



DOI: 10.31643/2025/6445.28

Metallurgy

Physical and chemical study of manganese dioxide sorbent after sorption of lithium from brines

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<p>Received: May 30, 2024 Peer-reviewed: June 23, 2024 Accepted: July 15, 2024</p>	<p>ABSTRACT The article presents the results of the study for the synthesized manganese dioxide sorbent after its saturation with lithium from brine. The sorbent was previously prepared. For this purpose the mixture of manganese oxide compounds was kept with lithium hydroxide in a wet state at 125 °C, calcinated at 450 °C and then the precursor was treated with dilute hydrochloric acid. The process intended to saturate the sorbent with lithium was performed by putting it in contact with a lithium-containing brine with a pH of 8.77 at T = 40°C for 24 hours in four cycles. The sorbent after saturation was studied using X-ray phase and thermal analysis methods. X-ray phase analysis showed that lithium-containing phases are represented by such compounds as $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ and $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$. The results of thermal analysis show the possibility of phases to be in the sorbent after saturation LiMn_2O_4 and $\text{Li}_{1.3}\text{Mn}_2\text{O}_4$ phases. The study results showed that ion-exchange interaction takes place between the lithium-ion from the brine and the proton from the manganese-oxide spinel composition to a greater extent during sorption. Besides, the redox nature of the interaction is present during the sorption of lithium. All lithium intercalation reactions proceed topotactically without significant changes in the main structure of the original sorbent.</p>
	<p>Keywords: lithium, brine, sorbent, manganese dioxide, sorption, exchange capacity.</p>
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Introduction

Lithium plays a key role in the advancement of energy storage technologies, electric mobility and wireless devices. It effectively addresses such significant problems as environmental pollution, climate change and fossil fuel shortages [[1], [2]].

Global emissions of carbon dioxide (CO₂) produced by fossil fuels increased and reached the highest level in history between 2021 and 2022 [[3], [4]].

Currently, we are intensely experiencing climate change every year - floods, forest fires, droughts and other major disasters due to the release of CO₂ gas and other gases into the atmosphere in large quantities. In this regard, international organizations intend to switch to renewable energy sources in order to reduce the spread of greenhouse gases and to reduce the load of fossil fuels [5]. The main human activity that produces CO₂ emissions is the combustion of fuels (coal, natural gas and oil) used to generate electricity and vehicles [[6], [7]].

One of the best solutions is to replace traditional modes of transport with electric vehicles to prevent the depletion of oil and gas reserves around the world, as well as environmental, economic and geopolitical problems. The main component of electric vehicles is lithium-ion batteries.

Lithium-ion batteries (LIBs) are popular power sources in various applications due to their high energy density, efficiency, reliability and variety of electrode configurations. Recently, there has been a steady trend towards the development of a new generation of lithium-ion batteries with increased capacity and energy density, intended for electric vehicles (EV), hybrid electric vehicles (HEV), space objects and autonomous electronic devices (for example, hybrid solar panels) [[8], [9], [10], [11], [12]].

Lithium is very relevant in the production of high-tech equipment [13]. The need for lithium is expected to increase in the coming decades with increase in demand for electric vehicles and renewable energy. According to McKinsey & Company forecasts, the demand for lithium-ion batteries will increase by 4,700 TWh by 2030, leading to the rapid development of lithium mining [14].

Currently, it is recommended to use various mineral raw materials and industrial wastes to extract strategically important metals [[15], [16], [17], [18], [19]]. Lithium is extracted mainly from hydromineral raw materials (brines), hard rocks, and also from waste lithium batteries [20]. Each of these sources has its advantages and disadvantages. One of the most attractive raw materials for lithium sources is natural brines since they require lower environmental and economic costs compared to mining from hard rocks. Brines contain dissolved lithium ions which can be extracted with the use of various methods such as evaporation, precipitation, liquid-liquid extraction, sorption and membrane methods [[21], [22], [23], [24], [25]]. One promising method is the sorption of lithium from brines. Methods for the sorption of lithium from brines can be performed with the use of both organic and inorganic sorbents. Cation exchangers based on sulfo groups and based on amino groups can effectively sorb lithium and can also be effective for the extraction of lithium from solutions, especially under certain pH conditions. But organic ion exchangers have selectivity not only for lithium but also for other ions. It can complicate the separation

and purification of recovered lithium and also result in the formation of organic waste which may require special disposal or treatment methods increasing the environmental burden of the process [26]. The synthesis and application of highly selective inorganic sorbents for lithium is a current scientific direction [[27], [28]].

