Review

The Technologies of Electrochemical Lithium Extraction Process from Lithium-Containing Solutions

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Abstract: With the rapid development of new energy vehicles and the digital electronics industry, the demand for lithium has surged, necessitating advanced lithium extraction technologies. Electrochemical methods, noted for their high selectivity and efficiency in extracting target ions from liquid sources in an environmentally friendly manner, have become increasingly vital. These methods are versatile, applicable in scenarios such as lithium extraction from saline lakes, mother liquor separation, and lithium enrichment. They include electrochemical deintercalation, electrochemical ion pumps, and electrodialysis, each offering unique benefits and challenges depending on the application context. This review provides a detailed exploration of the research progress in lithium extraction using electrochemical methods and discusses future prospects for these technologies, emphasizing their potential to meet the growing demand for lithium.

Keywords: electrochemistry; lithium extraction; recycling; lithium-ion battery

1. Introduction

With the continuous advancement of the new energy sector, lithium-ion batteries, which offer advantages such as long service life and mature technology, have been applied in various aspects of daily life [1–3]. Particularly in recent years, following the rapid growth of the new energy sector and the continuous expansion of the electric vehicle market, the consumption of lithium resources has been escalating annually [4–6]. In light of the Statistical Multifragmentational Model (SMM), the worldwide demand for lithium batteries witnessed a year-on-year growth of 52% in 2022, while the supply of lithium resources reached as high as 840 Kt [7]. From a global perspective, a notable mismatch in the regional supply and demand of lithium resources is evident. According to European battery regulation (2023) and The United States Department of Energy of Resource Recycling Policy, in view of the strategic importance of batteries, it is necessary to set out rules on the sustainability, performance, safety, collection, lithium recycling, and second life of batteries. It is important to create a harmonised regulatory framework for dealing with the recovery rate, purity of lithium compounds, and costing of batteries that are placed on the market in the union. Lithium ore exploitation resources in the upstream of the supply chain are mainly distributed in Australia, Chile, Argentina, and other regions in South America [8,9]. Thus, the extraction of lithium resources from secondary-resource lithium becomes the focus of researchers. Secondary lithium resources are generated along with the slag from lithium ore [10], with hydrometallurgical chemicals leaching the lithium from waste lithium batteries [11]. The evaporation, hydrometallurgical chemical leaching, solvent extraction, and adsorption/desorption are applied in lithium extraction. The evaporation technique can greatly reduce the use of chemicals and environmental impact, but high
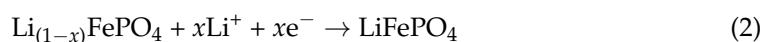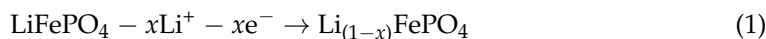
energy consumption and high carbon emissions restrict its future development. The hydrometallurgical chemical leaching precipitation technique has advantages of operation simplicity and low cost; disadvantages include poor selectivity, low lithium recovery, and the production of a large amount of wastewater requiring further treatment. The solvent extraction technique has the advantages of being a simple process with a high lithium recovery rate; the disadvantage is that it is only suitable for high-content lithium brine with fewer magnesium impurities, so the use of solvent extraction is limited. With the continuous expansion of the scale of lithium ore production and the recycling of waste lithium-ion batteries, the total amount of lithium-rich solutions shows an increasing trend year by year [12,13]. Therefore, efficient and convenient lithium extraction technology is worthy of study in the future.

Currently, a wide array of lithium extraction technologies are employed to recover lithium from lithium-containing solutions, including hydrometallurgy [14,15] and electrochemical recovery processes [16,17]. The primary technology utilized is the hydrometallurgical method, which employs the co-precipitation technique to recover metal elements from lithium solutions. These recovered metals are then processed and reproduced as chemical raw materials, facilitating the recycling of lithium resources. This approach allows for the efficient extraction and reuse of valuable metals, contributing to sustainable lithium resource management. The primary technology used is the hydrometallurgy method, which utilizes co-precipitation to recover metal elements from lithium solutions and reproduce them as chemical raw materials, thereby achieving the recycling of lithium resources [18–20]. Electrochemical extraction technology is an efficient lithium extraction technology that has been rapidly developing in recent years [17,21]. The electrochemical lithium extraction technology features high efficiency, environmental friendliness, and low energy consumption, with extensive prospects in the future [22,23]. This review aims to analyze the properties of various electrochemical lithium extraction methods from lithium-containing solutions, outline the current research status and technical characteristics, and promote the development of more efficient and environmentally friendly electrochemical lithium extraction technologies to meet the increasing demand for lithium extraction.

