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Review

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A perspective of solutions for membrane instabilities in olefin/paraffin separations: A review

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ABSTRACT:

Light olefins are mainly produced by the naphtha steam cracking, which is among the more energy intensive processes in the petrochemical industry. To save energy, some alternatives have been proposed to partially replace or combine with cryogenic distillation, the conventional technology to separate olefins and paraffins. Within this aim, facilitated transport membranes, mainly with Ag^+ cations as selective carriers, have received great attention owing to the high selectivity and permeance provided. However, to be used industrially, the undesirable instability associated to the Ag^+ cation should be considered. Poisonous agents and polymer membrane materials are sources of Ag^+ deactivation. In recent years, great achievements on the separation performance have been reported, but the current challenge is to maintain the selectivity in long-term separation processes. This work presents a critical analysis of the potential causes of Ag^+ deactivation and points out some alternatives that have been proposed to overcome the hurdle. This review highlights and critically analyses some perspectives of the ongoing development and application of facilitated transport membranes.

KEYWORDS: Olefin/paraffin separations; Facilitated transport membranes; Silver salts; Silver nanoparticles; Carrier poisoning.

1. INTRODUCTION

Light olefins are the principal raw material to the petrochemical industry.[1] In 2016, the global ethylene and propylene production was 146 and 99 million tons and the expected of demand growth rate, until 2025, is 3.6%/year and 4.0%/year, respectively.[2] Steam cracking (SC) is the main industrial process to manufacture light olefins from naphtha or light alkanes.[2–5] In petrochemical industry, SC is among the more energy-intensive processes, and, in 2016, the worldwide consumption have been estimated to be about $3.0 \cdot 10^{15}$ BTU.[6,7] After pyrolysis, separation section is the second large energy consumption step in SC (about $7.5 \cdot 10^{14}$ BTU).[2,5–7] The justification for this consumption is based on the cryogenic distillation of the cracked gases.[6,8,9]

Membrane processes have been proposed to save energy in the separation section by replacing or integrating with the current cryogenic distillation technology.[10–17]Membrane technology has achieved very promising results, specifically regarding the olefin/paraffin separations.[18–24] In a recent study, Lee et al.[25] identified the optimum membrane performance required to replace one typical C3 splitter. They found that a set of membrane modules with propylene permeance of 11.3 GPU (1 GPU=1×10^{-6} cm^3 (STP)/cm^2 s cmHg) and selectivity of 68 could substitute a typical distillation process. Since the replacement of the distillation column by membrane units with optimum performance is technically viable, the great challenge for membrane technology is to reach the suitable selectivity and permeability for the process and keep them over long-term operation. The operational conditions in which the membrane should be used are severe and can lead to the performance loss along the operation.[23,24,26–28]

Besides the steam cracking (SC) plants, which constitute the main target application, there are other two potential areas where membrane technology could be applied for olefin/paraffin separations. Olefin/paraffin separation membranes could be used in the recovery of propylene from FCC off-gas streams[29–32] and in vent streams of some kinds of petrochemical reactors, *e.g.*, polypropylene reactors.[33] The recovery of olefins from vent streams is very attractive because milder operational conditions are present (low level of sulfur and acetylene compounds) and the performance required is lower (selectivities of 3-5) than needed in SC process and FCC off-gas streams.[33] Maybe, this market niche can represent a previous favorable step before the attempt to replace distillation in the SC process or in the FCC off-gas streams that involves huge challenges to be overcome.[31,33]

Among membrane technologies, the alternatives based only on the solution-diffusion mechanism are not effective enough to discriminate olefin/paraffin pairs. The similarity between the physico-chemical properties of alkenes and alkanes is the main drawback that all dense-type membranes assigned to the separation face.[34] The carbon molecular sieve membranes suffer of the same problem, since there is a tiny difference between the molecular diameter of the molecules to be separated.[15] Nevertheless, many efforts have been focused to improve the separation using mixed matrix membranes by introduction of zeolites,[35,36] organic and metal−organic frameworks[37–41] in the polymer matrix. Other works focused on carbon molecular sieve membranes[10,42,43] that are brittle and difficult to scale-up the production.[25] To overcome these discriminative issues between the molecules, the facilitated transport of olefins has been explored, increasing simultaneously the permeance and the selectivity of the separation. The facilitated transport can be defined as a process in which chemically distinct carrier species form complexes with a specific component in the feed stream, thereby increasing the flux of this component relative to other components.[44] The facilitated transport membranes have surpassed the upper bound of the Robeson diagram for the olefin/paraffin separation in the last few years,[22,45] demonstrating the greater potential of this technological option.

Considering the potential applicability of the membrane technology for light olefins/paraffins separation, the goal of this work is to critically review the development of facilitated transport membrane for this separation highlighting the challenges and main drawbacks surpassed during the last decades. A comprehensive analysis of the instability/deactivation problems confronted by distinct kinds of membranes is carried out. The alkene/alkane membrane separation technology is presented describing the source of poisonous agents for the principal carrier used, *i.e.* the Ag^+. Finally, some recent strategies are pointed out as options that try to overcome the Ag^+ deactivation by smart solutions.

2. FACILITATED TRANSPORT MEMBRANES FOR OLEFIN/PARAFFIN SEPARATION

The development of new membranes based on polymeric materials or the modification of polymer structures that provide suitable selectivities for the olefin/paraffin separation has been largely investigated.[46–48] As the polymer films have become more selective to the olefins, they lose productivity due to the trade-off between selectivity and permeation flux, therefore, leading to the technical unfeasibility of the separation process.[15,49] Films where mass transport is based only on the solution-diffusion mechanism have shown, as best results, ideal selectivity of 27 (C_3H_6/C_3H_8) and 0.8 Barrer of propylene permeability.[48,49] These values are significantly lower than the performance reported for facilitated transport films that have shown mixture selectivities (C_2H_4/C_2H_6) higher than 100.[45]

The facilitated transport mechanism, when it takes place, plays in a complementary mechanism to the solution-diffusion transport. In the facilitated transport, a carrier agent interacts reversibly and selectively with the target molecule, that results in the increase in the driving force for the permeation flux of target molecule, and therefore, the permeate is enriched. This kind of transport is not accessible to the inert molecules that are not able to interact with the carrier agent, so that their concentration decreases in the permeate side (**Figure 1**). Thus, the facilitated transport membrane has a superior selectivity compared to the passive (solution-diffusion) membrane.[27,45,50,51] The carriers need to be effectively dispersed over the natural diffusional path of the gases (in the direction of the concentration gradient) and be present at a concentration high enough for transport activation. Furthermore, the carriers also need to be ready to the interaction with the target molecules inside the membrane, *i.e.*, the carriers should be not poisoned.[52,53]

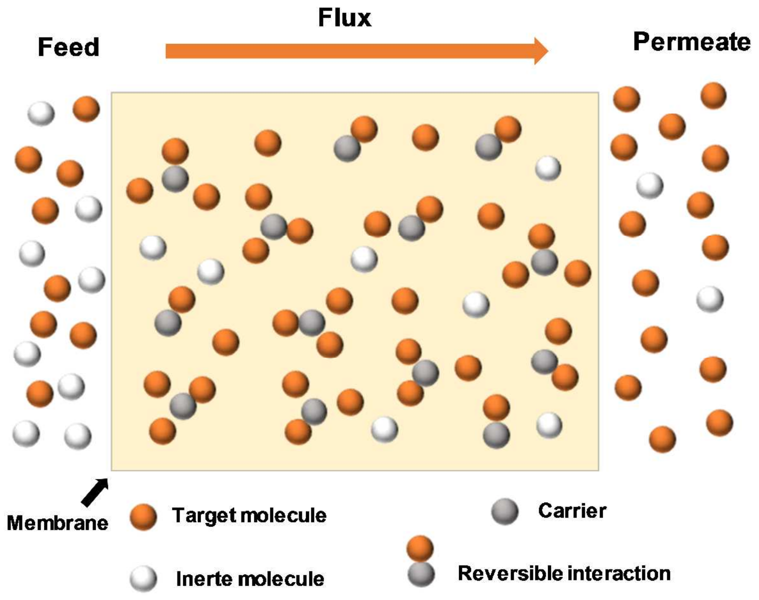

Figure 1. Representation of the facilitated transport mechanism through selective membranes.

