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AN OVERVIEW OF METHODS FOR LITHIUM SEPARATION

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Abstract:

Lithium (Li) is the lightest metal in nature. Natural lithium contains two stable isotopes ^{6}Li (7.43%) and ^{7}Li (92.57%), both playing a crucial role in the nuclear industry. Because of its high reactivity, pure elemental lithium is not found in nature. Instead, it may be seen as a constituent of salts or other compounds. Similarly, commercial lithium is available as lithium carbonate, a stable substance easily converted to other salts or chemicals. Production, processing, and purification of lithium are costly processes. The need to separate lithium appeared with the industry's transition from non-renewable to non-polluting. Recently, new techniques for lithium recovery have been developed at the laboratory scale with the potential for industrial production, such as adsorption-desorption cycling and diffusion dialysis pulsed electrochemical intercalation, and membrane separations [J. Hou et al., 2021]. The membrane-based separation processes have produced superior results for extracting Li^{+} and lithium isotopes enrichment. This overview will integrate the methods for lithium isotope separation using different types of membranes and their advantages and disadvantages.

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1. INTRODUCTION

Lithium is the 33rd most abundant metal on the planet. It is a highly reactive alkali metal that offers excellent heat and electrical conductivity, representing an element of great energy importance [H. Kazemzadeha et al., 2020]. These properties make it particularly useful for glass manufacturing, high-temperature lubricants, chemicals, pharmaceuticals, and lithium-ion batteries for electric cars and consumer electronics (figure 1) [W. Wu, S. Lu, 2023].

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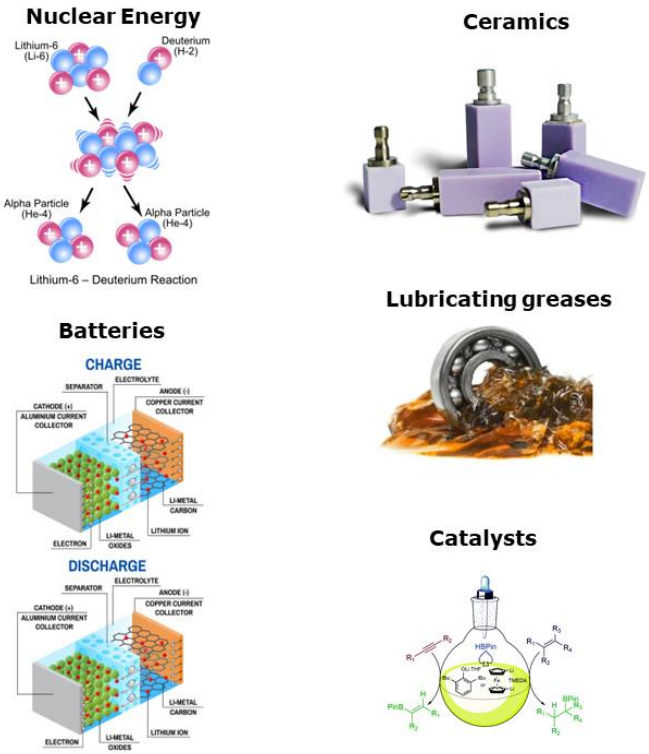

Figure 1. Various applications of Lithium

Nevertheless, pure elemental lithium is not found in nature but in salts or other compounds because of its high reactivity. Lithium is available in commerce as lithium carbonate, stable compound that can be easily transformed in other chemical substances. The need to separate lithium appeared with the industry's transition from non-renewable to non-polluting. Lithium isotopes are used in several fields of endeavor: ^{7}Li in the form of hydroxide (99.95%) is used in the cooling systems of pressurized water reactors-PWR; ^{7}Li as the essential component is a coolant with fluorine in molten salt reactors; also, ^{6}Li represents the source of tritium in nuclear fusion [de Oliviera et al., 2017]. Tritium (^{3}H) results from neutron absorption through the reactions below:

$$^{6}\text{Li} + n\,(\text{thermal}) \rightarrow {}^{4}\text{He} + {}^{3}\text{H} \quad (1)$$

$$^{7}\text{Li} + n\,(\text{fast}) \rightarrow {}^{3}\text{H} + {}^{4}\text{He} + n \quad (2)$$

The ^{7}Li reaction is an endothermal process requiring a neutron energy above 2.47 MeV, so most of the tritium production takes place in ^{6}Li, which is a strong neutron absorber affecting the reactor neutron economy, requiring extra fissile material in reactors with FLiBe. The reactor would be more efficient if ^{6}Li can be removed by isotope separation, an expensive process [J. T. Dolan, 2017].