Lithium-ion sieves (LIS) are considered one of the most promising materials for lithium recovery from low-lithium brines due to their high adsorption capacity and excellent lithium selectivity. Studies confirm manganese oxide (LMO) and titanium oxide (LTO) sorbents as effective methods for lithium recovery from brines [[29], [30], [31]].

Currently, there are two main classifications of LTO-type LIS: layered structures based on H_2TiO_3 and spinel structures based on $\text{H}_4\text{Ti}_5\text{O}_{12}$ [32]. The structure of H_2TiO_3 is explained by the main layered structure of the H_2TiO_3 precursor, similarly, the spinel structure of $\text{H}_4\text{Ti}_5\text{O}_{12}$ is derived from the spinel structure of its precursor - $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Titanium-based lithium-ion sieves have attracted attention due to their theoretical superior adsorption capacity but the practical adsorption capacity observed after extraction of lithium from brine or seawater is often lower [33].

Lithium-ion oxides based on spinel-type manganese oxide are currently the most popular selective sorbents. The scientists developed sorbents on such oxide-based manganese as $\lambda\text{-MnO}_2$, $\text{MnO}_2 \cdot 0.3\text{H}_2\text{O}$ and $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ from the precursors LiMn_2O_4 , $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ ($\text{Li}_4\text{Mn}_5\text{O}_{12}$) and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ($\text{Li}_2\text{Mn}_2\text{O}_5$) [[34], [35]]. These sorbents have excellent adsorption capacity; for example, sorbents made from precursors have the following sorption capacity: LiMn_2O_4 - 39.9 mg/g, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ - 59 mg/g, and the sorbent from the precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ has high capacity of 72.3 mg/g [36]. The advantage is their high selectivity for lithium, which avoids the sorption of other ions present in the solution [[37], [38]]. The specific adsorption of lithium relative to other coexisting ions occurs due to the unique ability of lithium ions in aqueous solution to selectively maneuver through layered gaps and occupy exchange sites relative to such competing ions as K^+ , Na^+ , Ca^{2+} and Mg^{2+} . This selectivity is due to the large ionic radii of ions such as K^+ (0.138 nm), Na^+ (0.102 nm) and Ca^{2+} (0.100 nm), in contrast to Li^+ (0.074 nm), which makes them unable to cross narrow channels [39]. Although Mg^{2+} (0.072 nm) has a similar ionic radius to Li^+ , its significantly higher free energy of hydration

compared to Li prevents its dehydration, thereby limiting its access to exchange sites [[28], [40]].

The study examined the conditions for obtaining a lithium-manganese precursor and its acid treatment, as well as the sorption characteristics and sorption capacity of the synthesized sorbent [41].

It is of great interest to study the composition of the saturated manganese dioxide sorbent to clarify and obtain additional information regarding the process of lithium sorption from brine.

Experimental part

Materials. Lithium hydroxide monohydrate $\text{LiOH}\cdot\text{H}_2\text{O}$ brand "puriss."; hydrochloric acid HCl qualification "puriss."; Mn_2O_3 "puriss. spec.", MnO "puriss.", brine from oil and gas fields.

Preparation of manganese dioxide sorbent. The preparation of sorbents consisted of three stages: 1) holding in an oven with treatment of a mixture of manganese oxide compounds and lithium hydroxide in an aqueous environment at 125 °C for 13 hours until dry at the end; 2) calcination of the processed product in a muffle furnace SNOL 7.2/1300 at 450 °C for 6 hours; 3) acid treatment of the precursor with dilute hydrochloric acid (0.5 mol/dm³) at 40 °C with stirring for 24 hours.

Methodology and analysis methods.
Experimental procedure. Sorption with saturation of manganese dioxide sorbent was performed under static conditions in a 3 dm³ glass, with a VELP Scientifica LS F201A0151 (Italy) mechanical stirrer installed above it, providing a fixed number of revolutions. The constant temperature was maintained with the use of an Aizkraukles TW 2.02 water bath thermostat (ELMI, Latvia). A given amount of sorbent was transferred into a glass filled with a given volume of brine, set to a given temperature and stirred for a certain time to carry out sorption. The solution was separated from the sorbent by decantation, and then contact of the sorbent with a fresh portion of brine was ensured after sorption. Saturation of the sorbent upon contact with fresh portions of brine was performed in 4 cycles. The saturated sorbent was washed and dried after sorption.

Determination of the capacity of sorbents. Static exchange capacity is calculated by the formula:

$$\text{SEC} = \frac{(C_0 - C_e) \cdot V}{m}$$

where, SEC – static exchange capacity; C_0 – metal concentration in the initial solution, mg/dm³; C_e – residual equilibrium concentration of metal in the solution, mg/dm³; V – solution volume, dm³; m – a mass of dry sorbent, g.

