Advanced Electrode Materials in Capacitive Deionization for Lithium Recovery

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Abstract. Demand for lithium batteries and lithium resources is growing because of the fast development of electric vehicles which will reach 900,000 metric tons per year by 2025. But the available lithium supplies are running out, and the future utilization of lithium resources will depend on strong productivity and resource recovery. However, current methods of extracting lithium ion resources still have the disadvantages of slow rates, unstable system outputs, and low purity. These methods can hardly compensate for the huge market demand in the future. The alternative technology, capacitive deionization (CDI) technology based on electrochemical ion pumping, provides a high capacity and rate of lithium resource recovery, which uses renewable electrode materials, reduces system waste generation, and has high lithium ion purity in the extract, which is sufficient to meet the future market demand. This mini-review analyzes the electrode materials used in CDI technology with a particular emphasis on the development of three materials, Olivine $LiFePO_4/FePO_4$, Spinel $LiMn_2O_4/\lambda\text{-}MnO_2$, and Spinel $LiNi_{0.5}Mn_{1.5}O_4$. The advantages and disadvantages of the current advanced materials are evaluated from various perspectives, and the feasibility of different electrodes is analyzed.

Keywords: Electrochemical Lithium extraction, Resource recovery, Capacitive deionization.

1. Introduction

Lithium is employed extensively in all facets of contemporary civilization since it is the lightest metal and the lightest solid element. The battery business has grown to be the greatest consumer of lithium in recent years due to the industry's quick expansion in new energy vehicles and the demand of lithium resources constant growth [1]. As the annual global demand for lithium resources increases at a rate of 8% - 11%, the stock of lithium resources can no longer meet the huge market demand in the future [2]. The lack in supply has led to the global average price of lithium from 8650 to 17000 $per metric ton from 2016 to 2020 [1, 2].

The distribution of globally available lithium resources is shown in Figure.1[2]. Since the boundaries of Chile, Bolivia, and Argentina constitute the "Lithium Triangle," where about half of the world's lithium deposits are concentrated and are present in salt lakes at concentrations as high as 220 to 3800 mg/L, current lithium resource extraction methods are mainly Lime-Soda Evaporation process aimed at the salt lake lithium resources [3, 4].

Although the evaporation method has the advantage of low cost, its slow process cycle and high water consumption make it not meet the requirements of sustainable development, which promotes the development of different processes, including precipitation, adsorption, solvent extraction, and membrane process. Unfortunately, the precipitation method cannot remove brine containing a high proportion of impurity salts, such as high concentration magnesium salts, and will cause serious precipitation waste pollution; The adsorption method has a severe test for the adsorption capacity and screening capacity of adsorbents; Solvent extraction can effectively separate various ions, but it is still unable to deal with brine with a high concentration of impurity salts. At the same time, the extractant will also cause container corrosion and even environmental pollution [1, 3]. The fatal defects of various processes show that developing sustainable lithium resource extraction technology is very important.

