



## OPEN ACCESS

## EDITED BY

Zenixole Tshentu,  
Nelson Mandela University, South Africa

## REVIEWED BY

Constantin Nechita,  
National Institute for Research and  
Development in Forestry Marin Dracea (INCDS),  
Romania

## \*CORRESPONDENCE

Dmitrii Butylskii,  
✉ d\_butylskii@bk.ru

RECEIVED 24 November 2025

REVISED 12 January 2026

ACCEPTED 19 January 2026

PUBLISHED 06 February 2026

## CITATION

Troitskiy V, Ponomar M, Ruleva V, Butylskaia T,  
Gorobchenko A, Dammak L, Mareev S,  
Sharafan M and Butylskii D (2026) Advanced  
strategies for designing the structure of lithium-  
selective membranes and its performance:  
a mini-review.  
*Front. Membr. Sci. Technol.* 5:1753282.  
doi: 10.3389/frmst.2026.1753282

## COPYRIGHT

© 2026 Troitskiy, Ponomar, Ruleva, Butylskaia,  
Gorobchenko, Dammak, Mareev, Sharafan and  
Butylskii. This is an open-access article  
distributed under the terms of the [Creative  
Commons Attribution License \(CC BY\)](#). The use,  
distribution or reproduction in other forums is  
permitted, provided the original author(s) and  
the copyright owner(s) are credited and that the  
original publication in this journal is cited, in  
accordance with accepted academic practice.  
No use, distribution or reproduction is permitted  
which does not comply with these terms.

# Advanced strategies for designing the structure of lithium-selective membranes and its performance: a mini-review

Vasily Troitskiy<sup>1,2</sup>, Maria Ponomar<sup>1</sup>, Valentina Ruleva<sup>3</sup>,  
Tatiana Butylskaia<sup>1</sup>, Andrey Gorobchenko<sup>3</sup>, Lasaad Dammak<sup>4</sup>,  
Semyon Mareev<sup>3</sup>, Mikhail Sharafan<sup>3</sup> and Dmitrii Butylskii<sup>1\*</sup>

<sup>1</sup>Laboratory of Advanced Lithium Recovery Technologies, Kuban State University, Krasnodar, Russia, <sup>2</sup>Platov South-Russian State Polytechnic University, Novocherkassk, Russia, <sup>3</sup>Kuban State University, Krasnodar, Russia, <sup>4</sup>Université Paris-Est Créteil, National Centre for Scientific Research (CNRS), East Paris Institute of Chemistry and Materials Science (ICMPE), Thiais, France

In recent years, the development of lithium-selective membranes (LSMs), among which the most widely used are ion-imprinted membranes (IIMs), lithium-ion sieve membranes (LISMs) and supported liquid membranes (SLMs), has attracted great interest due to the possibility of their use in direct lithium extraction (DLE) processes. This approach can be an alternative to the DLE sorption processes that are currently closest to commercialization. Although the efficiency of new LSMs has been widely discussed in original works and recent reviews, they are difficult to compare due to the different parameters used to estimate it. Fundamental principles of ion transport underlie the path to improved membrane performance. Success in membrane structure design on the way to its optimization are expressed by the «trade-off» effect: high selectivity of lithium extraction leads to low productivity. This mini-review presents the results of the analysis of recent studies in the field of design and testing of different types of lithium selective membranes. The performance and selectivity of the developed materials were evaluated using identical parameters: specific flux and selective ion separation coefficient. This facilitates an understanding of the path to improving LSMs and scaling it up for application in lithium extraction from brines and eluates of spent lithium-ion batteries.

## KEYWORDS

ion sieve membrane, ion-imprinted membrane, liquid membrane, lithium recovery, lithium selective membrane

## 1 Introduction

Direct lithium extraction (DLE) using lithium-selective membranes (LSMs) is an emerging technology aimed at efficiently recovering lithium from various sources, such as brines, seawater, and lithium-containing minerals (Foo and Lienhard, 2025; Saleem et al., 2025). LSM technology integrates the advantages of DLE based on sorbents with those of commercialized membrane processes such as selective electrodialysis (S-ED), membrane capacitive deionization, and nanofiltration (NF) (Xu L. et al., 2025; Yao et al., 2025). LSMs are generally designed to permit the passage of Li<sup>+</sup> ions while rejecting other ions, such as sodium, potassium, magnesium and calcium. This selectivity is achieved due to the

properties of the membrane material, which can include polymer, ceramic or composite structures exhibiting specific interactions exclusively with lithium ions.

LSM technology is gaining traction due to its potential to provide a more sustainable and environmentally friendly alternative to traditional lithium extraction methods. The combination of crushing, leaching and reduction, washing, heat treatment, filtration, evaporation, and related steps forms the basis of hydrometallurgical processes used for lithium extraction from brines in the Lithium Triangle countries (Chile, Bolivia, and Argentina), from mineral deposits in Australia, and from secondary resources worldwide (Tabelin et al., 2021; Butylskii et al., 2023). Moreover, in the Lithium Triangle countries and certain regions of China, evaporation ponds, where concentration and solution enrichment occur simultaneously, remain the traditional method (Ezama et al., 2018; King and Dworzanowski, 2021).

Integrated with other membrane-based methods, LSMs are designed to supplant the costly, energy-heavy processes currently used to separate and concentrate lithium from liquid sources, irrespective of the feed solution's origin (Butylskii et al., 2024). A major advantage of this technology lies in its versatility. It has potential applications in regions where climatic and topographic conditions preclude the use of traditional hydrometallurgical lithium extraction processes (certain lithium-producing areas of Russia, China, the United States, Portugal, and Serbia etc.), including pond evaporation.

However, when analyzing the potential of LSM technology, researchers often focus primarily on its high selectivity (Zhang J. et al., 2024; Abrishami et al., 2025), which is achieved through specific interactions in addition to the size and charge effects of ion exclusion inherent in various types of ion-exchange and filtration membranes. The increase in selectivity indicates the presence of barriers limiting the transport of ions and water, resulting in increased electrical and hydraulic resistance and directly affecting both performance and energy consumption. Thus, analyzing the success of LSM technology solely based on the concept of high selectivity is somewhat flawed.

The literature already contains numerous research and review articles presenting test results for individual LSM groups. However, few studies present a complete classification and compare individual LSM groups with each other. The difficulty lies in the fact that the original studies evaluate the performance of different LSM groups using different parameters. The goal of this paper was to present such a classification and evaluate LSMs from different groups and subgroups using the same parameters (specific flux and selective ion separation coefficient) for performance evaluation.

## 2 Design strategies for lithium-selective membranes

The explosive growth in the number of LSM types developed by researchers worldwide over the past 5 years highlights the need for a clear and systematic classification. Such classification facilitates cataloging and enables the correlation of the properties of newly developed membranes with those of their «relatives» within the same group or subgroup. Currently, the literature most commonly categorizes LSMs according to their fabrication methods and

constituent materials. Among these, the most frequently mentioned are ion-imprinted membranes (IIMs), ion sieve membranes (ISMs), and liquid membranes (LMs) (Figure 1).

### 2.1 Ion-imprinted membranes

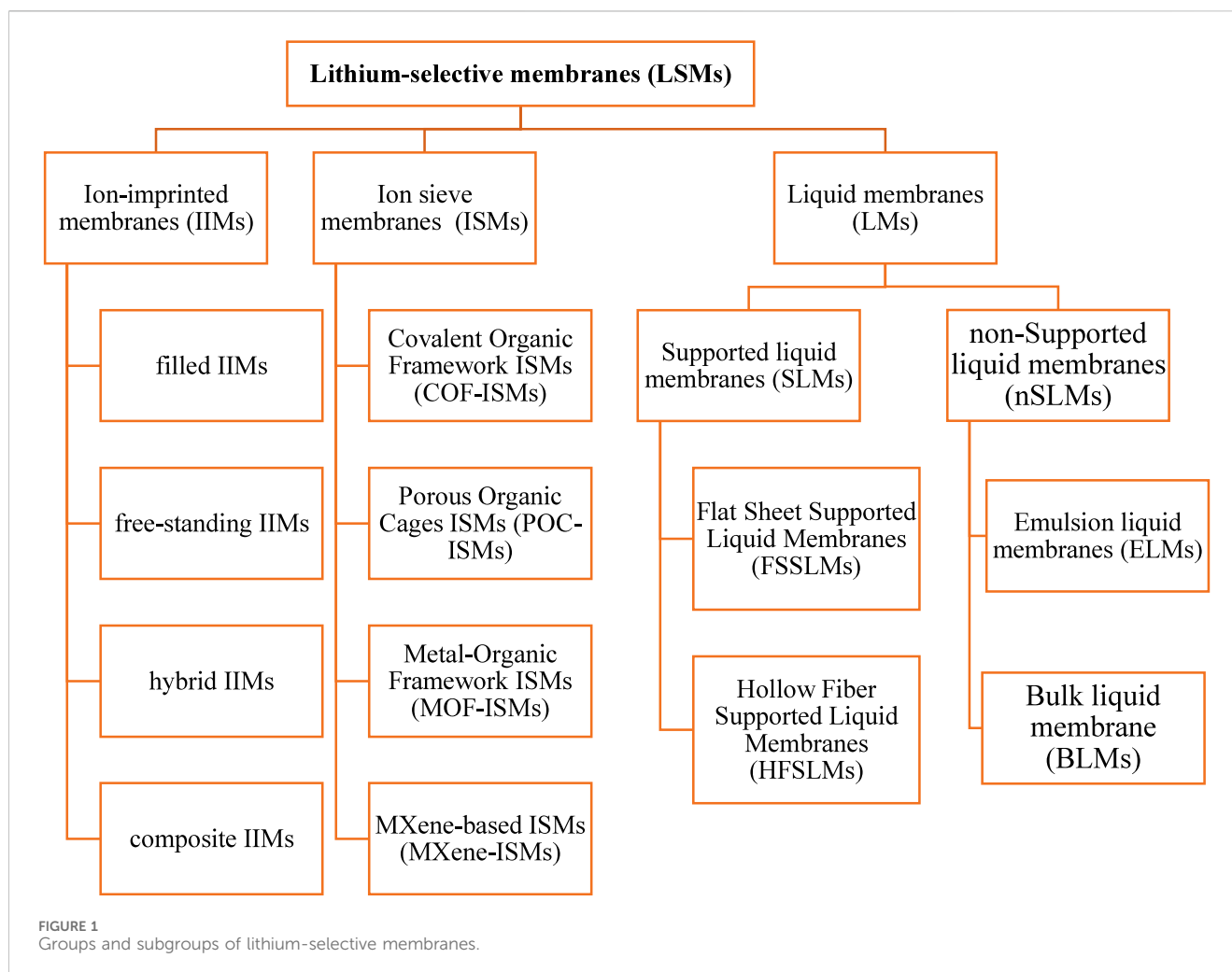
The synthesis of IIMs involves filling ion-imprinted polymers (IIPs), which are produced through the interaction of functional monomers, template ions and cross-linkers. This process results in the formation of specific recognition sites for target ions such as lithium. The template ion must then be leached from the polymer structure to obtain a gap equal to the size of the target ion. The efficiency of template removal and the integrity of the imprinted polymer structure after the leaching procedure determine the performance and efficiency of the final IIM. According to Zahir et al. (2024), IIMs can be classified into four main categories: filled IIMs, free IIMs, hybrid IIMs, and composite IIMs, depending on the synthesis method and composition.

