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ION SIEVES USED IN LITHIUM RECOVERY (Mn and Ti Oxides)

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Abstract

The growing global demand for lithium, driven by its critical role in battery technologies, has intensified research into efficient and sustainable recovery methods. Among these, lithium-ion sieves (LIS) based on manganese (Mn) and titanium (Ti) oxides have emerged as promising candidates due to their high selectivity, low energy requirements, and environmental compatibility. This study reviews the synthesis methods, structural characteristics, and adsorption mechanisms of MnO_2- and TiO_2-based ion sieves, evaluating their performance in lithium recovery from aqueous media. The advantages and limitations of various synthesis techniques, including solid-state, hydrothermal, sol-gel, and precipitation methods, are discussed in detail. Furthermore, recent developments in composite materials, doping strategies, and surface modifications are highlighted to improve stability and lithium retention capacity. Future perspectives are also addressed, emphasizing the integration of artificial intelligence (AI) and Internet of Things (IoT) technologies to optimize adsorbent design and process efficiency. The findings suggest that with continued innovation in materials engineering and process integration, LIS technologies could play a pivotal role in the sustainable extraction of lithium from both conventional and low-grade sources.

Keywords: Lithium-Ion sieve, Manganese Oxide, Titanium Oxide, Synthesis Methods, Future Perspectives

1. Introduction

Many processes (adsorption, solvent extraction, membrane, electrodialysis, etc.) are applied to recover lithium from lithium sources (ore, salt waters, geothermal waters, clays, etc.). [1], [2]. The methods used to obtain lithium from ore are acid process [3], alkaline process [4], chlorination process [5], and roasting process[6]. Among these processes, the method that causes the least corrosion in the equipment is the roasting method. However, this method also causes a lot of solid waste and waste gas pollution [7]. The methods used to recover lithium from aqueous sources are precipitation [8], solvent extraction [9], ion sieve adsorption [10], membrane separation [11], and electrochemical separation [12]. The most widely used method among these is the ion sieve adsorption method. Lithium-ion sieves with effective adsorbent properties have begun to be synthesized to obtain lithium ions in the solution medium and are still being studied by many researchers. These ion sieves are being investigated due to their high adsorption capacity, low cost, and toxicity properties [13], [14]. In addition, it is noteworthy that it provides separation efficiency with superior lithium selectivity and lower energy consumption compared to other methods. The dissolution problem and limited lithium capacity of the ion sieves used in this method are disadvantages for now [7].

Lithium exhibits a unique behaviour in sorption processes because it has the smallest ionic radius among monovalent cations. This small ionic radius allows lithium ions to move easily between gaps and small channels within the crystal structure [15]. In lithium adsorption, MnO_2-based ion sieves create a suitable environment for lithium ions to move and absorb effectively. The ion movement of manganese oxides with different valences and some defects in the crystal structure (point, line, and/or surface) allows lithium-ion movement. Thus, lithium selectivity and adsorption efficiency increases [15], [16]. TiO_2 ion sieves have fewer dissolution problems than manganese-based lithium-ion sieves. In other words, they have a stronger Ti-O bond energy [17]. Lithium titanium oxide shows low adsorption capacity due to aggregation and sintering problems resulting from the production method [18].

In this study, the synthesis methods of ion sieves and their efficiency in lithium recovery were investigated. Additionally, the importance of ion sieves in terms of future perspective was investigated.

2. Lithium-Ion Sieves Synthesis Methods

When practical application, cost, toxicity, and environmental treatment features are taken into consideration in material production, MnO_2 stands out. The multivalence of manganese valences (Mn^{2+}, Mn^{3+}, and Mn^{4+}) [19] that it has high oxidizability. Due to these features, it is a widely used material in heavy metal and dye removal [20]. In addition, MnO_2-based materials are used in important areas such as energy storage and conversion[21], electrochemical water oxidation [22], biomedical [23], and lithium recovery [15]. However, the high surface energy of this material can lead to clustering in adsorption processes. Their suspension in water, the presence of ions with different valences, and their structural solubility are disadvantages [19]. These disadvantages make it difficult to recover MnO_2-based materials and create application limitations because they are not practical [19], [24].

