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Ion-imprinted membranes for lithium recovery: A review

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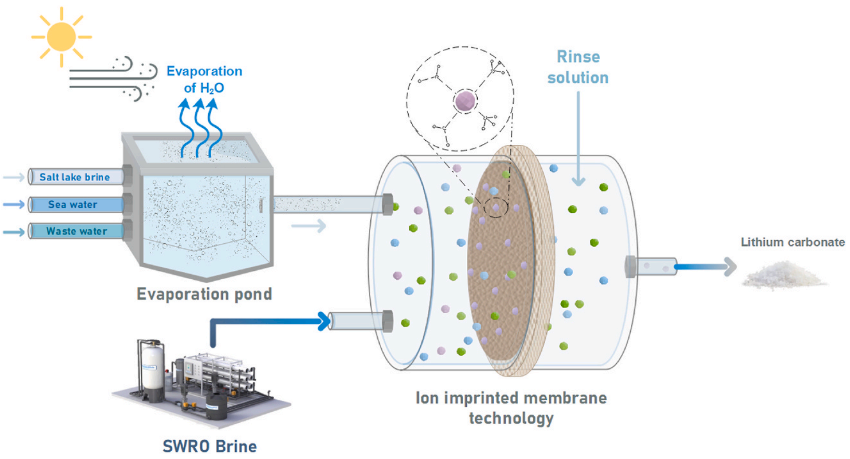
HIGHLIGHTS

- MST-based IIMs: Promising for scalable Li recovery.
- Investigates maximum Li + adsorption of 157 mg g^{-1}.
- Calls for refining IIM synthesis for higher capacity.
- Suggests bespoke monomers for targeted Li^+ capture.
- Highlights IIMs' potential in heavy metal recovery.

GRAPHICAL ABSTRACT



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ABSTRACT

This review critically examines the effectiveness of ion-imprinted membranes (IIMs) in selectively recovering lithium (Li) from challenging sources such as seawater and brine. These membranes feature customized binding sites that specifically target Li ions, enabling selective separation from other ions, thanks to cavities shaped with crown ether or calixarene for improved selectivity. The review thoroughly investigates the application of IIMs in Li extraction, covering extensive sections on 12-crown-4 ether (a fundamental crown ether for Li), its

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Recovery
Ion-imprinted membrane (IIM)

modifications, calixarenes, and other materials for creating imprinting sites. It evaluates these systems against several criteria, including the source solution's complexity, Li^+ concentration, operational pH, selectivity, and membrane's ability for regeneration and repeated use. This evaluation places IIMs as a leading-edge technology for Li extraction, surpassing traditional methods like ion-sieves, particularly in high Mg^{2+}/Li^+ ratio brines. It also highlights the developmental challenges of IIMs, focusing on optimizing adsorption, maintaining selectivity across varied ionic solutions, and enhancing permselectivity. The review reveals that while the bulk of research is still exploratory, only a limited portion has progressed to detailed lab verification, indicating that the application of IIMs in Li^+ recovery is still at an embryonic stage, with no instances of pilot-scale trials reported. This thorough review elucidates the potential of IIMs in Li recovery, cataloging advancements, pinpointing challenges, and suggesting directions for forthcoming research endeavors. This informative synthesis serves as a valuable resource for both the scientific community and industry professionals navigating this evolving field.

1. Introduction

Lithium (Li), the lightest metal with high electrochemical activity (Pramanik et al., 2020), is a critical component in various industries due to its unique properties, such as the highest specific heat capacity among metals. Li is essential in making lithium oxide (Li_2O) for glassmaking (Battistel et al., 2020), lithium carbonate (Li_2CO_3) for ceramics, and plays a significant role in the manufacturing of alloys, lubricants, and predominantly, lithium-ion batteries (Stringfellow and Dobson, 2021). Li's role is underscored by its booming demand in the electric vehicle market, which nearly doubled its share from 4.11% in 2020 to 8.57% in 2021 (Lambert, 2022), showcasing its versatility and significance.

Despite a 12% rise in Li production, consumption outpaced this with a 16% increase, resulting in a supply shortfall (European Commission, 2023; Mauk et al., 2021; Swain, 2018). As a reactive alkali metal, Li is abundant but not found in a free state; it is bound in minerals like lepidolite, petalite, spodumene, and in brines and seawater (Barbosa et al., 2023). However, the cost and complexity of current extraction and refining processes have prevented their widespread use, straining the market's ability to satisfy increasing demands (Hyun et al., 2020).

Li is recognized as a green energy metal, instrumental in transitioning from fossil fuels through its use in Li-ion battery technology. However, extracting it from solid and liquid reserves presents both technical and environmental hurdles. Improving recovery methods for better Li yields is critical. Given current trends, the industry anticipates a substantial deficit, ranging from 400,000 to 1.5 million tons annually by 2030. Therefore, investing in the production and refinement of Li has become increasingly vital (Zavahir et al., 2021).

Li is sourced from solid materials such as ores and clays, as well as liquid sources including brine, seawater, and oil fields. The industry primarily uses salt lake brine, geothermal brines, and spent Li electrolytes among liquid sources (Choubey et al., 2016; Zavahir et al., 2021). In particular, continental brine constitutes 59% of the global Li reserves (Krebs, 2006; Swain, 2017). Geothermal brine, found deep underground, contains Li at 10–20 mg L^{-1}, while surface-located salt lake brine has higher concentrations of 100–1000 mg L^{-1}. Although seawater holds about 230 billion tons of Li, its low concentration range of 0.1–0.2 ppm makes extraction economically unfeasible (Choubey et al., 2016; Grosjean et al., 2012; Li et al., 2018). Current research, therefore, focuses more on extracting Li from salt lake brine, as geothermal brine poses challenges due to the presence of other cations.

Diverse technologies exist for extracting and refining Li from salt lake brine, crucial for producing industrially valuable compounds. The main challenge in this process is the separation of Li from other cations, particularly Mg^{2+}, where the Mg^{2+}/Li^+ ratio often reaches 40 and can exceed 200 in certain cases (Song et al., 2017). Techniques range from traditional ones like solar evaporation, liquid-liquid extraction, and precipitation to more modern, promising methods.

1.1. Existing technologies for Li recovery from liquid resources

Solar evaporation, a conventional method for lithium recovery, leverages solar energy but is a lengthy procedure. Particularly effective in arid regions, it is energy-intensive and poses risks of soil and groundwater pollution. The precipitation method focuses on chemical precipitation, producing Li as either aluminate or carbonate salt when reacted with aluminum chloride or sodium carbonate, respectively (Zavahir et al., 2021). Its limitations emerge with high Mg^{2+}/Li^+ ratio brines, and despite its industry prevalence, it is resource-intensive, leading to significant waste. Liquid-liquid extraction, often termed solvent extraction, is adept at selectively isolating Li from other cationic mixtures using chelating agents. Yet, it is best studied for brines with low Mg^{2+}/Li^+ ratios. A major drawback is its dependence on substantial volumes of organic solvents, potentially inflicting environmental harm that outweighs the extraction benefits.

Recent Li recovery methodologies are categorized into three main types: membrane-based, electrochemical, and hybrid electro-membrane processes. Membrane-based strategies offer straightforward, continuous operation with lower energy demands, which are environmentally favorable (Li et al., 2019). They include methods like nanofiltration (NF), membrane distillation (MD) or crystallization (MDC), ion-sieve membrane (ISM), supported liquid membrane (SLM), and ion imprinted membrane (IIM). Hybrid techniques combine membranes with electrodes, such as in selective electrodialysis and capacitive deionization, to direct ion movement. Electrochemical processes, despite being newer, are gaining traction for their efficiency in Li capture (Zavahir et al., 2021), leveraging selective electrodes and the electric field between them to direct ion movement in solutions (Campione et al., 2018). Recent molecular dynamics simulations indicated that nanoporous graphene or graphyne electrodes, even without a selective electrode, can achieve high Li selectivity in mixed ion brines due to the optimal pore size facilitating Li ion association and dehydration, as well as the reverse migration of competing ions like Mg^{2+}, when subjected to an electric field of 0.2–0.4 V nm^{-1} (Li et al., 2022; Liao et al., 2022, 2023).

Among the membrane-based technologies, MD is a thermally driven process using a porous, hydrophobic membrane to allow only vapor molecules through, concentrating Li but requiring additional steps for isolation due to multi-ion presence. MD's main challenges are membrane fouling and the high energy required for heating. Conversely, NF utilized charged membranes, with positively charged ones proving more effective in Li recovery from complex multivalent solutions (Li et al., 2015). NF leverages steric properties and the Donnan exclusion principle, allowing selective passage of monovalent cations. (Gong et al., 2018). While widely applied across industries, NF faces issues with high salt solutions leading to increased viscosity and concentration polarization, affecting flux (Li et al., 2017). Despite this, NF is notable for large-scale potential, like MD. Both technologies, contend with membrane fouling, impacting permeability and selectivity (Somrani et al., 2013). Nevertheless, MD and NF are favored for their eco-friendly and sustainable approaches with minimal environmental impact. A summary of these Li recovery methodologies and their insights is presented in Table 1.

Li adsorption by ion sieve membrane operates on the intercalation principle, with notable membranes fabricated by grafting spinel-type $MnO_2{\cdot}xH_2O$ (where x varies) onto matrices like poly vinyl chloride (PVC) or polyvinylidene fluoride (PVDF) (Chung et al., 2008; Ji et al., 2012). Initially, ion sieve materials were tested by stacking crushed inorganic adsorbents in a column, but this proved inefficient due to material loss and pressure drop. Ion-sieve membrane have since demonstrated ineffectiveness in separating Li from solutions with Na^+ and Mg^{2+}, achieving separation factors of 454 and 4555, respectively (Zhu et al., 2014). This efficiency is partly due to larger free energy of hydration required by these coexisting ions, which limits their access to adsorption sites. Although this method offers high selectivity and chemical stability, its industrialization is hindered by issues like extractant leakage during prolonged operation.

Supported liquid membranes (SLM) are known for their low energy consumption and reduced heat generation compared to traditional liquid-liquid extraction (Maximini et al., 2006). In SLM, Li ions move from an aqueous feed phase to an aqueous stripping phase via an intervening organic phase. Various extractants, such as α-acetyl-*m*-dodecylacetophenone, tri-octyl phosphine oxide, di-2-ethyl hexyl phosphoric acid, tri-*n*-butyl phosphate and 1-alkyl-3-methylimidazolium hexafluorophosphate, have been used in different studies to form effective lipophilic metal-organic ligand species (Gao et al., 2018; Ma et al., 2000; Sharma et al., 2016). Research in this area focuses on enhancing long-term stability and solvent resistance, although solvent leakage remains a significant challenge.

IIM, synthesized from ion-imprinting polymer (IIP), exhibits a high affinity for specific template molecules over structurally similar ones. IIM has been widely used for recovering resources such as alkali metals, heavy metals, and rare earth metals, including Cd^{2+} and As^{3+} (Liu et al., 2011; Qiu et al., 2023). The Li^+-templated IIM technology, in particular, has attracted considerable attention for Li capture. Common functional monomers in IIMs include crown ether and calixarenes (Cui et al., 2018a; Sun et al., 2022), known for forming stable metal chelate complexes with Li ions due to their electron-rich cavities. The crown ring in crown ether and the cup-like structure of calixarene closely match the size of Li ions, leading to high selectivity for Li^+ over Na^+, Mg^{2+}, K^+ and Ca^{2+}. This results in efficient Li^+ extraction (He et al., 2022; Yang et al., 2022). While IIMs demonstrate notable separation performance with high selectivity and stability, challenges in membrane regeneration, primarily due to fouling and associated costs, persist (Cui et al., 2019; Luo et al., 2015).