## 2. Different Techniques of Electrochemical Lithium Extraction

2.1. Electrochemical Deintercalation Method

LiFePO$_4$ is a commonly used anode material in lithium-ion batteries. LiFePO$_4$ has a typical olivine-type crystal structure [23,24]. The crystal structure of LiFePO$_4$ is composed of [LiO$_6$] octahedra and [PO$_4$] tetrahedra, which facilitate the migration of lithium ions and electronic conduction through the Fe-O-Fe lattice planes. The chemical reactions involved in the removal and insertion of Li$^+$ in the LiFePO$_4$ crystal structure are depicted in Equations (1) and (2) [25] (Figure 1).

$$\text{LiFePO}_4 - x\text{Li}^+ - x\text{e}^- \rightarrow \text{Li}_{(1-x)}\text{FePO}_4 \tag{1}$$

$$\text{Li}_{(1-x)}\text{FePO}_4 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{LiFePO}_4 \tag{2}$$

Based on the above electrochemical delithiation theory, lithium iron phosphate is widely used for lithium extraction and lithium enrichment. Zhao et al. [26–29] conducted extensive research on lithium extraction using the LiFePO$_4$ electrode. They developed a "rocking chair" electrode system, which alternates between a lithium-rich LiFePO$_4$ electrode and a lithium-poor Li$_{(1-x)}$FePO$_4$ electrode. This system is divided by an anion exchange membrane, with the electrolytic cell containing initial liquid on one side and lithium-rich liquid on the other. Under a direct current electric field, the lithiation reaction occurred at the lithium-poor electrode (FePO$_4$ cathode), where lithium ions were absorbed from initial liquid, while the delithiation reaction occurred at the lithium-rich electrode (LiFePO$_4$ anode), diffusing lithium ions into the lithium-rich liquid. Anion exchange membranes are used, allowing Cl$^-$ ions to migrate from the cathode to the anode side to maintain charge balance. By switching the positions of the two electrodes and repeating the process, the selective enrichment of lithium ions is

achieved. The experimental results indicated that the maximum amount of lithium embedded reaches 38.93 mg/g after 10 h, while the maximum amount of embedded Mg^{2+} is 5 mg/g in $MgCl_2$ solution (220 mg/L). The selective enrichment of lithium ions has been confirmed in a simulated brine composed of LiCl and $MgCl_2$ solutions. The initial concentration of Li^+ was 220 mg/L, and the final Mg/Li ratio decreased from 60 to 45, demonstrating effective lithium-ion selectivity in the process.
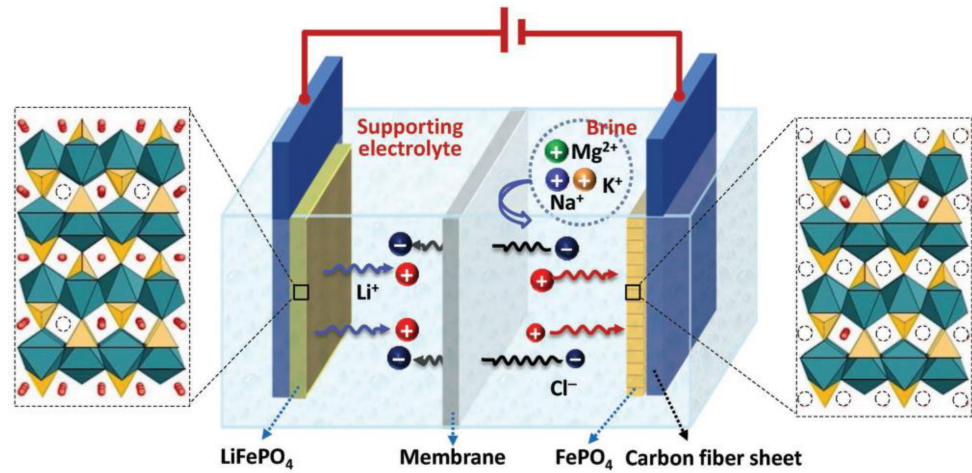
Figure 1. Structure of the $LiFePO_4/FePO_4$ electrolytic cell for lithium extraction reprinted from [26] under the terms of the CC-BY license.