A general classification of dry and wet methods in MnO_2 synthesis can be made. Solid state [25] and mechanochemical synthesis [26] [27], [28] methods can be considered in the dry process. Hydrothermal [29], sol-gel [30], and precipitation [31] methods can be considered among wet synthesis methods. In the *solid-state method*, $KMnO_4$ can react with different Mn(II) salts. This method has shown that MnO_2 can be obtained in a nano size. However, the milling time can cause aggregation in the product particles, and it has been found to affect the structural morphology of MnO_2 [32]. The *mechanochemical method* is a synthesis method in an environment without hazardous solvents [28] such as sulfuric acid. The final product does not clump and has a high surface area [33]. In the *hydrothermal method*, parameters such as Mn(II) precursors, reaction time, and temperature can affect the structure and morphology of MnO_2. In other words, the performance of MnO_2 depends on factors such as crystal structure, particle size, and surface defects [34]. Yand et al. (2013) synthesized α-MnO_2, β-MnO_2, and δ-MnO_2 by using the reaction temperature and reactant ratio parameters in their study. They reported that the properties of these products, such as surface area and pore volume, decreased in the order of δ-MnO_2>α-MnO_2>β-MnO_2 [35]. They reported that with increasing temperature, MnO_2 transformed from a sea urchin-like structure (90^0C) to a flower ball-like structure (160^0C). They reported that when the reaction time of the same structural change was extended from γ-MnO_2 microspheres (1 hour) to 9 hours, β-MnO_2 hollow microspheres were formed [36].The *sol-gel method* is a material synthesis method using water/alcohol and metal alkoxides. Ching et al. (1997) used this method with glucose and $KMnO_4$ to synthesize layered MnO_2. They reported that microporous MnO_2s were formed because of the reaction [37]. Chin et al. (1997) produced tunnel type MnO_2 by sol-gel method using $KMnO_4$ and fumaric acid as starting materials. They stated that layered MnO_2s could be obtained in highly concentrated solutions and tunnel type MnO_2s could be obtained in dilute solutions [38]. Hashemzadeh et al. (2009) used manganese acetate (($MnAc_2{\cdot}4H_2O$) and citric acid ($C_6H_70_8{\cdot}H_2O$) to synthesize MnO_2 by the sol-gel method. They reported that after drying and acid treatment, a brown blackish MnO_2 was obtained [39]. The *precipitation method* is the precipitation of the desired ion in the solution medium by adding a suitable ion. Pan et al. (2021) performed $KMnO_4$ reduction and urea hydrolysis reactions together to synthesize MnO_2. They studied the deposition temperature and deposition time parameters to obtain nanoparticles, nanorods, and nanowire MnO_2 [40]. Wu et al. (2013) used $Mn(NO_3)_2$ and KOH as starting materials. They reported that porous and hierarchical α-MnO_2 was obtained with this method. They stated that the calcination temperature was 400^0C as the optimum condition. However, they added that the residue of potassium ions could weaken the Mn-O bond [41].

Titanium oxide is used in many areas due to its physical and chemical properties. First, due to its low cost and good stability, many devices that use solar energy come to mind. TiO_2-based paints have been developed to convert sunlight into electricity. In addition, it could break down some pollutants with its most common and well-known photocatalyst feature [42]. In these applications, TiO_2 provides widespread use due to its specific surface area and structural morphology [43], [44] .