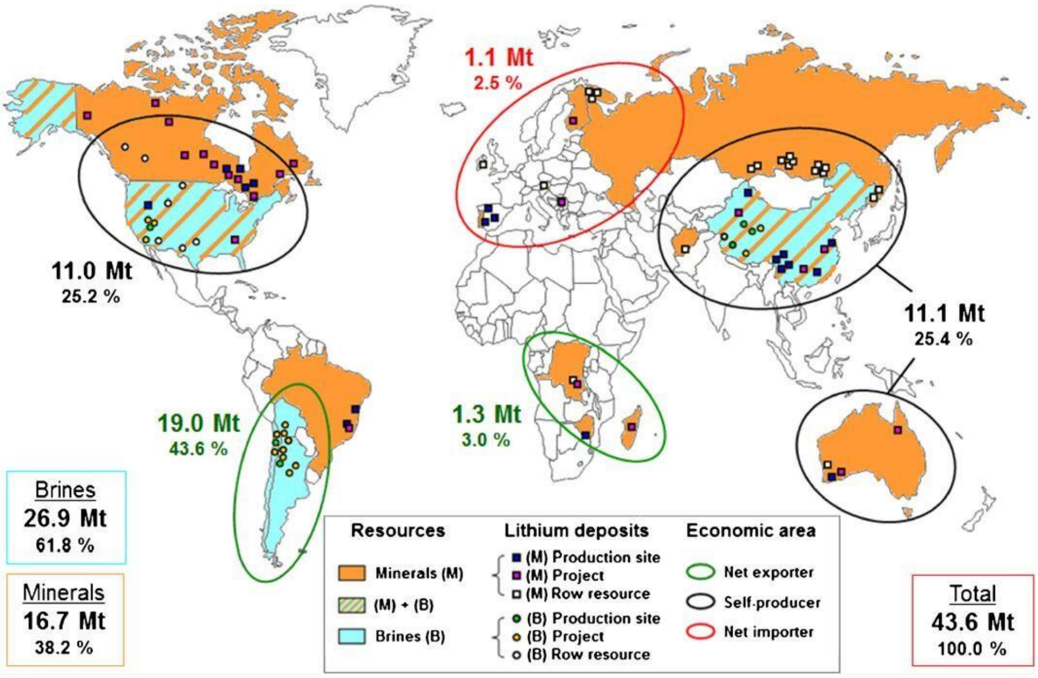

Figure. 1. Map of the distribution of available lithium resources [2]

In recent years, the process of recovering lithium-ions by capacitive deionization (CDI) methods has received extensive attention, research, and development due to its excellent recovery performance, development potential, and environmental protection during operation. Kim and colleagues created CDI systems, which combine oxidation generation electrodes (boron-doped diamond) and lithium recovery electrodes (lithium manganese oxide, LMO) to concurrently remove organic impurities and recover lithium resources. The test results in a lithium-rich solution of nearly 99% purity and a 65% reduction in contaminants [1, 2, 4]. Due to its excellent adsorption selectivity, cyclability, and environmental friendliness, capacitive deionization recovery is a successful process for removing lithium resources from brine and seawater. As a result, this review provides an overview of the most recent developments in lithium extraction and recovery in CDI systems, with a particular emphasis on the recovery capabilities of various electrode materials for distinct lithium resource types on Earth.

2. Lithium Resources on the Earth

The global lithium resources are currently spread out over several spheres of the earth. The lithium substratum on land is mostly made up of brine and ore, while the lithium substratum on oceanic surfaces exceeds the land-based resources, exceeding 230 billion tons [5]. Additionally, different forms of lithium in soil and organisms circulate in the biosphere. Since lithium resources have been heavily mined and used in recent years, many obsolete lithium resources (such as abandoned lithium batteries) exist in the anthroposphere. Resources of lithium on earth circulate throughout the earth in a variety of states and forms, just like other metal ions.

2.1. Lithium Species in the Oceansphere

The oceans, which make up 97% of the water on earth and cover 71% of its surface, are abundant in resources. According to the measurements and calculations, there are 231400 million tonnes of dissolved lithium in seawater, which is 17800 times the total on land [5, 6]. Because of these massive reserves, in the future, the ocean's lithium resources will provide a consistent source of lithium. Unfortunately, seawater has relatively little lithium present. The efficiency of directly introducing seawater into the extraction device is extremely low, resulting in energy waste and cost increases[4]. Currently, brine lithium resources are abundant. Lithium resources in seawater are typically overlooked due to their complex processes and high costs. However, as land-based lithium resources become depleted in the future, seawater lithium resources will become increasingly important.

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2.2. Lithium Ores in the Lithosphere

As a metal element, lithium resources are widely distributed in minerals. Lithium ore is the most important and direct source of lithium resources for human use. Lithium deposits in the world are not scarce. It is estimated that more than 30Mt lithium resources are distributed in Chile, Bolivia, China, Australia, and other countries [7]. At present, the terrestrial lithium resources are mainly brine-type and pegmatite-type, supplemented by sedimentary and other potential lithium deposits[6, 7]. At the same time, with the continuous exploration of lithium deposits in various countries, the pattern of world lithium resources may change at any time.