1.2. *Highlighting the need for ion-imprinted membranes (IIMs)*

Current Li recovery methods using membrane-based technologies face challenges including membrane fouling, high energy requirements, and inefficiencies in high Mg^{2+}/Li^+ ratio environments, as shown in Fig. 1. Hence, the development of a more effective system is essential. Fig. 2 shows that IIMs have been less investigated than other methods. Therefore, a in-depth examination of IIM materials, with a focus on the selective recovery of Li, is vital to gauge their effectiveness and potential for overcoming the issues prevalent in other membrane technologies. This discussion draws on research from the last decades to assess the readiness of IIMs for larger scale use, offering a detailed review of the advancements in IIM research and their prospective applications, while also identifying current hurdles and opportunities for enhancement in this nascent area, particularly relevant to Li extraction.

Unlike other reviews on Li recovery from liquid media that may only briefly mention IIMs among a wider array of membrane processes (Li et al., 2019), concentrate on size-exclusion methods like metal-organic frameworks (Hou et al., 2021), focus on separating Mg^{2+}/Li^+ as part of broader alkali and alkaline earth metal separation (Sun et al., 2021; Wang et al., 2021), or limit their scope to specific regional case studies (Liu et al., 2019; Xu et al., 2021), this review aims to be the basis for new researchers specializing in Li^+ separation with IIMs. It provides critical insights into tailoring new membrane materials by focusing on crucial factors such as adsorption efficiency, multi-ion solution selectivity, permselectivity, and the ability to regenerate.

2. Ion-imprinted membranes (IIMs)

Ion-imprinted membranes (IIMs) integrate the advantages of porous membrane technology with ion imprinting to selectively separate ions. While membranes have long been used as separation mediums, it is the nanofiltration membrane, which operates on principles such as Donnan exclusion, dielectric exclusion, and steric hindrance, that has advanced sufficiently for commercial-scale Li recovery. Despite its maturity, it is plagued by issues like membrane fouling and related high operation and maintenance costs. The concept of ion-imprinting, inspired by the selective nature of interactions between natural receptors and ligands in biological systems, paved the way for the development of ion-imprinted polymers (IIP). Within IIMs, these IIPs are anchored onto porous

Table 1
Literature highlights of existing membrane-based technologies.

Entry	Technology	Working principle	TRL	adsorption capacity/mg g^{-1}	Pros	Cons	Ref
1	Nanofiltration	Donnan exclusion, steric hindrance	full	0.1–40.9	low carbon footprint	high operational cost due to membrane fouling	(Bi and Xu, 2018; Bi et al., 2014; Guo et al., 2016; Somrani et al., 2013)
2	supported liquid membrane	solvent impregnation assisted selective transport of ions across a membrane	laboratory	1.1–36.2	low carbon footprint, high adsorption capacity and selectivity	use of large volumes of organic solvents and chemical reagents to assist recovery	(Lozano et al., 2011; Ma et al., 2000; Song et al., 2014; Swain et al., 2007)
3	ion-sieve membrane	selective adsorption of ions by intercalation	laboratory	10.3–58.58	high adsorption capacity and selectivity, enhanced chemical stability	use of reagents for desorption, leaching of ion sieve material lowering long term use	(Ji et al., 2012; Park et al., 2016; Saravaia et al., 2016; Zhu et al., 2014)
4	ion-imprinted membrane	selective adsorption of ions by chelation	laboratory	3.4–231.77	high adsorption capacity and selectivity	membrane fouling, use of acids/reagents for desorption	(Cui et al., 2018a, 2018b, 2019; Sun et al., 2017, 2018, 2022)
5	selective electrodialysis	ion transport driven by potential gradient	pilot	95%[a]	high selectivity for monovalent ions	membrane fouling	(Chen et al., 2018; Hoshino, 2013; Ji et al., 2017; Nie et al., 2017)
6	membrane distillation crystallization	ion transport driven by vapor pressure gradient across hydrophobic membrane	pilot	90%[a]	produces salt rich brine and fresh water in either side	membrane fouling promoted membrane wetting (loss of hydrophobicity)	(Quist-Jensen et al., 2016a, 2016b, 2016c)

[a] - Li^+recovery as a percentage.

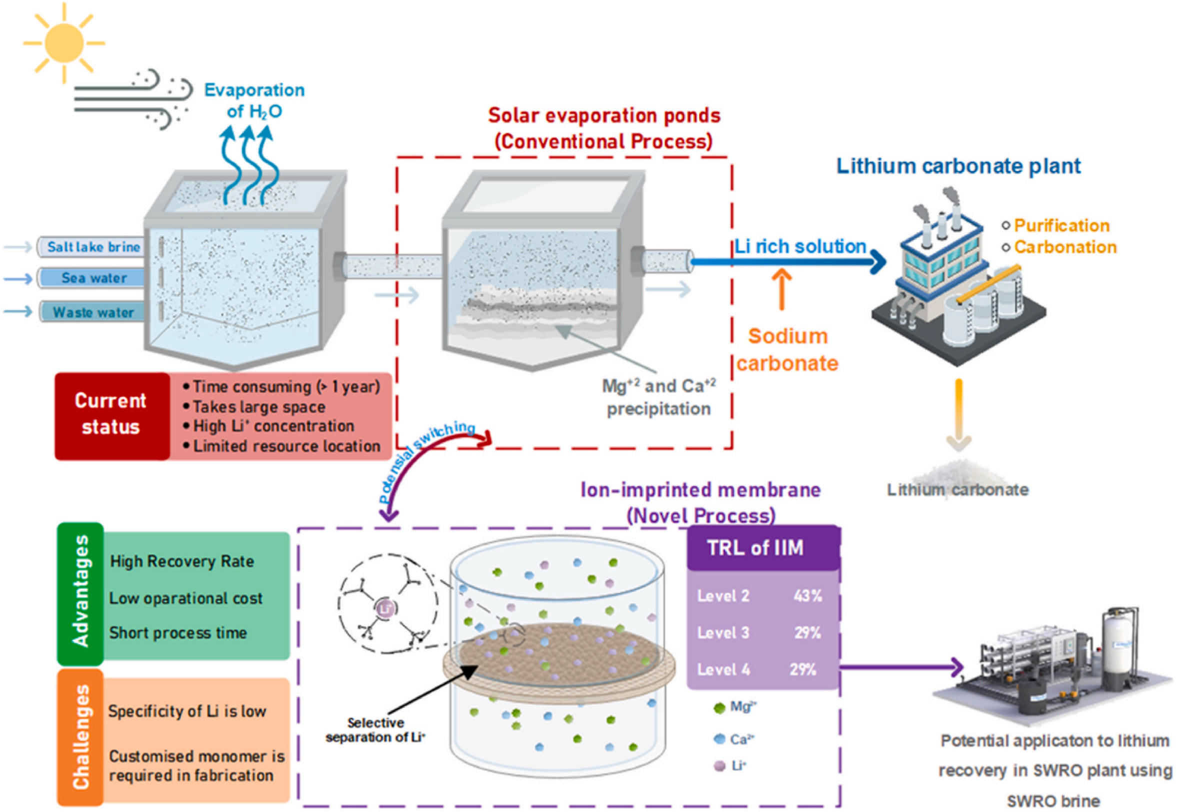

Fig. 1. Comparison summary of Li extraction using conventional solar evaporation versus a system utilizing IIM, including the advantages and disadvantages.

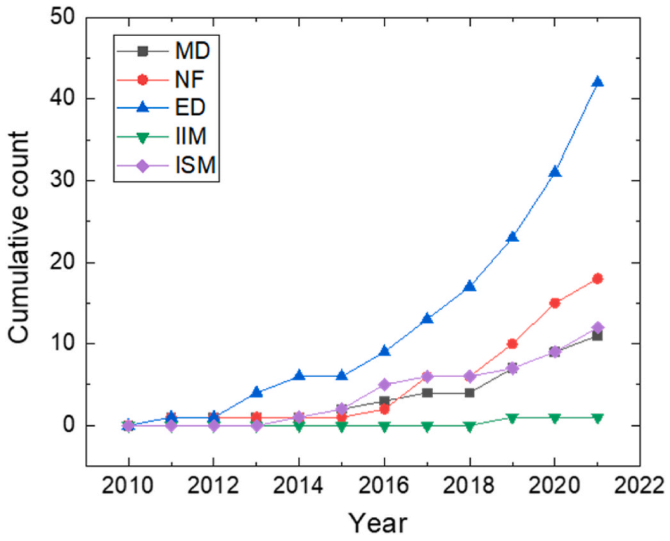

Fig. 2. A visual representation of the cumulative increase in research papers on Li recovery techniques, shown through a keyword search. Abbreviations refer to membrane distillation (MD), nanofiltration (NF), electrodialysis (ED), ion-imprinted membranes (IIM), and ion-sieve membranes (ISM).

polymeric membrane surfaces, enhancing sturdiness, reusability, and surface area. IIM fabrication typically involves a two-step (sometimes one-pot) process: first, synthesizing the IIP by crosslinking a templated ion with a ligand using a crosslinking agent, followed by embedding or grafting this IIP into a membrane matrix. This involves polymerizing the membrane monomer with IIP and an initiator. It is noteworthy that the term "functional monomer" has been inconsistently used in literature-sometimes referring to the ligand and other times to the matrix monomer. The careful selection of these components is pivotal, as it governs the membrane's selectivity and specificity.

The template ion, sometimes known as the target ion, is pivotal in the membrane's design. Once removed from the membrane matrix, it leaves an imprinted cavity tailored to selectively recognize and bind its counterpart during operation, forming a chelate. Due to this synthesis approach, IIMs are considered a highly promising solution for selective adsorption of metals in aqueous solutions. Their inherent high selectivity ensures efficient ion recognition and facilitate easy mass transfer (Xu and Guo, 2012).

2.1. Components of IIMs

2.1.1. Template molecule

The fundamental requirement for synthesizing any type of imprinted membrane is the presence of a template molecule or ion, in this case Li^+. The template molecule results in the creation of complementary specific recognition sites in the membrane matrix. It is essential to remove the template molecule from the membrane, as its presence reduces the number of rebinding sites in the matrix and negatively impacts recognition performance and efficiency (Donato and Drioli, 2021; Lorenzo et al., 2011; Madikizela et al., 2018).

The synthesis of IIMs is based on two main interactions (Sellergren et al., 1988; Wulff, 1995): covalent and non-covalent binding. Covalent bonds are found between the template molecules and functional groups of the membrane matrix molecules. Non-covalent interactions (Sellergren et al., 1988) are more commonly utilized in synthesis procedures as the weak chemical interactions make it easier to remove the template molecule from the membrane matrix once the synthesis and recognition process is completed (Alexander et al., 2006; Sellergren et al., 1988; Yan and Kyung, 2006). The earliest reported syntheses in 1949 used methanol extraction to remove templated ions. However, synthesis procedures have evolved since then and offer several physical or chemical pathways for removing the membrane matrix.