The development of IIMs originated from the concept of molecular imprinting polymers (MIPs), which, beginning with the pioneering work of G. Wulff (Wulff and Sarhan, 1972; Wulff, 2013), steadily gained attention in the field of selective particle extraction and expanded into various kinds of methods and applications. The principles underlying MIPs later served as the foundation for the IIPs creation. The first study on IIPs was published by Nishide et al. (1976), describing a chelating resin synthesized by cross-linking poly (4-vinylpyridine) in the presence of metal ion templates ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Hg}^{2+}$ ). Since then, both the materials and their morphology have been continuously improved. A variety of IIPs have been recently developed for the selective extraction of various ionic components such as Mn (II) (Khajeh and Sanchooli, 2011; Aravind and Mathew, 2020), Ni(II) (Saraji and Yousefi, 2009), Co (II) (Yusuf et al., 2019), Cd(II) (Singh and Mishra, 2009; Li et al., 2015), Cu (Kuras and Więckowska, 2015) and several others. Based on these materials, IIMs have been fabricated as thin films or layers, often supported by a porous material, that enable selective ion transport.

IIMs gained significant attention following the peak of applied interest in lithium extraction from brines, largely due to the particular challenge of separating lithium ions from the coexisting monovalent  $\text{Na}^+$  and  $\text{K}^+$  ions, which are present in excess. Selectivity toward  $\text{Li}^+$  ions is typically achieved by introducing a chelating agents such as 12-crown-4 ether (Cui et al., 2018), which is also commonly employed in the fabrication of another type of LSMs—liquid membranes (Swain, 2016). Furthermore, modified crown ethers (Sun et al., 2017), calix [4] arene (Yu et al., 2020), and other macrocyclic compounds can also act as chelating agents. Advances in the chemical composition of MIPs (Ali and Omer, 2022; Shen et al., 2023), IIPs, and particularly in IIMs, have been comprehensively summarized in recent reviews in this field (Branger et al., 2013; Shakerian et al., 2016; Lazar et al., 2023; Zahir et al., 2024).

### 2.2 Ion sieve membranes

The most significant progress in the development of LSMs has apparently been achieved in the case of ISMs. According to



the Scopus, from 2000 to the present, the number of publications on ISMs is almost four times higher than the number of publications on IIMs (6,929 records vs. 1,871 records, accordingly). Structurally, ISMs are composite materials featuring microporous frameworks ion channels. As the name implies, the fundamental mechanism of ion separation in these membranes is based on the pore-size sieving effect, where monovalent ions are partially or completely dehydrated to facilitate the transport (Xu et al., 2024). In this context, extensive research has focused on crystalline materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic cages (POCs), hydrogen-bonded organic frameworks (HOFs), and polyoxometalates (POMs), which form stable two- and three-dimensional porous structures permeable to ions (Yang et al., 2023; Chen et al., 2024; Jaïd et al., 2024). Among these materials, MOFs and COFs are the most widely utilized. MOFs are constructed by joining metal-containing units with organic linkers, using coordination bonds to create open crystalline frameworks with permanent porosity (Naka, 2014), whereas COFs are porous crystalline polymers consisting of covalently bonded organic units (Côté et al., 2005).

Although MOFs themselves have existed since the 1990s, originating from the pioneering work of R. Robson on the coordination of copper ions with organic linkers (Hoskins and Robson, 1989), and further developed and stabilized through the seminal contributions of Yaghi et al. (1995), Kondo et al. (1997), and Fujita et al. (1995), their application in membrane technology, particularly for selective lithium ion separation (2019–2025), has emerged only recently (Razmjou et al., 2019).

Currently, advanced strategies for constructing hierarchical structures such as MOF-on-MOF (Abdollahzadeh et al., 2022; Xiao et al., 2022) and COF-on-MOF (Li Y. et al., 2021; Xia et al., 2022) architectures with ordered pore arrangements are employed to control ion transport. For instance, carboxyl-functionalized UiO-66, followed by UiO-66 with amine functional groups, can be sequentially grown layer by layer on a porous anodized aluminum oxide (AAO) substrate membrane (Xiao et al., 2022). It has been reported that the incorporation of carboxyl groups enhances Li<sup>+</sup> transport in the presence of Mg<sup>2+</sup> ions.

Another noteworthy strategy involves the fabrication of an oriented MOF based on UiO-67 with a preferential growth direction along the plane (Xu et al., 2022). This approach

primarily addresses the challenge of reduced flux of the target  $\text{Li}^+$  ion with increasing membrane selectivity.

The construction of tailored structures within MOFs for enhanced monovalent ion selectivity of membranes is also of great importance. A study by Prof. T. Xu's group (Xu et al., 2024) demonstrated an *in situ* growth technology for crown ether@UiO-66 membranes, in which crown ethers are perfectly confined within the UiO-66 MOF structure. Similar hybrid architectures, such as MOF-in-COF structures (Fan et al., 2021), have also been reported in gas separation applications. These materials exhibit high permeability and selectivity due to the formation of MOF domains as chains of unit cells embedded within the one-dimensional channels of two-dimensional COFs.

Although POCs have been known in the literature for a long time (approximately from 1970s), they represent a relatively new class of crystalline materials actively studied for selective ion separation. The first hydrocarbon cage with a complete C–C backbone was reported in 1977 (Yang et al., 2023). Currently, cages with a mixed backbone of C–C and C–N bonds are being actively synthesized and studied. For selective ion separation, and particularly for lithium extraction, POCs can be assembled layer-by-layer on the substrate surface (Zhang Y. et al., 2024). They can pack in either crystalline or an amorphous solid state via noncovalent interactions. Their unique properties even enable porosity switching in response to specific chemical triggers (Jones et al., 2011; He et al., 2022; Ghaffar et al., 2023), which can be exploited to fine-tune pore size for targeted applications. Notably, thin POCs-based membranes hold great promise not only for selective ion extraction but also for use in lithium-ion batteries (LIBs), drug delivery, sensors, etc (Dai et al., 2022; Li et al., 2022).

Another effective approach to fabricating ISMs involves the use of precursors or powders of ion-sieve adsorbents (Sun et al., 2021). Various membrane designs have been reported for this class of materials, including those based on lithium ion conducting glass ceramic (Ounissi et al., 2020), first proposed by Hoshino (2015), as well as  $\lambda\text{-MnO}_2$  (Bao et al., 2023; Mojtahedi et al., 2025) or  $\alpha\text{-Al}_2\text{O}_3$  (Xue et al., 2020), etc. These membranes are typically formed either by incorporating a lithium-selective agent into the membrane bulk or by coating it onto the surface. In both cases, the lithium transport rate is constrained by the permeability of the ion-conducting pathways formed by the selective agent in the polymer matrix or by the thickness of the functional layer.

In recent years, MXene-based sieve structures have gained considerable attention in the design of ISMs (Lu et al., 2024; Chen et al., 2025). MXenes are 2D materials that are transition metal carbides or nitrides. In their structure layers of transition metal atoms (M) alternate with layers of carbon or nitrogen atoms (X) (Huang et al., 2018). They were first investigated by Naguib M. et al. (Naguib et al., 2011; Naguib et al., 2012), who reported a simple method for producing  $\text{Ti}_2\text{AlC}$ ,  $\text{Ta}_4\text{AlC}_3$ ,  $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$ ,  $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{AlC}_2$ , and  $\text{Ti}_3\text{AlCN}$  by immersing their powders in hydrofluoric acid (Naguib et al., 2012). Currently, MXene-based polymer membranes are being actively developed and evaluated using various techniques for selective ion separation (Mozafari et al., 2021). Among these, vacuum-assisted filtration, drop casting, and hot pressing are the most commonly employed (Lim et al., 2022).