2.1. Chemical interaction for olefin separation: Olefin π complexation.

The formation of complexes between some metals and the double bond of olefins has been well known since longtime. Nevertheless, only in 1827, the first metal-olefin complex was identified. The referred compound was the platinum (II) -ethene, which was known as Zeise complex. In the beginning of the 20th century, the first ideas of using silver (I) (Ag^+) salts in olefin absorption systems arose. However, only in 1951, Dewar[54] gave a satisfactory explanation to the interaction mechanism between the ethene and Ag^+. Shortly after, Chatt and Duncanson[55] advanced the Dewar`s explanation presenting the interaction mechanism called π-bond complexation.[13] This complexation takes place when the bonding orbital of the olefin donates electronic density to the empty outermost orbital of Ag^+ (5s) making a σ bond. The strength of this bond depends on the magnitude of the metal positive charge (*e.g.* silver, copper, and gold). The second bond formed is a π bond, resulting from the backdonation of the electronic density from the outermost atomic orbital 4d, which is electronically completed, to the π*- antibonding molecular orbital of the olefin (**Figure 2**).[56,57]

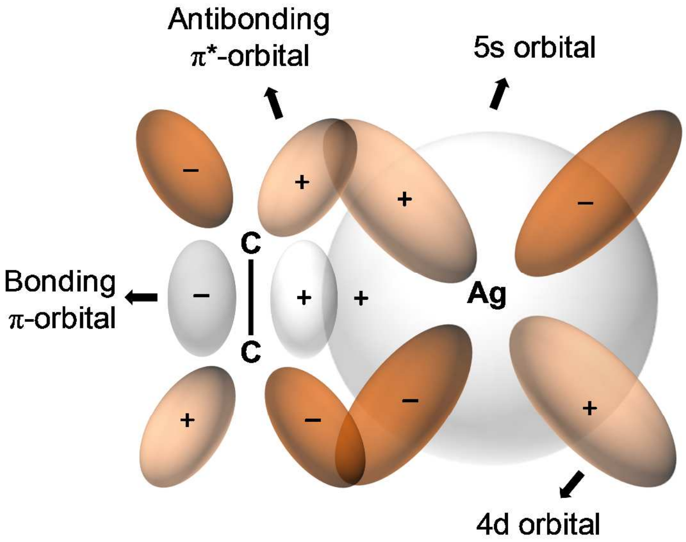

Figure 2. π complexation between olefin and Ag^+ ions (Adapted with permission from Eldridge.[58] Copyright 1993 American Chemical Society).

In 1960, Scholander[59] published a pioneering work that explored the facilitated transport in liquid membranes containing hemoglobin as carrier agent for oxygen transport. Thereafter, works that described membranes of facilitated transport have grown for several applications.[60] Over the following decades to the present day, the facilitated transport mechanism has attracted great attention of many researchers due to the separation potential compared to the simple mechanism of passive transport.

Practically, the development of facilitated transport membranes for light olefin/paraffin separations has been based on the feature of the reversible interaction among olefins and some transition metals, especially silver, copper and gold. Additionally, the π complexation should be strong enough to favor the interaction between the metal and at the same time allow the complexation reversibility under the appropriate operational conditions. Among transition metals, silver has one singularity related to π complexation. The silver electronegativity is 2.2, in the range 1.6 - 2.3 in which the reversible complexation can take place.[61] In addition, the silver salts that have been applied in facilitated transport of olefins have the lowest lattice energies compared to other metallic salts that can be also used for this goal. A salt with low lattice energy favors the solubility of the metal cation and hence it also favors its availability for the interaction with the olefin.[27,62] Owing to these features, silver is the metal most widely used in the preparation of facilitated transport membranes for olefin/paraffin separation. Nevertheless, the use of copper is the second option due to the lower price of this metal[25]. The price is a critical issue when the final goal is to scale up the production of this kind of membrane and therefore it should be considered. However, up to now, the use of the Cu^+ cation has not proved to be a feasible option for the facilitated transport of olefins due to the stability issues of this cation against oxidizing agents,[63] although some promising studies have recently been published about the use of ionic liquids as solvents that stabilize cuprous ions.[64]

Based mainly on the use of silver salts, the principal carrier, facilitated transport membranes for olefin/paraffin separations started to be developed initially as supported liquid membranes. After, in the search for superior mechanical stability, ion exchange and electrolyte membranes were applied to the olefin/paraffin separations.

2.2. Facilitated transport membranes.

2.2.1. Supported liquid membranes.

In 1973, Steigelmann and Hughes[65], working in the Standard Oil Company, started to develop films of cellulose acetate with silver nitrate solution in the pores of the membrane (support) (**Figure 3**). The solution is held in the pores of the support by capillary forces. The best initial result achieved for mixture selectivity (C_2H_4/C_2H_6) was *ca* 1280 and a mixture permeance of 30 GPU. Motivated by the preliminary results, they have developed these films for more than 10 years.[66] However, spite of all efforts, they have not had success in the commercialization of this technology. The main problem found by them was the poor stability of the Ag^+ solution in the membrane pores. During the separation process, the solution was gradually swept out from the pores due to the dragging effect of the gas stream, dropping the selectivity of the process. To solve this problem, some subsequent works[27,67–70] have focused on improving the stability of the solutions inside the pores of the membranes. However, the inherent instability of the supported liquid membranes continues to be a limiting feature in the commercial application of this membrane configuration.

Common performances of supported liquid membranes show selectivity values (α) ranging from 100 (α of C_3H_6/C_3H_8 using triethylene glycol/$AgBF_4$ 43 wt.% with humidified feed stream)[67] to 1000 (α of C_2H_4/C_2H_6 using $AgNO_3$ 4 M with humidified feed stream)[71] and permeances from 4 to 27 GPU of olefin, respectively. High permeances are achieved due to low mass transport resistance through liquid medium. The use of humidified feed stream is required to avoid the drying of solution held in support pores. The support can be prepared of microporous membranes made of cellulose, polyvinilydene diflouride (PVDF), and polytetrafluoroethylene (PTFE).[67,71–73] Indeed, the disadvantage for this membrane configuration are the real risks of dragging out the carrier solution from support pores.

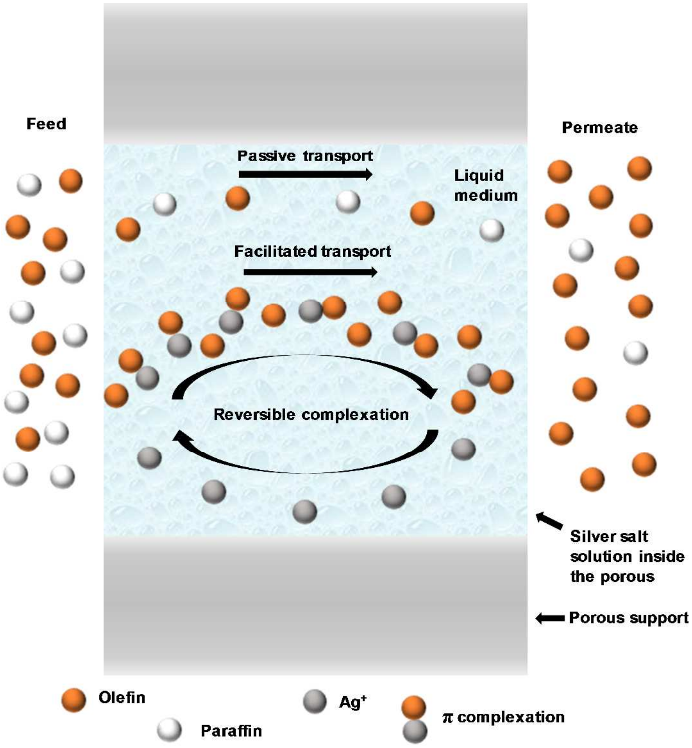

Figure 3. Supported liquid membrane.

2.2.2. Ion exchange membranes.

In the 1980`s, to solve the problems with the supported liquid membranes resulting from the Ag^+ solution sweeping out by the passage of the gas stream, LeBlanc and co-workes[74] proposed the use of ion-exchange membranes. From this work, several other groups started to research this kind of strategy.[18,75–81] The ion-exchange membranes are generally prepared by the addition of the silver salt to the membrane, which is formed by a polymer functionalized with an acid group, (*e.g.* sulfonic acid group) able to exchange H^+ for the Ag^+. To achieve the ion-exchange, the polymer should be immersed in the Ag^+ solution or other metallic salt solution. Next, the membrane should be humidified. Without water, the Ag^+ ions are so strongly attached to the anionic sites in the membrane that makes very difficult the interaction with the olefin (**Figure 4**). Working with humidified feed streams, several interesting works have been reported in literature. For instance, Eriksen et al.[75] applied Nafion (N-117), which was preswollen in glycerine and soaked in aqueous $AgBF_4$ 6 M, for separation of C_2H_4/C_2H_6 (1:1 molar ratio) humidified stream. The membrane provided a selectivity of 1930 and C_2H_4 permeability of 26800 Barrer or about 83 GPU.