According to data compiled by University of Michigan researchers Paul Gruber and Pablo Medina, brine lithium deposits make up 66% of the world's lithium resources, pegmatite lithium deposits make up 26%, and sedimentary lithium deposits make up 8% [5, 7].

2.2.1 Brine lithium deposits

Currently, brine lithium ore is the most important source of lithium resources. As shown in Figure 1, the "lithium triangle" in South America is the primary source of brine lithium ore[4, 6]. Brine lithium deposits are mostly concentrated in arid or plateau desert basins. Lithium can be enriched in underground brine, resulting in valuable lithium deposits [7]. The regional distribution of brine lithium resources in the world is shown in Table 1. Furthermore, many areas are currently unexplorable for lithium halide, indicating that lithium halide resources are plentiful.

Table 1 Estimated brine deposits lithium resources (Mt Li) [7].

Deposit	Li (Mt)
Uyuni, Bolivia	10.2
Atcama, Chile	6.30
Olaroz, Argentina	1.50
Zabuye, China	1.50
Rincon, Argentina	1.10
Diablillos, Argentina	0.90
Taijnar, China	0.90
Hombre Muerto, Argentina	0.80
Sal de Vida, Argentina	0.30
Clayton Valley, USA	0.20
Damxung, China	0.18
Total	21.60

Additionally, the extraction process of brine lithium ore is very simple; all that is required is to evaporate the brine naturally through the sun's action and pump it to each evaporation tank to gradually improve the concentration and purity of lithium [4, 7]. However, this is a time-consuming process. It takes more than three years, from the preliminary survey to the extraction of lithium resources to the final purification and precipitation of lithium carbonate [5, 6]. Simultaneously, the evaporation lithium extraction method will waste a lot of water resources, which should be considered, especially in arid areas. As a result, cleaner methods and technologies for extracting lithium ore from brine are required in the future, given the increased emphasis on sustainable development. Lastly, this method is incapable of responding quickly to sudden changes in market demand [4, 6, 7].

2.2.2 Pegmatite lithium deposits

Pegmatite deposits are widespread, primarily in ancient shields or geologically stable structures. Pegmatite is a type of granite and the main source of rare earth metals. Even though pegmatites are widely distributed, only 0.1% of them contain rare earth metals, and those with lithium resources are even scarcer [8]. Kesler estimated that lithium resource reserves of pegmatite ore are distributed across regions [7]. Spodumene is a common lithium-rich pegmatite, which used to be the first ore used to extract lithium resources for industrial production. Spodumene is a by-product of rare earth minerals including Tantalum (TA) and Rubidium (RB) that has significant economic advantages due to its high lithium concentration (1%–4%) and high recovery rates (60–70%) [4]. The advantage of extracting lithium resources from pegmatite deposits lies in the short production cycle and continuous production. However, the discovery and mining of lithium-rich deposits have grown more challenging as a result of the increasing demand for lithium resources. Meanwhile, mining and metallurgy will cause serious environmental hazards and energy waste.

2.2.3 Sedimentary lithium deposits and other lithium deposits

Sedimentary lithium deposits are less developed than the first two lithium deposits, owing to the low grade of most sedimentary lithium deposits. Lithium exists only in clay minerals through adsorption or isomorphism and has no industrial mining value [7]. However, the discovery of some clay lithium deposits with high lithium content in recent years has prompted the exploration and attention of sedimentary lithium deposits. Jadarite ore from the Jadar basin in Serbia is one of the most representative sedimentary lithium deposits, with a lithium content of 5.7%, which is higher than the lithium content of most lithium deposits [5, 7, 8]. Most sedimentary lithium deposits are still in the exploration stage, with only a few developed ore types, such as clay and tuff, which benefit from simple extraction and separation, low price, and high extraction rate [4]. As a result, sedimentary lithium deposits have enormous potential. At the same time, because the current survey of underground minerals is incomplete, many new lithium-rich minerals may emerge in the future, providing a significant supply of lithium resources.