Titanium oxide (TiO_2) exists in anatase, rutile, and brookite phases. Anatase and rutile have a tetragonal crystal structure. Each Ti^{4+} ion is in the shape of an octagon surrounded by 6 O^{2-} ions. The difference between the two phases is that the distance between Ti-Ti atoms is less in anatase [45]. The commonly used method for TiO_2 production is the *hydrothermal method* [46]. It is a process of TiO_2 synthesis in which the chemicals used (such as methanol, 1 and 4 butanol and toluene) [47], [48]are synthesized in an aqueous solution (hydrothermal) or a non-aqueous (solothermal) environment at high pressure and low temperature. Low temperature and high pressure improve solubility in most cases. Using water in this method is a more suitable method for synthesizing hydroxides, oxyhydroxides or oxides in the medium [45]. The hydrothermal method takes place in an autoclave where a certain pressure and temperature are applied. Then, calcination is performed to remove unwanted impurities for the desired phase and crystal structure. Sezer et al. (2023) calcined the TiO_2 they synthesized with the hydrothermal method at different temperatures ($400\text{-}1000^0C$). They reported that both anatase and rutile phases were formed at 900^0C, and only rutile phase was formed at 1000^0C [49]. Another synthesis method is the *combustion method*. This method is used in the production of many ceramic materials. However, the production of nanostructured materials, as in the hydrothermal method, is quite difficult [45], [50]. This method has the feature of exothermic reactions. The reaction occurs in the presence of an organic fuel and an oxidizer used as a reducing agent. The reaction proceeds spontaneously due to the enthalpy difference between the raw material and the product. Due to the high reaction rate and the effect of combustion, impurities leave the environment by evaporation. Thus, a high-purity product is obtained [51], [52]. Another method for the production of TiO_2 materials with different chemical and physical properties is the *sol-gel method* [53], [54], [55]. The sol-gel process consists of a liquid and a solid phase that is like a gel. This method can use two raw materials, alkoxide and non-alkoxide (inorganic salts) [56], [57], [58]. The synthesis process consists of the stages of completing the polymerization and removing the solvent. In other words, it is the transition from the liquid sol to the solid gel phase. Finally, the calcination process is carried out to remove impurities and obtain a powder product [59], [60], [61] .

3. Lithium-Ion Seives Studies

One of the commonly used methods for lithium recovery in solution is adsorption. The adsorbent material used in this method is called a lithium-ion sieve. The most common lithium-selective metal oxides are MnO_2 and TiO_2-based lithium-ion sieves. After these ion sieves are synthesized, they are activated with the help of acid [62], [63]. In other words, active surfaces that will hold lithium are provided. This creates a lithium memory effect. The most important factor in this mechanism is that the voids in the adsorbent material are equal to or smaller than the half diameter of the lithium ion [64]. After the adsorption process is performed, lithium is taken from the adsorbed surface with the help of an acid again. This lithium recovery method is safe, efficient, and simple [65], [66]. Other hydro or pyro metallurgical methods are used to obtain lithium in the desired form.

Manganese series spinel ion sieves have been widely used in lithium-ion adsorption, primarily including λ-MnO_2, $MnO_2.0.3H_2O$, and $MnO_2.0.5H_2O$, and $Li_{1.6}Mn_{1.6}O_4$ [67] [68] [69] after lithium removal by acidification from $LiMn_2O_4$ [70], $Li_4Mn_5O_{12}$ [71] [72] precursors.

The mechanism of lithium recovery from lithium manganese oxide (LMO) ion sieves has been tried to be explained by redox and ion exchange mechanisms. They stated that the sieve structure is important in the study of these mechanisms and that the regions where lithium settles can be formed because of these mechanisms. They divided the lithium settlement regions into three groups as redox type region (i), lithium specific ion exchange region (ii), and non-specific ion exchange region (iii) [73]. Shen and Clearfield (1968) reported that lithium can be completely replaced by protons in the ion exchange of LMOs as given in the chemical reaction (1). They also added that lithium protons will remain the same during ion exchange at the Mn (III) and Mn (IV) points in the sieve structure and therefore will provide high reversibility and specificity for lithium [74].

$$LiMn_2O_4 + H^+ \rightarrow HMn_2O_4 + Li^+ \tag{1}$$

Özmal and Erdoğan (2015) used $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ spinel powder lithium sieves to recover lithium from borogypsum ($2CaO.3B_2O_3.5H_2O$), a waste of Emet Boric Acid Plant. Although λ-MnO_2 sieve has a high lithium adsorption capacity, the fact that Mn also tends to dissolve reveals that this sieve will lose its Li retention ability in repeated uses. Although the nickel ion sieve has a longer usage time, its adsorption capacity was significantly lower than λ-MnO_2 sieve [75].

