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Highly selective polymer electrolyte membranes consisting of poly(2-ethyl-2-oxazoline) and $\text{Cu}(\text{NO}_3)_2$ for SF_6 separation

Woong Gi Lee & Sang Wook Kang

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Polymer electrolyte membranes consisting of $\text{Cu}(\text{NO}_3)_2$ and poly(2-ethyl-2-oxazoline) (POZ) were prepared for SF_6/N_2 separation. It was anticipated that repulsive forces would be operative between the negative charge of water and the F atoms of SF_6 when $\text{Cu}(\text{NO}_3)_2$ in the composite was solvated by water, and that the barrier effect of Cu^{2+} ions would be activated. In fact, $\text{Cu}(\text{NO}_3)_2$ solvated by water in the POZ membrane was observed to have more higher-order ionic aggregates than free ions or ion pairs, as confirmed by FT-Raman spectroscopy. Thus, when $\text{Cu}(\text{NO}_3)_2$ solvated by water was incorporated into the POZ matrix, the N_2/SF_6 selectivity increased to 28.0 with a N_2 permeance of 11.2 GPU at a POZ/ $\text{Cu}(\text{NO}_3)_2$ mole ratio of 1:0.7. The coordinative interaction of $\text{Cu}(\text{NO}_3)_2$ with the carbonyl group in POZ was confirmed by FT-IR spectroscopy and TGA, and the film thickness of the membrane was determined from SEM analysis.

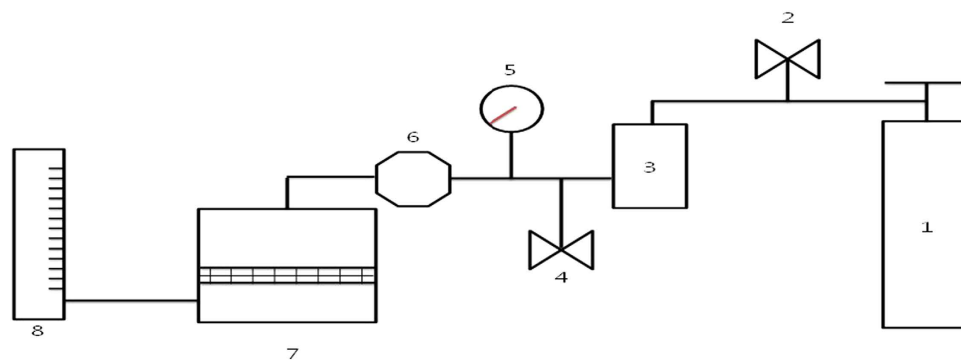
Separation of gas mixtures is very important in industrial fields¹. Sulfur hexafluoride (SF_6) gas is widely used in a variety of industrial processes, but it is one of the most potent greenhouse gases². SF_6 separation is very important given that its green house gas effect is 23900 times higher than that of CO_2 gas, and SF_6 is also a very stable gas with an atmospheric lifetime of 3200 years^{3,4}. To resolve these issues, techniques for SF_6 separation and decomposition have recently gained interest⁵.

Many studies have focused on developing technologies for separation of SF_6 and its derivatives, some of which have been partially commercialized. As an example of an SF_6 separation technique, a hollow fiber membrane was fabricated using a dry-wet phase inversion method. Separation of a N_2/SF_6 binary mixture using the hollow fiber membrane was investigated⁶. Furthermore, the plasma, electrical discharge, and spark methods are quite efficient methods for decomposition of SF_6 ^{7,8}. In another study, different porous materials were evaluated as absorbents for SF_6 . Stainless steel slag (SSS), which is rich in metal and silicon oxide, was reported to be an effective SF_6 decomposition agent⁹. Multi-walled carbon nanotubes (MWNTs) have also been evaluated for adsorption of SF_6 . Furthermore, zeolites, silicalite, and pillared clays were studied for adsorption of C1 to C4 alkanes and SF_6 gas^{10–13}. Metal organic frameworks (MOFs) such as DUT-9, Cu-BTC, and MIL-101 and porous coordination polymers (PCPs) have been used to separate SF_6 , CO, CO_2 , and CH_4 ^{14–18}.