3. Electrochemical Methods for Lithium Extraction and Recovery

Common brine lithium extraction techniques include precipitation (carbonate and aluminate precipitation), solvent extraction, ion exchange adsorption, nanofiltration, electrodialysis, and electrochemical lithium extraction [3, 4]. Compared with other brine lithium extraction methods, electrochemical lithium extraction is of great interest because of its high efficiency, energy saving, selectivity, safety, and environmental protection [1, 5]. Lithium-ion batteries' operating system serves as the foundation for electrochemical lithium extraction, using potential statically controlled Li^+ embedding/deletion of the salt lake brine in the electrode material to achieve lithium extraction.

Capacitive deionization (CDI), also known as electrosorption, is a technology that effectively removes salt ions from brine by adsorption through an electrochemical process to reach pure water (Figure 2).

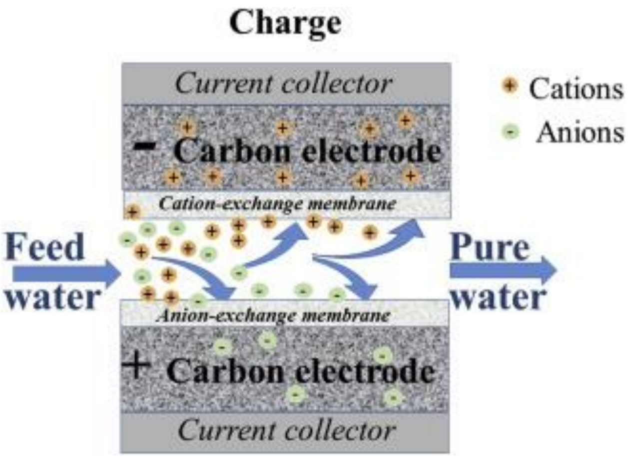

Figure 2. CDI working principle [9]

The benefits of CDI desalination technology are minimal equipment scaling, low energy use, and no contamination throughout the treatment phase. It has broad application prospects in industrial water softening, drinking water purification, and wastewater treatment. In the CDI desalination process, the electrode material can either be fixed to the collector or operated in a flowing manner in the electrode tank. CDI operating in a flowing manner is referred to as flowing electrode capacitive desalination (FCDI). Using FCDI technology, the continuous brine lithium extraction method described by Ha et al. has a maximum lithium adsorption capacity of up to 215 mol/m^2s at an initial feed solution concentration of 100 mg/L and a flow rate of 3 mL/min [2].All the research work confirms that CDI technology can achieve efficient and selective lithium extraction.

4. Electrodes for Lithium Extraction and Recovery

4.1. Olivine $LiFePO_4/FePO_4$

Because the purity and effectiveness of lithium extraction are impacted by the high concentration of sodium and magnesium plasma in naturally occurring lithium-containing solutions, the selectivity and adsorption capacity of CDI electrode materials become crucial considerations[8, 9]. Through the redox reaction of $FePO_4/LiFePO_4$, which has attracted a lot of research and interest, the $LiFePO_4$ battery charge and discharge completes the lithium-ion intercalation and unintercalation process. $FePO_4/LiFePO_4$ is a material utilized in battery cathode materials for electrochemical de-lithium because of its benefits, including stability and convenience of usage [1, 4]. Lithium-ions are easily inserted into octahedral positions thanks to their organized olivine structure in the following equation(1) [1]:

$$FePO_4 + Li^+ + e^- \leftrightarrow LiFeO_4 \tag{1}$$

In experiments for lithium-ion extraction and recovery, as early as 2012, Pasta used $LiFePO_4$ electrode materials. Its preparation technique became more refined within ten years, and the extraction rate increased gradually. The creation of an olivine $FePO_4$ electrode using sodium persulfate was studied by Xiong's team [10]. Additionally, in experiments involving the extraction and recovery of lithium, $FePO_4$ electrode preparation produced a cycling device with high selectivity. Li^+ was recovered from the brine to a degree of 85.30%, and in the final product, the Mg/Li ratio dropped from an initial 54.27 to 1.65. The process' average power densities were respectively 15.65 and 13.11 Am^{-2}. In their subsequent experiments, they attempted to extract lithium from brine using chemical redox, using the prepared $LiFePO_4$ electrode material. The outcomes showed that this new extraction technique enhanced the rate of extraction and the capacity of lithium-ions to adsorb, and the amount of lithium adsorption reached 9.13 $mg\cdot g^{-1}$ [10, 11]. This technique also showed good ion selectivity to produce lithium-ions with high purity and separation factors from Na^+, K^+, and Mg^+ [12].

Moreover, there are numerous ways to modify olivine $FePO_4/LiFePO_4$ electrode materials, and in Xu's study, a polymer having a large number of hydroxyl groups (PEG) modified porous $LiFePO_4/FePO_4$ electrode was developed in light of the high magnesium and salt content in brine or seawater [13]. With salt water, this electrode material may successfully attain an 82.3° contact angle. The utilization of carbon fiber reinforced material structures, which can improve cycling ability, considerably minimize the interstitial sodium side reaction, and significantly increase the rate of lithium-ion extraction, is another ground-breaking aspect of this experiment. The redesigned electrode significantly improves the poor current density of most of the electrode materials since the system may function with a higher unit capacity, cheaper manufacturing cost, and higher yield thanks to higher current density. From 62% to 92%, the system's present efficiency has increased. When the current density is 30 A/m^{-2}, the coulombic efficiency over 1000 cycles is 98.5% [13]. Future research into the modification of olivine $FePO_4/LiFePO_4$ electrode materials and the improvement of preparation procedures may further boost the efficiency and capacity of lithium extraction [5, 8, 13].

4.2. Spinel $LiMn_2O_4$/λ-MnO_2

In addition to the olivine LFP electrode, spinel LMO ($LiMn_2O_4$/λ-MnO_2) is another typical cathode electrode material. The selectivity and potential for Li^+ recovery for both electrode materials are adequate. A study on lithium extraction from λ-MnO_2/$LiMn_2O_4$ electrodes was reported by Joo et al., and it demonstrated that lithium could be extracted from brine with great efficiency and low energy consumption. However, the LMO electrode has higher recovery and selectivity[14]. Thus, more extensive and intense research has been done on LMO-based CDI extraction for lithium-ion recovery.

In fact, In the first effort to extract lithium ions electrochemically in 1993, the electrode material used was λ-MnO_2/Pt, but it was later discovered that the anode produced oxygen and chloride gas, which was detrimental to the lithium extraction procedure [1, 8]. Spinel LMO electrodes have since been the subject of numerous research. Using a 3D flow graphite felt electrode that is mesoporous and modified with λ-MnO_2/$LiMn_2O_4$, Mu et al. created a new FCDI lithium recovery method. The mesoporous electrode's high surface area creates a significant interface for lithium-ion jacking [15]. They created a method that efficiently extracted lithium at a rate of 75.06 mg/h per gram of $LiMn_2O_4$. The system is a quick and effective way to extract lithium ions due to its strong lithium selectivity, low energy consumption of 23.4 Wh/mol, and high Li/Mg separation ratio factor of 46. The work of Xu's group was centered on enhancing the operational stability of spinel-type LMO cathode materials [16]. Through microthermal smoothing, they created brand-new LMO-MST electrodes with a hybrid spherical interconnected tube microstructure utilizing urea and oxalic acid precipitant. Compared to other electrodes, the LMO-MST electrode can function at 10 degrees C for 1000 cycles with a capacity retention of 84.3% and a rate of up to 124.2 $mAh \cdot g^{-1}$, indicating high system stability and reaction rate. Additionally, by using an electrospinning technique, Choi et al. created inorganic spinel lithium manganese oxide ($LiMn_2O_4$) nanofiber materials with high lithium-ion selectivity. It was discovered that these materials' 90 nm diameter nanofibers were the best in terms of adsorption capacity and reusability, maintaining more than 90% of their initial capacity and nearly 25 mg/g of lithium adsorption in the fifth cycle [1].

