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# 고분자 전해질과 고분자 나노복합체를 활용한 올레핀 촉진수송 분리막에 대한 총설

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# Review on Facilitated Olefin Transport Membranes Utilizing Polymer Electrolytes and Polymer Nanocomposites

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요 약: 본 총설에서는 고분자와 은염으로 구성된 고분자 전해질 분리막과 장시간 안정성을 해결하기 위한 방안들이 정리되었다. 특히 이온성 액체를 활용하여 $AgNO_3$를 새로운 운반체로 사용하기 위한 방안, 새로운 고분자 매트릭스로서 poly(ethylene phthalate) (PEP)를 활용하는 방안과 가장 최근 알루미늄 염을 활용하여 운반체의 안정성을 부여하는 연구결과들이 정리되었다. 올레핀 촉진수송을 위한 고분자 나노복합체 분리막의 경우, 운반체인 은 나노입자 표면을 극성화시킬 수 있는 전자수용체의 종류와 특징들이 소개되었으며, 최근 투과도 성능을 향상시킬 수 있는 연구결과들이 정리되었다.

**Abstract:** In this short review, the polymer electrolyte membranes consisting of polymer and Ag salts were introduced and various approaches to solve the long-term stability were summarized. In particular, utilizing $AgNO_3$ as carriers with ionic liquid, the replacement of polymer matrix as poly(ethylene phthalate) (PEP) for strong coordinative interactions with Ag ions and the introduction of $Al(NO_3)_3$ to polymer/$AgBF_4$ complexes were introduced for long-term stable facilitated olefin transport membranes. For the polymer nanocomposite membranes, the role of electron acceptors as polarizer on the surface of AgNPs and the approach to solve the low permeance were introduced.

***Keywords***: *polymer electrolyte, polymer nanocomposite, olefin, carrier, facilitated transport*

## 1. Facilitated Transport

The theory of facilitated transport has been much interested in membrane fields due to their various applicability such as gas separation and fast ion transport [1-4]. Generally, it was very well known that the separation performance for membranes were observed to show the trade-off phenomena[1-4]. Thus, the selectivity for specific molecules would decrease with increasing permeance. However, both permeance and selectivity were surprisingly observed to be enhanced for facilitated transport membranes[1-4]. While fickian transport was generally observed in gas separation membranes, the carrier-mediated transport could be added in facilitated transport, resulting in fast transport selectively for specific molecules[3-4]. Thus, the enhancement in both selectivity and permeance could be observed in facilitated transport membranes[3-5].

Recently, the development of carriers for specific molecules has been researched for various gases such

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**Table 1.** Separation Performance of Polymer Electrolyte Membranes Consisting of Polymer and Ag Salts[21]

| | mixed gas selectivity (propylene/propane) | permeance (GPU) |
|---|---|---|
| POZ/$AgBF_4$ complexes | 60 | 36 |
| PVP/$AgBF_4$ complexes | 65 | 37 |

as carbon dioxide ($CO_2$) and olefin[5-10]. Representative carrier for $CO_2$ molecules was known as amine groups[2-3]. Thus, when some molecules have amine groups, the transport of $CO_2$ could be accelerated, resulting in the facilitated transport. For example, when 1-butyl-3-methylimidazolium nitrate ($BMIM^+NO_3^-$) among ionic liquids (ILs) was utilized as $CO_2$ membrane, $CO_2/N_2$ and $CO_2/CH_4$ selectivities were 4.7 and 5.8, respectively, with $CO_2$ permeance of 5.2 GPU (1 GPU = 1 × $10^{-6}$ $cm^3$ (STP)/($cm^2$ s cmHg))[5]. For the case of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$), $CO_2/N_2$ and $CO_2/CH_4$ selectivities were 5.0 and 4.8, respectively, with $CO_2$ permeance of 17 GPU[5]. Furthermore, when 1-methyl-3-octylimidazolium tetrafluoroborate ($MOIM^+BF_4^-$) to have relatively free anions was utilized, $CO_2/N_2$ and $CO_2/CH_4$ selectivities were 11.8 and 10.5, respectively, with $CO_2$ permeance of 20.3 GPU[5].

