멤브레인(Membrane Journal)
Vol. 34 No. 5 October 2024, 234-240

총 설

Print ISSN: 1226-0088
Online ISSN: 2288-7253
DOI: https://doi.org/10.14579/MEMBRANE_JOURNAL.2024.34.5.234

크라운 에테르 기능화 막에 의한 리튬 회수: 리뷰

토잔 탕베이*・라즈쿠마 파텔**,†

*연세대학교 언더우드국제대학 융합과학공학부 나노과학공학,
**연세대학교 언더우드학부 융합과학공학부 에너지환경융합전공

(2024년 7월 14일 접수, 2024년 10월 18일 수정, 2024년 10월 18일 채택)

Recovery of Lithium by Crown Ether Functionalized Membrane: A Review

Togzhan Tangbay* and Rajkumar Patel,†**

*Nano Science and Engineering, Integrated Science and Engineering Division, Underwood International College, Yonsei University, Incheon 21983, Korea
**Energy and Environmental Science and Engineering, Integrated Science and Engineering Division, Underwood International College, Yonsei University, Incheon 21983, Korea

(Received July 14, 2024, Revised October 18, 2024, Accepted October 18, 2024)

요 약: 에너지 저장 장치의 필수 요소인 리튬에 대한 필요성이 증가함에 따라 전 세계 리튬 침전물의 주요 공급원인 염수로부터 효율적인 리튬 회수 방법의 개발이 요구됩니다. 염수로부터 리튬을 회수하는 과정은 유사한 특성을 가진 공존하는 이온의 존재로 인해 복잡합니다. 크라운 에테르 기능화된 막은 선택적 리튬 회수를 위한 유망한 솔루션을 제시합니다. 이온-쌍극자 상호 작용을 통한 금속 이온에 대한 강한 친화력으로 유명한 크라운 에테르는 공동-이온 크기 호환성에 기반한 리튬 이온의 선택적 추출을 촉진하는 "호스트-게스트" 복합체를 형성합니다. 다양한 연구에서 크라운 에테르 이식된 막이 리튬 선택성을 향상시키는 데 효과가 있음이 입증되었습니다. 이 리뷰는 크라운 에테르 기능화된 막의 발전을 탐구하여 염수로부터의 리튬 회수 문제를 해결할 수 있는 잠재력을 보여줍니다.

Abstract: The increasing need for lithium, an essential element in energy storage devices, calls for the development of efficient lithium recovery methods from brines, the primary source of global lithium deposits. The recovery process of lithium from brines is complex due to the presence of co-existing ions with similar properties. Crown ether functionalized membranes present a promising solution for selective lithium recovery. Crown ethers, known for their strong affinity towards metal ions through ion-dipole interactions, form "host-guest" complexes that facilitate the selective extraction of lithium ions based on cavity-cation size compatibility. Various studies have demonstrated the effectiveness of crown ether-grafted membranes in enhancing lithium selectivity. This review explores the advancements in crown ether functionalized membranes, showing their potential to address the challenges in lithium recovery from brines.

Keywords: *crown ether, membrane, brine, lithium*

1. Introduction

Wastewater, which is produced during industrial processes, comprises a lot of different metal ions, which can be recovered and reused for other purposes[1]. One such metal ion is lithium, which is a very essential element in energy storage devices[2]. For instance, lithium is used as Li_2CO_3 in secondary batteries, as Li in primary batteries, and in other electronic materials[3]. As the world advances towards a technological future, the need for lithium is increasing rapidly, outpacing the immediate supply of the valuable

†Corresponding author(e-mail: rajkumar@yonsei.ac.kr; http://orcid.org/0000-0002-3820-141X)

metal. The substantial source of lithium is brine, accounting for about 70~80% of global lithium deposits[4]. However, extracting lithium from brines is challenging since brines also contain other co-existing ions with similar properties and high concentrations, complicating the extraction process. Consequently, various methods have been proposed to effectively extract lithium from brines.