2.1.2. *Functional monomer*

Functional monomers play a critical role in the assembly of membranes, as the assembly is significantly impacted by the interaction between the template ion and functional groups of the functional monomer. The selection of functional monomers is based on three criteria (Lu et al., 2019). Firstly, the functional monomer must have functional groups that can interact with the template ion, either through covalent or non-covalent interactions. Secondly, the functional groups on the functional monomer must not impede the polymerization of the membrane. And thirdly, the functional monomer must have excellent chemical stability during polymerization. Additionally, the size and charge of the template ion must match the specific binding capability of the functional monomer. For example, when recovering Li^+ with IIMs, crown ethers are a popular choice for functional monomers as their size complements Li ions.

2.1.3. *Crosslinking agent*

The role of crosslinking agents in the synthesis of IIMs is to ensure the stability of three-dimensional structures formed through the interaction between template ions and functional monomers (Lu et al., 2019). The choice of crosslinking agents is critical to the adsorption performance of the IIM. Care must be taken to ensure that the right amount of crosslinking agent is used, as either too little or too much can negatively impact the selectivity and performance of the IIM. The insufficient crosslinking agent can result in unstable mechanical properties and defective recognition sites, reducing the selectivity of the IIM. Conversely, the excessive crosslinking agent can lead to reduced flexibility in the IIM framework, decreased mass transfer performance, and reduced recognition sites, negatively impacting the rate and efficiency of adsorption.

2.2. *Fabrication technique of ion-imprinted polymers (IIPs)*

The synthesis of any type of IIMs involves filling the IIPs with customized recognition sites for the target ions. Depending on the synthesis process, IIMs can be divided into four main categories: filled IIMs, free-standing IIMs, hybrid IIMs, and composite IIMs, as shown in Fig. 3.

2.2.1. *Filled IIMs*

Filled IIMs, modeled after packed chromatographic column, are the simplest form of IIMs. They consist of terminal filler plates and IIPs sandwiched between them. While they offer versatile applications, including the simultaneous separation of multiple ions (Yoshikawa et al., 2016), their development has been limited in recent years. This is primarily due to the synthesis method, which requires grinding IIPs and risks destroying their ion recognition sites (Lu et al., 2019).

2.2.2. *Free-standing IIMs*

Unlike filled IIMs, free-standing IIMs are composed solely of crosslinked IIPs, eliminating the need for terminal filler plates (Yoshikawa et al., 2016). Their membrane-like structure is formed by mixing IIPs in a dispersed phase to create a casting solution (Kiełczyński and Bryjak, 2005). Various techniques like immersion precipitation, solvent removal, or polymerization can then be employed to produce the final membrane (Luo et al., 2023).

2.2.3. *Hybrid IIMs*

Hybrid IIMs are a variant of filled IIMs that incorporate both substrates and fillers to improve stability and simplify synthesis. IIPs are first synthesized and then mixed into the casting solution (Xu et al., 2012). Membranes are subsequently formed using methods like phase inversion. Although the grinding of IIPs may compromise ion recognition sites, the ease of preparation make hybrid IIMs a subject of ongoing research and application (Huang et al., 2017).

2.2.4. *Composite IIMs*

Composite IIMs feature a substrate membrane coated with a layer of IIPs. These are synthesized through *in situ* polymerization, grafting, or coating, offering a high degree of exposure to ion-imprinted recognition sites (Fu et al., 2015). They excel in adsorption capacity and selectivity for the target ion. The synthesis process is customizable and can be multi-staged (Chen et al., 2012), providing versatile membrane properties. Despite their advantages, composite IIMs have been less intensively researched than other types (Chen et al., 2012).

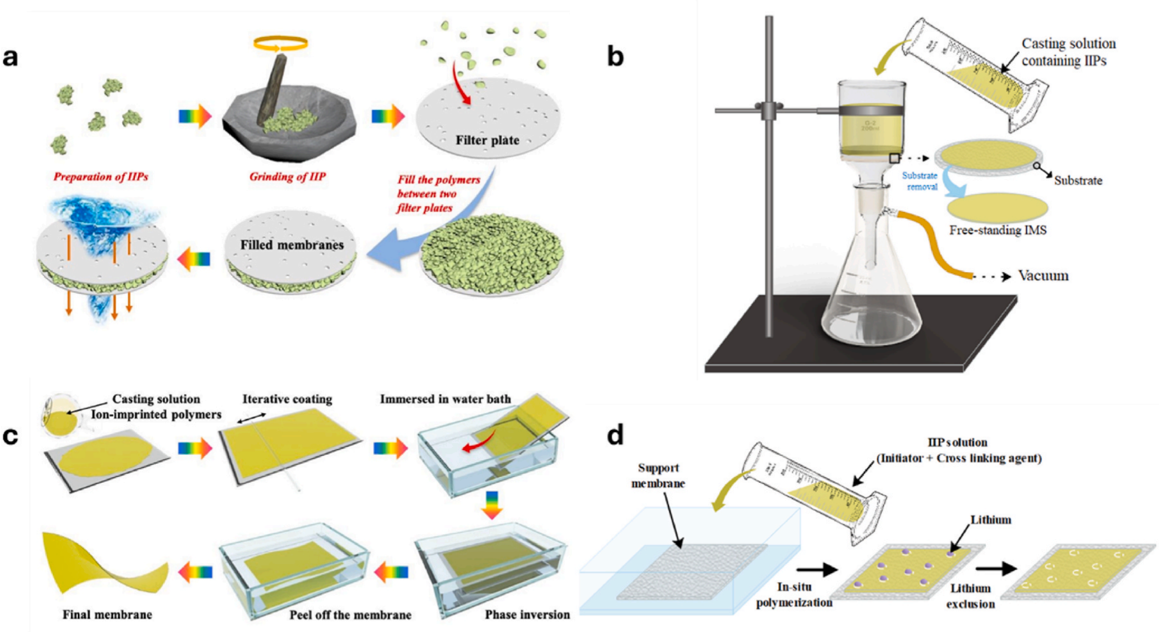

Fig. 3. Construction methods for various types of IIMs: (a) filled IIMs (reprinted from (Lu et al., 2019)), (b) free-standing IIMs, (c) hybrid IIMs (reprinted from (Lu et al., 2019)), and (d) composite IIMs.

2.3. Synthesis methods and working principle of IIMs

Multiple methods are used to synthesize IIMs, as illustrated in Fig. 4a and **4b,** which depict the general synthesis procedure and the Li adsorption/desorption cycle. Sun et al., (2017) used surface-imprinted polymerization for membrane fabrication. They prepared the functional monomer with overnight stirring, neutralization with methanol, and extraction via dichloromethane. The IIM was then synthesized by introducing a complexing agent, such as 12-crown-4-ether (12C4E) or its derivative, into a LiCl methanol solution, followed by refluxing in a nitrogen atmosphere. The Li^+ ions were subsequently eluted using 0.5 M HCl.

Surface-imprinted polymerization is advantageous for its efficient utilization and increase of adsorption sites. Improving this method, Huang et al. (2017) utilized dibenzo14-crown-14 (DB14C4), carbon nanotubes, and methacrylic acid to create Li-IIPs. Alternatively, suspension polymerization is another prevalent technique, where monomers, cross-linkers, and initiators undergo bulk polymerization into a dispersed phase (Lu et al., 2019), aided by continuous stirring and stabilizers to maintain the suspension, ensuring the stable development of the IIM structure.

2.4. Performance assessing parameters

IIMs performance is primarily gauged by two key metrics: adsorption capacity and selectivity. While both are important, selectivity takes precedence as it directly impacts the efficiency of the membrane system. Adsorption capacity, represented by Q_e, indicates the total number of adsorption sites, both specific and non-specific. This parameter can be calculated using Eq (1) (Lin et al., 2015; Lu et al., 2018, 2019).

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of Li^+ respectively, V is the solution volume in mL, and m is the mass of the membrane in mg.

The imprinting factor (α) quantifies the affinity between the imprinted polymer and the template molecule (Nantasenamat et al., 2007). It is calculated as the ratio of the retention factor (k') for imprinted (IIP) and non-imprinted (NIP) membranes as follows:

$$\alpha = \frac{k'_{IIP}}{k'_{NIP}} \tag{2}$$

To assess real-world applicability, especially in handling Li-containing liquid resources like seawater, salt lake brine, desalination brine, or leachate from Li based manufacturing plant (spent Li ion battery industry), several other parameters are examined. Thes include the distribution coefficient of Li (K_d, in mL g^{-1}), selectivity in the presence of other ions ($K_{Li/M}$), and relative selectivity (K').

$$K_d = \frac{(C_o - C_e)V}{C_e m} \tag{3}$$

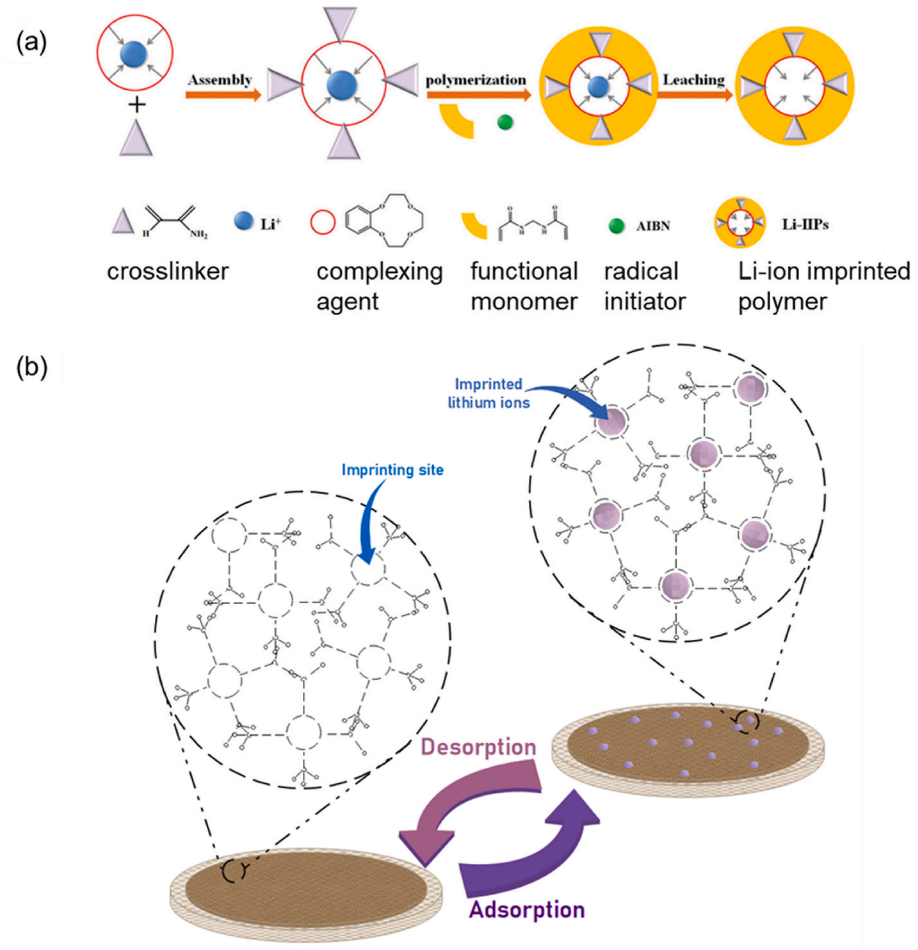

Fig. 4. A schematic of (a) general synthetic protocol for Li-IIM (reprinted from (Cui et al., 2018b)). (b) Representation of the Li adsorption-desorption mechanism of IIMs.

