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Polymer Electrolyte Membranes Containing Silver Ion for Facilitated Olefin Transport

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Introduction. Polymer electrolytes containing silver ions are of interest because of their potential application to facilitated transport membranes for the separation of olefin/paraffin mixtures. In the facilitated transport of olefins, silver ions confined to the membrane medium form reversible complexes with olefin molecules.[1,2] Olefin molecules donate π electrons from the occupied 2p orbitals to the empty s orbitals of silver ions to form σ-bonds. Back-donation of electrons from the occupied d orbitals of silver ions into the empty π^*-2p antibonding orbitals of olefin molecules results in π-bonding.[2] Because of such *reversible* and *specific* interaction of silver ions with olefin molecules, silver ions can act as olefin carriers for facilitated transport in the membrane and then lead a carrier-mediated transport in addition to a normal Fickian transport. Paraffins are unable to form complexes with silver ions and permeate only through Fickian transport. This results in high olefin/paraffin separation. Many investigators have studied olefin/paraffin separations by facilitated transport with various membranes.[3,4] In general, the facilitated transport phenomena have been typically observed in supported liquid membranes or ion exchange membranes containing silver ion carrier together with water.[3] However, despite extensive research on olefin/paraffin separations by facilitated transport membranes,[3] this technology has not been applied to industrial applications due to the evaporation of the liquid media in such liquid membranes. Here, we report the concentration effect of solid membranes containing silver polymer electrolytes as olefin carriers for the separation of propylene/propane mixtures.

Experimental Section. Poly(2-ethyl-2-oxazoline) (PEOx) ($M_W = 5 \times 10^5$) and poly(vinyl pyrrolidone) (PVP) ($M_W = 1 \times 10^6$) were purchased from Aldrich Chemical Co. and Polysciences, Inc., respectively. Silver tetrafluoroborate ($AgBF_4$) and silver triflate ($AgCF_3SO_3$) were purchased from Aldrich Chemical Co. All chemicals were used as received. Polymer electrolyte solution was prepared by dissolving a silver salt in 20% (w/w) polymer solution in water. The solution was coated onto asymmetric microporous substrate (SEAHAN Industries Inc., Seoul, Korea) using a RK Control Coater. After evaporation of water in a convection oven at 40 °C under nitrogen, the membrane was dried completely in a vacuum oven for 3 days at room temperature. The thickness of the top polymer electrolyte layer was ca. 1 μm. Gas flow rates represented by gas permeance were determined by a soap bubble flow meter. The unit of the gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg). Mixed-gas (50:50 vol % of propylene/propane mixture) separation properties of the membranes were evaluated by gas chromatography (Hewlett Packard G1530A, MA) equipped with a TCD detector. The stage cut (θ), the ratio of permeate to feed flow rates, was always less than 2%.

Results. Preliminary FT-IR and Raman spectroscopic experiments as well as ab initio calculations demonstrated that silver ions interact with the carbonyl oxygen of PEOx or PVP and exist as free ions, ion pairs, and/or higher ion aggregates according to the amount of silver salt loading in the polymer matrix.[5] The spectroscopic study showed that carbonyl groups of PEOx and PVP coordinate with silver ion up to a 1:1 mole ratio.[5]

The effect of silver salt concentration on propylene permeance was investigated. Figure 1 shows the propylene permeance through PEOx/silver and PVP/silver composite membranes with increasing amount of silver salt. As shown in this figure, the propylene permeance

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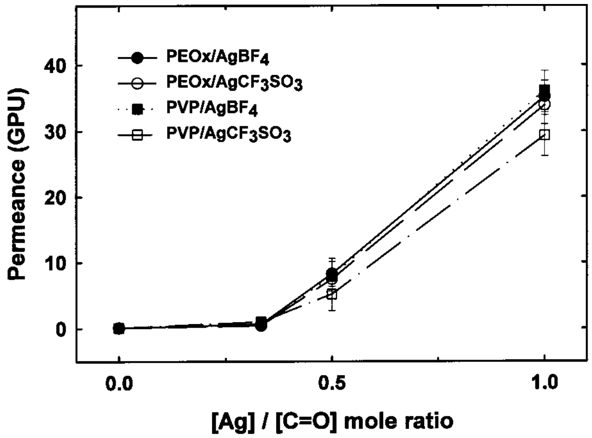

Figure 1. Propylene permeance with increasing carrier concentration in solid polymer electrolyte membranes containing silver ions (Δp = 413.5 kPa, T = 23 °C, 1 GPU = 10^{-6} cm^3 (STP)/(cm^2 s cmHg)).