As the carrier agent cannot be easily swept out from the membrane by the gas streams, the ion-exchange membranes have a vast advantage compared to supported liquid membranes. Despite their advantages, ion-exchange membranes formed by an ion-exchange polymer are usually more expensive and the required humidification is not desirable because it requires an additional operation step aimed at drying the outlet gas streams from the membrane unit.[27,28] For this kind of membrane configuration, olefin/paraffin selectivity values between 290 and 1900, and olefin permeances ranging from 5 GPU to 83 GPU have been reported (always with humidified feed streams). The main polymeric materials used as matrix for ion-exchange membranes are Nafion and sulfonated polyphenyleneoxide.[74,75]

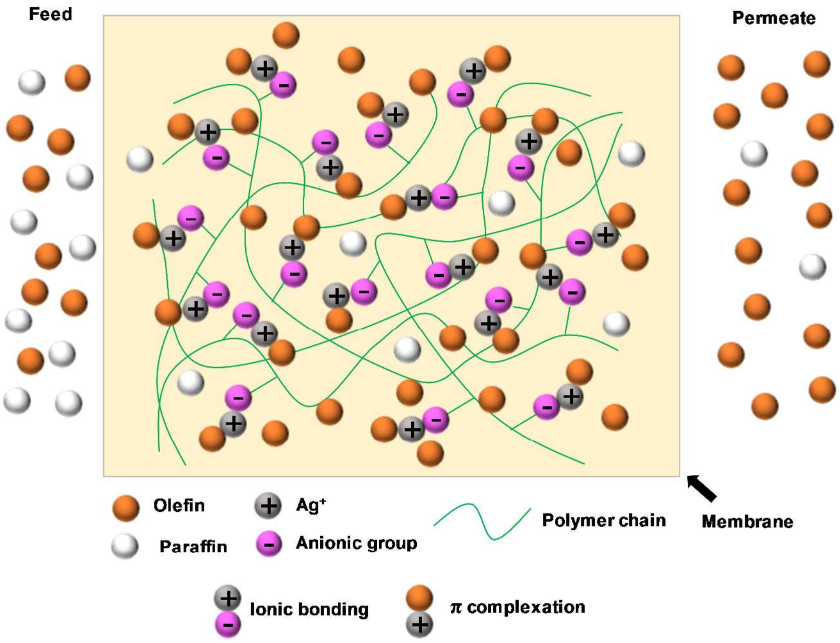

Figure 4. Ion-exchange membranes.

2.2.3. Electrolyte membranes.

During the 1990`s and 2000`s, to overcome the problems originated from the humidification dependence of the ion-exchange membranes, the development of dense materials denominated as polymer electrolyte membranes took place.[20,82–84] Among others, the research groups of Ingo Pinnau[83,85–87] and Yong Soo Kang[84,88–91] stood out during the last few years. Pinnau and Toy[83] reported that it was possible to dissolve silver salts in a hydrophilic polymer with polar functional groups able to coordinate with Ag^+ ion, *e.g.* polyether. In this kind of membrane, the facilitated transport was developed without humidification of the flowing gas, which represented a great achievement compared to the ion-exchange membranes. Kang et al.[45,51,62,84,92,93] followed this method and dissolved silver salts in others polar polymer matrices as poly(2-ethyl-2-oxazoline) (POZ), polyvinylpyrrolidone (PVP) and poly(styrene-b-butadiene-b-styrene) (SBS). The results obtained with polymer electrolyte materials have by far exceeded the previous results of supported liquid and ion-exchange membranes. In 2006, the Kang`s group,[45] using the polymer electrolyte membranes with different silver salts and polymers, was able to surpass the upper bound of Robeson diagram with selectivities and permeabilities never achieved before. For instance, the ideal separation factor (pure gas permeation) of propylene/propane was above 10,000 with 45 GPU of propylene permeance.[62] In the permeation of gas mixtures, the selectivity dropped to 40–60 due to the plasticization effect that occurred in the membranes.[51]

Inside the polymer matrix, the Ag^+ cations can be arranged as free ions, ion pairs or higher order aggregates.[94] In this context, the term “free ions” should be understood as the Ag^+ cations dissolved in the polymer matrix. The best way for the salt to be in the membrane is in the form of free ion, because the silver is more available to the interaction with the olefin.[90,94–96] To reach the desired amount of free ions in the electrolyte membrane, normally, the polymer should have suitable functional groups (*e.g.* ether, amide, lactam, ester, alcohol and aromatic or aliphatic double bond) to interact with the Ag^+ cations (**Figure 5a**). Polymers like poly(2-ethyl-2-oxazoline) (POZ), poly(ethylene oxide) (PEO), polyvinylpyrrolidone (PVP), polymethacrylates (PMA), poly(vinyl alcohol) (PVA), poly(styrene-b-butadiene-b-styrene) (SBS), poly(ethylene phthalate) (PEP),[45,51,62,84,92,93] poliurethanes (PU) based on polyether or polyester[21,97–99] and poly(ether-block-amide) (best known under the trademark Pebax®)[28,100,101] are used as suitable polymer matrix to maintain the dissolution of the silver salts in solid electrolyte membranes. The lower lattice energy of the salt is also crucial in this point to provide an easier way to dissolve the compound. Regarding this aspect, $AgBF_4$ is the most widely used salt due to its lowest lattice energy among ordinary silver salts for this purpose.[27,62] At this point, in an attempt to increase the degree of salt dissociation inside the polymer electrolytes, a couple of investigations have proposed the addition of asparagine[102] in the POZ/$AgBF_4$ membranes and the use of a mixture of silver salts[103,104] to improve the salt dissociation inside the polymer matrix.

Nevertheless, the interaction among the polymer functional group and the Ag^+ salt may cause the reduction of Ag^+ cation to Ag^0 metallic. Over the time, the Ag^0 growth and agglomeration cause the formation of some defects or holes at the interface between the metal particle and the polymer chains. Without discrimination, the gases can easily pass through this path with lower mass transport resistance that leads to selectivity loss in long-term permeation experiments.[26] Trying to solve this problem, several works have investigated solutions to overcome this drawback. In 2001, Jose et al.[105] retarded the formation of Ag^0 by incorporating phthalates to the membranes of PVP/$AgBF_4$ (**Table 1**). The stabilization of Ag^+ cation is due to the strong interaction between the carbonyl groups of phthalates and the Ag^+ that plays a key factor in slowing down the reduction induced by the lactam group of PVP. This was the pioneer work that started to report long-term experiments regarding the stability of polymer membranes containing silver salts. In attempt to avoid the Ag^0 growth and agglomeration, Park et al.[106] added a non-ionic surfactant (*n*-octyl β-D-glucopyranoside (8G1)) to the same kind of membrane to provide a steric hindrance effect hampering the metal particles coalescence. The protective layer onto the surface of formed silver particles was responsible to maintain the stability of membrane performance for 30 days (**Table 1**). However, the reduction problems were not solved by this strategy.

The reduction of Ag^+ by polymers like POZ normally results in an increase of H^+ ion concentration in the medium.[107] This is possible because the membrane contained a small amount of water favored by the hygroscopicity of salts like $AgBF_4$.[108] To suppress the Ag^+ reduction process, Kim et al.[89] proposed the introduction of HBF_4 in POZ/$AgBF_4$ membranes. The goal was to shift the equilibrium of the reduction reaction toward the regeneration of Ag^+, preventing the formation of metallic silver. To investigate this proposal, they performed permeation tests under UV irradiation. As a result, it was found that tiny amounts of HBF_4 could indeed suppress the reduction of Ag^+. A POZ/$AgBF_4$ membrane with the molar ratio of 1[carbonyl oxygen]:1[Ag^+] exhibited a selectivity of about 100 (50:50 vol.% of C_2H_4/C_2H_6) but, after 4 h under UV irradiation, the selectivity dropped to 1. When HBF_4 was introduced in the membrane with the molar ration of 1[carbonyl oxygen]:1[Ag^+]:0.2[HBF_4], the selectivity was maintained in the same initial value after 4 h under UV irradiation, thus having suppressed the Ag^+ reduction process inside the material. Although this procedure has been effective in laboratory studies, it seems an alternative difficult to implement on a large scale.