Crown ether functionalized membranes present a big promise for lithium recovery. Crown ether, a type of mycrocyclic ligand comprising of few ether groups, has a strong complexing affinity towards metal ions [4,5]. This affinity is demonstrated by the ability of the negatively charged oxygen atoms create complexes with metal ions via the ion-dipole interaction. These interactions are referred to as a "host-guest" complexes. The selectivity of crown ether regarding the desired metal ion depends on the cavity-cation size compatibility.

The possibility to recover metal ions by grafting polymeric membranes with crown ethers and achieving a successful host-guest ion segregation was investigated[6]. For example, Abdulazeez *et al.* proposed crown ether-grafted cellulose acetate polyelectrolyte membranes and showed that 12-crown-4 grafted CA membrane exhibited strong selectivity towards Li^+ ions[6]. Ge *et al.* showed that the membrane's ability to separate metal ions can be enhanced by appropriate CEs, such as 15-crown-5 hydroxymethyl ether (15C) grafted on graphene oxide[7]. The size of the 15C is ideal for the smaller diameter of lithium ions, which enables to selectively let lithium to endure a process known as "dual transport" and get through while inhibiting magnesium. To separate Li^+ from other metal ions such as Co^{2+}, Ni^{2+} and Mn^{2+} Sun *et al.* used benzo-15-crown-5 ether (B15C5) as extractant and showed that B15C5 exhibits effective coordination with Li^+ in comparison to other ions[8]. Hua *et al.* demonstrated an additional benefit of crown ether by employing it as a co-extractant in the tributyl phosphate-ionic liquid extraction system[9]. By forming hydrogen bond with the original system, crown ether enhances stability of the complex formed in the organic phase and, therefore, selectivity towards lithium ions. Other reports demonstrated utilizing crown ethers' selectivity towards lithium ions and the nanosheets' large surface area to create effective sorbents, such as PMBA-PMA-CE and 12-crown-4 passivated silicene[10,11]. Another unique approach of utilizing crown ethers was proposed by Huang *et al.*, the magnetic Li^+-imprinting polymer was developed, where the application of external magnetic field contributed to the solid-liquid separation[12].

Crown ether are made up of ethylene oxide in the form of cyclic structure. The presence of electronegative oxygen atom leads to the formation of coordination complex with electropositive metal ion. Polymeric membrane modified with the crown ether enhance the separation process of the separating film. At the same time the cavity of the crown math with the size of the lithium ion. Overall, crown ether functionalized membranes offer practical solutions to the problem of effective lithium recovery from brines. In this review, several approaches utilizing crown ether functionalized membranes are reviewed and discussed in detail.

2. Polymers

There are various polymers that form special property for application in membrane based separation process. Among them crown ether function polyimide and PVDF are popular membrane materials.

2.1. Polyimide

Hua *et al.* proposed a method of lithium recovery by developing a specialized contactor PI@14C4-SILM, which utilizes a crown ether functionalized polyimide membrane (Poly(DAB14C4-6FDA)) and a mixture of tributyl phosphate (TBP) and $[C_4mim][NTf_2]$ as the support and the liquid phase[13]. The findings indicate that the lithium penetration rate, initial flux, and Li/Mg selectivity have the following values: 0.354 μm/s, 0.128 mol/m^2 h, and 19.1 under particular conditions, that is, a feed phase magnesium-to-lithium ratio of 35 and a stripping phase of 0.5 mol/L HCl. Additionally,