The existing technology for separating lithium isotopes and enriching ^{6}Li is based on the use of mercury, generating severe environmental issues. In this respect, various solutions and or methods were sought and experimented: Two-Liquid-Phase Chemical Exchange Systems, Chemical exchange methods for lithium isotope separation, Lithium isotope separation by electromigration, Isotope separation by chromatography with Ion Exchange Resins, Resin-Supported Complexing Agents, Ion

Exchange Membranes, Laser Methods, Thermal Diffusion, Radiofrequency Spectroscopy, Electromigration, Distillation, Fractional Crystallization [A. Murali et al., 2021].

Lately, novel methods for lithium recovery have been developed at the laboratory scale with the potential to be applied in the industry: adsorption-desorption cycling, diffusion dialysis, pulsed electrochemical intercalation, and membrane separations [J. Hou et al., 2020]. The membrane-based separation produced good results for extracting Li^+ from the solution [S. Badea et al., 2022]. This overview will integrate the methods for lithium isotope separation using different types of membranes and their advantages and disadvantages. Due to low cost, low energy consumption, scalability, and high capacity for continuous processing, membranes have been widely applied in gas separation, water treatment, desalination, alcohol dehydration, and the dairy industry [J. Hou et al., 2021]. Membrane separation processes, such as nanofiltration (NF), electrodialysis, and electrolysis, can also be effective for lithium separation.

2. LITHIUM SEPARATION METHODS

2.1. Lithium separation by nanofiltration

This method involves a two-step separation process: Li recovery from brine via nanofiltration (NF) and membrane distillation (MD). Commercial membranes were polyamide (PA)-based NF membranes and a hydrophobic and porous polyvinylidene fluoride (PVDF) membrane. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to determine cation concentrations before and after Li recovery. The final Li concentration extracted from the brine is low due to poor separation from other remaining salt [Z. Yang, et al., 2016]. In this respect, NF membranes were used to filter out divalent cations, such as Ca^{2+} and Mg^{2+}, then the thinned brine was passed through the membrane distillation membrane to separate the remaining salts further and produce a Li-rich solution. The Li concentration after the two-step membrane process increased up to twelve times, so this simple two-step membrane process has excellent potential for Li recovery [Z. Yang et al., 2016].

Another study proposed a non-PA (non-polyamide), metal-coordinated NF membrane for separation processes in brines [L. Wang et al., 2021], which used polyether sulfone (PES) as the substrate, m-phenylenediamine (MPD) ligand solution, $CuCl_2$ metal solution, and $NaIO_4$ oxidant solution, and the Cu-MPD NF membrane was obtained (figure 2). The MPD, $CuCl_2$, and $NaIO_4$ solution was poured onto the surface of the PES substrate, followed by immersion of the surface-coated membrane into a GA/ethanol bath at 50°C to form a cross-linked Cu–MPD NF membrane.

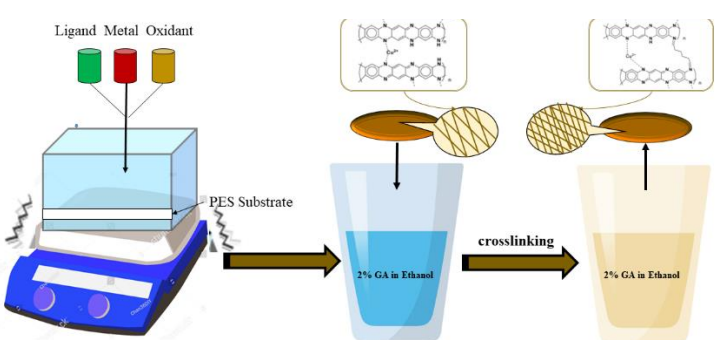

Figure 2. Membrane fabrication route and structural illustration of Cu–MPD NF membrane [L.Wang et al., 2021]

Due to poor Li^+/Mg^{2+} selectivity, the commercialized NF-PA based membranes are ineffective in lithium recovery processes. In this study, a copper metal and organic MPD complex were incorporated, the Cu^{2+} acting as both a cross-linking agent for MPD chains

and as positively charged sites. The obtained Cu-MPD NF membrane maintained an excellent water permeance and a good selectivity for Li^+/Mg^{2+}, much better than conventional NF membranes [Z. Yang et al., 2020].