Recently, gas separation has been widely studied using the electrolyte membrane. For example, the greenhouse gases CO_2 and CH_4 were separated from CO_2/N_2 and CO_2/CH_4 mixtures by using a polymer electrolyte. The polymeric gas separation membrane exhibited good performance. In one study, CO_2 was separated from a CO_2/N_2 mixture by using an electrolyte membrane with potassium fluoride (KF) in poly(vinylpyrrolidone) (PVP) solution. The potassium ion of KF was coordinated with the amide group of the PVP polymer to induce crosslinking. The interaction between the K^+ and CO_2 molecules facilitated CO_2 transport, resulting in enhancement of the CO_2 separation performance. As a result, the CO_2 permeance was 28.0 GPU and the selectivity (CO_2/N_2) was 4.1¹⁹.

In this study, we report the fabrication of an electrolyte membrane by simply adding $\text{Cu}(\text{NO}_3)_2$ to poly(2-ethyl-2-oxazoline) (POZ). The N_2 and SF_6 gas permeance of the electrolyte membrane is evaluated as shown in Fig. 1, demonstrating that the electrolyte membrane containing $\text{Cu}(\text{NO}_3)_2$ exhibits excellent separation performance. $\text{Cu}(\text{NO}_3)_2$ incorporated into the POZ membrane was found to have more higher-order ionic aggregates than free ions or ion pairs, as confirmed by FT-Raman analysis.

Department of Chemistry, Sangmyung University, Seoul 110-743, Republic of Korea. Correspondence and requests for materials should be addressed to S.W.K. (email: swkang@smu.ac.kr)



1 : Cylinder, 2, 4 : Needle valve, 3 : Massflow controller, 5 : Pressure regulator, 6 : Pressure gauge, 7 : permeation cell, 8 : Bubble flow meter

Figure 1. Experimental set-up for the gas permeation test.

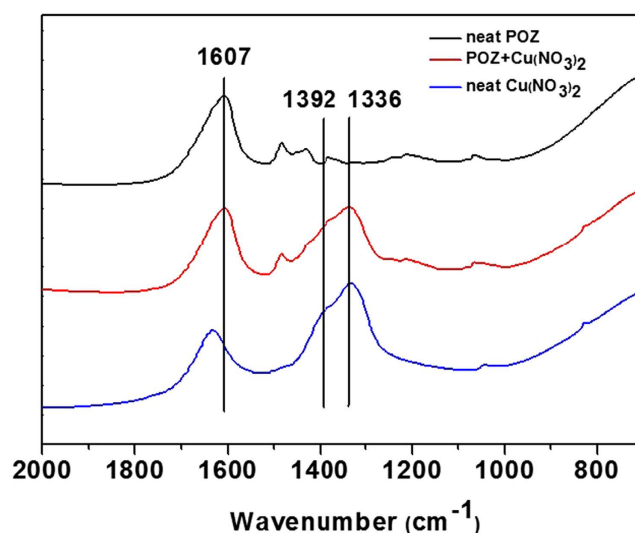


Figure 2. FT-IR spectra of neat POZ and POZ/Cu(NO₃)₂ electrolyte.

Results and Discussion

FT-IR. FT-IR measurements were performed on a Varian FTS3100 spectrometer; 64–200 scans were averaged at a resolution of 4 cm⁻¹. Thermogravimetric analysis (TGA) was performed with Mettler Toledo TGA devices at a heating rate of 10 °C/min. FT-Raman measurements were performed for Cu(NO₃)₂ and POZ/Cu(NO₃)₂ solutions at room temperature using a Horiba Jobin Yvon LabRam Aramis with a diode laser beam at an excitation wavelength of 785 nm.

The aggregates of copper nitrate were dispersed in the polymer chain. The ion aggregates were solvated by the partial positive charge of water. Therefore, the partial negative charge of water was localized on the exterior of the ion aggregates. Non-polar N₂ gas was transported through the polymer membrane by Fickian transport, but SF₆ gas having a high quadrupole moment experienced higher repulsion with the partial negative charge of water. Furthermore, the SF₆ molecules could be blocked by activated Cu cations in the polymer chains.