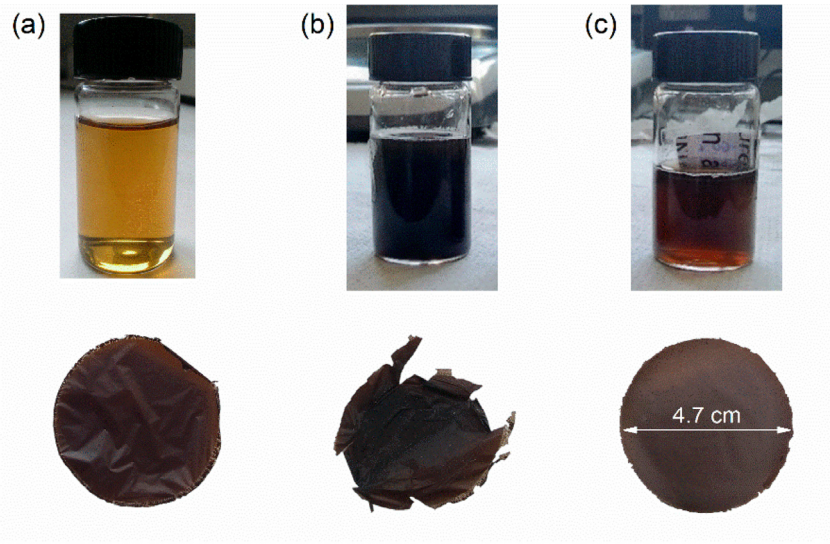

Fig. 1. Images of the formulations and f-GO membranes with the binders (a) GO, (b) PVDF, and (c) PVA (Reproduced from Baudino *et al.*[16], Copyright 2022, MDPI).

poly(DAB14C4-6FDA)-Li-NTf_2 and TBP-Li-NTf_2 displayed high binding energies of 163.26 and 182.1 kcal/mol, suggesting stable frameworks that contribute to the contactor's high lithium transfer efficiency. The rapid lithium transfer channel that forms between the liquid mobile phase and the crown ether structure is suggested to be the mechanism underlying this efficiency.

Another method, focusing on the improvement of hydrophilicity and stability, was proposed by Lu *et al.*[14]. Researchers created multilayered, highly selective lithium-ion-imprinted membranes (Li-IIMs) utilizing polyether sulfone substrates. These membranes comprise a composite structure consisting of an imprinting layer of lithium-ion-imprinted polymers, a hydrophilic layer of silicon dioxide nanoparticles, and an interfacial adhesion layer of polydopamine (pDA). With an imprinting factor of 2.51, these membranes exhibited the best selectivity coefficients for Li^+/K^+ (2.07) and Li^+/Na^+ (1.85). Additionally, a considerable selectivity for lithium was shown by the high permselectivity values of K^+/Li^+ (9.86) and Na^+/Li^+ (7.39). With an imprinting factor of 2.51, these membranes exhibited the best selectivity coefficients for Li^+/K^+ (2.07) and Li^+/Na^+ (1.85). Even after several adsorption/desorption cycles, the Li-IIMs' excellent rebinding efficiency of 90.3% demonstrated little degradation in binding capacity over time.

Yang *et al.* proposed a sustainable approach for lithium extraction, which involves nanofiber membranes composed of 14-crown-4-ether polyimide (14C4PI)[15]. These membranes were developed with a specific molecular weight and crown ether loading by a controlled electrospinning process. The 14C4PI-12 nanofiber membrane, characterized by its small diameter and large surface area, exhibited a high equilibrium capacity for lithium adsorption (Q_m = 40.17 mg g^{-1}). Additionally, Li^+ to Na^+, K^+, Mn^{2+}, Co^{2+}, and Ni^{2+} selective separation values reached 52.3, 54.97, 48.82, 41.05, and 35.04, correspondingly. The larger Gibbs free energy change of the 14C4PI-Li^+ combination (−113.99 kcal mol^{-1}) is suggested to be the contributing factor for the improved selectivity of 14C4PI to Li^+, as shown by the DFT computations.

2.2. PVDF

To extract lithium using pressure filtration and polymeric binders, Baudino *et al.* presented a unique method that uses a nanocomposite membrane composed of 12-crown-4-ether functionalized graphene oxide (GO) [16].