The ion exchange process was used in lithium recovery from Urmia Lake in Iran. For this purpose, spinel-type MnO_2 lithium-ion sieve with a diameter of approximately 40-90 nm and a length of 150-900 nm was synthesized by the hydrothermal method. The lithium uptake capacity of this synthesized ion sieve reached 9 $mmol.g^{-1}$ [76]. The role of spinel-type MnO_2 in lithium recovery has been shown to be effective in recovery due to the refilling effect of the gap created after lithium extraction, and perhaps only due to the ion exchange reaction between lithium and hydrogen ions [77], [78]. Acid treatment of spinel lithium manganese oxides, a lithium-ion sieve precursor, can cause almost all lithium ions to be removed upon extraction while preserving the spinel structure [77]. When lithium manganese spinel powder is added to an aqueous medium containing lithium ion, lithium ions can re-enter the displacement reaction [77], [79]. The selective adsorption method using manganese oxide ion sieves is considered as the most promising way to extract lithium ions from aqueous lithium sources such as seawater and salts due to its low cost, high selectivity towards lithium ions, high adsorption capacity, and environmental friendliness. Yang et al. (2018) synthesized lithium manganese oxide by the hydrothermal method using ethanol, $KMnO_4$, and $LiCl{\cdot}H_2O$ as precursors. They reported that the ion sieve has a hexagonal spinel structure with a thickness of 110 nm and a lateral dimension of 300-400 nm. They used the adsorption equilibrium isotherms data in the Langmuir model and predicted that it may show great potential for lithium recovery in brine or seawater [80]. Chen et al. (2016) obtained $MnO_2.0.5H_2O$ ion sieves (HMO) after acid treatment of $Li_{1.6}Mn_{1.6}O_4$ (LMO) synthesized by microwave pretreatment hydrothermal method and investigated their use in lithium recovery. $Li_{1.6}Mn_{1.6}O_4$ (LMO) and $MnO_2.0.5H_2O$ (HMO) ion sieves with possible pore sizes of about 20 nm were pretreated with microwave using commercial $Mn(NO_3)_2$, LiOH, and H_2O_2 mixed solution. Then, the hydrothermal method was applied at 100, 120, and 160 °C for 1 h. They investigated lithium adsorption after acid treatment. They reported that HMO ion sieve, as an improved material with high adsorption capacity and lithium selectivity, and chemical stability, may have promising applicability for lithium recovery from aqueous brine and seawater [81].

The most important Ti-based lithium-ion sieves are Li_2TiO_3 with a layered structure and $Li_4Ti_5O_{12}$ with a spinel structure [82] [83]. The lithium retention mechanism is like Mn-based lithium-ion sieves. Wang et al., (2024) synthesized Ti-based lithium-ion screen by high temperature solid state method. However, they stated that they had difficulties in this product tending to cluster and leaving lithium ions behind. To overcome these difficulties, they added magnetic Fe_3O_4 to the lithium-ion screen. They stated that the adsorption capacity reached 34.27 $mg.g^{-1}$ [84]. Qin et al., (2024) synthesized Ti-based lithium-ion sieves by the hydrothermal method in their studies. They used four surface-active materials to activate these sieves. These are sodium dodeacyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), hydroxypropyl cellulose (HPC), and tannic acid (TA), respectively. They stated that HTO-T adsorbent activated with tannic acid exhibited the lowest contact angle (8.8°) and the highest specific surface area (62.10 $m^2.g^{-1}$). They reported that lithium adsorption capacity was 33.61 $mg.g^{-1}$ [85]. Xiao et al., (2024) synthesized $Li_4Ti_5O_{12}$ by high high-temperature solid-state method. They made surface activation of this ion sieve with CTAB and F127. Surface-active ion sieves were converted into microspheres. Thus, they reported that they formed an open hierarchical mesoporous structure that allowed rapid ion exchange between Li^+ and H^+. They stated that lithium adsorption capacity was 57.90 $mg.g^{-1}$ [86]. Wang et al., (2019) investigated the lithium retention capacity of Mo-doped Ti-based ion sieve. They stated that Mo doping increased the stability of the lithium-ion sieve and reduced agglomeration. They reported that adsorption reached equilibrium in 10 hours, and the adsorption capacity was 78 $mg.g^{-1}$ [87]. Suyu et al., (2024) added Zr to the titanium lithium-ion sieve synthesized by the solid-state method. They stated that the lithium retention capacity was higher than the pure ion sieve. They stated that the lithium retention capacity of the pure ion sieve was 56.3 $mg.g^{-1}$, while the lithium retention capacity of the doped lithium sieve was 93.2 $mg.g^{-1}$ [88].