2.2. Lithium separation by electrodialysis

Electrodialysis (ED) is an electrochemical membrane separation process in which ions are transferred through selective ion-exchange membranes from one solution to another using an electric field as the driving force [A. Siekierka et al., 2022].

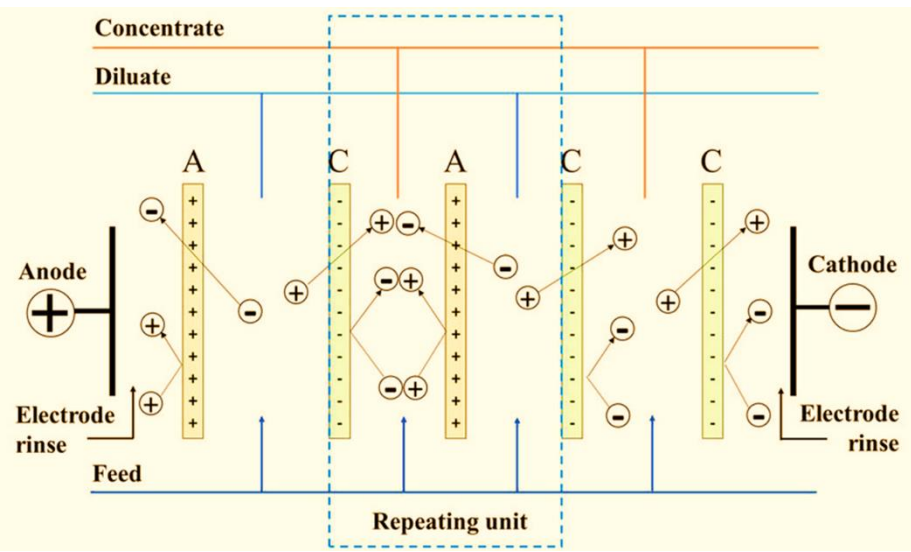

Figure 3. Schematic diagram of electrodialysis principles [A. Siekierka et al., 2022]

Only a few studies have been carried out without any membrane modification for the separation of lithium by the electrodialysis process. A selective cation exchange membrane within the electrodialysis process can be a promising recovery method for lithium ions from concentrated aqueous solutions [C. Huang al., 2007]. To be effective in the separation of lithium ions, ion exchange membranes require several modifications, such as increasing the membrane crosslinking, changing the ion exchange groups of the membrane, combining with conductive polymers, or modifying the membrane surface [H. Kazemzadeha al., 2020]. This last technique is widely used to improve membrane properties and performances. The synthesis process was optimized considering the flow of lithium ions and the molar selectivity of lithium ions over sodium ions. The CEM (cation exchange membrane) was prepared to separate Li^+ from Na^+ using electrodialysis [M. Bazrgar Bajestani et al., 2020]. The CEM was modified by in-situ polymerization of a polymer solution. To enhance the selectivity of the membrane for lithium ions separation, modified lithium manganese oxide ($LiCo_{0.5}Mn_{1.5}O_4$ with lithium adsorption capacity of 53.52 mg/g and molar adsorption ratio of lithium to sodium of 90.32) was added to the polymeric solution. The synthesis was optimized by considering two functions: lithium-ion flux and lithium-ion molar selectivity relative to sodium ion for the electrodialysis process to achieve proper results. The independent parameters for optimization were adsorbent weight percent, initiator weight percent, and molar ratio of acrylic acid to ethylene glycol (cross-linking agent) in the modification solution [C. Iurash et al., 1999].