To confirm the formation of the polymer electrolytes consisting of POZ and Cu(NO₃)₂, the interaction between copper ions and the carbonyl groups in the amide of the polymer was investigated using FT-IR spectroscopy. Figure 2 shows that the spectrum of neat POZ has an intense free C=O peak at 1607 cm⁻¹. When Cu(NO₃)₂ was incorporated into POZ, the shift of the free C=O peak at 1607 cm⁻¹ was negligible. Thus, the copper ion appeared not to interact with the carbonyl group. Furthermore, it was known that the stretching frequency of free NO₃⁻ occurs at 1336 cm⁻¹. When Cu(NO₃)₂ was incorporated into POZ, the intensity of the peak at 1392 cm⁻¹, which is the aggregated NO₃⁻, diminished and the peak of free NO₃⁻ at 1336 cm⁻¹ became dominant. This observation indicated that the ionic bonding of nitrate ions with the copper ions became weakened by interaction with the hydrogen bonds formed with water, resulting in the observed decrease of the stretching frequency.

Thermal analysis. Thermogravimetric analysis (TGA) was carried out to confirm the thermal stability of the polymer electrolyte using a Universal V4.5A (TA Instruments) apparatus. Figure 3 shows the TGA data for

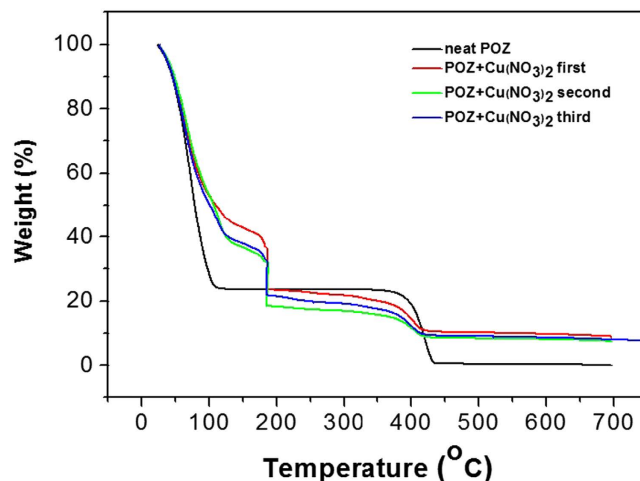


Figure 3. TGA analyses of neat POZ and POZ/Cu(NO₃)₂ (1:0.7 mol ratio).

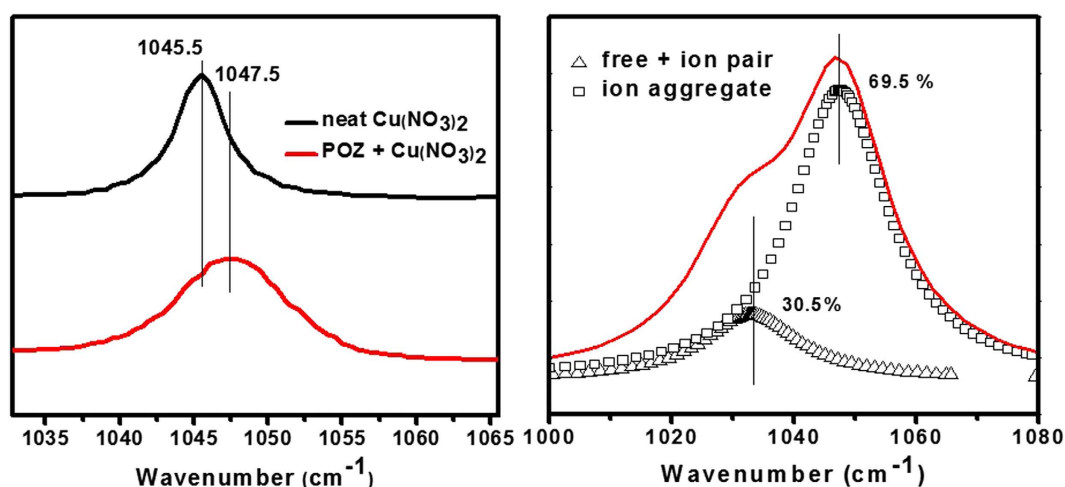


Figure 4. FT-Raman spectra of (a) neat Cu(NO₃)₂ and POZ/Cu(NO₃)₂ (1:0.7 mol ratio) and (b) the deconvoluted spectra for POZ/Cu(NO₃)₂.

neat POZ and POZ/Cu(NO₃)₂ (1:0.7 mol ratio), demonstrating 78% weight loss for neat POZ between 0 °C and 100 °C, attributed to evaporation of water. On the other hand, when copper nitrate was incorporated into the POZ polymer, water evaporation progressed at a higher temperature of above 100 °C, possibly due to solvation of copper nitrate by water. Therefore, the increase in the decomposition temperature was attributed to the strong interaction of copper with water. The boiling point of copper nitrate is known to be 170 °C. Thus, the loss of about 20% weight at about 170 °C was thought to be due to copper nitrate. Also, weight loss was apparent for all samples at around 400 °C due to degradation of the POZ polymer. It is deduced from this result that copper nitrate did not interact with the POZ polymer. Copper nitrate was solvated by water and thus the decomposition temperature of copper nitrate and water increased.