Deng et al. [30] carried out the electrochemical extraction of lithium using a $LiFePO_4/FePO_4$ electrochemical system. The electrode was modified using PEG-6000 as a poregen to obtain abundant pore structures of about 5–20 μm formed on the surface of the electrode. This modification increased the adsorption capacity to 17.10 mg g^{-1}, a 57.02% improvement. In this electrochemical system, delithium occurred at the $LiFePO_4$ electrode, while the lithiation reaction took place at the $FePO_4$ electrode. The system was effectively employed to recover lithium resources from geothermal water with a low lithium concentration. When the modified $LiFePO_4$ and $FePO_4$ electrodes were utilized in an H-type electrolytic cell with an operating voltage of 1 V, the retrieval rate of Li^+ reached 90.65% after eight cycles in the geothermal water, and the electrode structure of both the anode and cathode remained stable (Figure 2). For both the desorption of Li^+ from the $LiFePO_4$ electrode and the adsorption of Li^+ by the same electrode in the geothermal water tank, the current gradually decreased with time and cycle times.
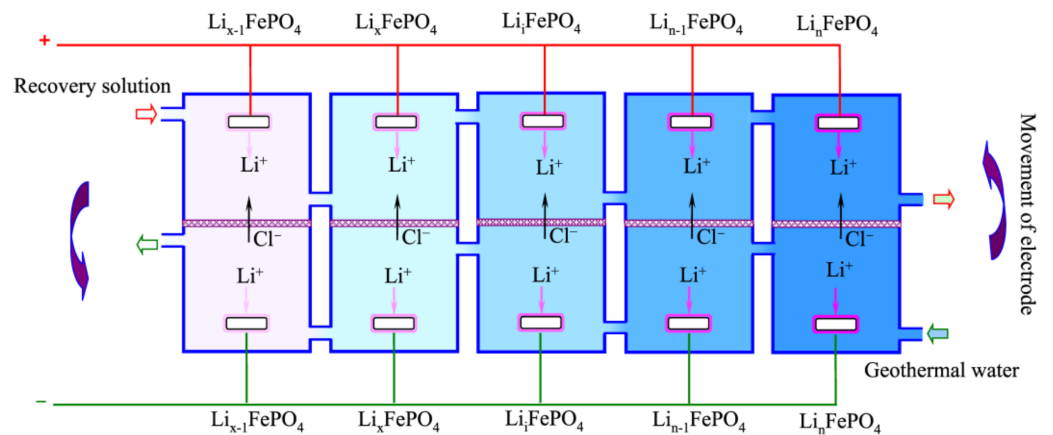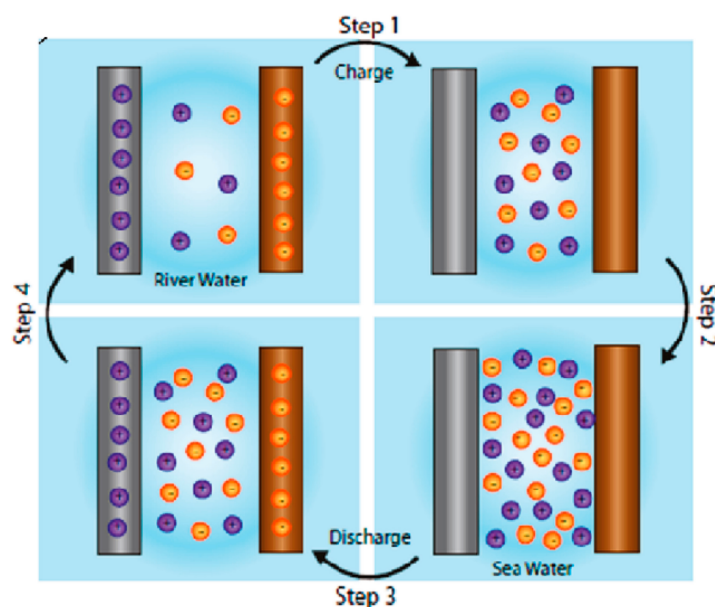

Figure 2. The schematic diagram of continuous electrochemical device proposed for Li^+ recovery from geothermal water. Reprinted from [30], Copyright 2020, with permission from Elsevier.

The electrochemical deintercalation method is commonly utilized for lithium extraction. Researchers have observed that the diffusion of anions is driven by the concentration differences of cations between the anode and cathode, leading anions to migrate towards the opposite electrode [31]. As a result, a small number of anions and impurity ions pass through the anion exchange membrane under the driving force of a concentration difference, and the separation rate of Li$^+$ declines. Specifically, in the treatment of Li$_2$SO$_4$ solutions, the relatively large ionic volume of SO$_4^{2-}$ increases the migration resistance. This not only necessitates higher voltages for the electrochemical adsorption reaction, prompting numerous side reactions, but also results in substantial electrical resistance and high energy consumption during the process [32].

While the electrochemical deintercalation method is straightforward and easy to operate, it has several drawbacks that require improvement. Specifically, the ionic conduction ability of the membrane and the stability of the electrode material need significant enhancements to optimize the process.