On the other hand, Kang et al.[109] interestingly suggested the introduction of $Al(NO_3)_3$ in POZ/$AgBF_4$ membranes (**Table 1**) to suppress Ag^+ ion reduction. The function of $Al(NO_3)_3$ is to weaken the interaction between the functional group of the polymer and the Ag^+ due to the favorable electrostatic interaction between Ag^+ and NO_3^-.[110,111] The mutual interaction between the ions, *i.e.* Ag^+/NO_3^- and Al^{3+}/BF_4^-, is responsible for changing the chemical environment of the Ag^+. Compared to the neat POZ/$AgBF_4$, the presence of $Al(NO_3)_3$ decreases the binding energy of the valence electron in the silver atom, which is verified by X-ray photoelectron spectroscopy (XPS) analysis. By modifying the electronic density of the silver atom, it is possible to adjust the intensity of the interaction between the Ag^+ and polymer functional group, reducing the oxidative power of the Ag^+ (**Figure 5b**). Using this strategy, it was possible to maintain the selectivity of the membrane for 14 days in long-term permeation tests.[109]

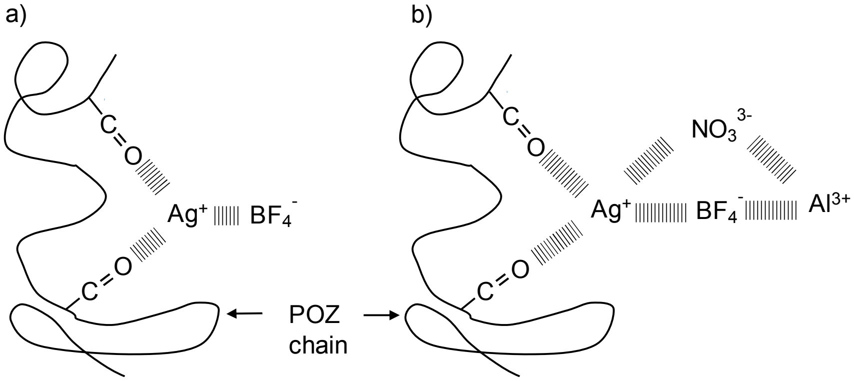

Figure 5. a) Interaction between the functional groups of POZ (amide C=O) with the Ag^+ from $AgBF_4$ and b) the mutual interaction between the Ag^+/NO_3^- and Al^{3+}/BF_4^- that weakens the former interaction between the C=O group of polymer.

Also in an attempt to solve the problems related to the essential instability of Ag^+ inside polar polymer matrices, Kang et al.[90] showed a way to disperse silver salts in polydimethylsiloxane (PDMS), which is an inert polymer matrix, and yet reach the facilitated transport (**Table 1**). The Ag^+ does not share the same interaction observed in polar matrixes, leading to the formation of silver salt aggregates trapped in the polymer domains. At first glance, it seemed that it would not work, since the preferable interaction with the olefin takes place with silver free ions. However, in permeation tests, when the olefinic gases began to pass through the membrane, the olefin complexation gradually dissolved the silver salt aggregates into free ions, promoting the facilitated transport. The time to reach the dissolution was about 100 h, after that, steady-state transport was achieved. Following this approach, it was possible to reach mixed gas selectivity of about 200, propylene permeance of about 15 GPU and keep the values constant for one week. This remarkable result brought the knowledge that introduction of silver salt in inert polymers, *i.e.* polymers that do not have functional groups to dissolve the silver salt, is feasible; and yet, they can promote the facilitated transport of olefins.

In the set of electrolyte membranes, the longest-term permeation test was performed in a PVP/$AgBF_4$/n-octyl β-D-glucopyranoside (8G1) membrane. Along 30 days, the presence of non-ionic surfactant (8G1) provided a stable membrane performance (mixture selectivity C_3H_6/C_3H_8 = 60 and mixed gas permeance of 34 GPU) with the highest permeance reported for electrolyte membranes.[106] The introduction of 8G1 only avoided the Ag^0 growth and agglomeration, however the reduction problems remained unsolved. Among attempts that indeed try to protect Ag^+ cation against reduction, POZ/$AgBF_4$/$Al(NO_3)_3$ membrane showed a stable performance (mixture selectivity C_3H_6/C_3H_8 = 21 and mixed gas permeance of 4.8 GPU) for 14 days.[109] The highest selectivity value was found in PDMS/$AgBF_4$ membrane with a stable performance (mixture selectivity C_3H_6/C_3H_8 = 200 and mixed gas permeance of 15 GPU) for 7 days.[90] In general, the selectivity values can vary from 5 to 200 and the mixed gas permeance from 0.5 to 34 GPU.[90,106,110] The time reported in long-term permeation tests ranges from 4 to 30 days.[90,110,112]

PVP is the most used polymer for electrolyte membranes of polar matrix; however, membranes made of PDMS, which is an inert matrix, have shown the highest selectivity values. Despite all efforts, the selectivity loss caused by Ag^+ cation reduction remains unsolved for permeation tests longer than 2 weeks. Considering simultaneously selectivity, permeance, and separation stability, the best result is performed by PDMS/$AgBF_4$ membrane, indicating that the use of inert matrixes is a promising strategy to develop new electrolyte membranes for olefin/paraffin separation. To avoid the reduction of Ag^+ inside the polymer matrix, besides the silicone-based polymers, other polymer class, which is well known by its intrinsic inertness, is thought to be used as membrane material. Fluoropolymers have been used in the latest works trying to solve the problem of Ag^+ instability.[22,113] In general, since Ag^+ is a stronger oxidant, the aim is that the polymer to be used as membrane does not have any group that could be oxidized by the Ag^+ cation.

Table 1. Results of long-term permeation tests of various electrolyte membranes.

Polymer	**Carrier/ stabilizer Fraction (%)**	**Separation performance (days)**	**Selectivity**[c]	**Mixed gas permeance (GPU)**	**Olefin purity (mol%)**	**Reference**
Electrolyte membranes of polar matrix						
PVP	$AgBF_4$/DOP 50.0[a*]/2.0[b*]	4.2	160	7.5	99.4	In 2001, Jose et al.[105]
PVP	$AgBF_4$/DPP 50.0[a*]/2.0[b*]	4.2	135	10	99.3	In 2001, Jose et al.[105]
PVP	$AgBF_4$/DBP 50.0[a*]/2.0[b*]	4.2	85	9	98.8	In 2001, Jose et al.[105]
PVP	$AgBF_4$/8G1 49.8/0.5[a]	30	50	34	98.0	In 2003, Park et al.[106]
PVP	$AgBF_4$/8G1 49.9/0.2[a]	30	60	34	98.4	In 2003, Park et al.[106]
PEP	$AgNO_3$ 50.0[a]	7	16.2	5.4	94.2	In 2006, Kang et al.[114]

a - molar fraction; b - weight fraction; a* - molar fraction relates only to the polymer; b* - weight fraction relates only to the polymer; c - mixed gas (50:50 vol % of propylene/propane mixture)

*Al(NO3)3·9H2O

PVP – polyvinylpyrrolidone; PEP – poly(ethylene phthalate); POZ – poly(2-ethyl-2-oxazoline); PEO – poly(ethylene oxide); PVA – poly(vinyl alcohol); PDMS – polydimethylsiloxane

DOP – dioctyl phthalate; DPP – diphenyl phthalate; DPB – dibutyl phthalate; 8G1 – n-octyl β-D-glucopyranoside.

Table 1. Continued.

Polymer	**Carrier/ stabilizer Fraction (%)**	**Separation performance (days)**	**Selectivity[c]**	**Mixed gas permeance (GPU)**	**Olefin purity (mol%)**	**Reference**
Electrolyte membranes of polar matrix						
POZ	$AgBF_4$/ $Al(NO_3)_3$[*] 47.6/4.8[a]	14	21	4.8	95.5	In 2013, Kang et al.[109]
PEO	$AgBF_4$/ $Al(NO_3)_3$[*] 49.9/0.2[a]	10	10	20	90.9	In 2015, Song et al.[115]
PVP	$AgCF_3SO_3$/ $Al(NO_3)_3$[*] 49.9/0.2[a]	4	5	0.5	83.3	In 2015, Sung et al.[110]
PVP	$AgCF_3SO_3$/ $Al(NO_3)_3$[*]/ $BMImBF_4$ 43.6/4.1/8.7[a]	4	9	0.5	90.0	In 2016, Park and Kang[112]
PVA	$AgBF_4$/ $Al(NO_3)_3$[*] 49.3/1.5[a]	6	17	11	94.0	In 2017, Park et al.[26]
Electrolyte membranes of inert matrix						
PDMS	$AgBF_4$ 73[b]	7	200	15	99.5	In 2004, Kim et al.[90]

a - molar fraction; b - weight fraction; a* - molar fraction relates only to the polymer; b* - weight fraction relates only to the polymer; c - mixed gas (50:50 vol % of propylene/propane mixture)

*Al(NO3)3·9H2O

PVP – polyvinylpyrrolidone; PEP – poly(ethylene phthalate); POZ – poly(2-ethyl-2-oxazoline); PEO – poly(ethylene oxide); PVA – poly(vinyl alcohol); PDMS – polydimethylsiloxane

DOP – dioctyl phthalate; DPP – diphenyl phthalate; DPB – dibutyl phthalate; 8G1 – n-octyl β-D-glucopyranoside.