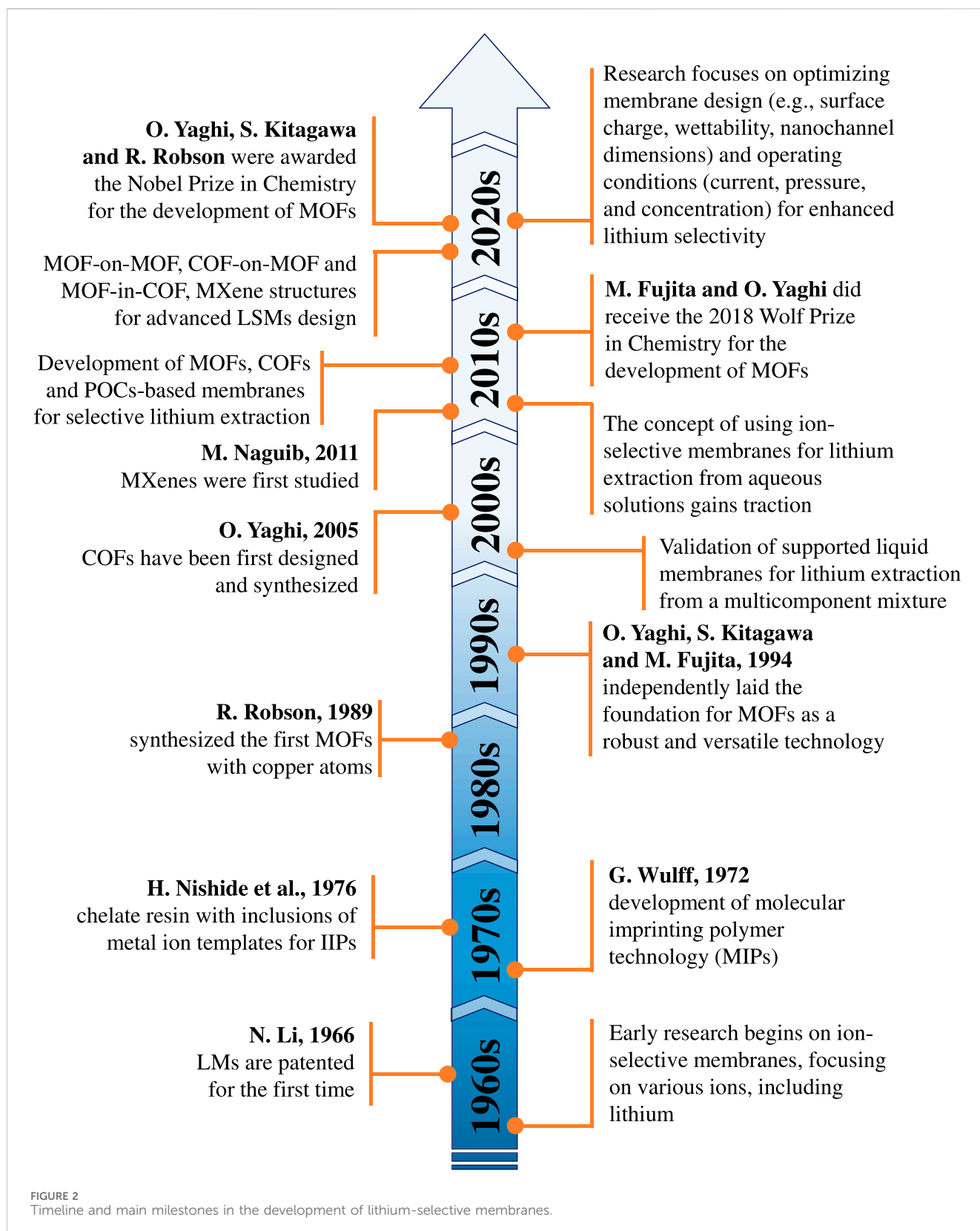
The broad range of modification methods explored for MXene-based polymer membranes enables the design of advanced strategies for enhanced conductivity, improved selectivity and thermal stability of polymer membranes.

More detailed information on the advances in the structure and properties of MOF-, COF- and POC-based membranes, as well as the ion transport mechanisms governing their performance, can be found in recent reviews (Li Y. et al., 2021; Hu et al., 2022; Lim et al., 2022; Yang et al., 2023; Xu T. et al., 2025; Zhang et al., 2025).

## 2.3 Liquid membranes

LMs represent a relatively prospective separation method for lithium extraction, despite having been first patented as early as 1968 by N. Li (Li, 1966; Li, 1971). Essentially, this membrane type can be regarded as an advancement of conventional liquid–liquid extraction technology (Swain, 2016). The technology utilizes an organic solvent containing extractants that selectively bind to target lithium ions (Demin et al., 2018). These extractants form lipophilic organometallic complexes with lithium ions, which diffuses from the treated solution into the organic solvent phase. This is followed by back-extraction of lithium into an aqueous solution and subsequent regeneration of the extractant. In theory, the method offers extremely high selectivity, as among all cations present in the treated solution ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), only  $\text{Li}^+$  should form such complexes and be transported across the selective liquid layer.

According to a 2023 mapping of DLE technologies conducted by the German company Extantia, sorption, ion-exchange, solvent extraction, electromembrane, and electrochemical technologies, have the highest potential for rapid commercialization (Werny, 2023). However, solvent extraction faces several challenges that limit its scalability, including the use of large volumes of solvents and extractants, high labor costs, and the need for skilled operation. Implementing the technology in the form of liquid membranes helps to mitigate these limitations and simultaneously enhances ion transport. In this configuration, a membrane impregnated with a liquid extractant functions as the organic phase or serves as a medium separator. Accordingly, LMs are generally classified into supported liquid membranes (SLMs) and non-supported liquid membranes (nSLMs), the latter including emulsion liquid membranes (ELMs) and bulk liquid membrane (BLMs). In SLMs, separation occurs on the membrane surface. In nSLMs it takes place within the bulk phase, either in the emulsion of ELMs (Björkegren et al., 2015) or in the extractant layer located between two microporous membranes, forming a BLM structure (Zhao et al., 2020). The structure of BLMs is particularly interesting, as ion transport occurs not only by diffusion but also via electromigration. Ions are transported the membrane to the other side, into a stream or layer containing an organic solvent with extractant. Back-extraction and extractant regeneration can occur simultaneously in the same system (Zhao et al., 2020). Lithium ions contained in the ligands diffuse to another membrane, forming a stream or layer containing the organic solvent. Lithium back-extraction into the receiving solution occurs through this stream or layer.



However, BLMs also have limitations: they possess a relatively small interfacial area, and the high resistance of the microporous membranes used in their design constrains their efficiency and scalability compared to SLMs (Belova et al., 2014).

Taken together, the advances in LSMs reflect a continuous refinement of strategies toward achieving high lithium selectivity, stability, and scalability. The timeline in Figure 2 shows the key technological milestones that have shaped this evolution over the past decades.

TABLE 1 Comparison of lithium extraction efficiency from solutions using different types of lithium-selective membranes.