This membrane was modified with a thin surface coating of spinel-type lithium selective adsorbent particles in poly (acrylic acid). This membrane was then incorporated with a layer of

lithium-selective adsorbent particles, the modified CEMs improving the cation selectivity. The membrane in artificial brine showed a molar Li^+ flux of 0.149 mol $min^{-1}m^{-2}$ and molar selectivity of 32.2, which was an 18.58% decrease and 62.3% increase, respectively, compared to pure one [M. Bazrgar Bajestani et al., 2020].

2.3. Lithium separation by electrolysis

A methodology was proposed for concentrating Li^+ in brines by coupling membrane electrolysis with crystallization to remove large concentrations of Na^+ [C. H. Diaz Nieto et al., 2020]. In this study, a three-compartment acrylic electrochemical cell was used. The anode (containing a titanium current collector in a buffer of carbonates) and middle (where brine was introduced) were separated by commercially available anion exchange membranes-AEM; likewise, the middle and cathode (containing stainless steel current collector) were separated by commercial CEM. Bicarbonate buffer was used for the anode, $NaHCO_3$ for the cathode, and brine (actual brine with/without Mg^{2+} and Ca^{2+} removed) for the middle zone. The first stage of electrolysis helped to remove any large divalent salts. The second stage drew Na^+ to concentrate the resulting brine with lithium further. The third stage, which highlighted the focus of the study, consisted of crystallization of the lithium in the form of lithium carbonate (Li_2CO_3) by introducing carbon dioxide [C. H. Diaz Nieto et al., 2020]. This method indicated a successful lithium carbonate recovery regardless of brine content or concentration, but the costs are an issue. Furthermore, other parameters must be considered: decreasing environmental impact, water by-product production, or process fastening.

2.4. Lithium separation by electromigration

Electromigration's separation of lithium isotopes represents one of the most friendly and promising environmental alternatives. Electromigration is the movement of atoms based on current flow through a material [Y. Kimura, Saka M., 2014]. If the current density is high enough, the heat dissipated within the material will repeatedly break atoms from the structure and move them (figure 4).

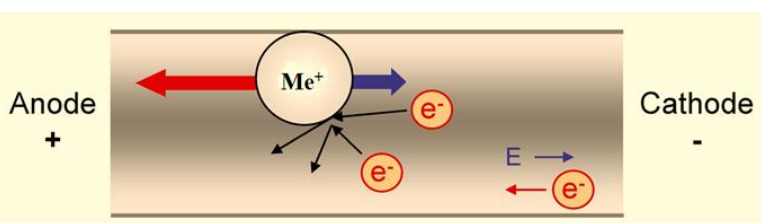

Figure 4. Schematic diagram of electromigration

The electromigration process is influenced by several factors, such as the pH variation of the electrolyte (pH variation of anolyte and catholyte), the time of migration, the applied voltage, and the catholyte used.

The effects of solute species and concentration in the catholyte with different voltages and migration time on the variation of pH in the electrolyte, lithium ions migration, and isotope separation were investigated [C. Wang et al., 2023]. This study selected four electrolytes as catholytes: HCl, $NH_3 \cdot H_2O$, NH_4Cl and NH_4HCO_3.These were chosen as the catholytes because digestion and evaporation could be cleaned out quickly when the samples need to be concentrated or determined. The electromigration experiments were conducted at 2 V and 16 V, respectively [C. Wang et al., 2023]. In this way, a system of "aqueous lithium salt solution - organic solution - aqueous solution was designed. The organic solution

contained 4-aminobenzo-15-crown-5 crown ether type, and for anode aqueous solution, cathode aqueous solution and organic solution were used a polypropylene film. The experiment results showed that during electromigration, the pH of the electrolyte changed dramatically. At high voltages, the higher the conductivity of the catholyte, the greater the variation in electrolyte pH. At the same time, the catholyte's pH influenced the anolyte's pH. The generation of H^+ in the anolyte causes competition for the complexation of lithium ions with the crown ether, which is detrimental to the migration of lithium ions. At the same time, the generation of OH^- in the catholyte leads to a decrease in the concentration of NH_4^+ or H^+ in the catholyte, which affects the migration of lithium ions from the organic solution to the catholyte [C. Wang et al., 2023].