$$K_{Li/M} = \frac{K_{d(Li)}}{K_m} \tag{4}$$

The kinetics of Li adsorption over time are also analyzed to determine the mechanism, be it pseudo first-order or second-order. The adsorption at a specific time, (t) is given by:

$$Q_t = \frac{(C_o - C_t)V}{m} \tag{5}$$

Here, Q_t is adsorption at time t. and C_t is the Li concentration at that time. While selectivity is key in assessing an IIM's performance, permeability is equally crucial for effective Li recognition. Standard permeation tests were conducted using a U-shaped device with tubular compartments with the membrane placed at the right middle. One tube contains a multi-ion solution while the other holds an equal volume of deionized water. Parameters like permeation flux (J, mg cm^{-2} h^{-1}), permeability coefficient (P, cm^2 s^{-1}), and permselectivity factor (β) are derived using the following equations:

$$J_i = \frac{\Delta C_i\ V}{\Delta t\ A} \tag{6}$$

$$P_i = \frac{J_i\ d}{C_{Fi} - C_{Ri}} \tag{7}$$

$$\beta = \frac{P_i}{P_{Li}} \tag{8}$$

These matrices are based on concentration data gathered at specific time intervals, typically analyzed through methods like inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or flame atomic absorption spectrometry (FAAS). Here, ΔC_i (mg L^{-1}) represents the concentration change of ion i in the receiving solution, A (cm^2) and d (cm) denote the effective membrane area and thickness, respectively, and V (mL) is the volume of receiving solution. C_{Fi}-C_{Ri} (mg L^{-1}) is the concentration difference of ion 'i' between the feeding and receiving solutions.

3. Case study discussions

Extensive research has been conducted on various aspects of ion-imprinted systems, as shown by numerous studies (Chitrakar et al., 2000, 2014; Cui et al., 2018b; Donato and Drioli, 2021; He et al., 2015; Huang et al., 2017; Jang and Chung, 2019; Liu et al., 2020a; Sato et al., 1997; Sellergren et al., 1988; Xu et al., 2016). The effectiveness of the membrane's adsorption capacity is influenced significantly by key factors such as the synthesis method, imprinting factor, and the choice of base polymer. For enhanced improve clarity and ease of reading, discussions on IIM systems developed for Li's selective recovery are organized into subsections based on the chelating agents used to form the imprinted sites.

3.1. 12-Crown-4-ether (12C4E) as chelating agent

Most ion-imprinted systems for Li recovery primarily use 12-crown-4-ether (12C4E) due to its size compatibility with Li$^+$ ions, facilitating the creation of tailor-made recognition sites. These membranes operate by selectively binding and rebinding Li$^+$ through chelation, and the ease of forming such chelates directly impacts the process efficiently. For example, Cui et al. (2018b) employed 12C4E as the complexing agent and acrylamide as the base polymer to create a wide-surface IIM. The membrane was synthesized using precipitation copolymerization, with *N,N′*–methylene bis-acrylamide (MBAM) serving as the crosslinking agent. An uncommon choice, $LiClO_4$, was used as the template ion during fabrication. The resulting membrane showcased an impressive adsorption capacity of 7.83 mg g^{-1} in a 60-mg L^{-1} Li $^+$ solution at pH 9, significantly outperforming non-imprinted membranes. This superior performance is attributed to the greater number of effective recognition sites formed during the polymerization of Li-IIP.

The study examined pH's influence on adsorption, revealing an increasing trend within the pH range of 4–9, as shown in Fig. 5a. This is attributed to the preferential binding of Li$^+$ in the engineered receptor sites. Lower pH levels result in competition between H$^+$ and Li$^+$ ions, reducing Li$^+$ attachment. Temperature also affects adsorption, showing an optimal rate at 30 °C (Fig. 5b). Above this, the adsorption decreases, likely because the Li-IIP complex becomes unstable at higher temperatures. These findings underscore the importance of both the membrane's thermal stability and that of the chelate in determining the IIM's industrial-scale operating temperature.

The IIM displayed high selectivity for Li over other ions like Na, K, Cu, and Zn: their respective selectivity values were $K_{Li/Na} = 5.34$, $K_{Li/K} = 6.47$, $K_{Li/Cu} = 23.05$, $K_{Li/Zn} = 27.13$. Additionally, the membrane retained its adsorption capacity across six reuse cycles when regenerated with 0.5 M HCl, as indicated in Fig. 5c.

The same research group explored another Li-IIM, utilizing 12C4E ligand and incorporating polydopamine in the interlayer with a graphene oxide-modified PVDF matrix, created through hydrolysis polymerization (Cui et al., 2018a). The polydopamine interlayer enhanced binding site availability, due to its catechol, amine, and imine surface groups. This design yielded a high adsorption capacity of 27.10 mg g^{-1} for a 50-mg L^{-1} Li $^+$ solution at pH 6. Adsorption decreased below pH 3 due to the protonation of the 12C4E's oxygen groups, limiting available Li$^+$ binding sites.

Adsorption behavior followed a Langmuir model, suggesting monolayer coverage (Fig. 5d), and confirmed a pseudo second-order rate model, indicating chemical adsorption as the dominant mechanism (Fig. 5e). In multi-ion solutions, the membrane showed high selectivity, as evidenced by separation factors like $K_{Li/K} = 5.38$, $K_{Li/Ca} = 21.94$, and $K_{Li/Mg} = 15.56$ (Fig. 5f). The membrane also demonstrated good regenerative capacity across 6 cycles, with a minor 8.2% reduction in capacity compared to the first cycle when regenerated with 1 M HCl.

In another study, Lu et al. used 12C4E and methacrylic acid (MAA) to fabricate a multilayered IIM featuring a polydopamine interfacial with a SiO_2 layer and a polyether sulfone (PES) matrix (Lu et al., 2018). The Li$^+$ template ions were introduced using LiCl. PES was selected as the backbone for its beneficial properties like high porosity and pressure resistance. When tested with a 50 mg L^{-1} LiCl solution at pH 9, the membrane showed its peak adsorption capacity of 27.55 mg g^{-1}. Evaluation of isothermal and kinetic behavior revealed conformity with the Langmuir isotherm and a pseudo-second-order rate constant, indicating that both physical diffusion and chemisorption contribute to adsorption mechanism. The membrane demonstrated notable reusability, maintaining 88.1% of its original activity across 10 cycles. However, its multi-layered structure seemed to compromise ion selectivity, as evidenced by low separation factors: $K_{Li/Na}$ at 1.85 and $K_{Li/K}$ at 2.07.

Cui et al. explored the fabrication of an eco-friendly, Li-selective IIM using a biodegradable matrix of cellulose acetate and chitosan, along with 12C4E as the complexing agent (Cui et al., 2019). The membrane featured a polydopamine interlayer anchored to TiO_2, which introduced nanochannels with surface hydroxyl groups to enhance antifouling properties. Tested with 100-mg L^{-1} Li $^+$ source solution, the membrane demonstrated a solid adsorption capacity of 20.08 mg g^{-1}. Additionally, the membrane retained 93% of its adsorption capacity over six regeneration cycles, using 0.01 M HCl for elution. Permselectivity tests (Fig. 6a and **b**) indicated that the separation mechanism is primarily driven by retarded permeation (Fig. 6c). As for its isothermal and kinetic behavior, the membrane conformed to Langmuir isotherm and a pseudo-second-order kinetic model, like most IIMs. While the membrane did show selectivity for Li over other ions, the separation factors were relatively low: $K_{Li/Na} = 1.78$, $K_{Li/K} = 2.43$, $K_{Li/Mg} = 2.60$, and $K_{Li/Ca} = 3.61$. The key advantage of this membrane, however, lies in its sustainable and straightforward fabrication process.

Yang et al. investigated an IIM prepared with 12C4E and TiO_2-incorporated PVDF, bypassing the need for a PDA interlayer (Yang et al.,

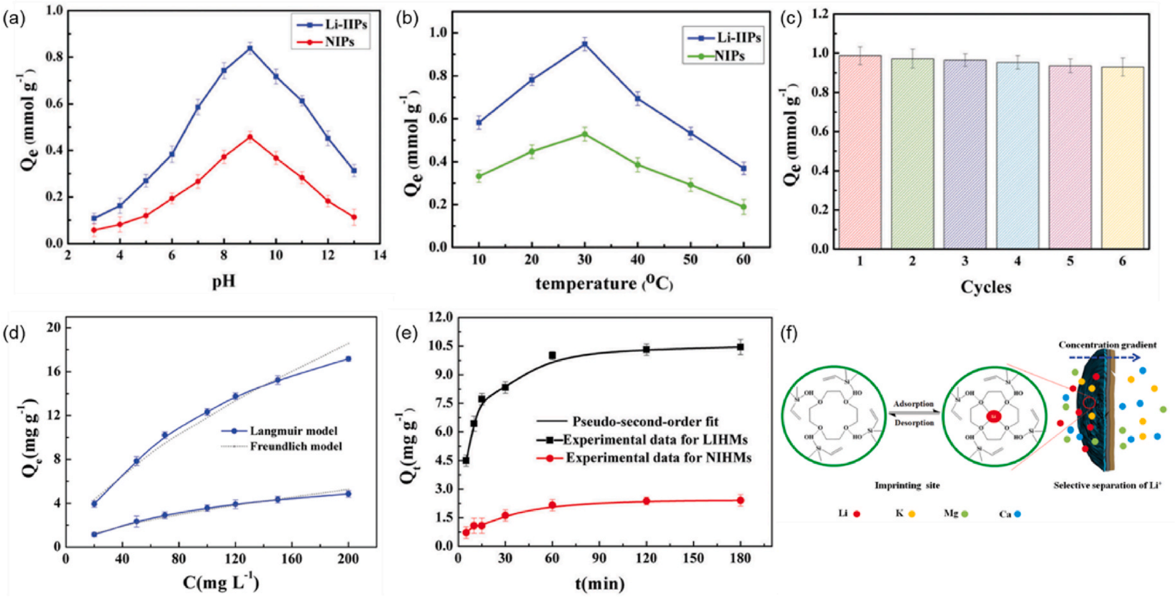

Fig. 5. (a) pH influence on the adsorption capacity (Q_e), (b) temperature effect on Q_e and (c) Q_e change with cycling of 12C4E/polyacrylamide IIM system (reprinted from (Cui et al., 2018b)). (d) Langmuir and Freundlich model fitting, (b) kinetic model fitting and (f) ion transfer mechanism of 12C4E/GO/PVDF IIM system (reprinted from (Cui et al., 2018a)).

