The Principle, Progress and Challenges of Lithium Extraction from Brine

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Abstract. With the great development of global electric vehicle and energy storage industry, the growing requirement for lithium resources is rising sharply. Efficient and green extraction of lithium from the brine of salt lakes with abundant reserves has become a key to ensuring the security of the lithium supply chain. As the current mainstream lithium extraction technology, absorption methods, membrane methods and electrochemical methods present their technical advantages. Also, they also face corresponding technical bottlenecks and scene limitations, especially in the salt lake brine in arid areas, where the extraction conditions are even more demanding. To adapting the lithium extraction strategy of low-energy, quick, sustainable, the text starts from the technical principles and elaborates on the extraction process in detail. It also reviews the latest research process and performance of each technology in terms of lithium extraction rate, selectivity and energy consumption. Based on it, the text discusses the current mainly challenge in material durability, system scalability, process collaboration, and economic efficiency in depth. Finally, the text predicts the future development trends of various technologies, aiming to offer theoretical references and technical insights for the development of the next generation of efficient, low-carbon, and sustainable lithium resource recovery technologies.

1 Introduction

Due to the development of global electric vehicle industry and increasing demand for large-scale energy storage, lithium-ion batteries, as the core energy storages devices, accounting for approximately 59% of the global demand, and the demand is still growing, which makes efficient and sustainable lithium extraction technologies extremely important. The currently reserves of lithium resources are approximately between 371 million and 436 million tons, mainly existing in salt lake brine (accounting for about 62%) and mineral deposits (accounting for about 38%) [1]. Among them, the brine becomes an important source of lithium resource supply, due to its large reserves and relatively lower mining costs.

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At present, the mainstream technologies for extracting lithium from brine mainly include extraction methods, membrane methods, adsorption methods, and electrochemical methods. However, these methods all have their own advantages while also facing their respective limitations: Although the extraction method has certain efficiency, the most promising system (such as TBP-$FeCl_3$) is limited by technical and economic factors and is difficult to achieve large-scale industrial application; In the adsorption method, the adsorbent must have high stability and high lithium selectivity. So far, the main research has mainly focused on manganese-based adsorbents and lithium-ion sieves, which can effectively adsorb lithium ions in high magnesium-lithium environments. However, powder-type adsorbents often face problems such as framework dissolution and performance degradation; Membrane method has the characteristics of low energy consumption and high efficiency, but is constrained by cost, flux, pollution, and selectivity contradictions; Electrochemical methods have the advantages of simple process, good sustainability, strong selectivity, and low operating costs [2], but they rely on external power supply, which to some extent limits their application in remote or energy-poor areas.

This text focuses on adsorption methods, membrane methods, and electrochemical methods. Through a systematic elaboration of the basic principles, key component design, performance, and research progress of these three methods, it analyzes the main challenges currently faced and envision their future development directions, with the aim of providing a reference for the development of a new generation of sustainable lithium extraction technologies.

2 Lithium resources: current status

Lithium is the lightest metal in nature. It has several uses because of its particular physical and chemical properties.In recent years , new energy vehicles and energy storage technology have grown quickly . So, the use of lithium in new energy materials has received much attention .

Salt lake brines have complex chemical makeups. They possess numerous chlorides, sulfates, carbonates, and borates of sodium, potassium, boron, calcium, and magnesium.The compositions of prominent salt lakes across the globe vary significantly.So, the ways to get lithium from salt lakes are also different.

China's lithium resources are primarily located in Qinghai and Tibet, with smaller deposits found in regions such as Xinjiang. Compared with foreign salt lakes, the majority of China’s salt lake brine lithium resources are characterized by a high proportion of Mg relative to Li and with a relatively high lithium concentration. This makes it harder to get lithium from the brine [3]. The Mg/Li ratio in Qinghai salt lake brine is from 30:1 to 1800:1. The crucial aspect of utilizing lithium resources from salt lakes lies in effectively separating magnesium from lithium. The brine from Tibet's salt lakes is rich in lithium and boron.Carbonate-type salt lake brines typically have a low Mg/Li ratio or contain little to no Mg^{2+}. Because of this, people can get lithium carbonate through natural evaporation. So, this kind of resource has a special advantage. Tibet salt lake brine has plenty of lithium resources and good prospects, but development is still limited and slow right now.

Lithium extraction from salt lake brine offers a significant cost advantage compared to lithium extraction from hard rock ore. Furthermore, the total lithium resources in seawater are vast, exceeding 10,000 times the total terrestrial lithium resources. In recent years, lithium extraction technology from seawater brine has garnered considerable attention from researchers both domestically and internationally, leading to notable advancements.

3 Lithium extraction technology

3.1 Electrochemical method

Electrochemical lithium extraction technology is based on the principle of reversible transfer of Li^+ between the solid-state electrode and the liquid electrolyte during the charge and discharge of lithium-ion battery cathode materials. Applying this principle in reverse for lithium extraction means that the discharge process uses lithium-containing brine/concentrated seawater to replace the organic electrolyte, achieving selective insertion extraction of Li^+. The charging process uses a recovery solution with a single component as a substitute, achieving extraction enrichment of Li^+. This process avoids the use of acidic or strongly oxidizing eluent required by the traditional ion sieve method and has advantages such as being environmentally friendly, causing little structural damage, and having low energy consumption ($\leq$30 W·h/mol Li^+). It is particularly suitable for selective separation of lithium in complex systems such as low grade, high magnesium-to-lithium ratio brine and concentrated seawater [4].