Du et al. developed core-shell nanorod electrodes made of λ-MnO_2/PPy/PSS and composite electrodes made of λ-MnO_2/graphene to study the recovery of lithium ions [17]. The results showed this system can adsorb 35.2 mg g^{-1} lithium ions with a high selectivity factor of 46.0. The composite electrode consisting of graphene and λ-MnO_2 demonstrated a high level of Li^+ selectivity [1, 8, 17].

4.3. Spinel $LiNi_{0.5}Mn_{1.5}O_4$

During the development of $LiMn_2O_4$ (LMO) electrodes, researchers found that the drawback lies in the inevitable dissolution of Mn during the cycle of lithium-ion adsorption and desorption, which can lead to serious problems such as capacity decay and poor cycling performance, among others [3, 18]. To address this issue, LMO electrodes are being improved to reduce Mn dissolution, and manganese spinel can be doped with other metal cations to lower the Mn^{3+} content in LMO, which will reduce Mn^{2+} dissolution and enhance electrochemical performance. Among these, the addition of Ni to LMO to create $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has demonstrated outstanding system cycling stability and a high potential to attract the interest of several researchers [1, 18, 19].

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) nanoparticles were prepared by Shang et al. as electrode materials used in HCDI for lithium resource recovery research. The experiments' findings demonstrated that lithium-ions could be quickly entered into and removed from the LNMO electrode while Na^+, K^+, Mg^{2+}, and other ions were inhibited, demonstrating the electrode material's high lithium-ion selectivity [1, 4, 9]. Additionally, the system has an adsorption capacity of around 260 mol/g, the stability of the LNMO system is enhanced by the doping of nickel in the electrode material, and the system can still operate at up to 86% of capacity after 100 cycles. Additionally, because of the dissolution issue in the LMO electrode, no dissolved Mn^{2+} and Ni^{2+} were discovered in the circulating solution of the LNMO electrode. LNMO is preferable to LMO for practical applications involving lithium recovery thanks to its good selectivity and strong stability [1, 7, 9].

Meanwhile, techniques for improving the stability of LNMO electrodes are being researched, and Wu et al. created a more stable LNMO-LLZTO electrode utilizing $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) modified LNMO electrode based on the premise of adding high-frequency electrophilic elements to protect the internal original electrode material and increase cycle life and stability[18]. The electrochemical performance of this electrode was similarly exceptional, with a capacity of 102.62 mAh g^{-1} for the LNMO-LLZTO cathode, capacity retention of 82.42% after 1000 cycles, and a high capacity of 100.87 mAh g^{-1} at 40 degrees C. Ji et al. used the sol-gel technique to produce novel $LiNi_{0.5}Mn_{1.5}$-xSr_xO_4 materials (x can be 0, 0.05, 0.1, 0.15, and 0.2) in a distinct examination of modified LNMO. The capacity retention of 86.63% after 500 cycles showed that the results showed enhanced cycling stability [19].

4.4. Other Electrodes

In addition to the three electrode materials listed above, there are many additional electrode materials that are ideal for the extraction and recovery of lithium resources utilizing CDI. Layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, Prussian Blue analogs, H_2TiO_3, etc., are a few examples. A lithium recovery electrode with a high discharge capacity, medium voltage plateau, and low cost is the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) electrode. In research conducted by Chung et al., an NCM electrode was employed to recover lithium ions from brine. The findings showed that by employing 2.60 Wh mol^{-1} Li^+, NCM could produce brine with 96.4% pure Li^+ [1, 2, 6].