Migration time was positively correlated with lithium ions concentration in the cathodic solution. An extremely high ^{6}Li isotope separation coefficient was obtained at a weak lithium-ion migration ratio, so the separation coefficient decreases rapidly as the migration ratio increases. It was found that the crown ether complexes with lithium ions or hydrogen ions in a ratio of 1:1 and with ammonium ions in a ratio of 2:1 [C. Wang et al., 2023]. When calculating the binding energy of the crown ether with the three ions, it resulted that the crown ether strongly chelates with hydrogen ions, followed by the ammonium ion and the weakest with lithium ions, which was consistent with experimental results [C. Wang et al., 2023]. This study provided important guidance to understand the electromigration process and select the better electrode solution and should be done to obtain a higher separation effect with this method.

3. MEMBRANE SEPARATION METHODS FOR LITHIUM ISOTOPES

Membrane separation processes are desirable as they can be highly selective for lithium ions and cost-effective. For more advanced separation performance, some modified membranes were obtained for composites to increase lithium-ion permeation while maintaining high rejection of other ions.

Various studies considered lithium isotope separation through membranes. One of the used membranes was a polysulfone-graft-monoazabenzo-15-crown-5 ether porous membrane (PSF-g-BN15C5), a membrane obtained using crown-ether [L. Yaolong et al., 2018].

Crown ether exhibits a high separation coefficient for lithium isotope separation owing to its precise size selectivity to cations. A crown ether-based solid−liquid extraction method for the lithium isotope separation with a high extraction efficiency is regarded as a valid alternative to the classic liquid−liquid method.

Dibenzo-15-crown 5-Ether (DB15C5) was used as an extractant, ionic liquid as a co-extractant, the solvent being anisole [Z. Zhang et al., 2020]. The lithium ions in the aqueous phase were extracted and isotopically separated by the organic liquid film method, the extraction equilibrium time being short. When 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was used as the co-extractant for LiI extraction, the obtained single-stage separation factor was 1.04, and the abundance of ^{6}Li isotope reached 7.8 %. The exchange process between ^{6}Li and ^{7}Li proved to be a spontaneous exothermic one ($\Delta H<0$, $\Delta S<0$). The results showed that the use of a crown ether and an ionic liquid can build an efficient system for the extraction and separation of lithium isotopes.

The PSF-g-BN15C5 was synthesized by nucleophilic substitution reaction from chloromethylated polysulfone (CMPSF) and BN15C5 (monoazabenzo-15-crown-5 ether). The porous membrane with a sponge-like structure was fabricated through noninduced phase separation-NIPS and characterized by FTIR spectrometer, XPS, ^{1}H NMR, and TGA. The PSF-*g*-BN15C5 membrane exhibited good lithium adsorption and separation performance by solid–liquid extraction system of H_2O-LiI/PSF-*g*-BN15C5. The maximum separation factor increased to 1.05,

which was higher than that obtained by free BN15C5 in the liquid–liquid extraction system of H_2O-LiI/$CHCl_3$-BN15C5 (figure 5) [L. Yaolong et al., 2018].