### 2.2. Electrochemical Ion Pump

The principle of the electrochemical ion pump involves extracting lithium under an inverse concentration gradient. The lithium ions are captured selectively by lithium absorption materials, while the counter electrodes (such as Pt and Ag) are adopted to capture anions [33–35]. Initially reported in the early 1990s by Kanoh and his team, the electrochemical ion pump method utilized λ-MnO$_2$ as the working electrode and a Pt wire as the counter electrode to extract lithium ions from a polycationic solution [36,37]. Subsequently, La Mantia and Yoon's group innovated this technique by replacing the Pt electrode with an Ag electrode, and its working principle is shown in Figure 3. The river water is low-salt water, and the seawater is high-salt water. The salt composition of seawater can be observably reduced by electrochemical ion pump technology. The λ-MnO$_2$ serves as the intercalating electrode, adsorbing and desorbing lithium ions, while the Ag electrode functions as the counter electrode, capturing and releasing chloride ions, thereby significantly reducing the power consumption during the electrochemical reaction [38].

Figure 3. The schematic diagram of electrochemical extraction lithium by ion pump. Reprinted with permission from [36], Copyright 2011 American Chemical Society.

In recent years, with continuous advancements in materials manufacturing technology, the scope of electrochemical ion pumping applications has notably expanded. Deng et al. introduced two 100 mL electrolytic cells, serving as the raw material cell and the recov-

ery cell, respectively, which were used for the recovery of Li$^+$. A green and innovative FePO$_4$/K$_2$NiFe(CN)$_6$ [FPO/KNiFC] electrochemical ion pump technique to recover lithium from low-concentration sources in geothermal water (Figure 4) was used. The performance of the LiFePO$_4$ electrode was enhanced by modifying it with multiwalled carbon nanotubes, improving both the insertion capacity and rate. Although the single insertion capacity stands at 14.88 mg/g, and the recovery efficiency reaches 95.81%, the recovery rate can be increased through cycle insertion–release processes [39]. Moreover, Kazuya Sasaki et al. developed a new electrochemical pumping technology for the extraction/recovery of lithium. This system comprises two power supplies, three electrodes, and a La$_{0.57}$Li$_{0.29}$TiO$_3$ (LLTO) electrolyte [40] (Figure 5). The distinctive structure enables the positive voltage of the third electrode in the cathode solution to be applied to the conventional battery through a secondary power supply. LLTO serves as an ideal solid electrolyte for high-purity lithium extraction and recovery, effectively blocking the permeation of cations other than lithium ions. Notably, this newly designed system demonstrates flexibility in adapting to a variety of commercial electrolytes and the capability of significantly enhancing the lithium collection rate of the mentioned main circuit [41]. Furthermore, an additional subcircuit provides effective control, accelerating the lithium absorption process by at least 464-times compared to traditional systems.
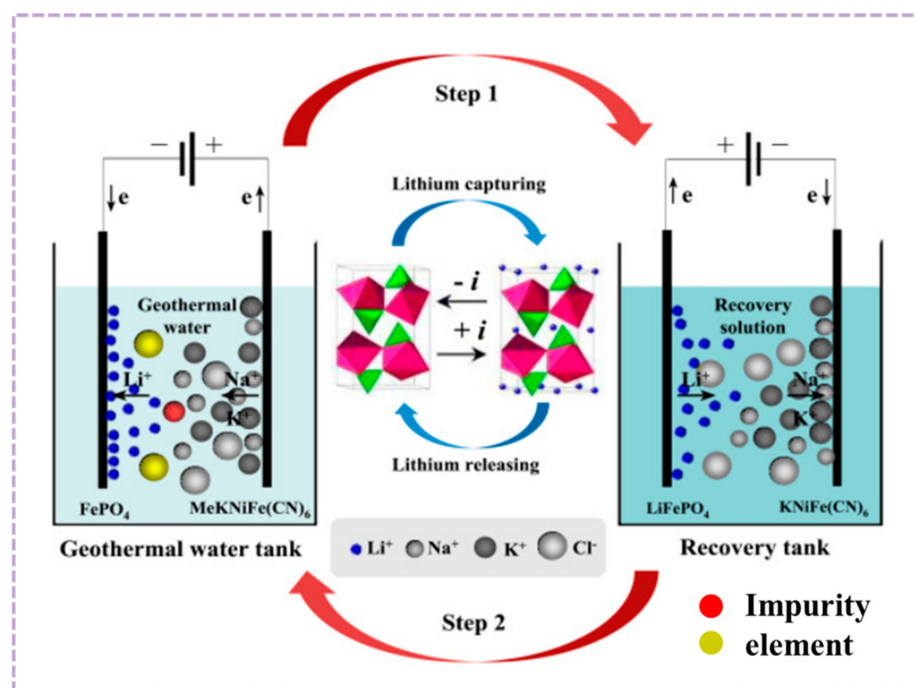
Figure 4. Apparatus and mechanism for lithium recovery from geothermal water by the FPO/KNiFC ion pump technique. Reprinted from [39], Copyright 2020, with permission from Elsevier.