Reference	Membrane	Membrane type	Feed solution	Experiment details	$j_{Li^+}$ , mol/(m <sup>2</sup> xh)	Competing cation, C <sup>n+</sup>	$j_{C^{n+}}$ , mol/(m <sup>2</sup> xh)	$S_{Li^+}/C^{n+}$
<b>Ion-imprinted membranes (IIMs)</b>								
Yang et al. (2022)	TiO <sub>2</sub> /PVDF-12C4E	Composite IIMs	0.1 g/L Li <sup>+</sup> 0.1 g/L Na <sup>+</sup> 0.1 g/L K <sup>+</sup> 0.1 g/L Mg <sup>2+</sup> 0.1 g/L Ca <sup>2+</sup>	H-type cell (diffusion) 1.1 × 10 <sup>-4</sup> m <sup>2</sup> 2 h	0.03	Na <sup>+</sup>	0.16	0.06
						K <sup>+</sup>	0.045	0.13
						Mg <sup>2+</sup>	0.036	0.25
						Ca <sup>2+</sup>	0.085	0.06
Li L. et al. (2021)	Sf-sg-AB12C4	Composite IIMs	3.5 g/L Li <sup>+</sup> 11.5 g/L Na <sup>+</sup> 19.55 g/L K <sup>+</sup> 12.1 g/L Mg <sup>2+</sup>	ED cell 2 V 3.1 × 10 <sup>-4</sup> m <sup>2</sup> 2 h	-	Na <sup>+</sup>	-	0.027
						K <sup>+</sup>	-	0.023
						Mg <sup>2+</sup>	-	0.03
						Ca <sup>2+</sup>	-	0.021
Yu et al. (2020)	PDMS-PDA-calix [4] arene	Composite IIMs	0.2 g/L Li <sup>+</sup> 0.2 g/L Na <sup>+</sup> 0.2 g/L K <sup>+</sup> 0.2 g/L Rb <sup>+</sup>	diffusion cell 0.5 × 10 <sup>-4</sup> m <sup>2</sup> 3 h	0.5	Na <sup>+</sup>	0.36	0.4
						K <sup>+</sup>	0.23	0.38
						Rb <sup>+</sup>	0.11	0.35
Yang et al. (2019)	M-co-0.50	Composite IIMs	0.35 g/L Li <sup>+</sup> 1.96 g/L K <sup>+</sup> , 1.2 g/L Mg <sup>2+</sup>	ED 4-compartment cell 50 A/m <sup>2</sup> 2.0 × 10 <sup>-3</sup> m <sup>2</sup> 1 h	0.33	K <sup>+</sup>	1.1	0.3
						Mg <sup>2+</sup>	0.15	2.2
Cui et al. (2019)	CA/CS-12C4E	Composite IIMs	0.1 g/L Li <sup>+</sup> 0.1 g/L Na <sup>+</sup> 0.1 g/L K <sup>+</sup> 0.1 g/L Mg <sup>2+</sup> 0.1 g/L Ca <sup>2+</sup>	H-type cell (diffusion) 2.5 × 10 <sup>-4</sup> m <sup>2</sup> 4 h	0.014	Na <sup>+</sup>	0.03	0.16
						K <sup>+</sup>	0.02	0.15
						Mg <sup>2+</sup>	0.04	0.1
						Ca <sup>2+</sup>	0.03	0.08
Sun et al. (2017)	PVDF- 2AM12C4	Composite IIMs	0.1 g/L Li <sup>+</sup> 0.1 g/L Mg <sup>2+</sup>	H-type cell (diffusion) 1.5 × 10 <sup>-4</sup> m <sup>2</sup> 3 h	1.67	Mg <sup>2+</sup>	0.09	5.3
<b>Ion sieve membranes (ISMs)</b>								
Jeong et al. (2025)	α-Al <sub>2</sub> O <sub>3</sub> /MLG	other	0.027 g/L Li <sup>+</sup> 10.8 g/L Na <sup>+</sup> 0.435 g/L K <sup>+</sup> 1.33 g/L Mg <sup>2+</sup> 0.364 g/L Ca <sup>2+</sup> 0.007 g/L Ni <sup>2+</sup> 0.01 g/L Co <sup>2+</sup>	H-type cell -1.5 V 2.1 × 10 <sup>-5</sup> m <sup>2</sup> 72 h (3 × 24 h)	7.1	Na <sup>+</sup>	0.26	3,260
Han et al. (2024)	2:1 [BMIM][AlCl <sub>4</sub> ]-MOF TFN	MOFs-ISMs	0.8 g/L Li <sup>+</sup> 1.27 g/L Mn <sup>2+</sup> 1.05 g/L Co <sup>2+</sup> 3.42 g/L Ni <sup>2+</sup> 0.03 g/L Cu <sup>2+</sup> 0.04 g/L Fe <sup>3+</sup> 0.05 g/L Al <sup>3+</sup>	NF cell 2.5 bar 0.9 × 10 <sup>-3</sup> m <sup>2</sup>	-	Mn <sup>2+</sup>	-	8.9
						Co <sup>2+</sup>	-	9.9
						Ni <sup>2+</sup>	-	10.1
Pang et al. (2023)	VmMS-1	Vermiculite-ISMs	1.4 g/L Li <sup>+</sup> 4.6 g/L Na <sup>+</sup> 7.8 g/L K <sup>+</sup> 4.9 g/L Mg <sup>2+</sup>	ED cell 200 A/m <sup>2</sup> 3 × 10 <sup>-5</sup> m <sup>2</sup> 1 h	1.3	Na <sup>+</sup>	0.09	14.9
						K <sup>+</sup>	0.07	19.1
						Mg <sup>2+</sup>	0.05	23.8
Eden et al. (2023)	CTA-S-60	MOFs-ISMs	0.69 g/L Li <sup>+</sup> 2.3 g/L Na <sup>+</sup>	H-type cell -1.0 - +1.0 V 0.96 × 10 <sup>-3</sup> m <sup>2</sup> 100 s	1.0 × 10 <sup>-11</sup>	Na <sup>+</sup>	-	1.2

(Continued on following page)

TABLE 1 (Continued) Comparison of lithium extraction efficiency from solutions using different types of lithium-selective membranes.

Reference	Membrane	Membrane type	Feed solution	Experiment details	$j_{Li^+}$ , mol/(m <sup>2</sup> ·xh)	Competing cation, C <sup>n+</sup>	$j_{C^{n+}}$ , mol/(m <sup>2</sup> ·xh)	$S_{Li^+/C^{n+}}$
Ahmadi et al. (2022)	GO-based membrane	other	3.5 g/L Li <sup>+</sup> 11.5 g/L Na <sup>+</sup> 19.5 g/L K <sup>+</sup> 12.1 g/L Mg <sup>2+</sup>	H-type cell 1 V 0.5 h	0.005	Na <sup>+</sup>	0.016	0.28
						K <sup>+</sup>	0.017	0.27
Ounissi et al. (2022)	Lithium Composite Membranes (LCM)	other	0.2 g/L Li <sup>+</sup> 2.0 g/L Na <sup>+</sup>	ED 4-compartment cell 5 A/m <sup>2</sup> 0.4 × 10 <sup>-3</sup> m <sup>2</sup> 4 h	0.087	Na <sup>+</sup>	2.35 × 10 <sup>-3</sup>	112
Lu Z. et al. (2021)	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -PSS	MXene-ISMs	1.4 g/L Li <sup>+</sup> 4.6 g/L Na <sup>+</sup> 7.82 g/L K <sup>+</sup> 4.9 g/L Mg <sup>2+</sup>	U-shaped cell 75 h	0.01	Na <sup>+</sup>	0.001	10
						K <sup>+</sup>	0.04	12
						Mg <sup>2+</sup>	0.016	25
Deng et al. (2021)	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	MXene-ISMs	1.4 g/L Li <sup>+</sup>	U-shaped cell 0.8 × 10 <sup>-3</sup> m <sup>2</sup> 24 h	0.01	-	-	-
Ounissi et al. (2021)	Lithium Composite Membranes (LCM)	other	0.1 g/L Li <sup>+</sup> 4.0 g/L Na <sup>+</sup>	DD and CID cell 0.78 × 10 <sup>-4</sup> m <sup>2</sup> 24 h	0.045	Na <sup>+</sup>	9.7 × 10 <sup>-5</sup>	5,543
						Na <sup>+</sup>	1.3 × 10 <sup>-3</sup>	931
Lu J. et al. (2021)	3D UiO-66-COOH	MOFs-ISMs	0.7 g/L Li <sup>+</sup> 2.4 g/L Mg <sup>2+</sup>	H-type cell 1.0 V 2 min	-	Na <sup>+</sup>	-	0.24
						K <sup>+</sup>	-	0.18
						Mg <sup>2+</sup>	-	136.5
Bajestani et al. (2020)	CEM/ LiCo <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>	other	13.9 g/L Li <sup>+</sup> 1.35 g/L Na <sup>+</sup>	EL cell 5 V 3 h	8.96	Na <sup>+</sup>	0.28	0.95
Sharma et al. (2020)	NC-4	other	0.5 g/L Li <sup>+</sup> 0.5 g/L Mg <sup>2+</sup> 0.5 g/L K <sup>+</sup> 0.5 g/L Na <sup>+</sup>	ED 4-compartment cell 2 cell pair 2 V/cell 0.0066 m <sup>2</sup> 2 h	4.32	Na <sup>+</sup>	0.6	2.2
						K <sup>+</sup>	0.25	3
						Mg <sup>2+</sup>	0.25	4.8
Zhang et al. (2020)	HSO <sub>3</sub> -UiO-66-0.6@PVC	MOFs-ISMs	0.28 g/L Li <sup>+</sup> 2.18 g/L Na <sup>+</sup> , 0.76 g/L K <sup>+</sup> 108.5 g/L Mg <sup>2+</sup>	2-compartment cell (diffusion) 0.5 × 10 <sup>-3</sup> m <sup>2</sup> 60 h	2.8 × 10 <sup>-5</sup>	Na <sup>+</sup>	0.8 × 10 <sup>-4</sup>	0.8
						K <sup>+</sup>	2.2 × 10 <sup>-5</sup>	0.6
						Mg <sup>2+</sup>	0.7 × 10 <sup>-3</sup>	4.7
Liquid membranes (LMs)								
Dong et al. (2025)	14C4PI(TBP-NaNTf <sub>2</sub> )	HFSLMs	0.7 g/L Li <sup>+</sup> 2.4 g/L Mg <sup>2+</sup>	MC cell 1.4 × 10 <sup>-3</sup> m <sup>2</sup> 120 h	0.18	Mg <sup>2+</sup>	0.017	15.8
Li et al. (2024)	EVAL/SPEEK-NW	FSSLMS	6.25 g/L Li <sup>+</sup> 97.2 g/L Mg <sup>2+</sup>	diffusion cell 5 cell pair 0.033 m <sup>2</sup> 11 h	0.83	Mg <sup>2+</sup>	<0.8 × 10 <sup>-2</sup>	>460
Hua et al. (2023)	PI@14C4	FSSLMS	0.7 g/L Li <sup>+</sup> 46 g/L Na <sup>+</sup> 3.9 g/L K <sup>+</sup> 2.4 g/L Mg <sup>2+</sup>	H-type cell 0.3 × 10 <sup>-3</sup> m <sup>2</sup> 96 h	0.15	Na <sup>+</sup>	0.83	4.1
						K <sup>+</sup>	0.03	6.1
						Mg <sup>2+</sup>	0.012	14.1
Zhao et al. (2020)	Sandwiched liquid-membrane	BLMs	1.0 g/L Li <sup>+</sup> 50.0 g/L Mg <sup>2+</sup> 6.9 g/L Li <sup>+</sup> 40.1 g/L Ca <sup>2+</sup> 23.0 g/L Na <sup>+</sup>	EL cell 3 V/cell 0.0036 m <sup>2</sup> 12 h	0.079	Mg <sup>2+</sup>	0.035	2.2
						Ca <sup>2+</sup>	1.2 × 10 <sup>-4</sup>	111
						Na <sup>+</sup>	1.3 × 10 <sup>-3</sup>	10

(Continued on following page)

TABLE 1 (Continued) Comparison of lithium extraction efficiency from solutions using different types of lithium-selective membranes.