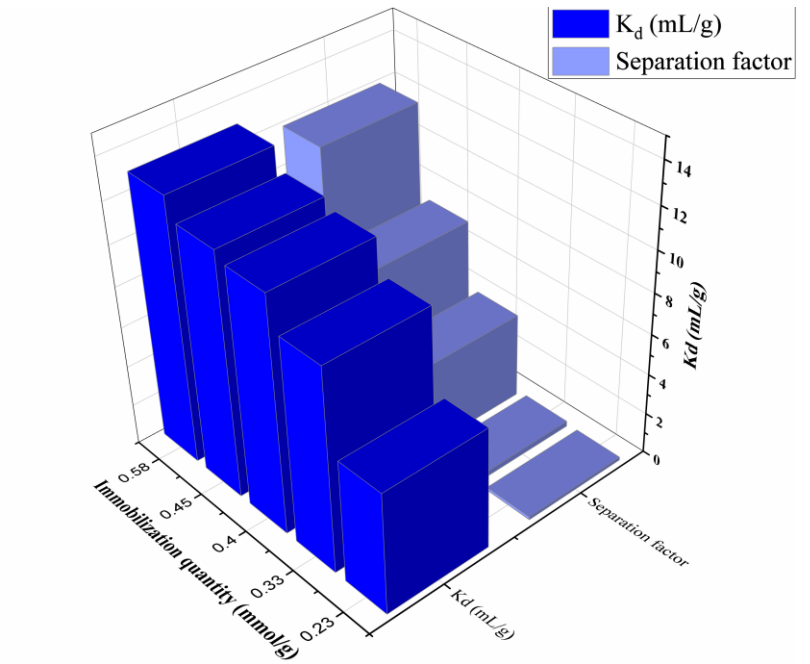

Figure 5. Effect of immobilization amount on distribution coefficient and separation factor (Lithium salt: LiI, 20°C)

Furthermore, the heavy lithium isotope (^{7}Li) was enriched in the aqueous phase, whereas the lighter one, ^{6}Li, was concentrated on the membrane phase [L. Yaolong et al., 2018]. These results revealed that PSF-g-BN15C5 offered an environmentally friendly method for lithium isotope separation with high extraction efficiency and can be considered for practical application.

Another membrane studied for lithium isotope separation was chitosan-graft-benzo-15-crown-5-ether (CTS-*g*-B15C5)/polyvinyl alcohol (PVA) porous blend membrane. The immersion-precipitation-phase inversion prepared this. Dynamic cyclic adsorption (solid−liquid extraction) was applied to determine the single-stage lithium isotope separation factor. After extracting, the concentration of lithium ions in the aqueous solution was determined by inductively coupled plasma optical emission spectrometry [Y. Zeng, et al., 2018].

The separation factor obtained by using the LiI−H_2O/CTS-*g*-FB15C5/PVA blend membrane extraction system reached 1.05, higher than those obtained by the CTS-g-FB15C5 film (1.03) and FB15C5 (4′-formoxylbenzo-15-crown-5 ether) (1.02). This indicated that grafting crown ether onto CTS (cellulose tri-stearate) polymers improved the lithium isotope separation. Furthermore, the heavy isotope, ^{7}Li, was enriched in the aqueous phase, whereas the lighter one, ^{6}Li, was concentrated in the film or membrane phase.

Figure 6 highlights the effects of the immobilization amount of crown ether on CTS, distribution coefficient (K_d), and single-stage separation factor (α). It can be seen from that K_d increased from 13.5 up to 49.3, and α increased from 1.008 to 1.046 with an increase of IA from 1.07 to 2.6 mmol·g^{-1}. The main reason was that the crown ether molecules dispersedly grafted on the CTS chains would increase the chance for each crown ether molecule to complex with lithium ions and enhance the efficiency of isotope adsorptive separation. The results were in good

agreement with the solid–liquid extraction results obtained by the LiI–H_2O/PVA-*g*-FB15C5 film system and the LiCl–methanol/PSF-*g*-AB15C5 polymer system [Y. Zeng, et al., 2018].

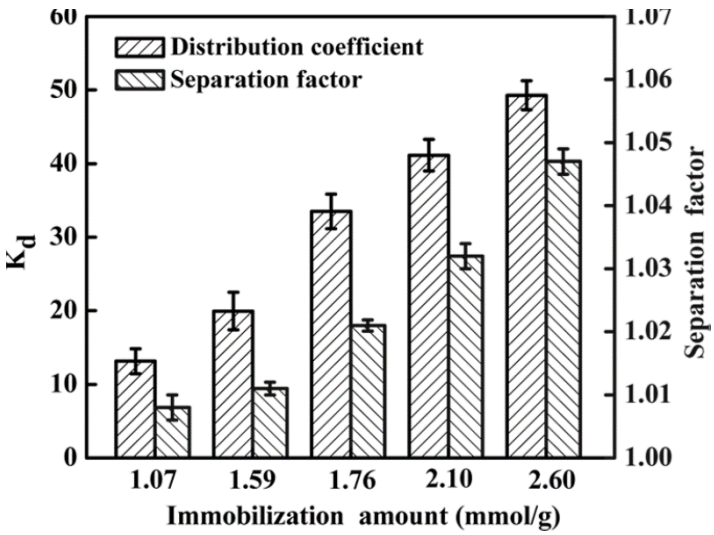

Figure 6. Effect of the immobilization amount on lithium isotope separation [Y. Zeng, et al., 2018].