For the facilitated olefin transport membranes, Ag ions and Ag nanoparticles (NPs) have been researched as carriers[6-19]. In this short review, polymer electrolytes and polymer nanocomposites to utilize Ag ions and Ag NPs as olefin carriers, respectively, were investigated and summarized.

## 2. Facilitated Olefin Transport Membrane by Utilizing Polymer Electrolytes

### 2.1. Polymer electrolytes

Ag ions generated from Ag salts such as $AgBF_4$, $AgCF_3SO_3$ and $AgClO_4$ were known to be reversibly interacted with olefin molecules[13]. $\pi$ electron of olefin molecules could be moved to vacant s-orbital in Ag ions and then the electron of d-orbital could be donated into olefin, resulting in the reversible interactions [13]. Among various Ag salts, $AgNO_3$ was inactive carriers since their lattice energy between Ag ions and counteranions was higher than other salts, resulting in the poor dissociation[20]. Thus, $AgBF_4$ salts were desirable for highly selective membranes due to relatively low lattice energy[20].

However, for the preparation of solid membranes to have Ag ions as carriers when organic solvents were evaporated, polymers capable of interacting with ions as coordinate bond should be utilized[13]. Thus, poly (2-ethyl-2-oxazoline) (POZ) and poly(vinylpyrrolidone) (PVP) to have amide groups, and poly(ethylene oxide) (PEO) to have ether groups have been utilized as polymer matrix for facilitated olefin transport membranes[7-8].

### 2.2. Separation performance

When $AgBF_4$ salts were incorporated into POZ, the selectivity of propylene/propane and permeance were 60 and 36 GPU, respectively as shown in Table 1[21]. Furthermore, PVP/$AgBF_4$ complex membranes showed 65 and 37 GPU for selectivity of propylene/propane and permeance, respectively[21]. These enhanced separation factor for mixture of propylene/propane was attributable to facilitated propylene transport generating from Ag ions as carriers. The high separation performance was expected to replace the distillation process to require high energy cost in petrochemistry fields.

### 2.3. Drawbacks

Even though these membranes to utilize Ag ions as olefin carriers could show the high separation performance, the practical applications have been limited due to serious drawback[13]. The crucial drawback was deterioration phenomena of separation performance in both mixed gas selectivity and permeance for propylene/propane mixtures with time[13]. Previous studies showed that Ag ions could be easily converted into Ag

**Table 2.** Separation Performance of Polymer Electrolyte Membranes with Long-Term Stability

| | mixed gas selectivity (propylene/propane) | permeance (GPU) |
|---|---|---|
| POZ/$AgNO_3$/$BMIMBF_4$ complex[20] | 32 | 5.4 |
| PEP/$AgBF_4$ complex[22] | 55 | 5.8 |
| POZ/$AgBF_4$/$Al(NO_3)_3$ complex[13] | 21 | 4.8 |
| PEO/$AgBF_4$/$Al(NO_3)_3$ complex[10] | 10 | 20 |

NPs with time, resulting in the decrease of separation performance[13]. Furthermore, the generated Ag NPs were readily aggregated and then played a role as barriers for gas transport. Therefore, many researches have been done to solve these problems.

### 2.4. Long-term stable membranes

For highly stabilized olefin transport membranes, $AgNO_3$ salts were utilized as new olefin carrier[20]. It was very well known that $AgNO_3$ salts were stable with time, not being converted easily into NPs[20]. However, $AgNO_3$ was inactive carriers when the salts were dissociated into polymer matrix due to their high lattice energy[20]. Thus, the use of $AgNO_3$ salts has been limited for facilitated olefin transport membranes even though they could show the long-term stability. To solve these problems, $BMIM^+BF_4^-$ as ionic liquid was incorporated into POZ/$AgNO_3$ complex membranes[20]. When POZ/$AgNO_3$/$BMIM^+BF_4^-$ membranes were utilized for propylene/propane mixtures, the selectivity of propylene/propane and permeance were 32 and 5.4 GPU, respectively as shown in Table 2 while the separation performance for POZ/$AgNO_3$ membranes without $BMIM^+BF_4^-$ was not observed[20]. The enhancement of separation performance was attributable to selective favorable interactions between $NO_3^-$ in $AgNO_3$ and $BMIM^+$ in ionic liquids, weakening the interactions between $Ag^+$ and $NO_3^-$. Thus, the Ag ions generating from $AgNO_3$ salts could play a role as olefin carrier for facilitated transport membranes.