Reference	Membrane	Membrane type	Feed solution	Experiment details	$j_{Li^+}$ , mol/(m <sup>2</sup> ×h)	Competing cation, C <sup>n+</sup>	$j_{C^{n+}}$ , mol/(m <sup>2</sup> ×h)	$S_{Li^+/C^{n+}}$
Zante et al. (2020)	PVDF/liquid membrane	FSSLMS	0.052 g/L Li <sup>+</sup> , 0.17 g/L Na <sup>+</sup>	1.8 × 10 <sup>-3</sup> m <sup>2</sup> 20 h	0.052	Na <sup>+</sup>	1.3 × 10 <sup>-4</sup>	400
			6.9 × 10 <sup>-3</sup> g/L Li <sup>+</sup> , 2.3 g/L Na <sup>+</sup>		0.18	Na <sup>+</sup>	1.08	16.7

\*EL, cell–electrolysis cell; ED, cell–electrodialysis cell; CID, cross-ionic dialysis cell; DD, diffusion dialysis cell; MC, cell–membrane contactor cell; NF, cell–nanofiltration cell.

### 3 Advantages of lithium selective membrane types

LSMs are expected to combine several key advantages, including high lithium-ion selectivity, high specific productivity (ion flux) and extraction efficiency, energy efficiency and continuous operation compared to traditional methods, as well as environmental sustainability through reduced reagent consumption. However, in practice, it is often impossible to achieve all these parameters simultaneously due to their inherently conflicting nature, a phenomenon known as the trade-off effect: increased productivity usually leads to reduced selectivity, while higher extraction efficiency tends to decrease energy efficiency, and *vice versa*. Consequently, most reports in the literature describe laboratory-scale LSMs that fulfill one or two sustainability criteria but rarely combine all the desirable characteristics.

Table 1 summarizes the results from recent studies proposing and testing various structures and compositions of ion-imprinted, ion-sieve, and liquid membranes. It should be noted that these results were obtained under diverse experimental conditions. The reported systems differ in driving forces (concentration, pressure, or electric field gradients), feed solution compositions (from ternary electrolytes containing lithium and magnesium salts to multicomponent solutions with monovalent ions such as Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup> to divalent ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup>), and in the design of test modules (ranging from simple laboratory H-type cells to multi-compartment electro dialysis cells with several repeating cell pairs).

Among the various types of ion-imprinted membranes, composite IIMs are likely the most widely used in lithium extraction. They are characterized by ease of fabrication and broad variability in component composition. Moreover, 12-crown-4 ether (12C4E) is most frequently employed as a chelating agent in such membranes (Sun et al., 2017; Cui et al., 2019; Li L. et al., 2021; Yang et al., 2022). The cavity size of 12C4E closely matches the ionic radius of lithium, enabling the formation of specific recognition sites through complexation with oxygen atoms. However, the structure remains permeable to smaller sodium and potassium ions. In addition, 12C4E can also interact with magnesium and calcium ions, forming sandwich structure. As a result, membranes of this type allow the transfer of not only lithium but also other coexisting ions (Yang et al., 2022), which leads to selective ion separation (or specific permselectivity) coefficient,  $S_{Li^+/C^{n+}}$ , often significantly lower than 1 (Table 1).

The selective ion separation coefficient (Equation 1) determines the ability of the membrane to preferentially

transport the target ion over coexisting ions in the feed solution and is defined as follows:

$$S_{Li^+/C^{n+}} = \frac{j_{Li^+}/j_{C^{n+}}}{c_{Li^+}^f/c_{C^{n+}}^f} = \frac{\Delta c_{Li^+}^p/\Delta c_{C^{n+}}^p}{c_{Li^+}^f/c_{C^{n+}}^f} \quad (1)$$

where  $j_{Li^+}$  and  $j_{C^{n+}}$  are the flux densities of Li<sup>+</sup> and coexisting C<sup>n+</sup> cations through the membrane, respectively;  $c_{Li^+}^f$  and  $c_{C^{n+}}^f$  are the concentrations of coexisting cations in the feed solution;  $\Delta c_{Li^+}^p$  and  $\Delta c_{C^{n+}}^p$  are the changes in concentrations of these ions in the concentrate (product) compartment over time.

This implies that, based on the physical meaning of the parameter  $S_{Li^+/C^{n+}}$ , IIMs are actually «selective» toward coexisting cations rather than lithium itself. Since the chelating agents incorporated in their composition exhibit specific affinity for lithium, the performance of IIMs is typically evaluated not only in terms of the selectivity coefficient but also by parameters such as diffusion permeability, sorption coefficients and adsorption capacity, that is, by characteristics obtained under equilibrium conditions or driven solely by concentration gradients. Luo et al. (2020) noted that for membrane applications in electric field-driven processes, it is essential to evaluate them under appropriate operating conditions. Moreover, both the specified current modes (Jiang et al., 2019; Zabolotsky et al., 2020; Golubenko and Yaroslavtsev, 2021) and hydraulic regimes (Zhang et al., 2021) can significantly influence membrane performance. Due to the coupled effects of concentration polarization and phenomena occurring at elevated (overlimiting) current densities, membranes can exhibit specific permselectivity only at current densities below the limiting value (Gorobchenko et al., 2022). Diffusion permeability, sorption coefficients, and adsorption capacities indeed play a major role at low current densities and when the proportion of the target component is high compared to coexisting components (20%–60%). This can then be used to calculate the selective ion separation coefficient (Luo et al., 2020). Therefore, while these parameters are important, specific permselectivity remains the key indicator, as it enables a direct assessment of the performance of different membrane systems and facilitates comparative analysis of the results independent of external factors.

Another parameter important for practical applications is the specific flux of the competing cations (Equation 2),  $j_k$ , mol/(m<sup>2</sup>×h):

$$j_{C^{n+}} = \frac{V}{s} \frac{dc_{C^{n+}}^p}{dt} \quad (2)$$

where  $V$  is the volume of feed or permeate solution,  $s$  is the membrane surface area,  $t$  is time of an experiment.

Although this parameter is as universal as the selective ion separation coefficient, it is not as widely used. Its definition and expression vary across different membrane-based methods. For example, in baromembrane concentration and separation processes (reverse osmosis and NF), which are widely used in water treatment processes (Jones et al., 2019), performance is typically evaluated by the membrane permeate flux,  $j_v$ , L/(m<sup>2</sup>×h). During NF treatment, lithium and other monovalent ions enter the permeate along with water molecules, whereas multivalent ions are predominantly retained in the retentate.

To develop integrated lithium extraction technologies and critically evaluate the progress of membrane-based methods, including those employing LSMs, it is essential to compare their performance using standardized parameters. Previously, we were the first to compile, calculate (when data were not explicitly provided in the original studies), and analyze the results of a wide range of membrane-based methods (ED, S-ED, BMED, EL, DD, CID, MCDI, NF, RO, etc.) for lithium extraction from both primary and secondary sources (Butylskii et al., 2023). The comparison was based on selective ion separation coefficients and specific ion flux. The analysis primarily focused on lab-made monovalent cation-selective and lithium-selective membranes. Although these membranes often demonstrate high selective ion separation coefficients, their technology readiness level remains too low for commercialization due to complex and costly fabrication procedures and testing performed only under simplified conditions using artificial brines. Therefore, a separate assessment was carried out for membranes and membrane technologies tested in either artificial or real multicomponent brines, as well as under near-industrial conditions (large effective membrane area, high total dissolved solids, integration with other processing stages, etc.) (Butylskii et al., 2024). This analysis highlighted the high potential of S-ED and NF methods for lithium extraction from mixtures containing divalent ions, as well as capacitive deionization, membrane capacitive deionization and electrobaromembrane methods for reagent-free separation of lithium from monovalent sodium and potassium ions.

Therefore, only comprehensive, multifactorial testing of the developed materials can provide a definitive conclusion regarding their applicability in lithium extraction technologies. Nevertheless, for preliminary assessments, the selective ion separation coefficient and specific flux values are sufficient.