A composite membrane PSf-g-BN15C5/NWF was prepared for adsorptive separation of lithium isotopes by noninduced phase separation, the equilibrium separation factor reaching 1.05 [Y. Liu et al., 2018]. It was stated that lighter-isotope was enriched in the solid (membrane) phase and the heavy one in the solution phase, respectively [Y. Liu et al., 2018]. According to Bigeleisen's theory, heavy isotopes can be easily concentrated in "stronger bonding environments" [J. Bigeleisen, 1965]. The use of polysulfone-graft-4′-aminobenzo-15-crown-5-ether (PSf-g-AB15C5) porous membrane as stationary phase packed in a chromatography column correlated with a four-stage tandem membrane chromatography method was also reported [H. Pei et al., 2019]. The relative abundances of ^{7}Li and ^{6}Li increased from 92.40 to 92.66% and from 7.60 to 7.80%, respectively [H. Pei et al., 2019].

To summarize, the blend membrane has great potential in developing green and highly efficient technologies, including membrane chromatography for lithium isotope separation [Y. Zeng, et al., 2018].

The dibenzo-15-crown-5-based polymeric membrane is another membrane used for lithium isotope separation at the laboratory scale. This was obtained by Troger's Base (TB) polymerization (PIM-DB15C5-TB), and it was also tested for lithium isotope separation [Y. Dong et al., 2022].

The first milestone in designing a selective membrane was how to facilitate its specific interaction with lithium ions. Derivatives of 15-crown-5 proved their effectiveness for the lithium isotope separation due to their cavity size similar with Li^+ diameter. The second milestone was that the membrane should have available mass transport channels, which could assure lithium isotope permeation. Furthermore, the membrane must be charge-neutral so that the electrostatic interactions compensate or eliminate the difference in the mobility between the two isotopes ($^6Li^+$ and $^7Li^+$). In this respect, two membranes (PIM-DB15C5-TB and Blend-DB15C5) were prepared [Y. Dong, et al., 2022]. The transport of $^6Li^+/^7Li^+$ across the membranes was measured by static ion diffusion in lab-made two-compartment diffusion cells. The $^6Li^+/^7Li^+$ selectivity for PIM-DB15C5-TB reached 1.08, while the value for Blend-DB15C5 was only 1.07. It was observed that the Li^+ permeation rate across the PIM-DB15C5-TB membrane ($1.3x10^{-7}$ cm^2/s) was higher than that across the Blend-

DB15C5 membrane ($1.2x10^{-10}$ cm^2/s). This was attributed to the introduction of highly rigid TB units, which obstructed the polymer chain from packing efficiently and provided PIM-DB15C5-TB with free volumes for Li^+ transport. The ion permeation rate through the Blend-DB15C5 membrane was extremely low due to the highly flexible and closely packed chain structure of Poly-acyl-DB15C5. The PIM-DB15C5-TB membrane exhibited a $^6Li^+/^7Li^+$ selectivity of 1.08 for a simulated $^6Li^+/^7Li^+$ mixture solution. A single-stage $^6Li^+/^7Li^+$ selectivity of 1.16 was achieved for a $LiNO_3$ solution with an electrodialysis cell assembled with PIM-DB15C5-TB (figure 7) [Y. Dong, et al., 2022].

