High Performance Membranes Using Lithium Additives: A Review

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Abstract— The easiest and reproducible methods to improve membrane performance is adding additives in casting solution. Different from common additives that usually used, inorganic additives like lithium seems to be very effective in the preparation of membranes with higher performance because of their small molecular weight and interaction behavior. Studies show that the use of lithium additives causes an increase in viscosity, porosity and conductivity, reduces hydrophobic, change membrane morphologies and enhanced membrane performance (permeability and rejection). Hence, lithium additives have a high potential for achieving high performance membranes, especially in membrane fabrication and application.

Index Terms— high performance, hydrophobic, lithium additives, membrane properties, membrane morphologies.

1 Introduction

Over the past decades, membrane technology has become an interesting and useful separation method due to higher efficiencies and with advances, lower energy requirements for operation [1]. Consider that many industries have started to utilize them as an alternative for many application processes ([2], [3], [4]). In addition, membranes technology is used to substitute chemical treatment of wastewaters to reduce chemical and costs, as well as to produce cleaner and more consistent effluent for discharge or recycle.

Membrane performances, such as permeability and rejection, are greatly influenced by the composition of dope solution [5], the method of casting the membrane ([6], [7]) and the thickness of the resulting membrane [8], which itself depends on many factors like dope concentrations and additives. The compatibility of polymers with additives can often play a significant role in the physical modification of the membrane-forming polymer. The role of organic and inorganic additives in dope solutions or spinning dopes has been reported as a pore-forming agent that enhances the permeation properties.

Polymer additives such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) were widely used to control membrane structure in the preparation of membrane [9]. Inorganic additives also known to change the solvent properties or the interaction between the macromolecular chains in casting solutions and was reported to be very effective in the preparation of membranes with higher performance [10]. Morever the use of inorganic additives like lithium additives have not been well reported and established, unlike PEG and PVP additives which have been well studied. According to this, the objective of this study is giving a brief overview on effects of lithium additives that change property and performance of membranes.

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2 Role of Lithium Additives in Improvement of Membrane Properties and Morphologies

2.1 Overview

Lithium additive are promising candidates for the fabrication of membranes with an appropriate structure and high performance. Cation such as: lithium, zinc, calcium and magnesium, and anion such as: chloride, bromide, iodide, nitrate, thiocyanate and perchlorate can gives good membranes property. Via ion-dipole interaction, these lyotropic salts form complexes with the carbonyl group in polar aprotic solvent such as with acetone, N,N-dimethylacetamide (DMAc), dimethylformamide (DMF), and N-methylpyrrolidone (NMP) [11].

2.2 Membrane Properties and Morphologies

Viscosity is considered one of the important parameters influencing the exchange rate between the solvent and affects the structure and performance of resultant membranes. Indeed, lithium additives significantly influenced the viscosity of the casting solutions. The viscosities of dope were observed to increase with the increase amount of additive used. This happen because some reasons such as (a) lithium additives-solvent interactions ([10], [12], [13]); (b) interactions between Li^+ cation and the strong electron-donating groups in polymer ([14] ,[15], [16], [17], [26]); and (c) competition between thermodynamic and kinetic effect of the additive ([15], [19], [20], [21]).

In membrane casting process, lithium additives in the solvent took more time to reach the surface and provided ample time for the polymer aggregates to form a fine porous structure and thus suppressed macrovoid formation [19]. The formation of porous structure and larger cavities was observed and these effects were enhanced with higher lithium content [10]. The larger cavities resulted in increasing of surface porosity ([13], [21], [22], [23]) and reducing pore size of membrane ([12], [14], [18], [24], [25]). The change of membrane morphologies from fingerlike to spongy layer also occurred ([14], [23]). The all effect of lithium additives in membrane properties and

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structure are presented in Table 1.

The increase in ionic conductivity with lithium additives is due to an increase in the number of mobile charge carriers and a decrease in the crystallinity of the host polymer. In addition, Li^{+} ion presence in the membrane does not change the amorphous structure [28]. Surface morphology of membranes becomes less uniform and homogenous, and mechanical property (tensile strength and elongation) decreases if lithium content increased [29]. If concentration of lithium additives (in example LiOH) was high (> 9 wt %) as reported, the ion conductivity decreased because the aggregation of ions [27]. An excess of ions can result in ionic interactions with the polymer chains, leading to restriction of the segmental relaxation of the polymer chain in the host polymer.

TABLE 1
SUMMARY OF LITHIUM ADDITIVES EFFECT IN MEMBRANE PROPERTIES AND MORPHOLOGIES

Lithium additives	Membrane properties			Membrane structure
	Porosity	Conductivity	Hydrophilicity	
Lithium chloride (LiCl)	H	-	H	Porous [10], fingerlike to spongy like [14]
Lithium bromide (LiBr)	H	H	H	Fingerlike to spongy layer [16], smooth surface [23]
Lithium flouride (LiF)	H	-	M	-
Lithium perchlorate ($LiClO_4$)	H	H	-	More porous inner skin ([17], [26])
Lithium hydroxide (LiOH)	-	H	-	Uniform and surface roughness increased [27]

H = High; M= Medium; L = Low; - = Not reported

Nowadays many commercial membranes made are strongly hydrophobic such as polysulfone; polyacrylonitrile (PAN); polyvinylidene fluoride (PVDF); polyether ketone (PEK); etc. The major reason for hydrophobic membrane fouling with organic compounds is that there are almost no hydrogen bonding interactions in the boundary layer between the membrane interface and water. This can lead to severe membrane fouling, decrease membrane performance, and cut down on membrane life spans. In this regard, some studies has shown hydrophilic property of the membrane could achieve by using lithium additives ([16,] [18], [23], [30], [31], [32]).