In Ref. (Yang et al., 2022), a composite IIMs TiO<sub>2</sub>/PVDF-12C4E was proposed. The membrane was fabricated using a PVDF matrix with the addition of TiO<sub>2</sub> to enhance overall hydrophilicity, while surface modification with 12-crown-4 ether imparted lithium-ion selectivity. The selective permeation ability of created membrane was measured in multicomponent solution with the same concentration of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> ions. The authors found that selective permeation ability varied in the following order: Li<sup>+</sup> < Mg<sup>2+</sup> < K<sup>+</sup> < Ca<sup>2+</sup> < Na<sup>+</sup>, which aligns with the transport mechanism previously described for IIMs and the relative hydrated ion sizes. It is noteworthy that the membrane exhibited close permeation ability for Li<sup>+</sup> and Mg<sup>2+</sup> ions, which can be attributed to their comparable hydrated ionic radii. According to our calculations, the membrane demonstrates a lithium flux of 0.03 mol/(m<sup>2</sup>×h) and a specific permselectivity  $S_{Li^+/Mg^{2+}} = 0.25$ .

Similar results were reported in Ref (Cui et al., 2019) for a CA/CS-12C4E hybrid membrane composed of cellulose acetate and

chitosan, further modified with TiO<sub>2</sub> and 12-crown-4 ether. However, in a mixed solution, the permeation ability differed and followed the order: Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Mg<sup>2+</sup> < Ca<sup>2+</sup>. This deviation can be attributed to structural differences in the substrate membrane and variations in the loading level of the chelating agent. Under identical feed solution concentrations and operating solely under a concentration gradient, the lithium flux through the CA/CS-12C4E membrane, according to our estimates is lower (0.014 mol/(m<sup>2</sup>×h)), compared with the TiO<sub>2</sub>/PVDF-12C4E membrane (Table 1).

In Ref. (Yu et al., 2020), a PDMS-PDA-calix [4]arene membrane was developed and tested using a different chelating agent (calix [4]arene). The enhanced lithium retention was attributed to its interaction with ester groups. However, based on the authors' data, the lithium flux through this IIM is approximately 0.5 mol/(m<sup>2</sup>×h), while the selectivity toward coexisting singly charged Na<sup>+</sup> and K<sup>+</sup> ions is nearly an order of magnitude lower than that achieved with membranes employing 12-crown-4 ether as the chelating agent (Table 1).

The performance of lithium extraction using IIMs can be improved by applying an electric current or pressure as an additional driving force alongside the concentration gradient. In Ref. (Li L. et al., 2021), a polysulfone-type membrane, Sf-sg-AB12C4, with 12-crown-4 ether, was synthesized and tested under a constant potential drop of 2 V. Unfortunately, the authors did not report specific flux values, and the available quantitative data are insufficient to perform an independent calculation. Nevertheless, it is worth noting that the membrane demonstrates significantly higher selective ion separation coefficient.

Thus, the analysis shows that although composite IIMs can exhibit high selective ion separation coefficients with respect to coexisting ions, they typically demonstrate low specific lithium fluxes. However, for this membrane type, low fluxes imply low lithium loss due to its removal with competing ions. This is because the target lithium product remains in the feed solution compartment rather than passing through the membrane, unlike in most other membrane processes.

The ISMs, conversely, are designed for the direct extraction of lithium by selectively transporting only Li<sup>+</sup> through the membrane, while coexisting ions are effectively excluded (Xu et al., 2024). Membranes of this type have been tested in both pressure-driven (Han et al., 2024), and electric-field-driven (Ounissi et al., 2022) processes.

MOFs-based ISMs deserve particular attention due to the rapidly increasing number of studies on their synthesis. In Ref. (Lu J. et al., 2021), a 3D UiO-66-COOH membrane was fabricated using an amino-functionalized PET-NC film whose pores were filled with carboxyl-functionalized UiO-66 crystals. This approach enabled the formation of subnanometer pores within a polymer nanochannel, resulting in a membrane that, according to our calculations, exhibits an exceptional selective ion separation coefficient for lithium over magnesium of 136.5 under an applied electric field. In Ref. (Han et al., 2024), a 2:1 [BMIM][AlCl<sub>4</sub>]-MOF TFN nanofiltration membrane was prepared on a PVDF film modified with MIL-101 grafted with different ionic liquids (ILs). Similar to other MOFs-based ISMs used in electrodialysis, the mechanism of lithium selectivity arises from a combination of the sieving effect and electrostatic interactions. In this membrane architecture, ionic liquids are employed to enhance electrostatic

exclusion, thereby improving selectivity. According to the authors (Han et al., 2024), the membrane exhibited lithium selectivity in the presence of  $Mn^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$ , with values ranging from 9 to 10 (Table 1).

Although MOFs-based ISMs frequently achieve high selectivity, the specific lithium flux through them is often low at practically reasonable lithium concentrations in the feed solution (up to 0.5 g/L). Another limiting factor for the practical implementation of MOFs-based ISMs technology is the complexity of MOF fabrication and their associated high production costs.

Reviews (Abrishami et al., 2024; Xu T. et al., 2025) summarize both the achievements and the limitations of MOFs-based ISMs, enabling an assessment of their prospects for integration into lithium extraction technologies. The authors highlight a significant gap between laboratory-scale samples and the large-area MOF-based ISMs required for industrial ion separation. However, MOF-based membranes for gas separation are being actively developed in parallel, with reports of the fabrication of ZIF-8 flat membranes with areas of up to 2,400  $cm^2$ , and even up to 4,800  $cm^2$  for spiral-wound membrane module (Yu et al., 2023).

A potential solution to the challenge of rapid scale-up is the use of less expensive materials for creating ISMs. MXene-based ISMs have recently emerged as a promising candidate in this regard. Deng et al. (Deng et al., 2021) reported the fabrication of a  $Ti_3C_2T_x$  membrane with a large area of up to 575  $cm^2$ . Although MXenes are two-dimensional materials, unlike MOFs, the interlayer gaps in their structures provide comparably effective pathways for lithium-ion separation. Lithium selectivity relative to  $Na^+$  and  $K^+$  can reach values of around 10, while selectivity relative to  $Mg^{2+}$  reaches 25, with a lithium flux of 0.08  $mol/(m^2 \times h)$  (Lu Z. et al., 2021).

The use of LMs for lithium extraction also shows significant promise. Membranes of this type are characterized by high specific permselectivity (Table 1). Zante et al. (2020) reported the development and testing of PVDF-based FSLMs employing heptafluorodimethyloctanedione (HFDOD) and tri-n-octylphosphine oxide (TOPO) as lithium-selective ligands. The selectivity toward  $Na^+$  reached 400, while the lithium flux in a concentration-gradient-driven system reached 0.052  $mol/(m^2 \times h)$ . Another similarly successful strategy is the use of BLMS. The sandwiched liquid-membrane developed by Zhao et al. (2020) incorporates a lithium-selective agent in the internal space between two ion-exchange membranes. The use of ionic liquids such as tri-n-butyl phosphate (TBP), which are well established in solvent extraction of lithium, enables high selectivity in the electric-field-driven process while simultaneously achieving enhanced lithium fluxes.

Similar to other membrane types, LMs also face surface area limitations that affect their performance and hinder broader adoption. In Ref. (Dong et al., 2025), 14C4PI(TBP-NaNTf<sub>2</sub>) HFSLMs designed as membrane contactors were fabricated and tested. Membrane contactors are devices equipped with polymer partitions that enable direct phase contact (gas-liquid or liquid-liquid) across an interface without dispersing one phase into the other. Their key advantage is efficient mass transfer between phases (Drioli et al., 2011). To maximize the effective use of the interface, membrane contactor configurations with the highest membrane surface area-to-volume ratio, namely, tubular or hollow-fiber membranes, are typically preferred. The 14C4PI(TBP-NaNTf<sub>2</sub>) membrane is made of 14-crown-4 ether functionalized

polyimide, the pores of which were filled with TBP and sodium bis(trifluoromethylsulfonyl)imide as a selective agent. With an area of  $1.4 \times 10^{-3} m^2$ , in  $Li^+$  and  $Mg^{2+}$  separation tests, the membrane demonstrated a lithium selectivity of 15.8 at a lithium flux of 0.18  $mol/(m^2 \times h)$  (Table 1).

Thus, this review demonstrates that, although numerous types of lithium-selective membranes and a wide range of implementation strategies have been reported in the scientific literature, moving to high levels of availability requires significant experimental development. Only a small fraction of laboratory prototypes has undergone detailed, long-term testing in multicomponent solutions for lithium extraction from natural brines. The complexity of fabrication methods, the need for continuous monitoring of membrane stability, the scarcity of comprehensive performance evaluations, and the inconsistent reporting of productivity, selectivity, and efficiency metrics (which vary depending on precursors, membrane type, and intended application) collectively hinder the implementation of LSM technologies for direct lithium extraction.

## 4 Conclusion

Direct lithium extraction using lithium-selective membranes represents a promising advancement in the field of lithium recovery. By leveraging the unique properties of specialized membranes, this method offers a more efficient, sustainable, and environmentally friendly approach to meet the growing demand for lithium. However, the present review highlights that the concept still faces a number of critical challenges. Despite achieving high selective ion separation coefficients, most LSMs exhibit relatively low specific lithium fluxes, necessitating productivity enhancement either through substantial increases in membrane surface area or by intensifying the driving force via pressure or electric field application rather than relying solely on concentration gradients. At the same time, the requirement for large membrane areas remains a major bottleneck for most LSMs. The cost of the precursors required for their fabrication and the overall complexity of the production technology continue to limit both productivity and industrial scalability. Furthermore, the productivity, selectivity, and efficiency of different types of LSMs are often expressed in non-uniform parameters, which complicates their comparison with other membrane types as well as with other processes that must be integrated into a complete extraction system. It is expected that continued research and development, aimed at improving LSM design and optimizing lithium extraction processes, will enhance the overall feasibility and efficiency of DLE systems.