Ion pump lithium extraction technology surpasses other electrochemical methods in selectivity, cycling stability, and energy efficiency, offering significant advantages for practical applications. The success of this technology hinges on electrode materials that exhibit high selectivity and a robust ion exchange capacity. Currently, the use of ion pump technology for lithium recovery remains predominantly within the realm of laboratory research. For it to transition to industrial applications, further extensive research is essential to address the practical implementation challenges and scale-up processes.
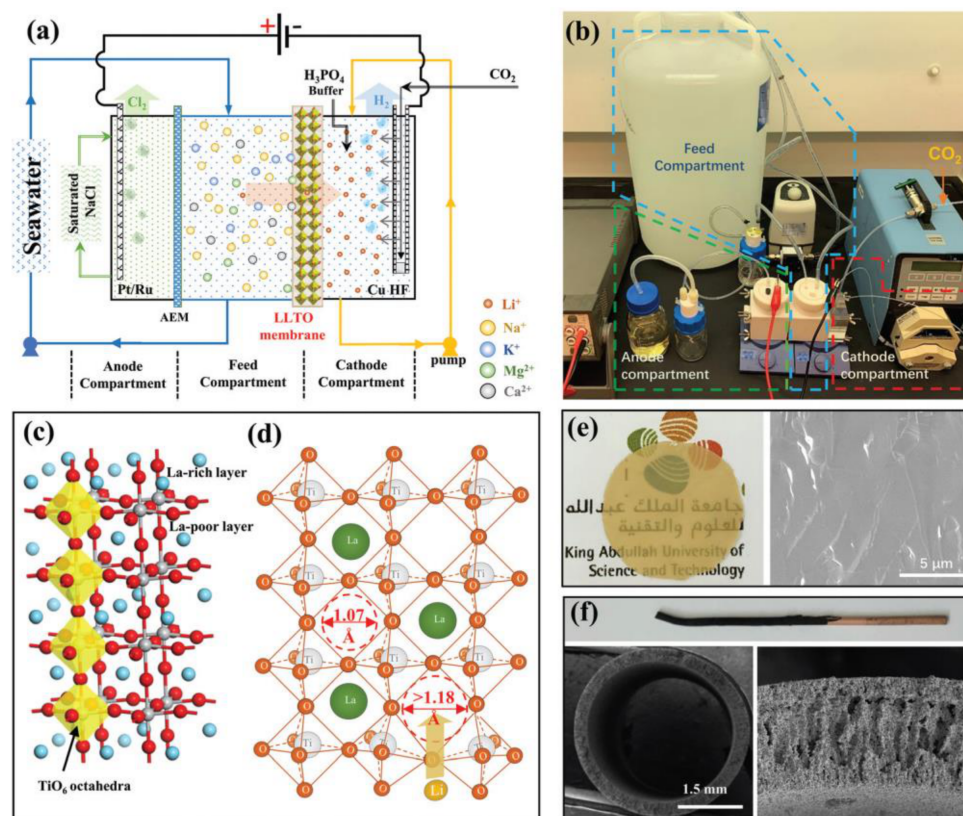
Figure 5. A Schematic of newly designed electrochemical pumping cell comprising a $La_{0.57}Li_{0.29}TiO_3$ (LLTO) electrolyte, Pt anode and cathode, a third Ni electrode, and main and secondary power supplies, thereby enabling mass transfer during Li ion extraction/recovery. (**a**) Schematic illustration of the three-compartment electrical cell to continuously enrich lithium from the feed solution to the cathode compartment and simultaneously generate H_2 and Cl_2 at the cathode and anode, respectively; (**b**) photographic image showing the enrichment setup; (**c**) the crystal structure of LLTO in ball-and-stick mode; (**d**) illustration of the percolation of lithium ions in the LLTO lattice; (**e**) images showing the glass-type LLTO membrane (~20 mm in diameter); (**f**) images showing the copper hollow fibre cathode, which is coated by catalytic Pt/Ru (dark colour) at one end. Reprinted from [41], Copyright 2008, with permission from RSC.
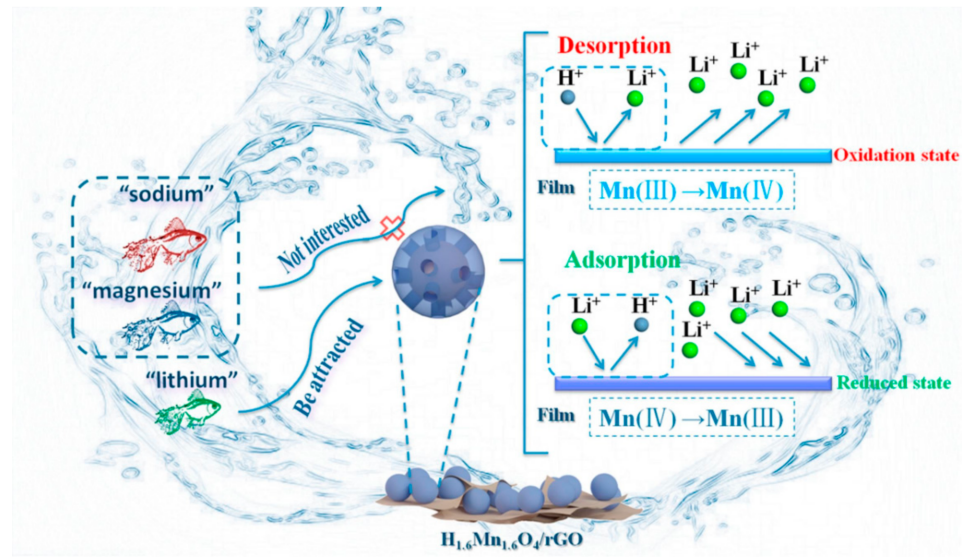
2.3. Electrodialysis Method