Compared with Ti-based adsorbents used in the adsorption method, Mn-based adsorbents with spinel structure exhibit a high adsorption capacity for Li^+ ions due to the spinel structure located in the tetrahedral region in the LMO crystal [79] [89], [90] and can reach 35~60 mg (Li^+)/g according to theoretical capacity [91]. In addition, it is easy to synthesize and exhibits different diffusion paths not only superficially but also in adsorbing lithium [92]. In contrast to these advantages of Mn-based adsorbents, lithium recovery from Ti-based adsorbents is quite low. However, it has low electronic conductivity and ion diffusion coefficient as the extraction reaction progresses, which causes restrictions on Li^+ transport. However, it is observed that the lithium retention capacity of Ti-based ion sieves increases with doping such as Fe, Zr, Mo.

4. Conclusion and Future Perspectives

In conclusion, MnO_2 and TiO_2-based ion sieves offer significant advantages such as high selectivity, low energy consumption, and environmental sustainability in the recovery of lithium from solution media. Although both types of ion sieves are promising candidates for lithium recovery technologies, it is of great importance to increase research on the development of synthesis methods, integration of material engineering approaches, and long-term stability analyses to overcome current limitations and optimize their performance.

Although lithium retention capacities are increasing day by day with the studies carried out, they still have some difficulties. Among these, their limited industrial use is the most important one due to their structural solubility. Structural dissolution problems have been tried to be reduced with various modifications. However, it is possible for the acid-doped ions to be used in the recovery of lithium from the structure to enter the environment. This can create a new problem, secondary pollution.

In order to ensure the industrial scale applicability of lithium ion sieves (LIS) in the coming years, it is of great importance to develop new generation composite adsorbents that are non-toxic and have high structural stability. Technologies such as electrospinning, 3D printing, and foam technology can be used in the production of new generation composites. In this way, both environmental impacts will be reduced and the service life of the adsorbents will be increased. Secondly, by understanding the adsorption mechanism of lithium at the molecular level and with artificial intelligence-supported material design, adsorbents optimized in terms of selectivity and capacity can be produced. Finally, in order to ensure the economic and technical sustainability of LIS technology, it should be aimed to develop combined processes that bring different processes together and to establish high-efficiency, low-cost, and environmentally friendly systems. These three strategies will contribute to the successful transfer of LIS technology from laboratory scale to industry.

In addition, in the future, artificial intelligence (AI) and the Internet of Things (IoT) will make revolutionary contributions to the industrial-scale application of lithium-ion sieve technology. By analyzing millions of experimental data, AI can optimize the most suitable adsorbent formulations, synthesis conditions, and process parameters; the most selective and durable material structures specific to lithium can be developed thanks to molecular modeling and machine learning algorithms. IoT-supported sensors monitor parameters such as lithium concentration, temperature, pH, and flow rate in real time, allowing the system to continuously adjust itself and maximize adsorption efficiency. Thanks to these intelligent systems, energy efficiency is increased, environmental risks are minimized, and production costs are reduced. As a result, with the integration of AI and IoT, lithium recovery processes become compatible with full automation, high accuracy, and sustainability principles, playing an important role in the transition to green technologies.

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