2022). Nano-sized TiO_2 was blended into the PVDF casting solution, forming microspheres during the gel phase inversion process. These were then immobilized in 12C4E through hydrolytic polymerization. When tested with a 300-mg L^{-1} LiCl solution, a 3.75 cm^2 piece of this IIM achieved rapid adsorption of 130.50 mg g^{-1} within just 10 min, reaching equilibrium at 132 mg g^{-1} after 40 min. By contrast, a non-imprinted membrane only managed 35.7 mg g^{-1}, resulting in an imprinting factor of 3.7. The enhanced adsorption capacity of the IIM was attributed not only to effective imprinting sites but also to their increased number. Selectivity tests in a multi-ion solution revealed a high affinity for Li, with the separation factors of $K_{Li/Na} = 24.6$, $K_{Li/K} = 17.0$, $K_{Li/Mg} = 6.80$, and $K_{Li/Ca} = 21.3$, consistent with other Li-selective IIMs.

XPS analysis of the O1s spectra indicated Li^+ chelation in the IIM both before and after adsorption. Initial spectra displayed two peaks at 531.6 and 532.06 eV (Fig. 6d), attributed to O–Si and C–O bonds, respectively. Post-adsorption, these evolved into three peaks at 531.8, 532.5, and 532.65 eV, corresponding to Li–O, Si–O, and C–O bonds (Fig. 6e). A minimum 0.5 eV shift for Si–O and C–O peaks signaled a change in their surrounding chemical environment, consistent with Li^+ coordinating with the crown ether's lone pair of electrons. The membrane relied on a delayed osmosis mechanism for ion separation and mass transfer, retaining 97% of its adsorption capacity after 6 cycles.

In an advanced membrane design, a 12C4E chelating agent and a PVDF base polymer were combined with a polydopamine interlayer anchored to SiO_2, significantly enhancing Li adsorption. The membrane achieved an impressive adsorption capacity of 231.77 mg g^{-1} when tested in a 200-mg L^{-1} Li^+ source solution at pH 7 over 180 min, using just 0.04 g of the IIM material (He et al., 2022). Unlike typical applications of polydopamine, which mainly focus on improving surface adhesion, this study used the compound to facilitate the uniform distribution of SiO_2 nanoparticles, thereby minimizing agglomeration in the ion-imprinted layer. Extended-Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory analysis revealed that the SiO_2 nanoparticles effectively boosted the membrane's surface electron donor tension. In-depth analysis using XPS and FTIR-ATR revealed the role of O-containing functional groups in MAA and 12C4E in the chelation of Li^+ ions. The as-prepared IIM exhibited XPS binding energies for the C–O–C/C–O peak at 285.9 eV and the O–C=O peak at 288.3 eV. After Li^+ adsorption, these peaks shifted to 286.11 eV and 289 eV, respectively. Concurrently, there was a notable reduction in peak intensity, which suggests the involvement of O-containing functional groups from both MAA and 12C4E in the Li^+ chelation process. In a similar vein, the transmittance spectra obtained from ATR-FTIR showed peak shifts from 1163 to 1722 cm^{-1} (before adsorption) to 1169 and 1730 cm^{-1} (after adsorption). Thus, the effective and selective Li^+ adsorption in this multi-layered ion-imprinted membrane is facilitated by a synergistic interplay of chelation between Li^+ and 12C4E, along with optimized spatial arrangement. The membrane exhibited enhanced cycling stability, retaining 90.4% of its adsorption capacity even after 10 regeneration cycles using 1 M HCl. In terms of selectivity, the calculated values were as follows: $K_{Li/K} = 4.36$, $K_{Li/Na} = 5.03$, and $K_{Li/Mg} = 3.55$.

3.2. *Modified crown ethers as chelating agent*

While 12C4E is commonly acknowledged as a chelating agent in imprinted systems, other branched or functionalized crown ethers have been investigated for their unique and advantageous molecular structures. 2-methylol-12-crown-4 (2M12C4) is one such example. It readily forms stable complexes with Li ions due to its similar cavity size to 12C4E. However, the lack of a double bond in its molecular structure precludes its direct use as a functional monomer in polymerization processes. This limitation means that 2M12C4 is not directly utilized in the fabrication of Li^+ ion-selective IIMs. To overcome this issue, 2M12C4 is chemically modified to create a double bond, resulting in 2-(allyloxy)methyl-12-crown-4 (2AM12C4). This modified form is then effectively employed in the preparation of Li^+ selective IIMs.

A basic Li-ion imprinted macroporous membrane was developed by Sun et al., incorporating the 2AM12C4 chelating agent with PVDF base polymer (Sun et al., 2017). The membrane was fabricated via surface imprinting polymerization, using a PDA adhesive layer to ensure a stable integration between PVDF and 2AM12C4. Testing in a 10 mL solution of 100 mg L^{-1} LiCl at pH 9 using a 0.07 g membrane sample resulted in Li adsorption of 27.1 mg g^{-1}. The membrane's macroporous structure provides numerous opportunities for creating artificial, yet specific, recognition cavities that enhance the affinity for Li ions. Adsorption behavior was found to follow the Langmuir isotherm, indicating that adsorption occurs at homogeneous sites within the membrane. The

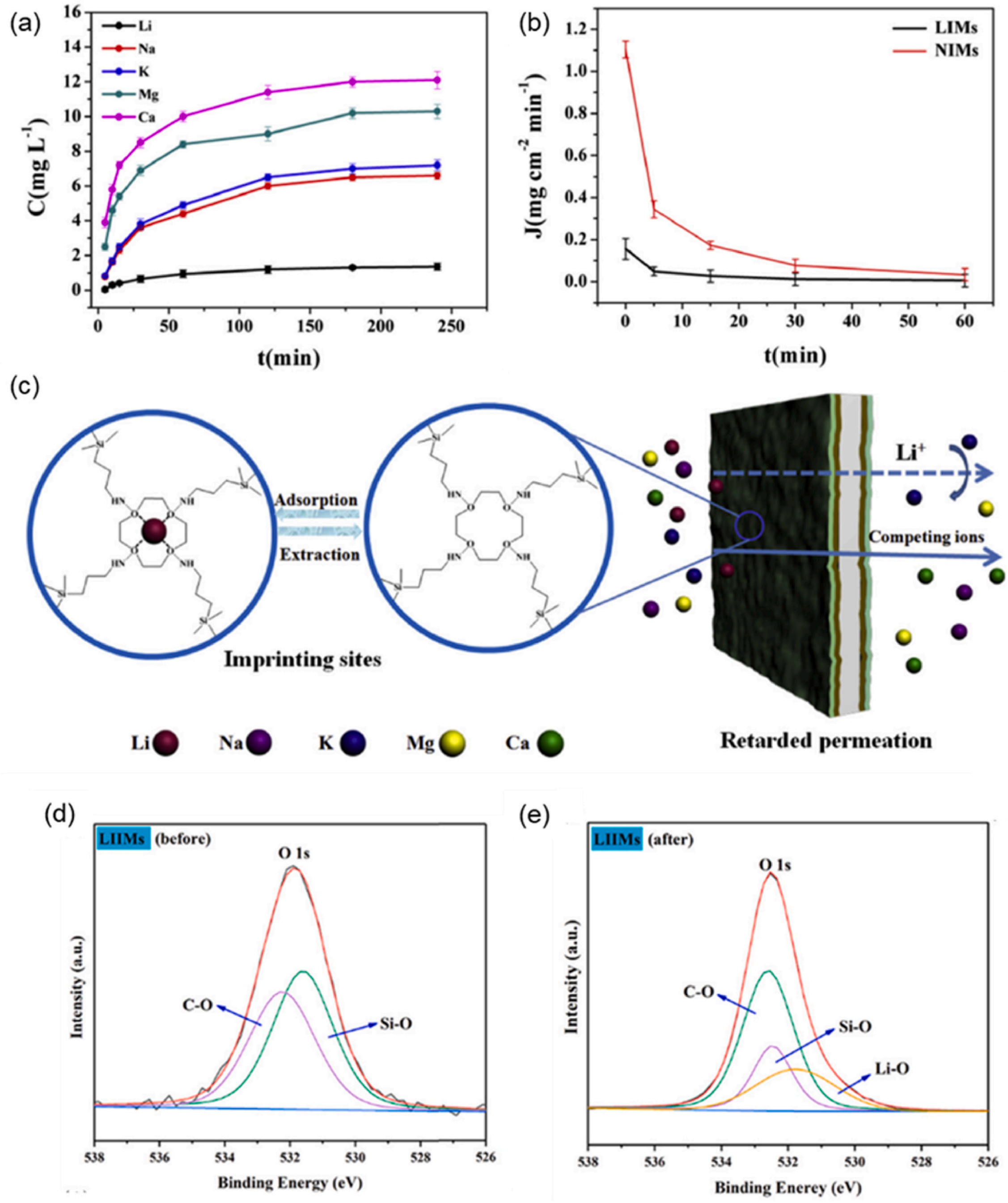

Fig. 6. (a) permeation performance in multi-ion solution, (b) time dependent permeation flux and (c) permselectivity mechanism of IIM of cellulose acetate and chitosan (reprinted from (Cui et al., 2019)). XPS spectra of O1s (d) before and (e) after Li $^+$ adsorbed on TiO_2/PVDF-IIM (reprinted from (Yang et al., 2022)).

selectivity factor for Li was measured to be 4.42 when compared to Mg ion uptake. This selectivity is attributed to the presence of specifically designed recognition cavities that are both sterically complementary and spatially oriented to match the size and shape of Li^+ ions. Additionally, the membrane demonstrated reusability across 6 cycles with only a 9.09% decline in its initial adsorption capacity.

Same research team developed a multilevel nanocomposite structure designed to selectively enrich Li^+ ions from solutions with high Mg and low Li concentrations, using 2AM12C4 as the chelating agent (Sun et al., 2018). The prime objective of this study was to create an anti-fouling membrane. To achieve this, silver nanoparticles (Ag NPs) were photo-deposited onto a PVDF membrane, utilizing a thin interlayer of self-polymerized PDA for adherence. This approach was necessary because Ag NPs could not be directly integrated into the PVDF membrane matrix. The inherent hydrophobicity of the PVDF membrane was mitigated by the presence of PDA layer and Ag NPs, shifting its property to hydrophilicity. This was confirmed by a reduction in water contact angle (WCA) measurements from 90.28° to 67.75°, indicative of an enhanced interaction between the membrane and water. Membrane disks, cut into 40 mm diameter circular shapes and weighing about 0.007 g, were able to adsorb 25.58 mg g^{-1} of Li^+ from a 10 mL solution containing 10 mg L^{-1} LiCl. When tested in high Mg, low Li brine, the selectivity factor for Li over Mg was measured at 4.75. The membrane demonstrated robust cycling stability for up to 10 cycles, retaining 92.1% of its adsorption capacity. It was regenerated using a 0.5 M HCl after each cycle. Antifouling tests conducted with bovine serum albumin

(BSA) showed that the presence of Ag NPs significantly improved the membrane's antifouling properties, thus enhancing both membrane regeneration and permeation.