Electrodialysis is an electrochemistry separation technology based on selective membranes, which was originally developed in the field of seawater desalination [42–44]. And with the development of membrane materials, electrodialysis began to be applied for lithium recovery from saline and other lithium solutions. The principle of electrodialysis technology is that a voltage is applied between the two electrodes, driving ion migration across the membranes to achieve the enrichment of target ions [45,46]. The working principle of the electrodialysis system is schemed in Figure 6. The figure depicts a schematic diagram of a typical electrodialysis cell constituted by a succession of anion and cation exchange membranes arranged in an alternating pattern between an anode and a cathode. Beneath an electrical potential applied between the anode and the cathode, the positively charged cations migrate towards the cathode, and the negatively charged anions proceed towards the anode. The electrodialysis system consists of repetitive units, including an cation exchange membrane (CEM) and an anion exchange membrane (AEM), which separate the concentration and dilution chambers alternately. The monovalent ions (e.g., Li^+, Na^+, K^+, and Cl^-) could permeate through these chambers and pass through the CEM and the AEM into the concentration chamber, while the divalent ions (e.g., Mg^{2+}, Ca^{2+}, SO_4^{2-}) are blocked by the ion exchange membrane and retained in the desalination chamber.
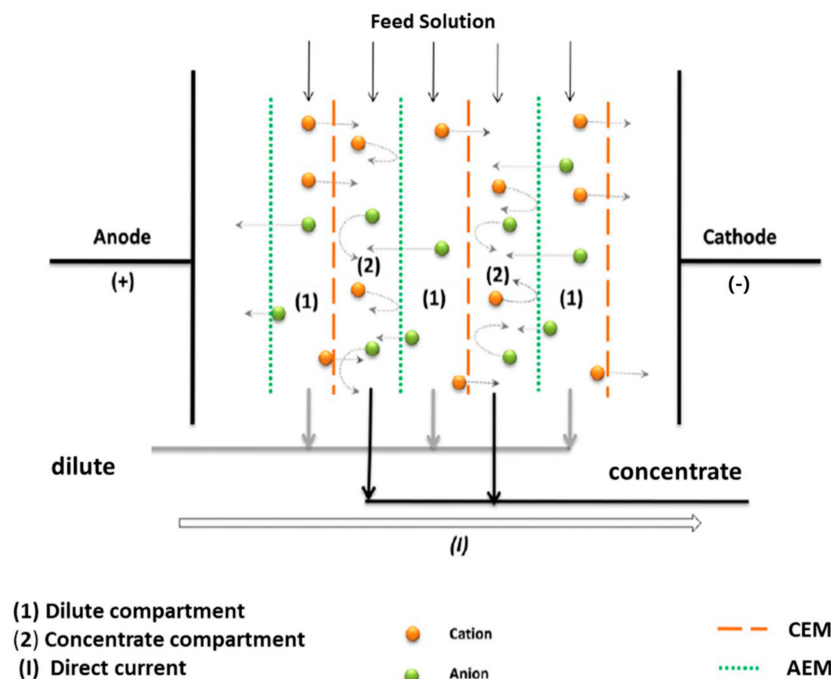
Figure 6. The schematic of electrodialysis. Reprinted from [46], Copyright 2019, with permission from Elsevier.