Electrochemical lithium extraction technology uses $LiFePO_4/FePO_4$ as the electrode material. It mainly relies on the reversible insertion and extraction reaction of lithium ions in the olivine structure. This method uses the big differences in the polarization behavior of Li^+, Na^+, K^+, and Mg^{2+} to get selective extraction. Zhao et al. did this research in 2013 [5]. The reduction peak of lithium is at about -0.197 V (vs. SCE), but the reduction peaks of sodium and magnesium are at more negative potentials, -0.511 V and -0.971 V, respectively. Potassium, but, shows limited insertion. So, by controlling the electrolysis voltage, like at 0.7 V, the co-insertion of impurity ions like magnesium and sodium can be well suppressed, and this achieves high selective separation of lithium.

The system's core parts include a $LiFePO_4/FePO_4$ composite working electrode, a foam nickel counter electrode, a saturated calomel reference electrode, and a two-compartment electrolytic cell separated by an anion exchange membrane. Operation is done in a potentiostatic mode, which helps electrode recycling and continuous lithium extraction by stepwise insertion and extraction processes. This setup is very good for high magnesium-to-lithium ratio brine systems.

In 2014, Liu et al. studied the interference of Na^+ on the lithium extraction process using this electrode system and found that by controlling the electrolytic voltage below 0.3 V (e.g., 0.25 V), the competitive insertion of Na^+ can be well suppressed, and this much improved the lithium selective extraction performance [6]. Under this voltage condition, after 10 cycles, the Li^+ concentration in the solution increased to 432 mg·L^{-1}, and the average lithium capacity of the electrode reached 38.6 mg·g^{-1} $LiFePO_4$.

Traditional methods have drawbacks. But electrochemical lithium extraction technology has advantages. First, it is very selective. It can block other ions like Mg^{2+} and Na^+ from interfering. Second, it uses little energy. The usual energy use is 1.4 to 20 W·h per mol of Li^+. Third, it does not need acid or base. So, it is good for the environment. Fourth, the electrode can be reused in place. And it works well after many uses.

3.2 Membrane methods

Membrane technology is a physical separation method based on the selective permeability of membrane materials, divided into two categories: nanofiltration (NF) and Electrodialysis (ED). Nanofiltration is studied due to its efficient separation performance and easy preparation ability. Electrodialysis is characterized by its strong ability to sieve monovalent/multivalent ions under the action of an electric field.

The research on nanofiltration for lithium extraction from salt lakes usually focuses on the separation of Mg^{2+}/Li^{+}, due to the extremely similar physical properties of Mg^{2+} and Li^{+}. The separation mechanism of nanofiltration includes size screening and Donnan effect, etc. It has excellent retention performance for polyvalent ions and has good permeation performance for monovalent ions.

Ren et al. tested the effect of nanofiltration in rare carbonate-type salt lakes. The three membranes, MNF-XZ, NF270, and DK, all had an interception rate of over 90% for SO_4^{2-}. However, the interception rate of Li by DK was only 15%. Nanofiltration showed good lithium osmotic effect in carbonate lakes [7], In the modification strategy, TANG et al. used the deposition method to form a negatively charged surface-active layer, achieving an interception rate of 98.6% for $MgCl_2$ [8]. This proves the great potential of the modification strategy in improving the lithium extraction efficiency.

Electrodialysis membrane technology involves the use of monovalent cation exchange membranes to prevent the passage of multivalent ions such as Mg^{2+} through the exchange membranes while allowing Li^{+} to pass through. Under the action of an external electric field, lithium ions and other cations are separated from anions.

Nie et al. used the CSO membrane, which, under optimized conditions, reduced the Mg/Li mass ratio in the simulated brine from 150 to 8, and the lithium recovery rate reached 95.3% [9]. However, traditional ion exchange membranes have problems such as decreased selectivity for cations and low energy efficiency when used in high-concentration salt water, which has led to the breakthroughs in the modification of ion-selective membranes. This is an important direction for electrodialysis methods.

Compared with nanofiltration membranes, electrodialysis membranes have lower energy consumption and higher energy efficiency. Although this technology can effectively remove divalent ions, it still has difficulty in separating lithium in salt water with a large number of similar-valence cations. Also, this technology still has shortcomings such as long processing cycle, unstable structure, and high operating costs, which affect the large-scale application of electrodialysis technology.

3.3 Adsorption method

The adsorption method involves the separation and extraction of lithium from brine in salt lakes using lithium-selective adsorbents, which is highly favored due to its simplicity and high cost-effectiveness. The current mainstream high-performance adsorbents can be classified into three major categories: aluminum-based, manganese-based, and titanium-based. All these materials achieve high selectivity in adsorbing lithium through their unique structural designs.