2.3. Challenges to avoid carrier instability.

Taking into account the results reached at laboratory scale by using polymer membranes with silver salts[45], the search for higher selectivities and permeabilities in the separation process is no more a big challenge. However, the maintenance of the membrane performance in long-term operation conditions has become a new target to be surpassed. Ag^+ cations incorporated in the electrolyte membranes report instability problems related to the tendency of them to react with other species, deactivating or poisoning the agent carrier in long-term operation.[28,31] The photoreduction or the exposition to reductant gases, *e.g.* hydrogen, inactivates the Ag^+ cation due to its reduction to metallic silver (Ag^0). The decontrolled formation of Ag^0 in the membrane can damage it with negative influence on the separation performance. The Ag^+ cation also can react with hydrogen sulfide (H_2S) and acetylene (C_2H_2) forming undesired compounds, principally silver acetylide that is extremely explosive and can pose a significant risk to the process. The deactivation reaction of Ag^+ are summarized in **Table 2**. It is worth emphasizing that small amounts (about 10 ppm) of these contaminants in the gas stream is enough to drastically decrease the process selectivity, in less than one week, impairing the membrane use.[28]

Table 2. Deactivation reaction of silver cation (Ag^+).

Reaction	Description
$Ag^+ + e^- \xrightarrow{uv} Ag^0$	Photoreduction
$2Ag^+ + H_2 \rightarrow 2Ag^0 + 2H^+$	Reduction by H_2

$C_2H_2 + 2AgX \rightarrow Ag_2C_2 + 2HX$	Formation of silver acetylide
$H_2S + 2AgX \rightarrow Ag_2S + 2HX$	Formation of silver sulfide

X is an anionic component of silver salt

Normally, the olefin/paraffin stream from naphtha steam cracking, which aims to be separated by membrane technology, contains some silver poisonous agents in low concentration, in ppm range. In the naphtha cracking furnace, it is necessary to operate with about 20 ppm of sulfur compounds in the feedstock to prevent the formation of undesired carbon monoxide. The function of sulfur is to passivate the nickel and iron catalysts sites in the cracking coil material of the furnace. The H_2S formed in the cracked gases is removed together with the CO_2 in the compression section using caustic solvents in absorption towers. Usually, CO_2 and H_2S concentration in the overhead stream of the absorption towers is below 0.2 ppm.[6,8]

Usually, hydrogen reduced compounds and acetylene (C2 and C3) are some byproducts of the SC. Hydrogen is removed at the lowest temperatures achieved in the chilling train, together with methane; they are overhead products of the demethanizer.[25] The acetylene species, *i.e.* acetylene, methylacetylene (MA), and propadiene (PD), are removed by catalytic hydrogenation processes that transform them into more saturated hydrocarbons. The content of acetylenic compounds in the outlet of the hydrogenation process is <0.5 ppm.[8] Typically, the specification of polymer grade ethylene and propylene from the SC is <1 ppm of H_2 and <4 ppm of acetylene species.[116]

This severe scenario corresponds to a typical petrochemical plant where membranes are intended to be implemented. In addition, there are other challenges not related to silver poisoning. To replace or integrate C2 and C3 splitters, the membrane should treat a feed stream under a pressure of 5-20 bar and produce a permeate stream at 1−3 bar. Governed by these conditions, plasticization effects may occur even in the most rigid polymer membranes.[11,117]

Thus, withstanding the negative influence of contaminants and avoid plasticization issues are essential challenges to be overcome by the next generation membranes.

3. ALTERNATIVES TO OVERCOME Ag^+ DEACTIVATION

In this context, some research groups have focused their efforts on proposing strategies to mitigate and/or overcome the problems imposed to the separation by the deactivation of the carrier. In the scientific literature, the most prominent efforts, proposing different solution lines to these problems, seem to not have a clear consensus on what would be the most promising strategy. The alternatives, which use dense polymeric films, are (i) the use of metallic nanoparticles as carrier, mainly silver nanoparticles, (ii) the use of ionic liquids for the stabilization of Ag^+, (iii) *in situ* regeneration of electrolyte polymeric membrane by using oxidizing agents, and (iv) the use of highly fluorinated polymers.

3.1. Silver nanoparticles as carrier.

As already seen, the reduction of Ag^+ to Ag^0 throughout the separation process causes deactivation of the carrier and consequently the loss of membrane selectivity. In 2004, Kang et al.,[52] when performing permeation tests on a polymeric membrane with silver salts, noticed that the selectivity was reduced from 52 to 31 in 150 h of experiment. In parallel, it was observed the formation of metallic silver nanoparticles (Ag NP), whose size increased from 14.75 to 27.75 nm. It should be noted that, even at the beginning of the experiment, Ag NP were formed, pointing to the difficulty in avoiding Ag^+ reduction. What was remarkable in this experimental observation was that, even with Ag NP of 27.75 nm in the membrane, the selectivity did not fall abruptly, only 40% reduction was observed. The hypothesis proposed for the maintenance of the

Ag carrier properties was the formation of a partial charge polarization on the Ag NP surface. The phenomena observed by these authors has initiated a new study framework involving facilitated transport nanocomposite membranes of light olefins in place of Ag^+ salts. The great advantage of this replacement is that the problems of reduction deactivation involving the Ag^+ ion would be bypassed. This would allow the maintenance of the separation properties of the membranes in long-term operation.[118]

In 2007, Kang et al.[53] presented the first paper introducing the idea of Ag NP as carrier for the facilitated transport of olefins. To polarize the surface of Ag NP more efficiently, p-benzoquinone (p-BQ), an electron acceptor, was used to this goal, since the polymer matrix (EPR-poly(ethylene-co-propylene)) used was non-polar. The membrane selectivity achieved working with 50:50 v/v propylene/propane mixtures was 11 (**Table 3**). After this work, others studies have begun to explore new molecules to polarize the surface of the Ag NP,[24,119–122] always aiming to improve the selectivity of separation. **Figure 6** shows a schematic representation of the possible polarization mechanism of the Ag NP surface by 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Table 3 shows the most promising results observed for the separation of light olefin/paraffin mixtures by membranes using Ag NP. Analyzing **Table 3**, there is a clear evolution in the carrier properties of the Ag NP due, mainly, to the suitable choice of the polarizing agent of the NP surface, but other factors are important such as the nanoparticle concentration, its size in the polymer matrix, and its adequate dispersion along the diffusional gas pathway. Although the concentration may vary from one work to another, it is noted that a concentration higher than 30 wt% of Ag NP, relative to the composite material, is required. In all works, where the facilitated transport of olefins by Ag NP with activator is verified, the NP have diameters smaller than 30 nm.[123] Therefore, Ag NP with sizes below this value can further improve the transport of the olefinic gases. Experimentally, the formation of the induced dipole on the interface between the Ag NP and the activator is checked by the X-ray photoelectron spectroscopy analysis (XPS). By changing the binding energy of the $d_{5/2}$ and $d_{3/2}$ silver orbitals to higher values, it is possible to verify the polarization of the NP surface.[53,119] Lee et al.[123] have reported an interesting study where the partial positive charge density of the surface of Ag NP was modulated by addition of TCNQ. These authors found that the amount of propylene adsorbed on the surface of the Ag NP could be correlated with the silver binding energy.

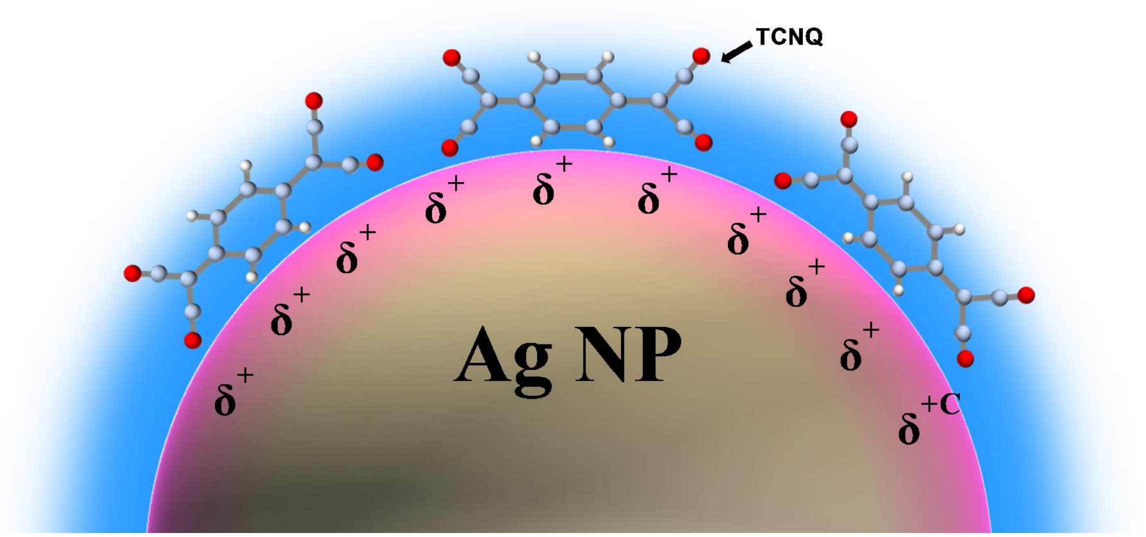

Figure 6. Schematic representation of the possible polarization mechanism of the Ag NP surface by 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Table 3. Main results of metallic nanoparticles as carriers for membrane facilitated transport of olefins.