## Author contributions

VT: Visualization, Writing – original draft, Formal Analysis. MP: Formal Analysis, Writing – original draft. VR: Formal Analysis, Writing – original draft. TB: Formal Analysis, Writing – original draft. AG: Formal Analysis, Writing – original draft. LD: Writing – review and editing, Conceptualization. SM: Conceptualization, Writing – original draft. MS: Conceptualization, Writing – original draft. DB: Writing – review and editing,

Writing – original draft, Supervision, Funding acquisition, Visualization, Resources, Conceptualization, Project administration.

## Funding

The author(s) declared that financial support was received for this work and/or its publication. We are grateful to the Russian Science Foundation and Kuban Science Foundation, project No 25-19-20153, <https://rscf.ru/en/project/25-19-20153/>

## Conflict of interest

The author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

## Generative AI statement

The author(s) declared that generative AI was not used in the creation of this manuscript.

## References

- Abdollahzadeh, M., Chai, M., Hosseini, E., Zakertabrizi, M., Mohammad, M., Ahmadi, H., et al. (2022). Designing angstrom-scale asymmetric MOF-on-MOF cavities for high monovalent ion selectivity. *Adv. Mater.* 34, e2107878. doi:10.1002/adma.202107878
- Abrihami, S., Gonbadi, M., and Razmjou, A. (2024). Is MOF a suitable starting material for industrial lithium extraction? *Ind. Eng. Chem. Res.* 64, 731–739. doi:10.1021/ACS.IECR.4C03740
- Abrihami, S., Xiao, H., Asadnia, M., Low, Z.-X., and Razmjou, A. (2025). Recent advances in the design principles of lithium selective membranes. *Water Res.* 283, 123724. doi:10.1016/j.watres.2025.123724
- Ahmadi, H., Zakertabrizi, M., Hosseini, E., Cha-Umpong, W., Abdollahzadeh, M., Korayem, A. H., et al. (2022). Heterogeneous asymmetric passable cavities within graphene oxide nanochannels for highly efficient lithium sieving. *Desalination* 538, 115888. doi:10.1016/j.desal.2022.115888
- Ali, G. K., and Omer, K. M. (2022). Molecular imprinted polymer combined with aptamer (MIP-aptamer) as a hybrid dual recognition element for bio(chemical) sensing applications. *Review. Talanta* 236, 122878. doi:10.1016/j.talanta.2021.122878
- Aravind, A., and Mathew, B. (2020). Nano layered ion imprinted polymer based electrochemical sensor and sorbent for Mn (II) ions from real samples. *J. Macromol. Sci. Part A* 57, 256–265. doi:10.1080/10601325.2019.1691451
- Bajestani, M., Moheb, A., and Dinari, M. (2020). Preparation of lithium ion-selective cation exchange membrane for lithium recovery from sodium contaminated lithium bromide solution by electrodialysis process. *Desalination* 486, 114476. doi:10.1016/j.desal.2020.114476
- Bao, L., Xu, Z., Guo, W., Lin, S., and Sun, S. (2023). Enhancement of lithium extraction from low grade brines by highly hydrophilic blend membranes using MnO<sub>2</sub> ion sieve as adsorbents. *Colloids Surfaces A Physicochem. Eng. Asp.* 674, 131884. doi:10.1016/j.colsurfa.2023.131884
- Belova, V. V., Kostanyan, A. E., Zakhodyaeva, Y. A., Kholkin, A. I., and Logutenko, O. A. (2014). On the application of bulk-supported liquid membrane techniques in hydrometallurgy. *Hydrometallurgy* 150, 144–152. doi:10.1016/j.hydromet.2014.10.011
- Björkregren, S., Karimi, R., Martinelli, A., Jayakumar, N., and Hashim, M. (2015). A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals. *Membr. (Basel)* 5, 168–179. doi:10.3390/membranes5020168
- Branger, C., Meouche, W., and Margailan, A. (2013). Recent advances on ion-imprinted polymers. *React. Funct. Polym.* 73, 859–875. doi:10.1016/j.reactfunctpolym.2013.03.021
- Butylskii, D. Y., Dammak, L., Larchet, C., Pismenskaya, N. D., and Nikonenko, V. V. (2023). Selective recovery and re-utilization of lithium: prospects for the use of membrane methods. *Russ. Chem. Rev.* 92, RCR5074. doi:10.57634/RCR5074
- Butylskii, D. Y., Troitskiy, V. A., Smirnova, N. V., Pismenskaya, N. D., Wang, Y., Jiang, C., et al. (2024). Review of recent progress on lithium recovery and recycling from primary and secondary sources with membrane-based technologies. *Desalination* 586, 117826. doi:10.1016/j.desal.2024.117826
- Chen, C., Shen, L., Lin, H., Zhao, D., Li, B., and Chen, B. (2024). Hydrogen-bonded organic frameworks for membrane separation. *Chem. Soc. Rev.* 53, 2738–2760. doi:10.1039/D3CS00866E
- Chen, Z., Du, J., and Shi, J. (2025). Mxene-based lithium-ion sieve polymer membrane for sustainable lithium adsorption. *Sep. Purif. Technol.* 354, 129316. doi:10.1016/j.seppur.2024.129316
- Côté, A. P., Benin, A. I., Ockwig, N. W., O’Keeffe, M., Matzger, A. J., and Yaghi, O. M. (2005). Porous, crystalline, covalent organic frameworks. *Sci.* 310, 1166–1170. doi:10.1126/science.1120411
- Cui, J., Zhou, Z., Liu, S., Zhang, Y., Yan, L., Zhang, Q., et al. (2018). Synthesis of cauliflower-like ion imprinted polymers for selective adsorption and separation of lithium ion. *New J. Chem.* 42, 14502–14509. doi:10.1039/C8NJ03249A
- Cui, J., Zhou, Z., Xie, A., Liu, S., Wang, Q., Wu, Y., et al. (2019). Facile synthesis of degradable CA/CS imprinted membrane by hydrolysis polymerization for effective separation and recovery of Li<sup>+</sup>. *Carbohydr. Polym.* 205, 492–499. doi:10.1016/j.carbpol.2018.10.094
- Dai, C., Gu, B., Tang, S.-P., Deng, P.-H., and Liu, B. (2022). Fluorescent porous organic cage with good water solubility for ratiometric sensing of gold(III) ion in aqueous solution. *Anal. Chim. Acta* 1192, 339376. doi:10.1016/j.aca.2021.339376
- Demin, S. V., Shokurova, N. A., Demina, L. I., Kuz'mina, L. G., Zhilov, V. I., and Tsvadze, A. Y. (2018). Effects of side-chain substituents in Benzo-15-Crown-5 on lithium extraction. *Russ. J. Inorg. Chem.* 63, 121–127. doi:10.1134/S0036023618010059
- Deng, J., Lu, Z., Ding, L., Li, Z.-K., Wei, Y., Caro, J., et al. (2021). Fast electrophoretic preparation of large-area two-dimensional titanium carbide membranes for ion sieving. *Chem. Eng. J.* 408, 127806. doi:10.1016/j.cej.2020.127806
- Dong, B., Hua, J., He, J., Du, J., Xiao, J., and Li, J. (2025). A hollow fiber supported ionic liquid membrane contactor for continuous extraction of lithium from high magnesium/lithium ratio brine. *Water Res.* 279, 123451. doi:10.1016/j.watres.2025.123451
- Drioli, E., Criscuoli, A., and Curcio, E. (2011). *Membrane contactors: fundamentals, applications and potentialities*. 1st Ed. Elsevier Science.
- Eden, N. T., Scalzo, M. T., Hou, R., Ghasemiestahbanati, E., Konstas, K., and Hill, M. R. (2023). Sulfonated metal-organic framework mixed-matrix membrane toward direct lithium extraction. *ACS Appl. Eng. Mater.* 1, 2336–2346. doi:10.1021/acsanm.3c00196
- Ezama, I., Raúl de los Hoyos, C., Cortegoso, P., and Braun, T. (2018). “Direct extraction lithium processes: the challenges of spent brine disposal SRK consulting.”

Any alternative text (alt text) provided alongside figures in this article has been generated by Frontiers with the support of artificial intelligence and reasonable efforts have been made to ensure accuracy, including review by the authors wherever possible. If you identify any issues, please contact us.