Aluminum-based adsorbents for lithium extraction are mainly lithium-aluminum layered double hydroxides (Li/Al-LDHs), with the formula $LiX\ m\ Al(OH)_3{\cdot}nH_2O$ (where X refers to denotes anions). The Li^{+} adsorption mechanism is based on the selective occupation of octahedral vacancies in the aluminum hydroxide layers by Li^{+}: the ionic radius of Li^{+} is well-matched with the vacancy size, while larger interfering ions (e.g., Mg^{2+}, Na^{+}) are excluded via steric hindrance [10]. Meanwhile, the interlayer anion-ion hydration energy difference further enhanced the lithium adsorption selectivity. In practical applications, the adsorption performance of Li/Al-LDHs is significantly impacted by the interlayer anions. In sulfate-type brines, sulfate ions tend to replace the interlayer chloride ions, causing structural distortion and reducing the desorption efficiency. To address these issues, metal atom doping is commonly used to modify the adsorbent to reduce the problems of dissolution and loss. In 2024, Huo et al. proposed a cobalt-doped and sulfate-intercalation co-modified aluminum-based adsorbent (Co-LDHs-SO_4). The lithium adsorption capacity in sulfate-type salt lake

brines reached 10 mg/g, and it exhibited extremely high separation coefficients for Mg^{2+}, Na^{+} and K^{+} [11].

Manganese-based adsorbents are also known as lithium manganese oxide (LMO) ion sieves, and they are mainly derived from spinel precursors (e.g. $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$, $Li_{1.6}Mn_{1.6}O_4$). Their adsorption mechanism consists of two key steps: Firstly, the Li^{+} in the spinel structure exchange with H+ in acidic solutions, forming hydrogen-type manganese oxides (HMO) and generating vacant crystal sites; Secondly, these vacant crystal sites selectively adsorb lithium ions from brine by virtue of the ion radius matching property, while excluding larger interfering ions (e.g. Mg^{2+}, Na^{+}) [12]. Manganese-based adsorbents commonly encounter issues including manganese leaching and structural instability during adsorption process. Qian et al. successfully doped one-valent potassium ions in the spinel structure of $Li_{1.6}Mn_{1.6}O_4$. This adsorbent achieved a lithium adsorption capacity of 26.0 mg/g in actual brine, and the adsorption capacity remained at 90.8% of the initial value after 6 cycles, which also decreased the manganese dissolution rate from 5.4% to 4.0% [13].

Titanium-based adsorbents (LTO) mainly originate from two types of precursors: layered $Li_2\ TiO_3$ (converted from acid washing to H_2TiO_3) and spinel $Li_4Ti_5O_{12}$ (converted to $H_4Ti_5O_{12}$). Their adsorption mechanism is mainly based on ion exchange, where hydrogen ions in H_2TiO_3 or $H_4Ti_5O_{12}$ selectively exchange with lithium ions in the brine. At present, the main problems of titanium-based adsorbents include high mass transfer resistance, slow adsorption and desorption rates, and the possibility of crystal transformation during the acid washing process which leads to a sudden drop in adsorption capacity. By means of element doping modification, introducing metallic or non-metallic elements can regulate the crystal structure of the adsorbent, optimize the adsorption active sites, and broaden the lithium-ion transmission channels, which can effectively improve the aforementioned deficiencies. In some practical cases, the Fe-doped titanium-based adsorbent attained a maximum adsorption capacity of 34.8 mg/g in actual salt lake brine, with a titanium dissolution rate of $\leq 1\%$ during the cycle. The Mo-doped material had an adsorption capacity of 78 mg/g in a 1.8 g/L LiOH solution. The La-doped material could increase the adsorption capacity of the material by 8.2% compared to the modified version [14].

4 Conclusion

This article provides a comprehensive review of three mainstream technologies for extracting lithium from salt lake brine - electrochemical method, membrane method, and adsorption method, which systematically summarizes the technical principles, performance characteristics, and application bottlenecks. The electrochemical method is based on the reversible insertion and extraction of lithium ions. It uses $LiFePO_4/FePO_4$ as the core electrode and achieves high-selective separation of lithium in a high-magnesium-to-lithium ratio system through voltage regulation. It stands out for its low energy consumption, no consumption of acids and bases, and the ability to regenerate the electrode in situ. However, relying on an external power source has limited its application in remote areas with scarce energy resources. The membrane method is divided into nanofiltration and electrodialysis. It realizes ion separation through the selective permeation of membrane materials, which has the characteristics of low energy consumption and high efficiency. However, their practical implementation is hindered by membrane contamination, high preparation costs, and difficulties in separating covalent cations of the same valence. The adsorption method is widely concerned due to its simple process and high cost-effectiveness. The core is three types of adsorbents: aluminum-based, manganese-based, and titanium-based. They can be adapted to different types of salt lake brine through modification. Nevertheless, some key technical barriers remain such as adsorbent dissolution, insufficient cycle stability, and difficulties in solid-liquid separation of the powder.

Authors contribution

All the authors contributed equally and their names were listed in alphabetical order.

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