The research team further innovated by modifying the base matrix of the membrane, while retaining 2AM12C4 as the chelating agent. In this novel iteration, the base was still composed of PVDF, but it was additionally modified with anchored graphene oxide and TiO_2 (GO-TiO_2) (Sun et al., 2022). GO was selected for its capability to form 2-D nanochannels and its ease of functionalization. However, GO alone did not provide adequate structural stability. To address this, TiO_2 was incorporated for its chemical stability, cost-effectiveness, and proficiency in pollutant degradation. Interestingly, the Li adsorption capacity in this novel membrane was comparatively low at 13.3 mg g^{-1}, when tested in a 10 mg L^{-1} LiCl solution, as opposed to 27.1 mg g^{-1} achieved with PVDF-only base. Despite this, the selectivity factor for Li over Mg in a co-existing solution was 6.5, outperforming the PVDF-only base membrane (4.42) and the Ag-PVDF membrane (4.75). Tests also revealed greater permeation of potentially competing ions such as Na^+, K^+ and Mg^{2+} over Li^+, affirming that selective Li^+ binding occurred at specific recognition sites, thereby inhibiting Li^+ transmission. Additional data suggested that ion permeation operated through a "delayed" osmotic mass transfer mechanism. Impressively, the membrane exhibits excellent reusability, sustaining only an 11.9% decrease in its initial adsorption capacity over 20 cycles.

Luo et al. introduced a novel IIM that utilized 2AM12C4 as the chelating agent and a unique polymer matrix as its base (Luo et al., 2017). The team employed hydrophilic poly (2-hydroxyethyl methacrylate) (PHEMA) with brush-like morphology, synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. PHEMA is rich in surface hydroxyl and ester groups, contributing to its hydrophilic nature and facilitating the rapid uptake of metal ions into the IIM's cavities. Previous studies have highlighted PHEMA's efficacy in mitigating interference from proteins in biological media (Zhang, 2014). Motivated by these findings, the membrane in the present study was tested for Li^{+} capture from complex simulated solutions containing representative pollutants like SiO_2 NPs (inorganic) and organic compounds such as polyacrylamide.

While the PHEMA-brush-grafted IIM's Li^+ adsorption capacity of 5.30 mg g^{-1}, from a 30 mL solution of 50 mg L^{-1} LiCl at pH 6, may not seem impressive compared to other IIMs, its selectivity metrics are noteworthy. It exhibits superior selectivity against a variety of ions commonly found in industrial waste streams, with selectivity values of $K_{Li/Na} = 14.74$, $K_{Li/K} = 18.26$, $K_{Li/Cd} = 25.23$, $K_{Li/Cu} = 9.93$, and $K_{Li/Co} = 11.06$. Additionally, the membrane demonstrated robust cycling stability, retaining 88.43% of its original adsorption capacity over 10 cycles when regenerated with 0.5 M HCl.

The same research team developed a highly selective IIM featuring remarkable selectivity factors, including $K_{Li/Na} = 50.88$, $K_{Li/K} = 42.38$, $K_{Li/Cu} = 22.5$, and $K_{Li/Zn} = 22.2$ (Luo et al., 2015). During the fabrication of this IIM, the 2AM12C4 chelating agent was coupled with a base membrane. This base was prepared using Fe_3O_4 NPs coated with silica and functionalized with 3-(trimethoxysilyl) propyl methacrylate (MATES), as depicted in Fig. 7. With the aim of applying this IIM for Li^+ capture from wastewater streams, Fe_2O_3 particles were incorporated

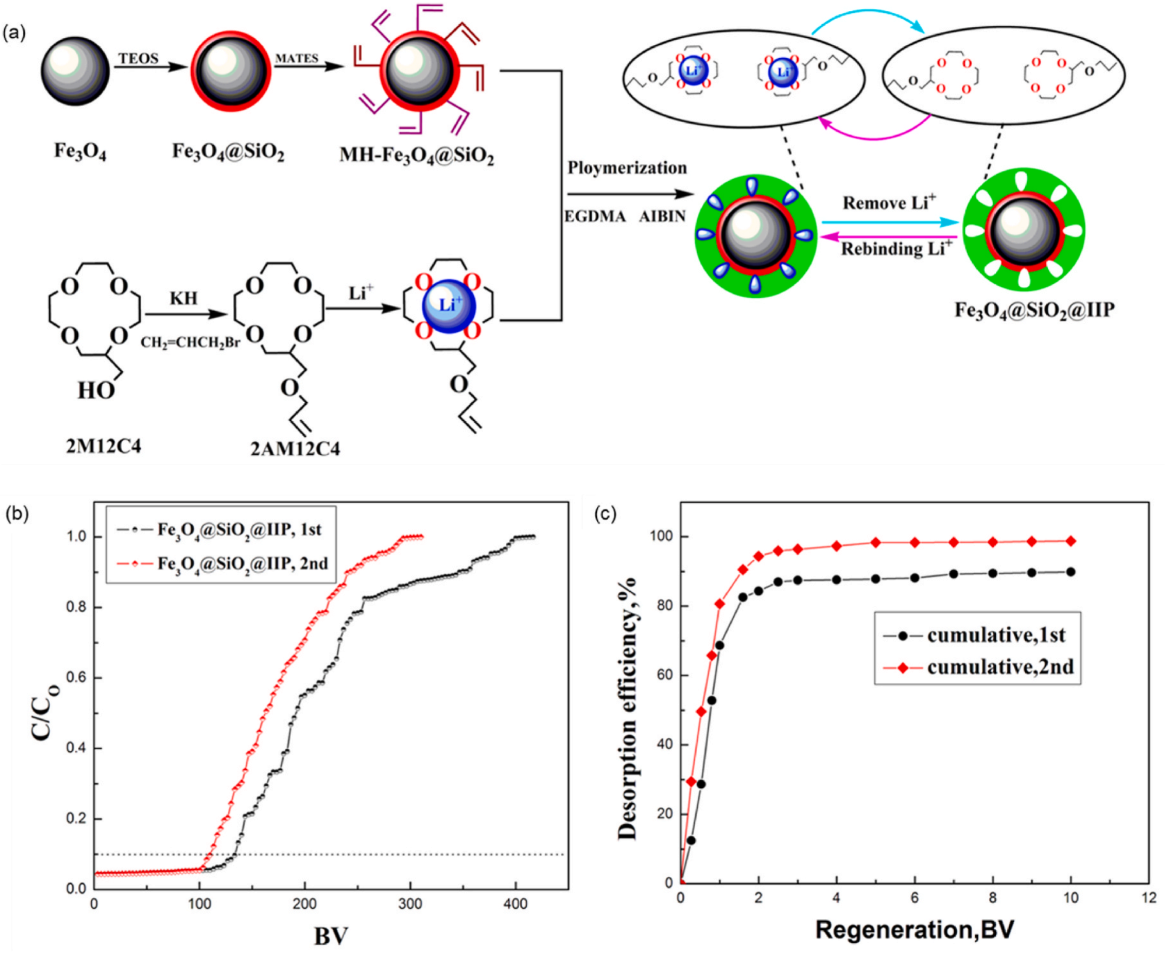

Fig. 7. (a) synthetic procedure of Fe_2O_3@SiO_2@IIP fabrication, (b) performance of fixed bed column adsorption test, and (c) regeneration performance by desorption efficiency of the same IIM (reprinted from (Luo et al., 2015)).

into the matrix to allow for easy magnetic separation. To enhance the graft ratio, these NPs were enveloped in a silica shell, thereby increasing the number of surface hydroxyl groups. While the membrane exhibited high selectivity in multi-ions solutions, its inherent adsorption capacity was somewhat low, registering at just 4.04 mg L^{-1} when tested in a 15 mmol L^{-1} LiCl solution at pH 6. Nevertheless, the membrane showed strong cycling stability, retaining 92% of its original adsorption capacity over five cycles. Regeneration between each cycle was achieved with 0.5 M HCl. Additionally, the membrane was successfully tested in real-world wastewater treatment applications using a fixed bed column. In the initial run, the column treated 140 bed volume units, and a second run under identical conditions treated 110 bed volume units. An impressive 89.8% of captured Li^+ was recovered by elution with 0.5 M HCl. They estimate that treating one ton of wastewater in this manner could result in the recovery or recycling of 4.3 kg of LiCl, translating to economic benefit of ¥240.8 for companies in industries like spent lithium-ion battery recycling or other sectors generating Li waste.

Liu et al. (2020b) developed a Li-selective IIM using a novel unipolar pulsed electropolymerization technique. The chelating agent employed was 2-hydroxymethyl-12-crown-4-ether (2HM12C4), while pyrrole served as both the conductive and cross-linking agent. The resulting IIM exhibited homogenous adsorption sites and high selectivity for Li^+ ions. In a 40 mg L^{-1} LiCl solution at pH 1.0, the membrane achieved a maximum adsorption capacity of 16.40 mg g^{-1}. During the electro-capturing process, a potential of −0.2 V was applied for 80 min to enhance adsorption. The research team also investigated the membrane's adsorption capacity across varying pH levels. In tests using an initial 10 mg L^{-1} LiCl solution, adsorption capacities were observed to be 5.45, 10.17, and 20.23 mg g^{-1} at pH levels of 1.0, 3.0, and 7.0, respectively. The variation in adsorption capacity between acidic and neutral environments was attributed to the crown ether's protonation state. In acidic conditions, the partially protonated nature of the crown ether reduced the number of available adsorption sites. Conversely, in neutral conditions, the deprotonated state of the crown ether enhanced its chelating ability for Li^+ ions. The membrane exhibited a high selectivity for Li^+ at highly acidic pH, with selectivity values including $K_{Li/Na} = 4.20$, $K_{Li/K} = 4.11$, $K_{Li/Mg} = 4.13$, $K_{Li/Al} = 4.30$, and $K_{Li/Fe} = 4.28$. This high selectivity is attributed to the well-matched size of the imprinted sites and the capturing agent: Li^+ has an ionic radius of 76 nm, while the chelating agent, 2HM12C4, has a radius of approximately 75 nm. Despite the low initial concentration of Li^+ in the solution, the membrane displayed notably improved adsorption capacity compared to existing adsorbents in highly acidic condition. This performance is due to the electrochemically switch ion exchange (ESIX) mechanism, rather than traditional acid-based elution methods involving H^+ replacement. Normally, adsorption in acidic solutions is complicated by the competition between Li^+ and H^+ ions for the same adsorption sites. Regarding reusability, the membrane's performance was evaluated over 5 cycles, using ultrapure water for regeneration. This approach differs from common practices, where acidic solutions of various concentrations ranging from 0.1 M to 1 M are typically used for regeneration. With a 1.0 V of applied potential, the membrane retained an impressive 95.88% of its initial adsorption capacity.

