Journal of Membrane Science 733 (2025) 124333

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Structural tailoring of poly(quaternary ammonium) thin-film composite membranes for efficient lithium recovery from concentrated salt-lake brine

Hansoo Kim [a,1], Juyeon Choi [a,1], Hyunjung Kim [b], Sungkwon Jeon [c,*], Jung-Hyun Lee [a,**]

[a] Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea
[b] Department of Earth Resources and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea
[c] Department of Polymer Science and Engineering, Kumoh National Institute of Technology, 61 Daehak-ro, Gumi, Gyeongbuk, 39177, Republic of Korea

ARTICLE INFO

Keywords:
Thin-film composite membrane
Li recovery
Nanofiltration
poly(quaternary ammonium)
Positively charged membrane

ABSTRACT

The application of conventional polyamide nanofiltration (NF) membranes to lithium (Li) recovery from high-salinity salt-lake brine is challenging, despite their high separation efficiency, owing to their intrinsic negatively charged nature. Herein, we developed highly Li-selective, positively charged poly (quaternary ammonium) (PQA) thin-film composite NF membranes *via* an interfacial Menshutkin reaction by varying the structure of the linear tertiary amine monomers used. Less bulky tertiary amine monomers with shorter alkyl chain spacers and/or fewer amine groups produced a denser, more Li-selective PQA membrane with a strongly positive surface charge. Hence, the PQA membrane fabricated with the least bulky tertiary amine monomer exhibited the highest magnesium ion (Mg^{2+}) rejection (~99.4 %) and Li^+/Mg^{2+} selectivity (~90) under high-salinity mixed-salt conditions (10,000 ppm, Mg^{2+}:Li^+ mass ratio = 20:1). This performance considerably exceeded that of other reported Li-selective NF membranes, underscoring the potential of the PQA membrane for efficient Li recovery from concentrated salt-lake brine. The superior Li selectivity of the PQA membrane was attributed to its strongly positive surface charge and moderate molecular density. Our study provides a versatile means to fabricate advanced membranes for resource recovery or hazardous matter removal and elucidates their structure–property–performance relationship.

1. Introduction

Lithium (Li) is an indispensable metal that is used in various industrial fields, including ceramics, batteries, pharmaceuticals, and nuclear plants [1]. Because Li-containing salt-lake brine accounts for ~69 % of the world's total Li resources, Li extraction from salt-lake brine has attracted considerable attention [2]. Unfortunately, salt-lake brine also contains large amounts of magnesium ions (Mg^{2+}), hindering efficient Li recovery because Mg^{2+} and Li^+ have similar hydrated radii (Mg^{2+} = 4.3 Å, Li^+ = 3.8 Å) and chemical properties [3,4]. Various technologies for Li recovery, including solvent extraction [5], solar evaporation [6], precipitation [7], and nanofiltration (NF) [8], have been explored. Among these methods, NF holds significant promise for Li recovery because it enables Li recovery in a continuous process with relatively high Li selectivity, achieving high energy and separation efficiency [2,9]. In addition, NF is considered an environmentally friendly process because it does not require toxic chemicals, unlike conventional Li recovery processes (*e.g.,* solvent extraction and precipitation), thereby enabling sustainable Li recovery [10].

Conventional NF membranes feature a polyamide (PA) selective layer formed through interfacial polymerization (IP) between diamine (*e.g.,* piperazine [PIP]) and trimesoyl chloride (TMC) monomers on a porous support, resulting in a thin-film composite (TFC) configuration [11,12]. However, conventional PA NF membranes exhibit negative surface charges, which preferentially enhance the permeation of Mg^{2+} *via* electrostatic attraction, thereby impeding selective Li^+ separation [13]. Hence, various strategies to design positively charged PA NF membranes, including the surface deposition or incorporation of cationic materials (*e.g.*, quaternized bipyridine, diethylenetriamine, quaternary imidazolium salts, aminated quantum dots) [10,14–16] and application of amine-abundant monomers (*e.g.*, polyethyleneimine, polyallylamine) [17,18], have been proposed. Although the resultant

* Corresponding author.
** Corresponding author.
E-mail addresses: skjeon@kumoh.ac.kr (S. Jeon), leejhyyy@korea.ac.kr (J.-H. Lee).
[1] These authors equally contributed to this work.

https://doi.org/10.1016/j.memsci.2025.124333
Received 28 March 2025; Received in revised form 3 June 2025; Accepted 12 June 2025
Available online 13 June 2025