Polymer	Carrier/ activator Fraction (%)	Separation performance (days)	Selectivity[c]	Mixed gas permeance (GPU)	Olefin purity (mol%)	Reference
EPR	Ag NP/p-BQ 35.1/29.8[b]	3.5	11	0.45	91.7	In 2007, Kang et al.[53]
PVP	Au NP 81.1[b]	—	22	1.2	95.7	In 2008, Kang et al.[50]
SLM*	Ag NP/ $BMImBF_4$ 41.2/58.8[b]	5	17	2.7	94.4	In 2008, Kang et al.[121]
POZ	Ag NP/PVP 29.8/35.1[b]	15	21	1.3	95.5	In 2008, Kang and Kang[52,124]
PVP	Ag NP/ TCNQ 33.1/0.7[b]	5.5	50	3.5	98.0	In 2011, Chae et al.[119]
PVP	Ag NP/TTF 33.3/33.3[a]	—	145	2.5	99.3	In 2014, Choi et al.[120]
PEO	Ag NP/p-BQ 27.8/2.8[a]	10	10	15	90.9	In 2014, Hong et al.[125]
PVP	Ag NP/ F4-TCNQ 48.8/2.4[b]	1.5	112	1.8	99.1	In 2014, Chae et al.[122]
PU	Ag NP/$(OTf)^-$ 21.0/29.1[b]	—	24.4[d]	—	—	In 2016, Rezende et al.[126]

a - molar fraction; b - weight fraction; c - mixed gas (50:50 vol % of propylene/propane mixture); d - ideal solubility selectivity of propylene/propane

*Supported liquid membranes. Support of polyester microporous membrane

EPR – poly(ethylene-co-propylene); PVP – polyvinylpyrrolidone; POZ – poly(2-ethyl-2-oxazoline); PEO – poly(ethylene oxide); PU – polyurethane

Ag NP – silver nanoparticle; Au NP – gold nanoparticle

p-BQ – p-benzoquinone; BMImBF4 – 1-butyl-3-methylimidazolium tetrafluoroborate; TCNQ – 7,7,8,8-tetracyanoquinodimethane; TTF – tetrathiafulvalene; F4-TCNQ – 2,3,5,6-tetrfluoro- 7,7,8,8-tetracyanoquinodimethane; $(OTf)^-$ – triflate anion.

The membranes with Ag NP have reached higher selectivity values compared to membranes made of PVP[119] with the same weight ratio of Ag^+ and with the advantage of being resistant to light and hydrogen gas.[24] To further investigate the viability of Ag NP as promising carriers for the facilitated transport of olefins, Kang et al.[24] verified the deactivation resistance against C_2H_2. Surprisingly, the NP activated with TCNQ as a polarizing agent proved to be resistant to the formation of silver acetylide. Therefore, this is an additional evidence of the superior chemical stability that the Ag NP reports compared to Ag^+ salts. To become even more feasible, the chemical stability of Ag NP membranes against hydrogen sulfide and other sulfur compounds needs to be investigated. Other source of instability for the separation is the inherent instability of the polarizing agents, which is few mentioned in the literature. Compounds like p-BQ, TCNQ and tetrathiafulvalene (TTF) work as electron acceptor; thus, they have a tendency of withdrawing electrons from other molecules. This feature makes polarizing agents susceptible to chemical attack similarly as it is found in Ag^+ cation. For instance, depending on the condition, p-BQ can easily withdraw electrons from other chemical species and consequently being transformed in hydroquinone,[127,128] which is unable to polarize the surface of Ag NP. Therefore, p-BQ could be deactivated as polarizing agent by suffering a reduction process.

Other aspect that should be addressed is related to the permeance of this kind of membranes. Generally, the flux of Ag NP membranes need to be improved. For industrial application, high fluxes are required because it is necessary to reach the target high production of industrial plants. Thus, Hong et al.[125] prepared a membrane of poly(ethylene oxide) with Ag NP activated by p-benzoquinone seeking out the permeance increase. The composite membrane showed a selectivity of 10 and a mixed-gas permeance of 15 GPU for 10 days, the highest permeance reported for Ag NP membranes.

The use of Ag NP was also tested in membranes of polyurethane (ether based) (PU). Rezende et al.[126] measured the sorption values of propylene and propane in Ag NP/PU membranes (**Table 3**), in which the Ag NP were synthesized *in situ* into PU matrix using UV light radiation and silver triflate ($AgCF_3SO_3$) as salt precursor. It was found an ideal solubility selectivity of 24.4 in the Ag NP/PU membranes that could indicate an essential contribution of the sorption selectivity in propylene/propane separation by this kind of membrane.

3.2. Ionic liquids for the stabilization of Ag^+.

The introduction of ionic liquids (IL) to stabilize Ag^+ salts in facilitated transport membranes is another alternative that the literature has reported as promising. For instance, the use of POZ/$AgNO_3$ membranes could reach stable separation performance (mixed gas permeance of 5.6 and selectivity of 32) during 150 h by the addition of small amount of 1-butyl-3-methylimidazolium nitrate ($BMImNO_3$).[96] Another example is the use of PVP/$AgBF_4$ membrane with $BMImNO_3$ that was able to maintain a selectivity of 7.2 with 3.6 GPU nearly constant along 160 h of permeation (**Table 4**).[129]

In the search for higher stability, in the last few years, dense composite membranes incorporating ionic liquids have received much attention.[22,112,129–132] In this configuration, IL/Ag^+ system is embedded in the polymer so that Ag^+ cations are distributed between the polymer matrix and a liquid phase entrapped inside it. This Ag^+ distribution through the membrane promotes the fixed and mobile carrier facilitated transport mechanisms, leading to higher permeabilities and selectivities.[133] In this line, Ortiz et al.[22,134] developed a material with promising characteristics for the separation of light olefin/paraffin mixtures. Previous to the material choice, a thorough investigation on the most suitable IL to form the IL/silver salt pair was carried out[135,136]. Among several pairs, 1-butyl-3-methylimidazolium tetrafluoroborate/silver tetrafluoroborate ($BMImBF_4/AgBF_4$) was selected. Additionally, the fluoropolymer poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was used as polymer matrix to avoid the potential reduction of Ag^+ by the polymer chain.

The results obtained with the composite films of PVDF-HFP/$BMImBF_4$–$AgBF_4$ behave satisfactorily providing a mixture selectivity C_3H_6/C_3H_8 = 700, and propylene permeability of 6630 Barrer or about 55 GPU in the separation process (**Table 4)**. This remarkable performance was maintained for 10 days. The IL could stabilize the Ag^+ in a long-term experiment in this kind of membrane. To prove the potential of this type of material it is necessary to perform tests under the presence of the deactivating agents and verify the behavior of the composite membranes with ionic liquid against the simulated industrial operational conditions.[22]

On the other hand, different tests were made using thermoplastic polyurethanes (TPU)/IL membranes, but without taking into account the problems related to instability of the olefins transport. Wang et al.[97] synthesized several PU membranes with different silver salt/IL pairs. The IL used contained the 1-butyl-3-methylimidazolium cation ($BMIm^+$). Among all membranes prepared with IL, the highest selectivity (C_3H_6/C_3H_8 = 18.3) was found for the $AgBF_4/BMImBF_4$/TPU (weight fraction 10/20/70) membrane. The highest olefin permeability (8400 Barrer) was observed for the $Ag(Tf_2N)/BMImTf_2N$/TPU (weight fraction % 10/20/70) membrane. In general, the IL enhanced the selectivity of the TPU membranes by favoring the coordination of olefin with the Ag^+ ions inside the dense polymeric matrix. However, the best result (C_3H_6/C_3H_8 = 38 and 8512 Barrer) were reported for the $Ag(Tf_2N)$/TPU (weight fraction % 10/20/70) membrane without adding IL (**Table 4)**.

Table 4. Results of membrane performance with ionic liquids for protection against the reduction of Ag^+.