While IIMs often exhibit high selectivity and adsorption capacity, the location of the binding sites deep within the polymer matrix can sometimes limit the rate of ion elution and rebinding. To optimize the full use of cavities and facilitate complete ion removal, it is advantageous for the recognition sites to be situated at or near the surface of the carrier materials. In this context, multi-walled carbon nanotubes (MWCNTs) are particularly appealing due to their high specific surface area and robust mechanical properties. Building on this idea, Huang et al. designed a novel IIM using dibenzo-14-crown-4 (DB14C4) as the chelating agent, MWCNT as the carrier, and MAA as the base polymer through surface imprinting polymerization (Huang and Wang, 2018). The template ion for Li^+ was introduced using $LiNO_3$. DB14C4 was selected specifically for its size compatibility with Li^+ ions. In tests using a 300 mg L^{-1} LiCl solution and a 15 mg sample of the IIM, the membrane showed a Li^+ adsorption capacity of 9.4 mg g^{-1}. Like other Li-selective IIMs, adsorption behavior followed a Langmuir isotherm, although kinetic experiments indicated a pseudo-first-order rate model. When the membrane was subjected to 10 consecutive recycling runs and using 1 M HNO_3, a 10.3% reduction in its original adsorption capacity was observed. Selectivity is a crucial feature for IIMs, especially when applied in solutions containing multiple salts. In tests with a 50 mg L^{-1} multi-ion solution of Na^+, K^+, Cu^{2+} and Zn^{2+} at pH 6 and using 15 mg of adsorbent, the membrane displayed selectivity factors of $K_{Li/Na} = 3.66$, $K_{Li/K} = 3.01$, $K_{Li/Cu} = 2.05$, and $K_{Li/Zn} = 2.10$.

The same research team explored the use of clay minerals as an alternative carrier material, specifically replacing MWCNT with vermiculite clay (Huang and Wang, 2019). While attapulgite and zeolite have been previously studied for selective element recovery in IIM systems, vermiculite offers low-cost, high surface area option. The unique clay features a central layer of magnesium octahedral sheets flanked by two layers of silica tetrahedral sheets. The new membrane, which utilized vermiculite as a carrier, displayed a notable increase in Li^+ adsorption capacity, reaching 19.68 mg g^{-1} from a 10 mL sample of a 10 mg L^{-1} LiCl solution. Furthermore, the selectivity factors more than doubled compared to the MWCNT-based systems, with values of $K_{Li/Na} = 9.2$, $K_{Li/K} = 10.7$, and $K_{Li/Mg} = 3.9$. For Li detection, the study employed a colorimetric method, using acetone, KOH, and thorium as supporting reagents to serve as the reaction medium, pH regulator, and chromogenic reagent, respectively. The Li concentration was quantified by measuring the absorbance peak at 488 nm using a UV–visible spectrophotometer, based on a standard curve.

Among crown ethers, 14-crown-4 (14C4) seems to offer an ideal size fit for Li^+ ions, with a diameter ranging from 1.2 to 1.5 Å. A common issue in IIMs is inefficient Li^+ adsorption and desorption due to the uneven distribution and deep embedding of binding sites. To address this, Zhu et al. proposed the incorporation of chelating crown ether units directly into the repeat units of the base polymer backbone (Fig. 8a–c). This modification aims to offer more precise control over the location of the chelating agent (Zhu et al., 2020), thereby enhancing the Li^+ adsorption capacity. Using condensation polymerization, they created a copolymer-type IIM by combining di(aminobenzo)-14-crown-4 (DAB14C4) with 4,4′-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA). The resulting membrane showed an adsorption capacity of 34.05 mg g^{-1} for Li^+ from a 100 mL solution of 500 mg L^{-1} Li at pH 7, under a flowrate at 15 mL min^{-1}. While the adsorption capacity was satisfactory but not exceptional, the membrane's selectivity factors were remarkable: $K_{Li/Na} = 45.6$, $K_{Li/K} = 48.3$, $K_{Li/Mg} = 23.5$, and $K_{Li/Ca} = 41.2$. In addition, the membrane showed only a 2.3% reduction in adsorption capacity after 5 regeneration cycles using 0.1 M HCl. The authors further substantiated the Li^+ capture performance by calculating adsorption energies through DFT calculations (Fig. 8d and **e**), and these computational results were consistent with the experimental observations.

3.3. *Calixarene as chelating agent*

Calixarene is a class of macrocyclic organic ligand specifically engineered for their unique cavity structures that can be tailored to match the size and shape of target ions, making them widely applicable in the field of ion separation. Among the various types of calixarenes, calix [4]arene is particularly well-suited for matching the radius of Li^+ ions. Yu et al. developed an IIM that used neat calix [4]arene and its derivative, 4-*tert*-butylcalix [4]arene, in combination with polydimethylsiloxane (PDMS). Known for its chemical stability, tunable hardness, superior permeability, and non-toxicity, PDMS serves as the base membrane material (Yu et al., 2020). In batch adsorption experiments, the membrane adsorbed 50.87 mg g^{-1} of Li^+ from a 10 mL, 200 mg L^{-1} LiCl solution. Notably, the membrane was eluted with EDTA rather than a common acid, thus bypassing the usual H^+ replacement method. Optimal elution was achieved using a concentration of 0.2 M

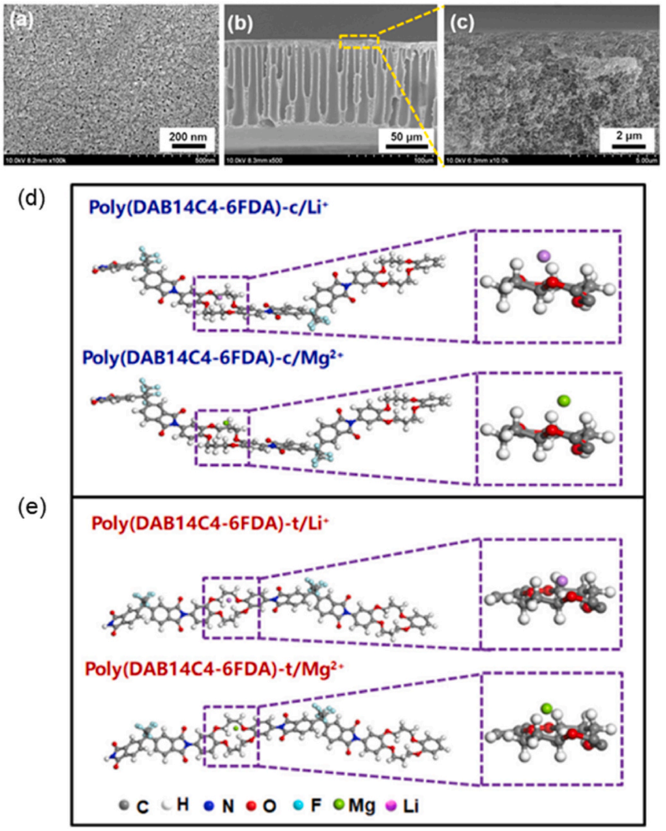

Fig. 8. SEM images of DAB14C4-FDA IIM (a) top surface, (b) cross section and (c) enlargement of cross-sectional skin layer. (d) space structure of DAB14C4-FDA IIM in one configuration after adsorbing-Li^+ (top) and Mg^{2+} (bottom) and (e) space structure of DAB14C4-FDA IIM in the second configuration after adsorbing-Li^+ (top) and Mg^{2+} (bottom) (reprinted from (Zhu et al., 2020)).

EDTA. The membrane demonstrated reusability across four cycles, showing a 13.62% loss in adsorption capacity when tested with 10-day intervals between each cycle and regenerated using 2 M EDTA. FTIR was used to evaluate the membrane's characteristics before, during, and after adsorption and elution. Peak shifts were observed in the –C═O and –C–O stretching bands, moving from their original positions at 1635 cm^{-1} and 1412 cm^{-1} to 1618 cm^{-1} and 1401 cm^{-1}, respectively, during the adsorption process. These shifts affirm the involvement of the ester linkage in chelate formation and returned to their original positions after elution.

3.4. *$\lambda-MnO_2$ as chelating agent*

$\lambda-MnO_2$ is recognized as a Li selective adsorbent in Li-ion sieves, its functionality primarily arises from the ion intercalation and deintercalation that occur during the capture and release of Li^+ ions, respectively. However, in a novel approach, Du et al. synthesized an inorganic-organic hybrid film consisting of $\lambda-MnO_2$ embedded in polypyrrole (PPy) and polystyrene sulfonate (PSS), arranged in a core–shell nanorod morphology. This innovative Li-selective IIM was developed using unipolar pulse electrodeposition (Du et al., 2016). The ESIX technique facilitated the capture (adsorption) and release (desorption) of Li^+ ions. When subjected to an applied potential of −0.2V in a 200 mL LiCl solution with a concentration of 30 mg L^{-1} (mirroring seawater conditions), the membrane exhibited an adsorption capacity of 35.2 mg g^{-1} within a span of less than 2 h. Notably, the membrane demonstrated remarkable selectivity for Li^+ over Na^+, with a selectivity factor of $K_{Li/Na} = 46.0$ in a 1:1 co-ion solution. The authors attributed this selectivity to the low ion transfer resistance and the strong high electric driving force inherent in their design. Furthermore, the membrane showcased commendable durability, retaining 98.9% if its adsorption capacity over 5 cycles. The ESIX-driven adsorption and desorption necessitate particular solution conductivities to enable ion transfer. As a result, the regeneration was performed using a 30 mg g^{-1} Li^+ solution at an anodic potential of 1.0 V.

3.5. *Blended chitosan as chelating agent*

In a move towards large-scale application of IIMs for Li^+ recovery, Das et al. explored a pilot-scale study using a chitosan-based IIM to recover Li^+ from the leachate of Li coin cell (LCC) cathodes (Das et al., 2022). They innovated by employing chitosan with different acetylation levels, affecting viscosity, combined with different amounts of glutaraldehyde as a crosslinker. During membrane synthesis, Li^+ was introduced in different amounts to the chitosan-glutaraldehyde mixture, and after extracting Li^+, specific cavities remained that were adept at recognizing and capturing Li^+. The effectiveness of this approach is attributed to chitosan's rich amine and hydroxyl groups. The membrane was then used to recover Li^+ from actual LCC leachate.

The top-performing chitosan IIM nanofiber exhibited a pore size of about 2.29 μm, fiber width of roughly 176.5 μm, and ion exchange capacity of 8.45 meq g^{-1}. It achieved an exceptional Li adsorption rate of 100 mg g^{-1}, notable distribution coefficient (6969.7 mL g^{-1}), and a separation factor of 90 in a complex metal ion mix. The adsorption was consistent, suggesting a uniform monolayer formation, and the process was spontaneous and endothermic, with a ΔG value of −20.3 kJ mol^{-1}. The fiber's selectivity was evident, with relative Li sorbed (RLS) values over 20 and relative Li released (RLR) above 9. The adsorption fit a pseudo-first-order kinetic model, indicative of a fast, physisorption-dominated mechanism. The IIM also proved to be durable, withstanding up 9 regeneration cycles using 0.05 M HCl and retaining 99.1% of its adsorption capacity.

The examined case studies (Table 2) show a preference for using LiCl as the primary Li^+ source during IIM synthesis, with $LiClO_4$ and $LiNO_3$ as less common alternatives. In the fabrication process, PDA is often used to strengthen the bond between the chelating agent (crown ether) and the membrane's base polymer. PVDF is favored for its structural stability, with its hydrophilicity often enhanced by additives such as TiO_2, Ag, GO, GO-TiO_2, or SiO_2. Other substrates like pyrrole, polystyrene sulfonate, polyether sulfone, and methacrylic acid are also utilized, with bio-inspired material like cellulose acetate and chitosan being considered for IIMs.