3 EFFECT LITHIUM ADDITIVES IN ADDITIVES ACT AND MEMBRANE PERFORMANCE

Apparently, the concentration of additive is very crucial as it influences membrane property such as porosity, conductivity, hydrophilicity, morfology; and effect in additives acts (Table 2). If LiF and $LiCl_4$ acted as a pore former at very low concentration [22], LiBr acted as pore former in 3 wt % [23].

The suppressed macrovoids in the membrane structure reported could improve membranes performance ([13], [18], [21], [30]). Lithium additives also reported improving pure water permeability ([13], [23], [33], [34]). However, compared to the membrane without any additives, lithium additives presence improved the overall membrane performance in flux and rejection ([26], [32], [34]).

TABLE 2
LITHIUM ADDITIVES ACTS IN MEMBRANE CASTING

Lithium additives	Additives acts				Referencee
	Pore former	Pore inhibitor	Pore filler	Source of charge	
Lithium chloride (LiCl)	√	-	-	-	[10], [21], [35]
Lithium bromide (LiBr)	√	√	√	√	[23], [32], [36], [40]
Lithium flouride (LiF)	√	-	-	-	[22]
Lithium perchlorate ($LiClO_4$)	√	-	-	√	[17], [26], [29] [37], [38], [39]
Lithium hydroxide (LiOH)	-	-	-	√	[27], [28]

4 MEMBRANE FABRICATION AND APPLICATION

The selection of a technique for membrane fabrication depends on a choice of polymer and desired structure of the membrane. The most commonly used techniques for preparation of polymeric membranes with lithium additives shown in Table 3. However among these techniques, phase inversion and microwave irradiation techique are the most favorite method in the fabrication of polymeric membranes with lithium additives.

Summary of the use lithium additives in membrane application is shown in Figure 1. Most of lithium additives (LiCl, LiBr, anf LiF) in used in separation prosses like ultrafiltration (UF), nanofiltration (NF), gas permeation, and membrane distillation (MD). Many researchers used $LiClO_4$ as additives, which can be easily washed out during membrane preparation for gas permeation membrane or as additive to enhanced electrical properties or ionic conductivity for electrolyte membrane ([29], [38], [39]).

TABLE 3

Lithium additives	Fabrication techiques	Type membrane
LiCl	Phase inversion ([20], [33]); microwave irradiation technique [30]	Hollow fibre; flat sheet
LiBr	Interfacial polymerization [16]; microwave irradiation technique [23]; phase inversion [32]	Hollow fibre; flat sheet
LiF	Microwave irradiation technique [22]	Flat sheet
$LiClO_4$	Phase inversion [17]; immersion-precipitation [26]; casting solution [29] [38]; emulsion polymerization [39]	Hollow fibre; flat sheet
LiOH	Solution casting ([27],[28])	Thin sheet

Differently from other lithium additives, LiOH is potential to developed as a source of charge on the polymer electrolyte. Electrolyte membranes are often used to replace the liquid electrolyte type for benefit and broad application reasons. Several studies were using LiOH as electrolyte composite membrane components with the addition of filler in the form of nanoparticles in situ ([27], [28]).

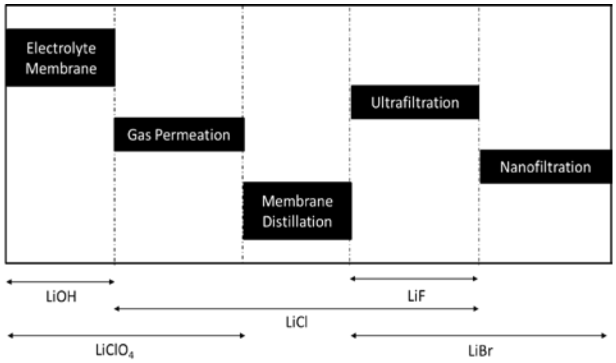

Fig 1. Summary lithium additives used in different membrane processes

It is considerable point that, what was mentioned is only part of opportunities for using lithium additives to improve membrane property and performance. Whereas, this additives can also expand usability of membrane application in other ways. For instance, due to its different effect on membrane property, many research tried to combine lithium additive with common additives like PEG or PVP or nanoparticle. In addition, Zhang and Zhang found the synergy effect between LiCl and PEG could increase the flux remarkably than the use of single additive [31]. When the PEG content was higher than LiCl, the pure water flux was relatively high. While with increasing of LiCl content, the membrane tensile strength increased.

5 Conclusion

Various property of membrane can be enhanced or reduced depend on the concentration the additives. The presence of lithium additives in dope solutions appears to increased porosity, conductivity and lowered the hydrophobic property. The additives could alter membrane morphological structure thus directly affecting membranes performance. This effect sometimes been explained by Li^+ ion interaction, thermodynamic-kinetic effect or additives-solvent interaction. The lithium additive concentration has been proven to be one of the most influential parameters in membrane fabrication. Obviously, there is an opportunity for the use single or combine of lithium additives to fabricate and obtain the membrane with desirable properties due the application of membrane. Hence, lithium as additives has a high potential for achieving high performance membrane.

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