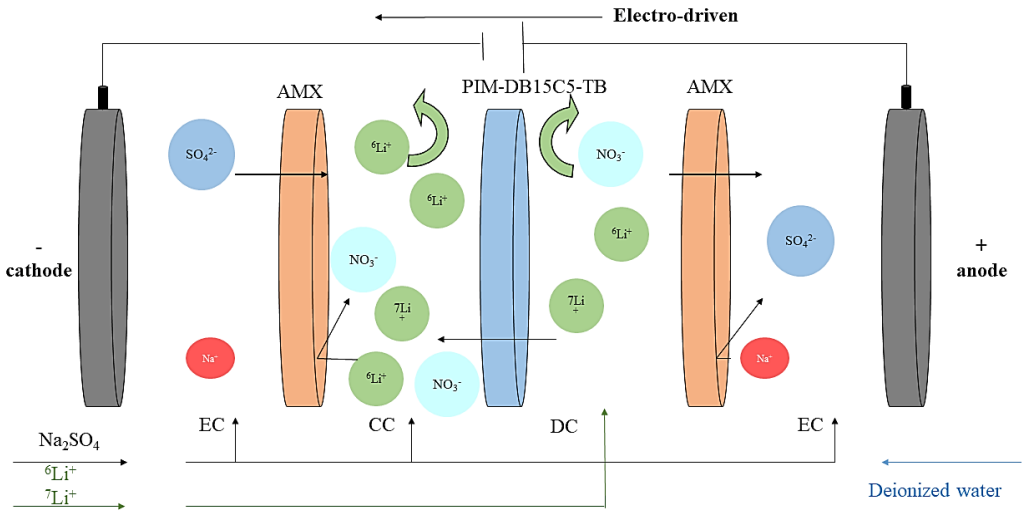

Figure 7. Schematic diagram of an electrodialysis cell for lithium isotope separation [Y. Dong, et al., 2022].

It can be concluded that dibenzo-15-crown-5-based polymeric membranes with highly rigid backbone structures and abundant free-volume elements can be considered a promising solution for $^6Li^+/^7Li^+$ separation. The goal was to categorize the membranes for selective separation of lithium ions. To improve the selectivity, the membranes were modified using crown ethers, which proved their efficiency at laboratory scale.

A membrane chemical exchange process for isotope separation was introduced to separate lithium isotope using solvent resistant polyethylene vinyl alcohol (EVAL) hollow fiber membrane [Z. Yang et al., 2020]. For ^7Li enrichment (up to 93%), a multistage cascade membrane chemical exchange system was built and azo chelating agents were used as the organic phase. The used membrane showed mechanical and lithium flux stability for hundreds of hours, in a laboratory-scale experiment [Z. Yang et al., 2020]. The work can be considered as the fundament for future application of membrane chemical exchange process for isotope separation.

4. CONCLUSIONS

Lithium recovery from different sources benefits lithium-ion battery production, water purification, brine waste reduction, and the nuclear industry. Lithium isotopes separation represents a significant milestone in nuclear science and industry taking into consideration the current environmental and energetic situation.

Nanofiltration, electrodialysis, electrolysis, and electromigration using membranes are ion-separation processes effective for lithium extraction from monovalent and

multivalent metal ion solutions. The most technically viable techniques for the separation of lithium isotopes are two-phase chemical exchange (using crown ethers), displacement chromatography and electromigration, the latter being technically more difficult. Electromigration and electrodialysis methods proved to be one of the most eco-friendly and promising alternatives for the separation of lithium isotopes. Still, the experimental approaches must be optimized and scaled up. However, only the separation using two-phase chemical exchange with crown ethers produced separation factors comparable to those of the classical separation method. Other experimental approaches using the electrochemical isotope effect are expected to emerge in the coming years. Displacement chromatography methods are one of the old but still used methods for the separation of lithium isotopes. Among them, the ion exchange method using crown ethers grafted on polymers seems to be one of the most innovative and studied methods, although only lab-scale experiments were reported.

Membrane separation processes are desirable as they can be highly selective of lithium ions and cost-effective. To improve the separation performance, some studies have modified the membranes to increase the permeation of lithium ions and the rejection of other ions. These studies have shown varying results, some better than others, but lithium recovery, particularly by membrane filtration, is an area that requires further investment. However, the various combinations of composite membranes and separation processes revealed the vast potential for further innovative lithium recovery.

A techno-economic analysis and life cycle appraisal for each of the Li separation or Li isotopes enhancement must be required to further estimate the environment impact, energy demand, costs, productive capacity and potential scale-up. A suggested route can be the investigation of the synergies between the mentioned methods. A strategic merger of two or more of these methods can diminish their individual issues.

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