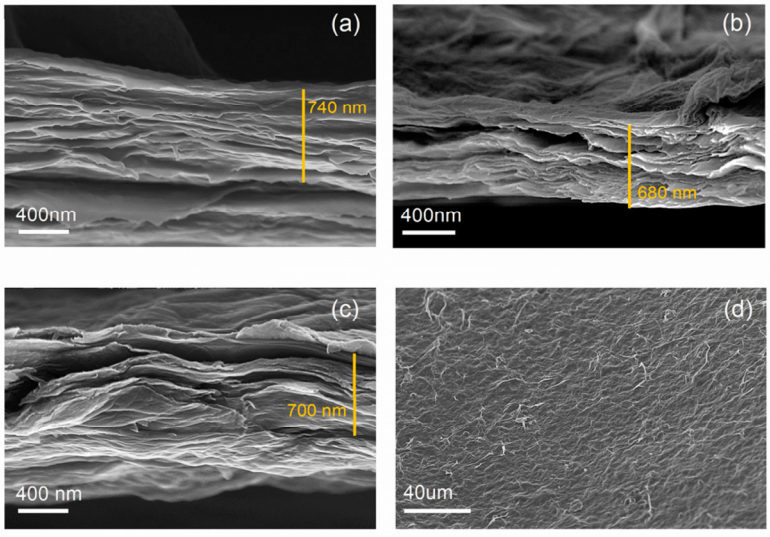

Fig. 2. FESEM images of (a) pure GO membrane, (b) f-GO membrane, (c) nanocomposite membrane, and (d) top view of the nanocomposite (f-GO+PVA) membrane (Reproduced from Baudino *et al.*[16], Copyright 2022, MDPI).

To enhance the mechanical characteristics of the membrane, carbodiimide esterification was used to alter the GO flakes prior to the incorporation of polymeric binders, such as poly(vinylidene fluoride) (PVDF), poly(vinyl alcohol) (PVA) and pristine GO. The modified membrane was examined using nitrogen gas in a dead-end pressure arrangement, which accelerated the process of lithium extraction. The results demonstrated that the membrane effectively recovered 70 % of lithium, even from solutions with low concentrations (7 mgLi/L), averaging 5 mgLi/g of lithium absorption in less than 30 minutes of filtration.

Li *et al.* presented the synthesis of a new ion-imprinted membrane (SP-IIM) with an adhesive layer made of chemically modified polydopamine (PDA) oxidized by sodium periodate (SP-PDA@PVDF)[17]. The PDA was cross-linked during the oxidation process at pH 5.0, enhancing the membrane's chemical stability and reusability. The resultant SP-PDA@PVDF's flaky microstructure increased the surface area that could be loaded with 12-Crown-4 (12C4). After being incubated in a 200 mg/L lithium solution for 180 minutes, the membrane showed the best capacity for lithium adsorption of 42.58 mg/g. Additionally, the selective separation factors of Li^+/Mn^{2+}, Li^+/Co^{2+}, Li^+/Ni^{2+} reached 6.71, 5.84, and 3.03, correspondingly. The SP-PDA@PVDF layer's intermolecular cross-linking, due to sodium periodate's oxidation of the PDA, decreased the likelihood of the ion-imprinted layer's separation from the membrane and enhanced the SP-IIM's reusability, which was proven to decrease only by 4.6% after 5 adsorption/desorption cycles.

Qu *et al.* developed TiO_2/PVDF-based lithium ion-imprinted membranes (LIIMs) employing a sustainable hydrolysis polymerization approach[18]. Li^+ showed the selective separation factors for Fe^{2+}, Cu^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, K^+, and Na^+ to be 10.93, 19.30, 22.66, 23.49, 26.14, 27.57, and 39.00, accordingly, indicating that the LIIMs had a reasonable sensitivity for lithium in the leaching solution. The interaction between Li^+ and oxygen present on the crown ether was the fundamental mechanism driving the selective adsorption of LIIMs. As a highly selective sustainable material, the LIIMs provide a broad spectrum of potential applications in the recycling of wasted LIBs.

Another TiO_2/PVDF-based lithium ion-imprinted membranes (LIIMs) but containing 12-crown ether-4 were developed by Yang *et al.*[19]. After being placed in a 300 mg/L LiCl solution, the LIIMs' best adsorption capacity for Li^+ was determined to be 132.00

mg/g, attributed to a significant affinity force and an abundance of binding sites. Data from Langmuir isothermal adsorption demonstrated the homogeneity of the imprinting sites on LIIMs. The selective separation factors of Li^+ to Mg^{2+}, K^+, Ca^{2+}, and Na^+ corresponded to 6.80, 17.00, 21.30, and 24.60, respectively. Following 6 cycles, the adsorption capacity of LIIMs was stable nearly 97%. These findings demonstrated that the LIIMs have high selective adsorption capacity to Li^+ because of their high affinity, numerous rebinding sites, and suitable cavity.