Polymer	**Carrier/ stabilizer Fraction (%)[a]**	**Separation performance (days)**	**Selectivity[b]**	**Mixed gas permeance (GPU)**	**Olefin purity (mol%)**	**Reference**
POZ	$AgNO_3$/ $BMImNO_3$ 58.8/7.0	6	32	5.6	84.8	In 2006, Kang et al.[96]
PVP[f]	$AgBF_4$/ $BMImNO_3$ 8.9/86.6	6.5	7.2	3.6	87.8	In 2007, Kang et al.[129]
PVDF-HFP	$AgBF_4$/ $BMImBF_4$ 60.2/7.8	10	700	55[d] 6630[e]	99.9	In 2013, Fallanza et al.[22]
TPU	$AgBF_4$/ $BMImBF_4$ 10/20	—	18.3[c]	3000[e]	94.8	In 2017, Wang et al.[97]
TPU	$Ag(Tf_2N)$/ $BMImTf_2N$ 10/20	—	9[c]	8398[e]	90.0	In 2017, Wang et al.[97]
TPU	$Ag(Tf_2N)$ 30	—	38[c]	8512[e]	97.4	In 2017, Wang et al.[97]

a - weight fraction; b - mixed gas (50:50 vol % of propylene/propane mixture); c – tests under 2 bar transmembrane pressure; d – olefin permeance; e – olefin permeability in Barrer

POZ – poly(2-ethyl-2-oxazoline); PVP – polyvinylpyrrolidone; PVDF-HFP – poly (vinylidene fluoride-*co*-hexafluoropropylene); TPU – thermoplastic polyurethane Elastollan®

$BMImNO_3$ – 1-butyl-3-methylimidazolium nitrate; $BMImBF_4$ – 1-butyl-3-methylimidazolium tetrafluoroborate; $BMImTf_2N$ – 1-butyl-3-methylimidazolium bis(tri fluoromethanesulfonyl)imide.

3.3. In situ regeneration using oxidizing agents.

Merkel et al.[28] have continued the research line focused on the development of polymer electrolyte membranes using polyethers which can provide a facilitated transport without the matrix humidification. This group further discussed the instability of the Ag^+ cation caused by deactivating agents listed in **Table 2**. The material used to produce the membranes was the Pebax® 2533 with various levels of silver tetrafluorobate ($AgBF_4$). It is an elastomeric thermoplastic material composed of blocks of polyether (PE) and polyamide (PA). Specifically, the poly (ether-b-amide) used was prepared from nylon 12 and polytetramethylene oxide.

The Pebax® 2533/$AgBF_4$ membranes were tested against the deactivating agents in the separation of ethylene/ethane mixtures, and as expected, the selectivity in the separation process has collapsed. However, by exposing these membranes to hydrogen peroxide vapors combined with tetrafluoroboric acid (H_2O_2/HBF_4) or immersing directly in a bath of H_2O_2/HBF_4, the membranes were able to return partially or completely to the original selectivity values (**Table 5**).

This *in situ* regeneration, by using these oxidative treatments, has reversed the deactivation caused by light, H_2 and C_2H_2; however, the membranes deactivated by H_2S have not shown any reversion. In the light and H_2 cases, the explanation for the regeneration is that the Ag^0 formed in the deactivation process is oxidized and returns to the Ag^+ form, becoming active again for the facilitated transport. However, the deactivation process caused by H_2 seems to be more aggressive than light deactivation, since the required time to restore the same level of selectivity was longer in the case of H_2 deactivation (60 h). According to Merkel et al.,[28] the understanding of the phenomenon involved in the regeneration of membranes inactivated by C_2H_2 still demands more detailed studies. Nevertheless, taking into account the chemical reaction of silver acetylide formation it can be thought that the regeneration is not caused by the oxidizing agent itself, but by the presence of HBF_4, which shifts the equilibrium of the reduction reaction toward the Ag^+ regeneration.[137]

Table 5. Results of the deactivation and regeneration processes of Pebax® 2533 + 80 wt% $AgBF_4$ membrane with original selectivity of 40 and olefin permeance of 87 GPU (adapted from Merkel et al.[28] with permission from Elsevier).

Deactivation process	**Selectivity[a] drop**	**Regeneration process**	**Selectivity[a] regeneration**
Membrane exposed to ambient light for 34 days	-95%	Immersion in a H_2O_2/HBF_4 bath[b] for 30 s	100%
Membrane exposed to ambient light for 34 days	-95%	Contact with the H_2O_2/HBF_4 vapors[c] for 16 h	50%
7 days of hydrogen permeation	-95%	Contact with the H_2O_2/HBF_4 vapors for 60 h	50%
Membrane exposed to 10 ppm of acetylene in the ethylene feed for 5 days	-85%	Immersion in a bath of H_2O_2/HBF_4 for 60 s	69%
Membrane exposed to 10 ppm of hydrogen sulfide in the ethylene feed for 7 days	-92%	Immersion in a bath of H_2O_2/HBF_4 or contact with the H_2O_2/HBF_4 vapors	0%

a – mixed gas (65:35 vol % of ethylene/ethane); b - 1:1 mixture of 35 wt% H_2O_2 in water and 50 wt% HBF_4 in water; c - membrane in contact with the vapor of a 1:1 H_2O_2/HBF_4 aqueous solutions at room temperature.

From the possibility of *in situ* membrane regeneration, the research group believes that it will be possible to extend the service life of the membrane by applying cyclic regeneration steps, thus enabling the practical application of the membranes made of Pebax® 2533/$AgBF_4$. Analyzing this proposal, it is noted that the deactivation by H_2S was not solved and the cyclic regeneration steps should be evaluated against the commercial application feasibility of the technology.

3.4. Current technological options.

At the beginning of this decade, Innovative Membrane Technologies (Imtex) presented a system called Permylene^{TM} that uses a flat sheet composite structure based on chitosan material and silver cations as facilitating agents in spiral wound membrane elements.[138–140]The chitosan layer thickness is estimated to be between 2 to 4 microns. The system also uses an aqueous silver nitrate solution as continuous closed loop of hydration. This company claims that the system is able to operate with stable performance over 1000 hour. However, impurities (hydrogen, acetylene, sulfur compounds, and carbon dioxide) can affect the performance of the membrane and should be managed. More recently, in 2016, the Compact Membrane Systems (CMS) Company unveiled the separation system called Optiperm^{TM}. By this olefin/paraffin separation system, the company has claimed resistance against common poisonous agents in feed stream, including hydrogen and acetylene.[141,142] Probably, the reason of stability is the membrane based on highly fluorinated polymers, which are extremely resistant to chemical and thermal harsh conditions.[23] To prepare the membrane, Ag^+ cations are incorporated to the polymer matrix by ion-exchange with the H^+ from sulfonic groups of the fluorinate polymer. Unlike previous works,[27,75,78,80] in which the membrane was immersed in a silver salt aqueous solution to achieve ion-exchange, in this case the polymer and the Ag^+ salt are solubilized in the same solvent. After, the solution is casted to form a polymeric film called silver ionomer, responsible for the facilitated transport of olefins.[23]

As in any typical structure of thin film composite membrane used for industrial gas separations, the selective layer has the task of distinguishing the molecules to be separated and it should be thin (0.1-1 μm) to provide high permeances. A thin layer does not have enough mechanical strength and it is necessary to deposit it onto the surface of a porous support (150–

200 μm) with negligible mass transport resistance. In addition, another high diffusion layer can be added to protect the selective layer and plug any defects eventually present. This protective layer prevents damage during the manipulation of the membrane and protects the exposed surface of the selective layer from contaminants present in the stream to be separated.[143,144]

In the Optiperm™ system,[23] the high diffusion layer is made of glassy polymer based on perfluoroether and chlorotrifluoroethylene groups, which are resistant against oxidation by the Ag^+ cation. For the selective layer, amorphous perfluoropolymers are used to maximize Ag^+ cation stability. The fluoropolymer inertness and the protection offered by the protective layer are responsible for the resistance against poisonous/deactivating agents.

According to the information reported in a patent assigned to CMS,[23] the best results (**Table 6**) were achieved by using the following materials for the membrane layers. The high diffusion layers are composed of Teflon® AF 2400, a copolymer with 83% (molar percentage) of perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) and 17% of tetrafluoroethylene. The porous support is made of PAN350, an ultrafilter made from polyacrylonitrile. Two selective layers with the same amount of $AgNO_3$ are tested. One layer has higher permeance and lower selectivity (selective layer 1) and the second one has lower productivity and higher selectivity (selective layer 2). The selective layer 1 is composed by a silver ionomer of sulfonic acid based on the PDD/VF (vinyl fluoride)/PPSF (perfluoro sulfonylfluorideethylvinyl ether) terpolymer (T_g 58 °C). The selective layer 2 is made of the Aquivion®D79-25BS,[113] a perfluorosulfonic acid polymer made from perfluorosulfonylfluoridevinyl ether monomer. The patent, doesn't report information related to long-term stability and tests of resistance against poisonous agents. The permeation tests were conducted using humidification of the feed stream and N_2 as a sweep gas.

Regarding the humidification need issue related to the ion-exchange membranes,[145] Feiring et al.[146] tested different configurations to provide the required moisture in highly fluorinated silver ionomer membranes. In the configuration 1, they humidified the sweep gas (N_2) and the feed mixture. In the configuration 2, the feed was dried, and the sweep gas was a water vapor under vacuum. Finally, the configuration 3 employed a dried feed and vacuum. As expected, the best results corresponded to configuration 1. Surprisingly, the configuration 2 and 3 provided equivalent high olefin/paraffin selectivity but 30% and 60% smaller olefin permeance respectively. The presence of the inert sweep gas in the permeate stream implies a further separation step. Thus, configuration 2, which does not use the N_2 as sweep gas, shows an advantage since the permeate stream only has moisture, olefin; and eventual small amount of paraffin. A subsequent drying stage may be considered in the separation train, but it seems an easier task than removing the inert gas from the outlet stream of the membrane unit.