FT-Raman spectroscopy. To investigate the ionic constituents (i.e. free ions, ion pairs, and higher-order aggregates) of NO₃⁻ in neat Cu(NO₃)₂ and POZ with Cu(NO₃)₂, FT-Raman spectra were acquired as shown in Fig. 4. The ionic constituents of NO₃⁻ are known to present stretching bands at 1034, 1040, and 1045 cm⁻¹, assigned to free ions, ion pairs, and ion aggregates, respectively²⁰. When copper nitrate was incorporated into the POZ polymer, the wavenumber of the NO₃⁻ species increased negligibly from 1045.5 to 1047.5 cm⁻¹ as shown in Fig. 4(a), indicating that Cu(NO₃)₂ incorporated into POZ existed mostly as ion aggregates. In the case of Cu(NO₃)₂ incorporated into POZ, the relative percentage of free ions, ion pairs, and aggregates is shown in Fig. 4(b). New peaks were observed at 1029 and 1034 cm⁻¹. These peaks were attributed to free ions and ion pairs. The peak areas for each configuration were measured to be 14.829, 15.664, and 69.501% as shown Fig. 4(b). Based on these results, Cu(NO₃)₂ incorporated into the POZ polymer formed more higher-order ion aggregates than free ions or ion pairs and the ion aggregates were dispersed in the membrane chain.

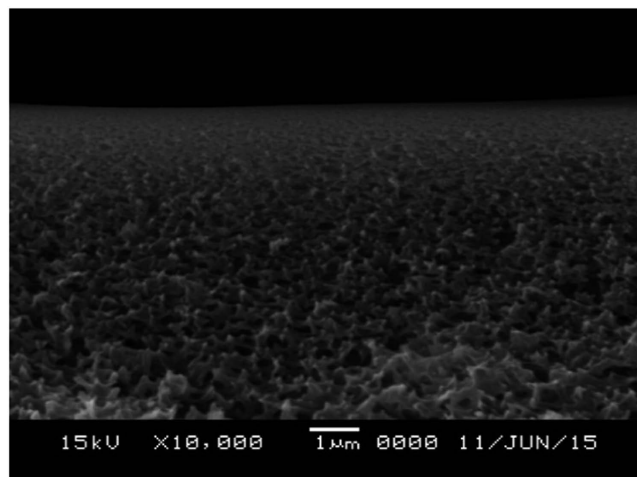


Figure 5. SEM image of POZ/Cu(NO₃)₂ (1:0.7 mol ratio) electrolyte polymer membrane.

mol ratio (POZ : Cu(NO ₃) ₂)	gas permeance (GPU)		selectivity (N ₂ /SF ₆)
	N ₂	SF ₆	
1:0.5	4.2	0.7	6.0
1:0.7	11.2	0.4	28.0

Figure 6. Gas permeance and selectivity of polymer electrolyte at different compositions.

Structural morphology. Scanning electron microscopy (SEM) was used to investigate the thickness of the polymer electrolyte on the polysulfone macroporous membrane supports, as shown in Fig. 5. When the polymer electrolyte solution was coated onto the supports, the thickness of the selective layer was about 1 µm.

Separation performance. After the electrolyte membrane was coated with the control coater, the membrane was applied as the SF₆ separation membrane. Figure 6 showed the single gas permeance and selectivity of N₂/SF₆ through the copper nitrate ion aggregate membrane. The N₂ gas permeance at each mol ratio (1:0.5 to 1:0.7) was about 4.2 and 11.2 GPU while the SF₆ gas permeance was about 0.7 and 0.4 GPU. 1:0.7 mol ratio of POZ/Cu(NO₃)₂ gave rise to the highest N₂ gas permeance with the lowest SF₆ gas permeance. In addition, after 2 d, the SF₆ gas permeance decreased to about 0.2 GPU. Therefore, the selectivity of the POZ/Cu(NO₃)₂ (1:0.7 mol ratio) membranes was the best at 28.0. Thus, because Cu(NO₃)₂ was solvated by water, the repulsive force between the negative charge of water and the F atoms of SF₆ increased, and the barrier effect of activated Cu²⁺ ions was also enhanced as shown in Fig. 7.