2.3. Others

Cheng *et al.* produced a chitosan (CS) nanofiber membrane with a high specific surface area of 111.55 m^2/g via a low-temperature phase separation approach[20]. The crown ether (CE) modified chitosan nanofiber membranes (CS-CE) were developed by attaching 2-(Hydroxymethyl)-12-crown 4-Ether ($2H_{12}C_4$), which possesses a distinct cavity structure, onto the surface of CS with the goal of achieving superior Li^+ selection. The optimal Li^+ adsorption capacity of the CS-CE membrane was found to be 297 mg/g after it was subjected to a Li^+ solution with the concentration of 1000 mg/L. It demonstrated outstanding reusability with a little decrease by 8.8% in adsorption capacity over 5 cycles, and it retained a significant selectivity for Li^+ with the separation coefficient between 1.33 and 34.05, regardless of the presence of other co-existing metal ions.

An interfacial polymerization approach was used by Li *et al.* to create a unique nanofiltration (NF) membrane[21]. The polyethyleneimine (PEI) was hydrogen-bonded to 15-crown-5 ether (15C5), and reacted with trimesoyl chloride (TMC) to form Li^+ transport pathways that are supported by 15C5's selectivity for Li^+. The membrane showed a constant separation factor for Li^+ over Mg^{2+} of 14, and a permeability of 8.0 L m^2/h bar. This resulted in a considerable reduction of the Mg^{2+}/Li^+ mass ratio from 20 to 1.7. With an initial Mg^{2+}/Li^+ mass ratio of 50, a three-stage NF process employing the PEI@15C5-TMC membrane further improved this separation, yielding a final permeate with a Mg^{2+}/Li^+ mass ratio of 0.1, comprising 24 ppm Li^+ and 2.7 ppm Mg^{2+}.

Through unipolar pulsed electropolymerization, Liu *et al.* developed a lithium ion imprinted membrane (Li^+-IIM), incorporating pyrrole as a conductive and crosslinking agent, 2-hydroxymethyl-12-crown-4 ether for the capture, and lithium ion as a template[22]. Li^+-IIM demonstrated an optimal capacity for lithium ion adsorption of 16.40 mg/g at a pH of 1.0 from a 40 mg/L Li^+ solution, achieving this in a span of 80 minutes. The selectivity factors of Li^+ to Na^+, K^+, Mg^{2+}, Al^{3+}, and Fe^{3+} were found to be 4.20, 4.11, 4.13, 4.30, and 4.28, accordingly. Additionally, the Li^+-IIM demonstrated outstanding regeneration characteristics as it retained 95.88% of its adsorption capacity following 5 cycles of adsorption and desorption.

The liquid rubidium (Rb(l)) is commonly found with lithium in Salt Lake brine and saltwater. Therefore, Meng *et al.* focused on the goal of removing rubidium (Rb(I)) by developing two types of polymer inclusion membranes (PDA-PIM and PDT-PIM)[23]. These membranes used polyvinyl chloride (PVC) and dicyclohexano 18 crown 6(DCH18C6) as carriers. Moreover, the plasticizers used were tricaprylmethylammonium chloride (Aliquat 336) for PDA-PIM and trioctylphosphine oxide (TOPO) for PDT-PIM. The separation of Rb(I) requires an electric field; higher voltage enhanced Rb(I)'s permeability coefficient and separation factor. PDT-PIM and PDA-PIM had PRb of 2.39 μm/s and 12.08 μm/s at 180 volts, and SRB/NA of 14.44 and 11.21, accordingly. In addition, the PDT-PIM demonstrated efficient low-concentration Rb(I) extraction, achieving a 3.02-fold enrichment of Rb(I) over 81.5 hours and just 4.6% drop in PRb over 4 cycles.