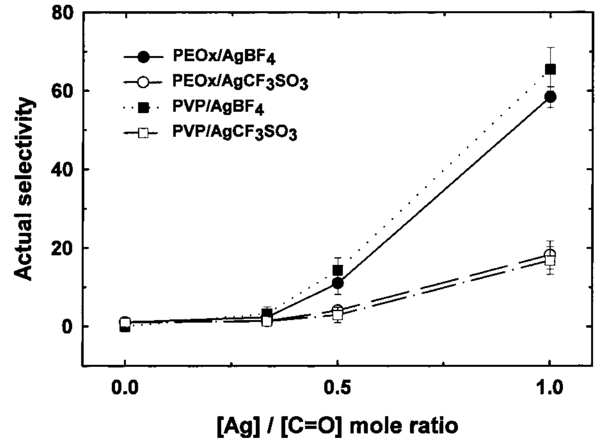

Figure 2. Actual selectivity with increasing carrier concentration in solid polymer electrolyte membranes containing silver ions (Δp = 275.6 kPa, θ < 0.02, T = 23 °C).

through pure PEOx and PVP membranes was very low and was not detected being below the practical lower limit of the bubble flow meter. There is no significant improvement of the propylene permeance through PEOx/silver and PVP/silver until the mole ratio of silver to carbonyl reached ca. 0.34. However, permeance increased up to 30 GPU with increasing silver ion content. This dependence of the carrier concentration is consistent with the mathematical model proposed by Kang et al. to interpret the facilitated transport behavior in solid state.[6] Meanwhile, the propane permeance through the membrane was unmeasurably small (less than 0.1 GPU) no matter what the concentration of silver ion is. The ideal separation factors for olefin/paraffin in mixture were determined by the ratio of permeance of olefin to the permeance of paraffin; therefore, the ideal separation factor is at least 300 at the mole ratio of 1, implying that silver polymer electrolytes could be successfully used as a facilitated transport membrane material for the separation of olefin/paraffin mixtures. The propylene permeance of PEOx and PVP containing $AgBF_4$ or $AgCF_3SO_3$ show similar trends with increasing silver salt contents.

The mixed-gas separation properties of polymer electrolyte membranes were evaluated in order to obtain the actual selectivity. The actual selectivities were determined by the ratio of mole fractions of the gas components in permeate and in feed streams, and the results are shown in Figure 2. The facilitating effect of the silver ions increases with increasing mole ratio of silver to carbonyl functional group. The anion of the silver salt had a significant effect on the facilitated transport while there is no significant dependence on polymer matrix, PEOx or PVP in these experimental conditions. The polymer electrolyte membranes containing $AgBF_4$ showed greater separation properties than those containing $AgCF_3SO_3$. In the environment of the polymer electrolyte membrane, the silver ions have several possibilities for interaction with the salt anion, the carbonyl group of polymer matrix, and double bond of olefin. The relative strengths of these interactions would be important and affect the facilitated transport. Therefore, the reversible complex-forming reaction rate between metal ions and the double bonds of the hydrocarbon would be varied by the nature of the polymer matrix and silver salt. The details of the effect of silver salt in polymer electrolytes are under investigation in this laboratory.

Summary. Solid polymer electrolyte membranes containing silver ions exhibit facilitated transport of propylene. The propylene permeance and its ideal separation factor over propane increased from less than 0.1 GPU to 30 and from ca. 1 to 300, respectively, when the mole ratio of silver to carbonyl group reaches 1. This excellent performance is predominantly attributed to the extraordinary high loading of silver ions in PEOx and PVP solvents. As shown in the mixed-gas results, the polymeric matrix, PEOx or PVP, had little effect in the membrane performance of our polymer electrolyte membrane systems. However, the anion of the facilitated transport carrier, BF_4^- or $CF_3SO_3^-$, had a significant effect on the facilitated transport property.

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