This study presented a simple method for the preparation of an electrolyte membrane containing Cu(NO₃)₂ aggregates as a barrier material. The membrane was simply fabricated by adding Cu(NO₃)₂ to the POZ solution followed by preparation of the composite by using a control coater. The N₂ permeance achieved with a 1:0.5 mol ratio of POZ/Cu(NO₃)₂ was 4.2 GPU, which increased to 11.204 GPU in the case of a 1:0.7 mol ratio of POZ/Cu(NO₃)₂. On the other hand, the SF₆ permeance decreased at a 1:0.7 mol ratio of POZ/Cu(NO₃)₂. Therefore, the highest selectivity of 28.0 was achieved with a 1:0.7 mol ratio of POZ/Cu(NO₃)₂.

Methods

Materials. Poly(2-ethyl-2-oxazoline) (POZ) and copper nitrate hydrate (Cu(NO₃)₂·xH₂O) were purchased from Sigma-Aldrich and used without further purification.

Fabrication process. A polymer solution was prepared by dissolving POZ in water (20 wt%). To prepare the polymer electrolyte solution, the amount of Cu(NO₃)₂·xH₂O added to the polymer matrix was determined according to the mole ratio of the copper ion to the monomeric unit of POZ. This solution was stirred for one day at room temperature. This polymer electrolyte solution was coated onto polysulfone macroporous membrane supports (Toray Inc., Japan) using an RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). To contain the water moistly, the polymer electrolyte membranes were dried for 10 minutes at room temperature. The gas flow rates were measured using a bubble flow meter. The unit of gas permeance is GPU, where 1 GPU = 1 × 10⁻⁶ cm³ (STP)/(cm²·s·cmHg).

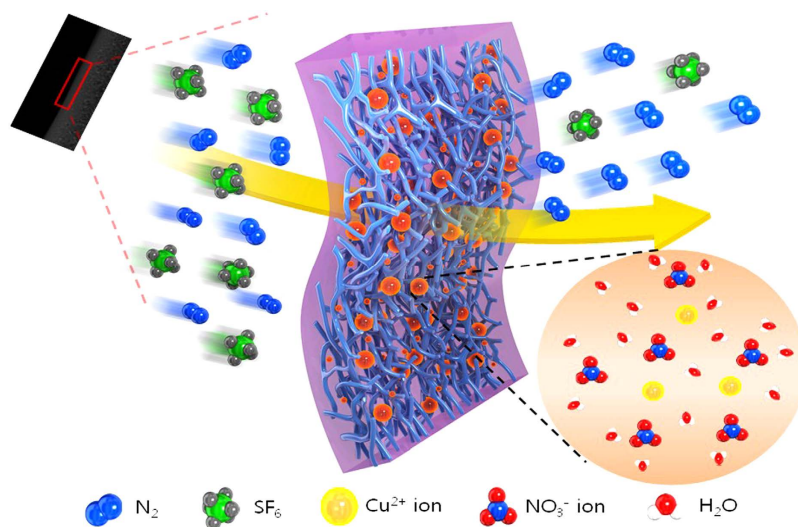


Figure 7. Polymer electrolyte membrane for SF₆ separation.

Characterization

FT-IR measurements were performed on a Varian FTS3100 spectrometer; 64–200 scans were averaged at a resolution of 4 cm⁻¹. Thermogravimetric analysis (TGA) was performed with Mettler Toledo TGA devices at a heating rate of 10 °C/min. FT-Raman measurements were performed for Cu(NO₃)₂ and POZ/Cu(NO₃)₂ solutions at room temperature using a Horiba Jobin Yvon LabRam Aramis with a diode laser beam at an excitation wavelength of 785 nm.

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Author Contributions

S.W.K. led the project, conducted the data analysis and reviewed the manuscript. W.G.L performed the experiments, collected the data and wrote the paper.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

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