A transition metal hexacyanoate is known as Prussian Blue Analogues (PBA). It has a bulk chalcogenide face-centered cubic structure. Rapid lithium-ion intercalation and unintercalation processes can occur quickly in this material due to its channeled structure. Poor cycling stability is a challenge for PBA, though, and it has an impact on its capacity to grow commercially. To increase the system's cycling stability and lithium extraction efficiency, Wei et al. looked into encapsulating sodium hexacyanophenyl propionyl ferrate (NaNiHCF) in a very stable shell part. The final results revealed that the system's adsorption capacity was 59.38 $mg \cdot g^{-1}$ and that, after 50 cycles, it still retained 87% of its initial capacity [20].

In addition, H_2TiO_3 has been the subject of extensive study and attention as an electrode material with superior lithium adsorption capabilities. Liu et al. looked into a solid-state approach for creating spherical layer-structured H_2TiO_3 ion sieve (LSTIS) particles that used spray drying as an aid [21]. The outcomes demonstrated superb adsorption and selective qualities. The system's equilibrium adsorption capacity was 30.08 $mg \cdot g^{-1}$ (averaged over five cycles at 25.85 $mg \cdot g^{-1}$). In brines with several coexisting cations, the adsorption capacity reached 27.45 $mg \cdot g^{-1}$. Marthi et al. looked at how well titanium slag-derived H_2TiO_3 immobilized on DE and performed as a lithium adsorbent. The system's great selectivity (selectivity factor >40) and maximum adsorption capacity of 27.4 mg/g were shown [22].

Each electrode has undergone ongoing development and improvement, leading to varying degrees of advancements in the system's cyclic stability, lithium-ion selection, and adsorption capacity. The inability to directly compare the effects of various electrodes due to variations in analytical conditions highlights the necessity for method standardization. In contrast to other electrode materials, LNMO and NMC have undergone fewer investigations, and there is a discrepancy between their theoretical maximum adsorption performances. LMO also exhibits outstanding ion selectivity but requires improvement in system stability. In contrast, PBA and HTO, the two electrode materials, have undergone more research and have reached a more advanced stage of development. However, the selectivity and adsorption of each of the aforementioned electrode materials can be further improved in the future to increase the commercial viability of CDI for lithium-ion recovery.

5. Conclusion

This paper focuses on the main electrode materials for CDI technology in the field of lithium resource extraction and the contribution of novel electrode materials and processing techniques to improving lithium extraction efficiency. The traditional methods of lithium extraction and recovery, including precipitation, extraction, and adsorption, have their own advantages and disadvantages, such as the precipitation method using carbonate and aluminate as precipitant, which has a low magnesium-lithium ratio and is appropriate for lithium extraction from salt lake brine, with high yield and simple process, but at the same time, it will generate a lot of waste slag and high salt wastewater, which is high energy consumption and high pollution technology and is not conducive to sustainable development. The high magnesium-lithium ratio brine is extracted using an extractant, which has the benefits of a high separation coefficient, a cheap cost of production, and a high yield, but also has the problems of serious equipment swelling and extractant dissolution loss in the reverse extraction process. To solve these problems, CDI has been studied and proven to have the ability to recover lithium resources with high selectivity and no pollution. Through the continuous development of innovative synthesis methods, improvements in stability and extraction capacity, and rate have been achieved in electrode materials. Additionally, the invention of novel electrode materials may significantly boost the effectiveness of the separation of lithium and magnesium, but it also has to put an emphasis on the economics, effectiveness, and stability of the CDI lithium extraction process. At the same time, the coupling improvement of electrode materials needs specific consideration, and efforts should be made to break through the capacity, selectivity, and system operation stability technology of CDI lithium extraction. In conclusion, the development of new electrode materials is to enhance the rate and stability of lithium-ion extraction, which is a way to provide a high-speed production idea for the future large demand. The comprehensive utilization of lithium resources also needs to effectively solve the scientific, technical, and engineering problems faced in the industrialization process in the future and strive to improve the lithium extraction performance and operational stability of the CDI system through the development of electrode materials and build an efficient way of lithium extraction by CDI.

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