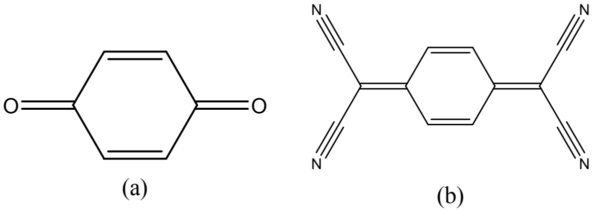
To solve the poor long-term stability for polymer electrolyte membranes, new polymer matrix was suggested[22]. When poly(ethylene phthalate) (PEP) was suggested as new polymer matrix, the long-term stability was observed with time even though unstable $AgBF_4$ salts were utilized[22]. Actually, the selectivity of propylene/propane and permeance were 55 and 5.8 GPU, respectively, and these separation performance remained constant with time[22]. These enhanced long-term stability for Ag ions was attributable to strong coordination between Ag ions and the phthalate groups of PEP[22]. The strong interactions between Ag ions as olefin carriers and phthalate structure caused Ag ions to be interrupted to get electrons, not being easily converted into NPs[22]. From these results, it was concluded that the strong coordination for Ag ions as olefin carriers could enhance the long-term stability for facilitated olefin transport membranes.

Recently, $Al(NO_3)_3$ was incorporated as additives for long-term stable facilitaed olefin transport membranes [13]. When $Al(NO_3)_3$ was incorporated into POZ/$AgBF_4$ complex membrane, the selectivity of propylene/propane and permeance were 21 and 4.8 GPU, respectively[13]. Surprisingly, the separation performance remained constant over more than 14 days[13]. Furthermore, the film of POZ/$AgBF_4$/$Al(NO_3)_3$ complexes had a persistent white color after exposure at room temperature over more than 3 months, indicating that Ag ions were quite stably existed as ionic states in the polymer matrix[13]. The long-term stability by addition of $Al(NO_3)_3$ was explained by the formation of ionic aggregates between $Ag^+$ of $AgBF_4$ and $NO_3^-$ of $Al(NO_3)_3$[13]. The ionic aggregates generated between $Ag^+$ of $AgBF_4$ and $NO_3^-$ of $Al(NO_3)_3$ were attributable to the favorable strong interactions between F atoms of $AgBF_4$ and $Al^{3+}$ of $Al(NO_3)_3$[13].

Very recently, the research was reported to improve the permeance of polymer/$AgBF_4$/$Al(NO_3)_3$ complex

**Table 3.** Separation Performance of Polymer Nanocomposite Membranes

| | mixed gas selectivity (propylene/propane) | permeance (GPU) |
|---|---|---|
| EPR/Ag NPs/*p*-BQ composite[19] | 11 | 0.5 |
| PVP/Ag NPs/TCNQ composite[14] | 50 | 3.5 |
| PEO/Ag NPs/*p*-BQ composite[11] | 10 | 15 |



(a) (b)

**Scheme 1.** Structure of (a) *p*-benzoquinone and (b) 7,7,8,8-tetracyanoquinodimethane

membranes[10]. As reported for POZ/$AgBF_4$/$Al(NO_3)_3$ complex membranes, their permeance was relatively low 4.8 GPU[13]. To improve the permeance for facilitated olefin transport membranes to utilize the $Al(NO_3)_3$ salts, PEO as a new polymer matrix was suggested since it has higher flexibility than glassy POZ and PVP[10]. Actually, when PEO was utilized as new polymer matrix, the selectivity of propylene/propane and permeance were 10 and 20 GPU, respectively[10]. Furthermore, the separation performance remained constant with time even though the enhanced permeance was observed[10]. From these results, it could be concluded that $Al(NO_3)_3$ salts played a role as restrainer for reduction of Ag ions, regardless of polymer species.

