Separation Technology. *Ind. Eng. Chem. Res.* 2002, 41, 1393–1411.
(57) O’Brien, K. C.; Koros, W. J.; Barbari, T. A.; Sanders, E. S. A New Technique for the Measurement of Multicomponent Gas Transport Through Polymeric Films. *J. Membr. Sci.* 1986, 29, 229–238.