Abuliti Abudula et al. developed a novel lithium-ion separation composite membrane composed of $H_{1.6}Mn_{1.6}O_4$ nanoparticles and reduced graphene oxide (rGO) by vacuum filtration technology [47]. The membrane's effectiveness in selectively extracting low-concentration lithium ions from aqueous solutions is attributed to the selective adsorption properties of $H_{1.6}Mn_{1.6}O_4$ and the excellent conductivity of rGO (Figure 7). There exist lattice protons in $H_{1.6}Mn_{1.6}O_4$/rGO composite films. Generally, ion exchange between Li^+ ions and H^+ ions is conducted during the chemical adsorption/desorption process. The results show that the lithium-ion adsorption capacity of $H_{1.6}Mn_{1.6}O_4$/rGO composite membranes reached an equilibrium of 38.78 mg/g after 5 h. Impressively, the adsorption capacity of these composite membranes was maintained at 99%, even after five cycles. Specifically, during selective adsorption experiments with initial molar ratios of Li^+/Na^+ and Li^+/Mg^{2+} set at 1:1, the adsorption ratios achieved were 10.39 for Li^+/Na^+ and 10.23 for Li^+/Mg^{2+}, respectively, demonstrating significant selectivity in ion exchange.

Shao et al. [48] contrived the multi-stage selective electrodialysis (S-ED) process with high-performance monovalent cation exchange membranes (MCEMs) to handle simulated penetration water from a one-stage nanofiltration (NF) process. The mussel-inspired gallic acid/polyethyleneimine- assembled membrane (M-GA/PEI) with specific architecture and charge properties manifested superior separation performance compared to CSO (a commercial MCEM) during the multi-stage S-ED process. They designed a multi-stage selective electrodialysis (S-ED) process utilizing high-performance monovalent cation exchange membranes (MCEMs), as shown in Figure 8. These MCEMs were tailored to treat simulated osmotic water produced by a one-stage nanofiltration (NF) process. Leveraging the specific architectural and charge characteristics, the M-GA/PEI achieved a Li^+-rich solution with a high concentration (approximately 8.33 g/L) and purity over 96.4% simultaneously, under a volume ratio of 10:1 (under DC:CC converter) during both the first- and second-stage S-ED processes.

Figure 7. Schematic of the adsorption and desorption on the $H_{1.6}Mn_{1.6}O_4$/rGO composite film. Reprinted from [47], Copyright 2019, with permission from Elsevier.
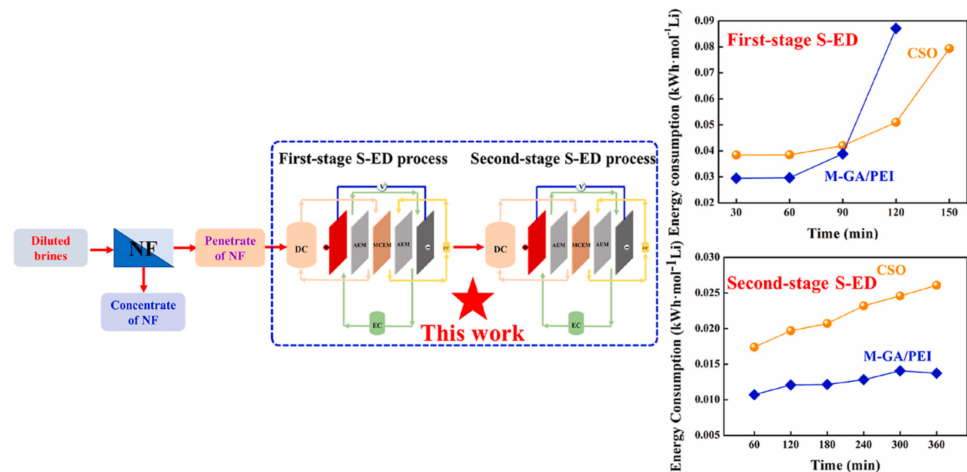
Figure 8. The configuration of the designed selective electrodialysis. Reprinted from [48], Copyright 2023, with permission from Elsevier.