## Publisher’s note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/frmst.2026.1753282/full#supplementary-material>



- Saraji, M., and Yousefi, H. (2009). Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water samples. *J. Hazard. Mater.* 167, 1152–1157. doi:10.1016/j.jhazmat.2009.01.111
- Shakerian, F., Kim, K.-H., Kwon, E., Szulejko, J. E., Kumar, P., Dadfarnia, S., et al. (2016). Advanced polymeric materials: synthesis and analytical application of ion imprinted polymers as selective sorbents for solid phase extraction of metal ions. *Trac. Trends Anal. Chem.* 83, 55–69. doi:10.1016/j.trac.2016.08.001
- Sharma, P. P., Yadav, V., Rajput, A., Gupta, H., Saravaia, H., and Kulshrestha, V. (2020). Sulfonated poly (ether ether ketone) composite cation exchange membrane for selective recovery of lithium by electrodialysis. *Desalination* 496, 114755. doi:10.1016/j.desal.2020.114755
- Shen, Y., Miao, P., Liu, S., Gao, J., Han, X., Zhao, Y., et al. (2023). Preparation and application progress of imprinted polymers. *Polym. (Basel)* 15, 2344. doi:10.3390/polym15102344
- Singh, D. K., and Mishra, S. (2009). Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer. *J. Hazard. Mater.* 164, 1547–1551. doi:10.1016/j.jhazmat.2008.09.112
- Sun, D., Zhu, Y., Meng, M., Qiao, Y., Yan, Y., and Li, C. (2017). Fabrication of highly selective ion imprinted macroporous membranes with crown ether for targeted separation of lithium ion. *Sep. Purif. Technol.* 175, 19–26. doi:10.1016/j.seppur.2016.11.029
- Sun, Y., Wang, Q., Wang, Y., Yun, R., and Xiang, X. (2021). Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine. *Sep. Purif. Technol.* 256, 117807. doi:10.1016/j.seppur.2020.117807
- Swain, B. (2016). Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review. *J. Chem. Technol. Biotechnol.* 91, 2549–2562. doi:10.1002/jctb.4976
- Tabelin, C. B., Dallas, J., Casanova, S., Pelech, T., Bournival, G., Saydam, S., et al. (2021). Towards a low-carbon society: a review of lithium resource availability, challenges and innovations in mining, extraction and recycling, and future perspectives. *Min. Eng.* 163, 106743. doi:10.1016/j.mineng.2020.106743
- Werny, M. (2023). Mapping DLE. Available online at: <https://www.adionics.com/mapping-dle/>.
- Wulff, G. (2013). Forty years of molecular imprinting in synthetic polymers: origin, features and perspectives. *Microchim. Acta* 180, 1359–1370. doi:10.1007/s00604-013-0992-9
- Wulff, G., and Sarhan, A. (1972). Use of polymers with enzyme-analogous structures for resolution of racemates. *Angew. Chem. Int. Ed.* 11, 341–345.
- Xia, Q.-Q., Wang, X.-H., Yu, J.-L., Xue, Z.-Y., Chai, J., Liu, X., et al. (2022). Tale of COF-on-MOF composites with structural regulation and stepwise luminescence enhancement. *ACS Appl. Mater. Interfaces* 14, 45669–45678. doi:10.1021/acsmi.2c12606
- Xiao, H., Chai, M., Abdollahzadeh, M., Ahmadi, H., Chen, V., Gore, D. B., et al. (2022). A lithium ion selective membrane synthesized from a double layered Zr-based metalorganic framework (MOF-on-MOF) thin film. *Desalination* 532, 115733. doi:10.1016/j.desal.2022.115733
- Xu, R., Kang, Y., Zhang, W., Zhang, X., and Pan, B. (2022). Oriented UiO-67 metal-organic framework membrane with fast and selective lithium-ion transport. *Angew. Chem. Int. Ed.* 61, e202115443. doi:10.1002/anie.202115443
- Xu, T., Wu, B., Li, W., Li, Y., Zhu, Y., Sheng, F., et al. (2024). Perfect confinement of crown ethers in MOF membrane for complete dehydration and fast transport of monovalent ions. *Sci. Adv.* 10, eadn0944. doi:10.1126/sciadv.adn0944
- Xu, L., Zhao, B., Zhang, X., Liu, W., Rau, D., Wu, D., et al. (2025). Membrane and electrochemical separations for direct lithium extraction. *Nat. Chem. Eng.* 2, 551–567. doi:10.1038/s44286-025-00250-6
- Xu, T., Liu, Z., Li, X., and Xu, T. (2025). The evolution of metal-organic framework membranes: from laboratory innovation to industrial implementations. *Ind. Eng. Chem. Res.* 64, 9847–9866. doi:10.1021/acs.iecr.5c00781
- Xue, F., Zhang, X., Niu, Y., Yi, C., Ju, S., and Xing, W. (2020). Preparation and evaluation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported lithium ion sieve membranes for Li<sup>+</sup> extraction. *Chin. J. Chem. Eng.* 28, 2312–2318. doi:10.1016/j.cjche.2020.05.006
- Yaghi, O. M., Li, G., and Li, H. (1995). Selective binding and removal of guests in a microporous metal-organic framework. *Nature* 378, 703–706. doi:10.1038/378703a0
- Yang, S., Liu, Y., Liao, J., Liu, H., Jiang, Y., Van der Bruggen, B., et al. (2019). Codeposition modification of cation exchange membranes with dopamine and crown ether to achieve high K<sup>+</sup> + electrodialysis selectivity. *ACS Appl. Mater. Interfaces* 11, 17730–17741. doi:10.1021/acsmi.8b21031
- Yang, J., Qu, G., Liu, C., Zhou, S., Li, B., and Wei, Y. (2022). An effective lithium ion-imprinted membrane containing 12-crown ether-4 for selective recovery of lithium. *Chem. Eng. Res. Des.* 184, 639–650. doi:10.1016/j.cherd.2022.06.039
- Yang, X., Ullah, Z., Stoddart, J. F., and Yavuz, C. T. (2023). Porous organic cages. *Chem. Rev.* 123, 4602–4634. doi:10.1021/acs.chemrev.2c00667
- Yao, X., Zheng, Q., Tjambiru, V. T., Wu, P., Li, Z., Miyamoto, A., et al. (2025). High-selectivity separation of lithium from spent lithium-ion battery leachates using surface-modified commercial nanofiltration membranes. *Environ. Sci. Technol.* 59, 23542–23555. doi:10.1021/acs.est.5c05864
- Yu, C., Lu, J., Dai, J., Dong, Z., Lin, X., Xing, W., et al. (2020). Bio-inspired fabrication of Ester-functionalized imprinted composite membrane for rapid and high-efficient recovery of lithium ion from seawater. *J. Colloid Interface Sci.* 572, 340–353. doi:10.1016/j.jcis.2020.03.091
- Yu, C., Cen, X., Zhang, Z., Sun, Y., Xue, W., Qiao, Z., et al. (2023). Step-nucleation *in situ* self-repair to prepare rollable large-area ultrathin MOF membranes. *Adv. Mater.* 35, e2307013. doi:10.1002/adma.202307013
- Yusof, N. F., Mehamod, F. S., and Mohd Suah, F. B. (2019). Fabrication and binding characterization of ion imprinted polymers for highly selective Co<sup>2+</sup> ions in an aqueous medium. *J. Environ. Chem. Eng.* 7, 103007. doi:10.1016/j.jece.2019.103007
- Zabolotsky, V. I., Achoh, A. R., Lebedev, K. A., and Melnikov, S. S. (2020). Permselectivity of bilayered ion-exchange membranes in ternary electrolyte. *J. Memb. Sci.* 608, 118152. doi:10.1016/j.memsci.2020.118152
- Zante, G., Boltoeva, M., Masmoudi, A., Barillon, R., and Trébouet, D. (2020). Highly selective transport of lithium across a supported liquid membrane. *J. Fluor. Chem.* 236, 109593. doi:10.1016/j.jfluchem.2020.109593
- Zavahir, S., Riyaz, N. S., Elmakki, T., Tariq, H., Ahmad, Z., Chen, Y., et al. (2024). Ion-imprinted membranes for lithium recovery: a review. *Chemosphere* 354, 141674. doi:10.1016/j.chemosphere.2024.141674
- Zhang, C., Mu, Y., Zhang, W., Zhao, S., and Wang, Y. (2020). PVC-based hybrid membranes containing metal-organic frameworks for Li<sup>+</sup>/Mg<sup>2+</sup> separation. *J. Memb. Sci.* 596, 117724. doi:10.1016/j.memsci.2019.117724
- Zhang, X.-C., Wang, J., Ji, Z.-Y., Ji, P.-Y., Liu, J., Zhao, Y.-Y., et al. (2021). Preparation of Li<sub>2</sub>CO<sub>3</sub> from high Mg<sup>2+</sup>/Li<sup>+</sup> brines based on selective-electrodialysis with feed and bleed mode. *J. Environ. Chem. Eng.* 9, 106635. doi:10.1016/j.jece.2021.106635
- Zhang, J., Gao, Q., Han, B., and Zhou, C. (2024). Mechanism of lithium ion selectivity through membranes: a brief review. *Environ. Sci. Water Res. Technol.* 10, 1305–1318. doi:10.1039/D3EW00769C
- Zhang, Y., Hao, Z., Hussein, I., Wang, Z., and Zhao, S. (2024). Tunable ionic sieving membrane *via* reactive layer-by-layer assembly of porous organic cages. *Adv. Funct. Mater.* 34, 2315750. doi:10.1002/adfm.202315750
- Zhang, H., Zhang, J., Wang, D., Fan, H., Xu, Y., Zhao, F., et al. (2025). Advances in metal organic framework-based membranes for ion-selective sieving. *Sep. Purif. Technol.* 374, 133623. doi:10.1016/j.seppur.2025.133623
- Zhao, Z., Liu, G., Jia, H., and He, L. (2020). Sandwiched liquid-membrane electrodialysis: lithium selective recovery from salt lake brines with high Mg/Li ratio. *J. Memb. Sci.* 596, 117685. doi:10.1016/j.memsci.2019.117685