The performance of IIMs is primarily evaluated by their selectively in separating Li from multi-ion solutions, with the separation factor ($K_{Li/M}$) indicating the efficiency of Li over competing ions. PVDF-based membranes, whether modified or not, typically exhibit separation factors for Na ($K_{Li/Na}$) and Mg ($K_{Li/Mg}$) below 10. Exceptional selectivity is noted in certain systems such as 2AM12C4 in MATES-modified SiO_2-coated Fe_2O_3 NP ($K_{Li/Na} = 50.88$ and $K_{Li/K} = 42.38$). However, the validity of comparing adsorption capacities in mg g^{-1} is questioned due to variations in IIM amount, and the volume and concentration of Li^+ solution across studies. A uniform reporting standard is suggested for clarity.

Research indicated that Li adsorption often follows a monolayer pattern at uniform adsorption sites, with a chemisorption-based pseudo-second-order kinetic mechanism. However, a pseudo-first-order rate model was observed in DB14C4-based chitosan IIMs. Notably, IIMs demonstrate strong reusability across various compositions, with up to 20 cycles tested and less than 15% decrease in adsorption capacity. This reusability is advantageous over ISM with metal adsorbents, which face significant performance decline due to dissolution and leaching during acid-regeneration cycles (Yu et al., 2022). In IIM systems, the integrity of membranes is maintained even after regeneration with mineral acids, while electrochemical adsorption prefers ultrapure water or a conductive Li^+ salt solution. For calixarene-based IIMs, despite limited data availability, EDTA is the preferred eluent.

Table 2
Highlights of existing studies on Li selective IIMs.

Entry	chelating agent	base polymer	selectivity for target ion relative to competing cations	adsorption capacity/mg g^{-1}	regeneration capacity retention/%	adsorption cycles	reference
1	12C4E	acrylamide	$K_{Li/Na} = 5.34$, $K_{Li/K} = 6.47$, $K_{Li/Cu} = 23.5$, $K_{Li/Zn} = 27.13$	7.83	high	6	Cui et al. (2018b)
2	12C4E	GO/PVDF	$K_{Li/K} = 5.38$, $K_{Li/Ca} = 21.94$, $K_{Li/Mg} = 15.56$	27.10	91.8	6	Cui et al. (2018a)
3	2AM12C4	PVDF	$K_{Li/Mg} = 4.42$	27.1	90.9	6	Sun et al. (2017)
4	2HM12C4	PPy	$K_{Li/Na} = 4.20$, $K_{Li/K} = 4.11$, $K_{Li/Mg} = 4.13$, $K_{Li/Al} = 4.30$	16.40	95.9	5	Liu et al. (2020b)
5	$\lambda-MnO_2$	PPy and PSS	$K_{Li/Na} = 46$	35.2	98.9	5	Du et al. (2016)
6	4-*tert*-butylcalix [4] arene	PDMS	$K_{Li/Na} = 1.71$, $K_{Li/K} = 4.56$, $K_{Li/Rb} = 3.80$	50.87	86.4	4	Yu et al. (2020)
7	12C4E	TiO_2/PVDF	$K_{Li/Na} = 24.60$, $K_{Li/K} = 17.0$, $K_{Li/Mg} = 6.8$, $K_{Li/Ca} = 21.3$	132.0	97	6	Yang et al. (2022)
8	2AM12C4	Ag/PVDF	$K_{Li/Mg} = 4.75$	25.58	92.1	10	Sun et al. (2018)
9	2AM12C4	GO-TiO_2/PVDF	$K_{Li/Mg} = 6.5$	13.3	88.1	20	Sun et al. (2022)
10	12C4E	SiO_2/PVDF	$K_{Li/Na} = 5.03$, $K_{Li/K} = 4.36$, $K_{Li/Mg} = 3.55$	231.77	90.4	10	He et al. (2022)
11	12C4E	PES	$K_{Li/Na} = 1.85$, $K_{Li/K} = 2.07$	27.55	88.1	10	Lu et al. (2018)
12	12C4E	cellulose acetate and chitosan	$K_{Li/Na} = 1.78$, $K_{Li/K} = 2.43$, $K_{Li/Mg} = 2.60$, $K_{Li/Ca} = 3.61$	20.08	93	6	Cui et al. (2019)
13	2AM12C4	$SiO_2@Fe_2O_3$ on MATES	$K_{Li/Na} = 50.88$, $K_{Li/K} = 42.38$, $K_{Li/Cu} = 22.5$, $K_{Li/Zn} = 22.2$	4.04	92	5	Luo et al. (2015)
14	DB14C4	vermiculite clay/MAA	$K_{Li/Na} = 9.2$, $K_{Li/K} = 10.7$, $K_{Li/Mg} = 3.9$	19.8	86.9	10	Huang and Wang (2019)
15	DB14C4	MWCNT/MAA	$K_{Li/Na} = 3.66$, $K_{Li/K} = 3.01$, $K_{Li/Cu} = 2.05$, $K_{Li/Zn} = 2.10$	9.4	89.7	10	Huang and Wang (2018)

There has been growing interest in retrieving Li from various spent battery materials, from the simple $LiCoO_2$ to the more intricate $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ compositions, particularly as the first batch of electric vehicle batteries reach their end of life (Nayaka et al., 2016; Zhuang et al., 2019). Usually, while metals like Ni, Cu and Co are recovered by hydrometallurgical or pyrometallurgical methods, Li typically ends up in waste sludge (Moazzam et al., 2021). Most research on recovering Li from spent Li-ion batteries has involved dissolving the waste in purely organic solutions such as iminodiacetic acid (IDA) or maleic acid (Nayaka et al., 2016), or in a blend of organic and mineral acids like citric acid with H_3PO_4 (Zhuang et al., 2019), or using a deep eutectic solvents like oxalic acid (Lu et al., 2021). The extracted Li is then typically isolated via semi-continuous column adsorption to minimize lag time (Purnomo et al., 2018), or by precipitating it as Li oxalate or through sulfation roasting (Liu et al., 2022).Although the use of IIMs for Li recovery from spent Li ion batteries has not been thoroughly explored, their precisely tailored ion imprinted sites promise high selectivity for Li, despite the complexity of the battery waste.

The progress of IIMs in Li recovery was assessed using their Technology Readiness Level (TRL). Fig. 9 provides an overview of the TRL for these projects in comparison with other studies (Zavahir et al., 2021). The TRL scale, which goes from 1 to 9, gauges the level of technological development: level 1 represents the initial concept stage, based on basic principles, and level 9 indicates a technology that has been intensively proven in operational environments. This scale is crucial for gauging a technological evolution from conceptualization through to practical operation, providing a framework to identify potential risks, uncertainties, and investment needs for further development.

The criteria for assessing the studies included their adsorption capacity, synthesis methodologies, and ability to regenerate the materials. The majority of the research reviewed remains in the conceptual stage, with only 29% advancing to detailed laboratory testing, underscoring the fact that IIM technology for Li^+ recovery is still in its infancy, lacking any implementation on a pilot scale.

4. Conclusion

The escalating global demand for Li has intensified the quest for scalable, cost-effective, and highly selective technologies recovery solutions. MST-based IIMs stand out as a promising solution in this context. This paper offers a detailed yet concise overview of factors that influence the efficiency of these imprinted membranes. Yet, numerous challenges persist that hinder the realization of this technological potential. The conclusion offers insights and future research directions to enhance the selective recovery efficiency of IIMs.

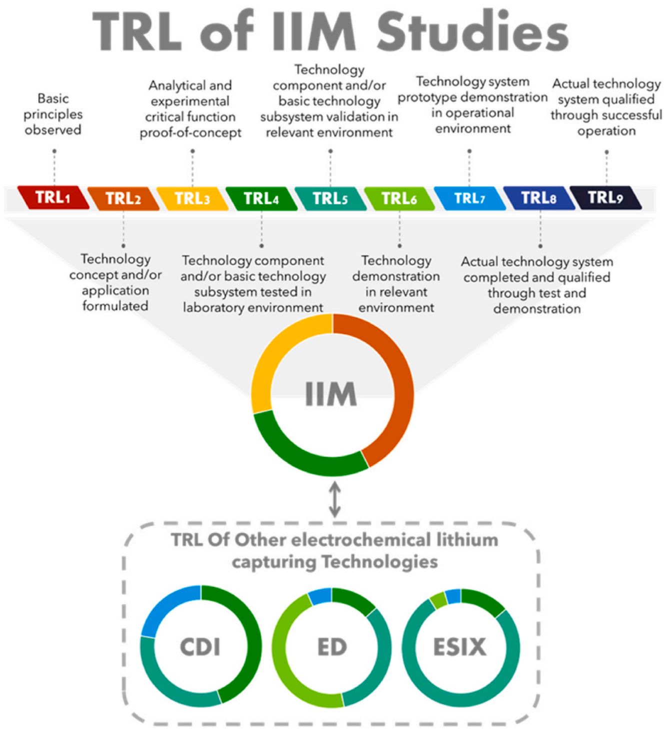

Fig. 9. TRL of existing studies on recovery of Li vs. TRL of technologies such as ED, ESIX, and CDI, adapted from (Zavahir et al., 2021).

Ongoing advancements in IIM research have brought forth diverse synthesis approaches. The literature cites a maximum Li^+ adsorption capacity of 157 mg g^{-1}. Translating this capacity to an industrial scale demands significant resources and infrastructures. Thus, before any transition towards full-scale implementation, it is imperative that this adsorption capacity is corroborated by independent studies. Furthermore, for this technology to be economically viable at an industrial scale, it must consistently deliver high adsorption capacities. Beyond simply verifying existing adsorption capacities, there is a pressing need to perfect the synthesis techniques to further increase the selective adsorption capacity of IIMs for Li^{+}.

Moreover, the recognition sites within IIMs are formed using functional monomers. This approach, however, is not without its pitfalls. These universal monomers can occasionally demonstrate selectivity for non-target ions or molecules, potentially diminishing the efficacy of IIMs. This underscores the necessity to innovate and design bespoke monomer tailored for Li^{+} recovery in IIM synthesis. One promising avenue might involve integrating monomers with crown ethers, which have consistently shown an affinity for Li^{+} ions. In addition, there is a noticeable research gap in the fabrication of IIMs targeting heavy metal recovery, given their intricate imprinting challenges. Future explorations in this domain could offer a broader perspective on the versatility of imprinted membranes.

This paper critically examines the myriad studies centered around Li^{+} extraction using IIMs. It is projected that IIMs will be pivotal in selectively harvesting Li^{+} from seawater brine, championing benefits like elevated recovery rates, cost-efficiency, and unparalleled selectivity for the targeted cation. As such, accelerating research endeavors to enhance the efficiency of IIMs and scrutinizing their scalability for industrial applications is of paramount importance. This stride will be instrumental in averting the looming Li scarcity threatening the global market.

CRediT authorship contribution statement

Sifani Zavahir: Writing – original draft, Conceptualization. **Najamus Sahar Riyaz:** Writing – original draft. **Tasneem Elmakki:** Visualization. **Haseeb Tariq:** Visualization. **Zubair Ahmad:** Writing – review & editing. **Yuan Chen:** Writing – review & editing. **Hyunwoong Park:** Writing – review & editing. **Yeek-Chia Ho:** Writing – review & editing. **Ho Kyong Shon:** Writing – review & editing. **Dong Suk Han:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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