3. Conclusions

The efficient recovery of lithium from brine faces significant challenges due to the presence of other co-existing ions. Various crown ethers are used to sequester lithium ions. Crown ether functionalized mem-

branes have emerged as a promising solution, offering high selectivity for lithium ions due to its strong affinity due to the matching cavity size of the host and the guest.

Methods utilizing polyimide-based membranes modified with crown ether have shown high lithium penetration rates, initial flux, and selectivity, tailoring them for environmental applications. PVDF-membranes have shown durable mechanical properties, chemical stability, and reusability, making them effective for lithium extraction even from low-concentrations. Other novel methods, including the use of chitosan nanofiber membranes and nanofiltration techniques, exhibited outstanding regeneration characteristics and minimal degradation over multiple cycles.Overall, the successful implementation of crown ethers significantly contributes to the sustainable recovery of lithium metal. Modification of various other type of polymeric membrane with crown ether can be explored to enhance the applicability of the membrane to lithium ions and beyond.

Reference

1. Y. Chen, J. Tang, S. Wang, L. Zhang, and W. Sun, "Bimetallic coordination polymer for highly selective removal of Pb(II): Activation energy, isosteric heat of adsorption and adsorption mechanism", *Chem. Eng. J.*, **425**, 131474 (2021).
2. Y. Zhang, Y. Zhang, Y. Liu, H. Wu, M. Zhou, P. Gu, and Z. Li, "Chitosan grafted with crown ether with high selectivity and adsorption on lithium-ion", *Fullerenes Nanotubes Carbon Nanostructures*, **31**, 538-548 (2023).
3. Y. Tachibana, T. Kalak, and M. Tanaka, "Chromatographic purification of lithium, vanadium, and uranium from seawater using organic composite adsorbents composed of benzo-18-crown-6 and benzo-15-crown-5 embedded in highly porous silica beads", *ACS Omega*, **7**, 27410-27421 (2022).
4. Y. Xiong, T. Ge, L. Xu, L. Wang, J. He, X. Zhou, Y. Tian, and Z. Zhao, "A fundamental study on selective extraction of Li^+ with dibenzo-14-crown-4 ether: Toward new technology development for lithium recovery from brines", *J. Environ. Manage.*, **310**, 114705 (2022).
5. I. Oral and V. Abetz, "A highly selective polymer material using benzo-9-crown-3 for the extraction of lithium in presence of other interfering alkali metal ions", *Macromol. Rapid Commun.*, **42**, 2000746 (2021).
6. I. Abdulazeez, B. Salhi, N. Baig, and A. Al-Saadi, "Molecular dynamics simulation of the fractionation of lithium and magnesium-ions on crown ether-grafted cellulose acetate polyelectrolyte membranes", *J. Mol. Liq.*, **376**, 121475 (2023).
7. M. Ge, C. Wei, T. Fang, and X. Liu, "Molecular insight into the separation mechanism of crown Ether-Based channels for lithium Extraction", *Sep. Purif. Technol.*, **338**, 126415 (2024).
8. Y. Sun, M. Zhu, Y. Yao, H. Wang, B. Tong, and Z. Zhao, "A novel approach for the selective extraction of Li^+ from the leaching solution of spent lithium-ion batteries using benzo-15-crown-5 ether as extractant", *Sep. Purif. Technol.*, **237**, 116325 (2020).
9. J. Hua, J. He, H. Pei, J. Du, X. Ma, and J. Li, "A remarkable improved Li^+/Mg^{2+} selectivity and Li^+ recovery simultaneously by adding crown ether to tributyl phosphate-ionic liquid extraction system as co-extractant", *Sep. Purif. Technol.*, **335**, 126162 (2024).
10. M. Zhou, G. Yang, X. Tian, S. Xue, H. Li, and J. Pan, "Selective capture of lithium on crown ether functionalized hybrid polymer nanosheets prepared by one-step emulsified Pickering O/W/O double emulsion droplet reactors", *J. Environ. Chem. Eng.*, **10**, 106997 (2022).
11. I. Abdulazeez, "Size-controllable crown ether-embedded 2D nanosheets for the host-guest ion segregation and recovery: Insights from DFT simulations", *J. Phys. Chem. Solids*, **171**, 110983 (2022).
12. Y. Huang, X. Li, L. Chen, G. Luo, D. Tao, J.