## 3. Facilitated Olefin Transport Membrane by Utilizing Polymer Nanocomposites

### 3.1. Metal nanoparticles as olefin carriers

The development of new olefin carriers has been interested and many investigations were researched[11, 14-19]. Representative examples were to utilize the metal NPs such as Ag or Au. Since the favorable interactions between Ag or Au ions and olefin molecules existed, it was expected that if the surface of metal nanoparticles were positively polarized by specific electron acceptors such as *p*-benzoquinone (*p*-BQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and ionic liquids as shown in Scheme 1, the interactions between nanoparticles and olefin could be enhanced, resulting in the facilitated olefin transport[16,17,19].

**Table 4.** The Electron Affinity of Electron Acceptors

| Substance | eV |
|---|---|
| *p*-benzoquinone (*p*-BQ) | + 1.86 |
| 7,7,8,8-tetracyanoquinodimethane (TCNQ) | + 2.8 |

### 3.2. Separation performance

For the preparation of polymer nanocomposite membrane, poly(ethylene-co-propylene) (EPR) and *p*-BQ were selected as polymer matrix and electron acceptors, respectively[19]. The selectivity of propylene/propane and permeance were 11 and 0.5 GPU, respectively as shown in Table 3. These results indicated that the positively polarized Ag NPs could be reversibly interacting with olefin molecules, resulting in the facilitated transport[19]. Furthermore, these membranes containing NPs showed the long-term stability with time, indicating the Ag NPs were highly stabilized by strong interactions with electron acceptors[19].

Recently, for the enhanced separation performance of polymer nanocomposites, TCNQ was suggested as new electron acceptors[14]. As shown in Table 4, the electron affinities for *p*-BQ and TCNQ were 1.86 and 2.8 eV, respectively[14]. Thus, it could be expected that if TCNQ was applied as electron acceptors instead of *p*-BQ, the surface of Ag NPs could be more positively polarized due to high electron affinity[14]. Actually, the selectivity of propylene/propane and permeance for PVP/Ag NPs/TCNQ composite membranes were 50 and 3.5 GPU, respectively as shown in Table 3[14].

These enhanced separation performance was attributable to higher electron affinity of TCNQ, inducing the increased polarity onto surface of Ag NPs[14].

### 3.3. Drawbacks and solution for enhanced permeance

Even though high stability of polymer/Ag NPs/electron acceptors, their low permeance compared with polymer electrolytes interrupted the practical applications. Thus, PEO as a new matrix was suggested for polymer nanocomposites since it has relatively high flexibility[11]. When *p*-BQ was incorporated into flexible PEO/AgNPs composites, the selectivity of propylene/propane and permeance for PEO/Ag NPs/*p*-BQ composite membranes were 10 and 15 GPU, respectively, with long-term stability[11]. The positive polarity was confirmed by x-ray photoelectron spectroscopy (XPS) and it was observed for the binding energy to be increased, indicating that the surface of Ag NPs was properly modified for reversible interactions with olefin molecules[11].

## 4. Conclusions

In this short review, the definition of facilitated transport and various facilitated olefin transport membranes were introduced. In particular, the carriers for facilitated olefin transport were investigated in detail. Representative olefin carriers were Ag ions and Ag NPs for polymer electrolyte and nanocomposite membranes, respectively. Even though polymer electrolyte membranes to utilize Ag ions could show the high separation performance for olefin/paraffin mixtures, they have serious drawback such as poor long-term stability with time. To solve these problems, various approaches such as (1) utilizing $AgNO_3$ as carriers with ionic liquid, (2) the replacement of polymer matrix as PEP for strong coordinative interactions with Ag ions and (3) the introduction of $Al(NO_3)_3$ to polymer/$AgBF_4$ complexes have been researched. For the polymer nanocomposite membranes to utilize the AgNPs as olefin carriers, the electron acceptors such as *p*-BQ and TCNQ were required to induce the surface of NPs to be positively polarized, resulting in the reversible interactions with olefin molecules. Since the polymer nanocomposite membranes containing NPs showed the low permeance even though they showed the excellent selectivity, PEO was recently suggested as new polymer matrix. As a result, the selectivity of propylene/propane and permeance for PEO/Ag NPs/ *p*-BQ composite membranes were 10 and 15 GPU, respectively, with long-term stability.

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