Liu et al. introduced an innovative electrodialysis technology, which utilized $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), a lithium superionic conductor, and incorporated an assisted charge balance (ACB) system [49]. The electrodialysis technology was operated under low-voltage and ultra-low-current conditions (Figure 9). The excellent ion selectivity of LATP, coupled with the improved recovery of ACB, enables this technology to achieve exceptionally high separation efficiencies and significantly reduced energy consumption. By implementing a two-stage extraction process on aged brine, the battery-grade Li_2CO_3 is produced directly with a purity of 99.93%. Remarkably, when applied to pristine brine, the technology achieves an impressive Li/Mg separation coefficient as high as 5924. This simplified production process is expected to significantly reduce the cost of Li_2CO_3 production.
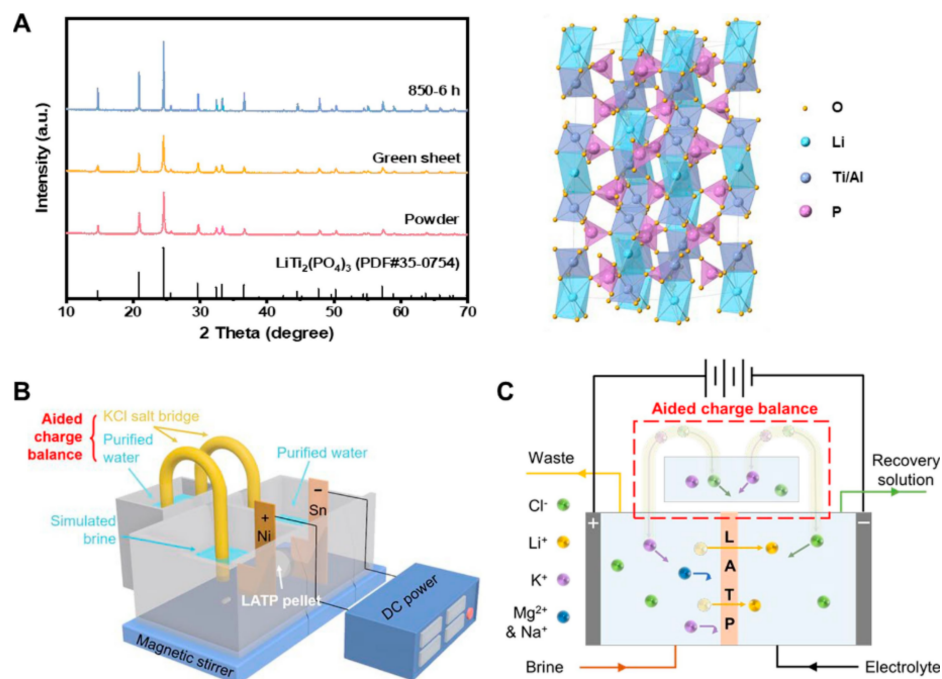
Figure 9. (**A**) XRD pattern and the crystal structure of LATP, and the schematic illustration of (**B**) LES and (**C**) the extraction process. Reprinted from [49], Copyright 2024, with permission from Elsevier.

The electrodialysis method offers significant advantages in terms of cost efficiency, environmental sustainability, and effective separation of lithium ions from bivalent cations. However, its effectiveness in separating lithium from sodium ions is limited. Additionally, the presence of specific anions in the solution, particularly high concentrations of SO_4^{2-}, can dramatically reduce the lifespan of the electrodialysis membranes [50,51]. Another challenge with this method is the generation of substantial amounts of wastewater that require further treatment. Moreover, the migration rate of lithium ions during electrodialysis is relatively slow, leading to lengthy processing times. Consequently, while electrodialysis presents potential benefits, its application in lithium extraction requires more in-depth study to overcome these operational challenges.

3. Conclusions

Electrochemical technology holds promising prospects in lithium extraction and adsorption, encompassing methods such as electrochemical deintercalation, ion pumps, and electrodialysis. These techniques offer advantages, such as low cost, environmental sustainability, and reusability. Despite their potential, many of these technologies are still under development, facing significant barriers to commercialization. To advance the field of electrochemical lithium extraction, further research should focus on the following aspects:

(1) Electrochemical materials play a crucial role in determining the performance of lithium extraction systems. The effectiveness of both the anode and cathode materials in the electrochemical system, the ion exchange active materials in electrically controlled setups, and the membrane materials in electrodialysis processes directly influences the efficiency of lithium extraction. Therefore, there is a pressing need to enhance basic research into the development of new materials. Challenges such as low ionic mobility and suboptimal cycling stability persist in current materials. Addressing these issues could involve doping and coating materials, as well as engineering electrodes with perforations to modify their microstructures and chemical compositions, thereby improving their functional properties. In electrodialysis, the choice of membrane materials is critical for effectively separating monovalent from polyvalent ions. Advancements in this area should focus on increasing the ion conductivity, minimizing electrochemical impedance, and enhancing the chemical stability of these membranes. Such improvements will not only boost the performance

of lithium extraction but also enhance the overall sustainability and efficiency of the electrochemical methods employed.

(2) Optimization of electrochemical processes. In the past, the industrial production of lithium primarily focused on generating industrial-grade Li_2CO_3. However, advances in electrochemical production technology are now paving the way for the direct one-step production of battery-grade lithium compounds such as Li_2CO_3, LiOH, and LiCl. This shift enables not only a transition from single to multiple electrochemical processes but also a transformation of the industry towards refining chemicals and achieving battery-grade production through process optimization. Electrochemical lithium extraction optimally utilizes lithium-containing solutions and recovers lithium from low-concentration and economically unviable brines efficiently. As global efforts to reduce carbon emissions continue to evolve, industrial practices must adapt to minimize environmental impacts, carbon emissions, energy, and freshwater consumption. Upgrades in electrochemical lithium extraction technology are essential for significantly improving these parameters, which, in turn, will accelerate the rapid industrialization and commercialization of lithium extraction processes. This evolution is critical for supporting the growing demand for lithium in various high-tech applications, including electric vehicles and renewable energy storage solutions.

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