Table 6. Performance of facilitated transport membranes based on highly fluorinated polymers after the results of Majumdar et al. *(*2016*)*.[23]

Polymer	Carrier Fraction (%)[a]	Selectivity[b]	Olefin permeance (GPU)	Olefin purity (mol%)
(PDD/VF/PPSF)	$AgNO_3$ 16.7[b]	95.7	276	96.0
Aquivion®D79-25BS	$AgNO_3$ 16.7[b]	52.1	311	92.9

a - weight fraction;
b - mixed gas (20:80 vol % of propylene/propane feed mixture)
PDD – perfluoro(2,2-dimethyl-1,3-dioxole); VF – vinyl fluoride ; PPSF – perfluoro sulfonylfluorideethylvinyl ether.

4. SUMMARY AND CONCLUSIONS

The global demand of light olefins has experienced a significant growth related to the increasing demand of different polymers over the last decades. The principal process to produce olefins is the naphtha steam cracking process, the most energy intensive process in the petrochemical industry. In an attempt to save energy in the process, some alternatives have been proposed to replace or integrate with the current cryogenic distillation separation of olefins and paraffins. Among several technologies, facilitated transport membranes have stood out owing to the combination of high selectivity and permeance. However, to be used in the industrial separation, some instability issues should be considered.

The Ag^+ cation, the main carrier for the facilitated transport membrane, suffers deactivation by poisonous agents present in the gaseous stream to be separated. Even without the presence of deactivating agents, the Ag^+ cation can be reduced by the chemical environmental of the polymer matrix from which the membrane is made. After achieving superior performance by using silver salts dissolved or dispersed in polymer matrix, the current arduous task is to maintain the selectivity in long-term separation process. To attain this goal, some clever alternatives have been proposed to overcome the hurdle.

By adding small amounts of HBF_4 or non-ionic surfactants, it is possible to confer certain stability to Ag^+ cation. In addition, the introduction of $Al(NO_3)_3$ in electrolyte membranes can weaken the interaction between the functional group of the polymer and the Ag^+ salt, providing a more stable chemical environment to the Ag^+. A remarkable result was reached with a POZ/$AgBF_4$/$Al(NO_3)_3$ membrane. The selectivity was maintained during 14 days. The use of another interesting carrier, Ag NP, overcome the problem related to the reduction of Ag^+. To be useful, the Ag NP should be activated by a suitable polarizing agent. Experimental tests showed the resistance of Ag NP against acetylene, which is one of the poisonous agents. Therefore, Ag NP reveal higher resistance compared to Ag^+. The best results reached by Ag NP composite membranes achieved a selectivity of 10 and a mixed-gas permeance of 15 GPU for 10 days.

To avoid the Ag^+ cation reduction inside the polymer matrix, more inert polymers have begun to be applied as a host matrix to silver salts. Specially fluoropolymers, which are well known by their intrinsic inertness, have been used as material to the preparation of Ag^+ facilitated transport membranes. A PVDF-HFP matrix was used for hosting a system of $AgBF_4$/$BMImBF_4$. IL have been demonstrated as another type of agents able to stabilize Ag^+ against reduction. Joining these features, a membrane of PVDF-HFP/$BMImBF_4$–$AgBF_4$ reported a mixture selectivity of 700 and propylene permeability of 6630 Barrer (about 55 GPU) in a 10 days separation test. Claiming resistance against common poisonous agents in the feed stream, a thin film composite membrane based on a highly fluorinated polymer was developed by Compact Membrane Systems Company. Beyond the intrinsic inertness of the membrane material, additional protection arises from the configuration of the composite membrane. A thin separation layer composed by fluorinated silver ionomer, which is responsible for the facilitated transport of olefins, is between two high diffusion protective layers. This configuration seems to avoid the poisoning of the Ag^+ cation that are ionic bonded in the ion-exchange polymer; however, the membrane humidification dependence was not solved. If the problems related to poisoning are still present in the membrane process, other alternative is to try an *in situ* regeneration using vapor of the oxidizing system (H_2O_2/HBF_4) to recover the separation performance and extend the service life of the membrane.

Most of the results reported in the literature didn't consider the presence of poisonous agents in the permeation experiments. The main concern is still the stability of Ag^+ inside the polymer matrix, but it seems that this challenge has started to be overcome using stabilizing agents and inert polymer matrix. Issues related to the plasticization effects are not yet a problem discussed intensively by the works concentrated in the facilitated transport membrane for the olefin/paraffin separation. Probably, the future efforts will be dedicated to understand deeply the problems regarding the poisonous agents, trying to figure out a more robust solution. Due to the lower performance required and milder condition operation, the initial commercial application of the membrane technology to olefin/paraffin separation could be in the vent streams of some kinds of petrochemical reactors. This application could make a step forward in the use of commercial olefin/paraffin membrane units before the challenging task aimed to replace the distillation unit in the steam cracking process or in the FCC off-gas streams.

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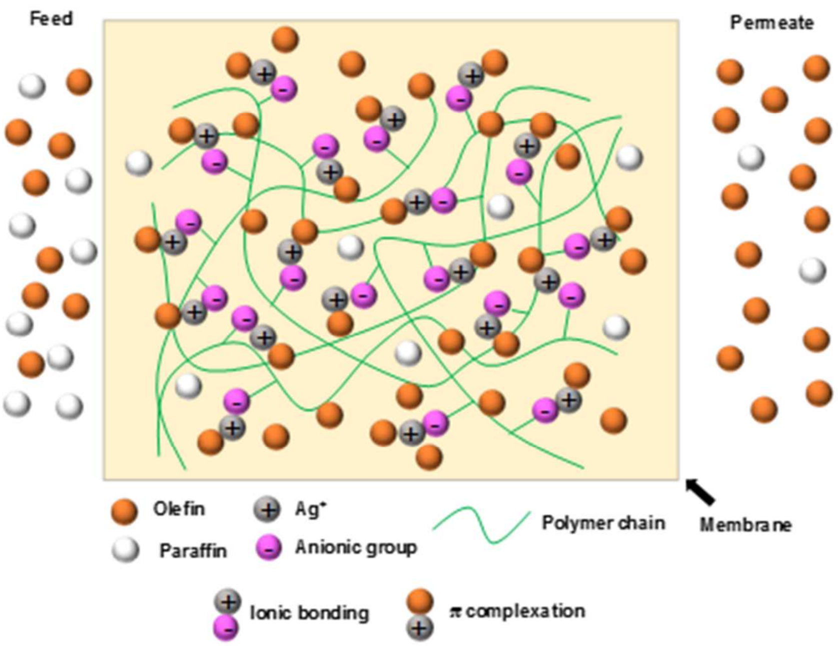

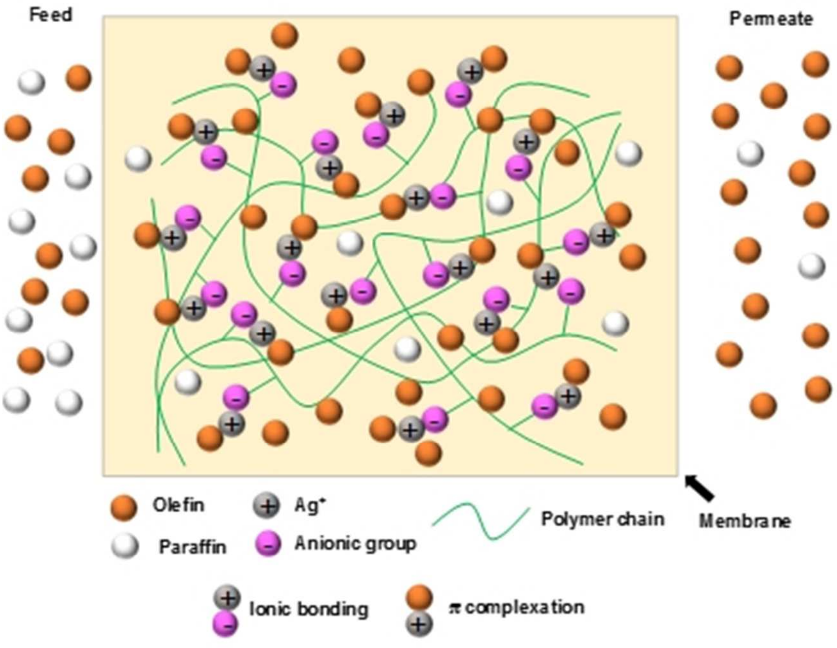

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