Sun, Z. Qiu, Y. Chao, and W. Zhu, "Synthesis of a magnetic crown ether ion imprinted polymer material for the selective adsorption of lithium", *New J. Chem.*, **47**, 3134-3139 (2022).
13. J. Hua, J. He, H. Pei, X. Ma, S. R. Wickramasinghe, and J. Li, "Supported ionic liquid membrane contactor with crown ether functionalized polyimide membrane for high-efficient Li^+/Mg^{2+} selective separation", *J. Membr. Sci.*, **687**, 122038 (2023).
14. J. Lu, Y. Qin, Q. Zhang, Y. Wu, J. Cui, C. Li, L. Wang, and Y. Yan, "Multilayered ion-imprinted membranes with high selectivity towards Li^+ based on the synergistic effect of 12-crown-4 and polyether sulfone", *Appl. Surf. Sci.*, **427**, 931-941 (2018).
15. F. Yang, L. Li, J. Hua, J. He, X. Ma, and J. Li, "Electrospun nanofiber membrane of dibenzo 14-crown-4-ether polyimide for efficient selective lithium recovery from discarded lithium-ion batteries", *Sep. Purif. Technol.*, **334**, 126018 (2024).
16. L. Baudino, A. Pedico, S. Bianco, M. Periolatto, C. F. Pirri, and A. Lamberti, "Crown-ether functionalized graphene oxide membrane for lithium recovery from water", *Membranes*, **12**, 233 (2022).
17. Z. Li, G. He, G. Zhao, J. Niu, L. Li, J. Bi, H. Mu, C. Zhu, Z. Chen, L. Zhang, H. Zhang, J. Zhang, B. Wang, and Y. Wang, "Preparation of a novel ion-imprinted membrane using sodium periodate-oxidized polydopamine as the interface adhesion layer for the direction separation of Li^+ from spent lithium-ion battery leaching solution", *Sep. Purif. Technol.*, **277**, 119519 (2021).
18. G. Qu, J. Yang, Y. Ran, B. Li, H. Wang, and Y. Wei, "Adsorption performance and mechanism of TiO_2/PVDF-based lithium-ion imprinted membrane in leaching solution of spent lithium-ion batteries", *J. Clean. Prod.*, **442**, 140982 (2024).
19. J. Yang, G. Qu, C. Liu, S. Zhou, B. Li, and Y. Wei, "An effective lithium ion-imprinted membrane containing 12-crown ether-4 for selective recovery of lithium", *Chem. Eng. Res. Des.*, **184**, 639-650 (2022).
20. Q. Cheng, Y. Zhang, X. Zheng, W. Sun, B. Li, D. Wang, and Z. Li, "High specific surface crown ether modified chitosan nanofiber membrane by low-temperature phase separation for efficient selective adsorption of lithium", *Sep. Purif. Technol.*, **262**, 118312 (2021).
21. H. Li, Y. Wang, T. Li, X. K. Ren, J. Wang, Z. Wang, and S. Zhao, "Nanofiltration membrane with crown ether as exclusive Li^+ transport channels achieving efficient extraction of lithium from salt lake brine", *Chem. Eng. J.*, **438**, 135658 (2022).
22. W. Liu, G. Yan, E. Zhang, Q. Liang, L. Qin, M. Wang, X. Liu, and Y. Yang, "Extraction of lithium ions from acidic solution using electrochemically imprinted membrane", *Desalination*, **496**, 114751 (2020).
23. X. Meng, Y. Tian, M. Tang, and R. Qiao, "Separation and enrichment of Rb(I) in dicyclohexano 18 crown 6(DCH18C6)/PVC polymer inclusion membrane assisted by electric field", *J. Environ. Chem. Eng.*, **9**, 106712 (2021).