Analysis methods. The quantitative content of the studied elements in brines is determined with the use of an Optima 8300DV atomic emission spectrometer with inductively coupled plasma and a SHIMADZU atomic absorption spectrophotometer type AA-7000 (Japan). X-ray phase analysis (XPA) was performed on a D8 ADVANCE diffractometer "BRUKER AXS GmbH", (Germany) $\text{Cu-K}\alpha$ radiation, PDF-2 database of the International Center for Diffraction Data ICDD (USA).

Thermal analysis of the saturated sorbent sample was performed with the use of an STA 449 F3 Jupiter simultaneous thermal analysis device. Before heating, the furnace space was evacuated (evacuated per cent level ~ 92 %) and then purged with inert gas for 5 minutes. Heating was performed at a rate of 15°C/min. in an atmosphere of highly purified argon. Cooling was performed at a rate of 17 °C/min. The total volume of incoming gas was maintained within 50 ml/min. The results obtained with the STA 449 F3 Jupiter were processed with the use of the NETZSCH Proteus software.

Results and Discussion

The manganese dioxide sorbent for lithium sorption was synthesized according to the conditions presented above and may have a composition close to $\text{MnO}_2 \cdot n\text{H}_2\text{O}$; the process presumably occurs via the ion exchange mechanism. X-ray phase analysis (XRD) of the sorbent and its precursors is shown in Figure 1 (a, b, c). As can be seen from Figure 1a, lithium manganese oxide (LMO) was formed with the composition LiMnO_2 with an orthorhombic crystal lattice structure (space group Pmnm) as a result of holding a mixture of oxide compounds of manganese (II), (III) and lithium hydroxide in a wet state in a drying oven at 125 °C for 13 hours until it was dry. The oxidation of manganese present in the trivalent state to tetravalent with the transformation of the main phase of the LMO LiMnO_2 to $\text{Li}_{1,6}\text{Mn}_{1,6}\text{O}_4$ occurs with further calcination of the resulting LMO at 450 °C for 6 hours. It represents a face-centred cubic system

(space group $Fd3m$) with a lattice constant of 8.14 Å (Figure 1 c). It can be noted that the main phase of the resulting sorbent is represented by manganese (IV) dioxide as a result of acid treatment of the precursor after calcination; the diffraction pattern retained the cubic structure with only a slight decrease in the constant lattice to 8.036 Å (Figure 1 c). It may indicate that the acid treatment with the extraction of lithium from the precursor proceeds topotactically with the preservation of the cubic structure of the crystal lattice [42].

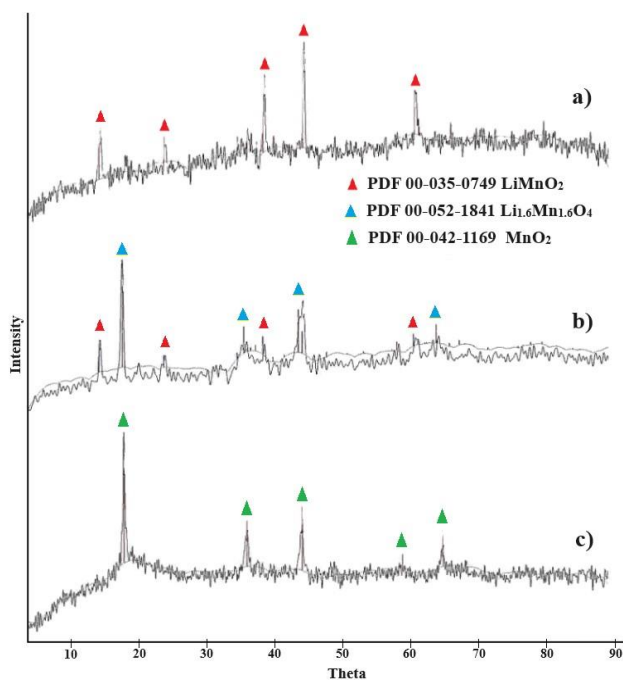


Figure 1 - Diffraction patterns of lithium-manganese oxide of the first stage of processing (a), precursor after calcination (b), and sorbent (c).

As can be seen from Figure 1 b, some part of underoxidised orthorhombic LiMnO_2 also remains after calcination. Orthorhombic LiMnO_2 adopts an ordered rock salt structure consisting of zigzag sheets of edge-sharing MnO_6 octahedra, separated by octahedrally coordinated lithium ions (Figure 2). According to work [43] the delithiation reactions which occur between orthorhombic LiMnO_2 and acid depend on the physical form of the material. On exposure to acid, a single crystal of LiMnO_2 was observed to undergo a delithiation reaction as described in reaction (1) to form a phase of composition MnO_2 :

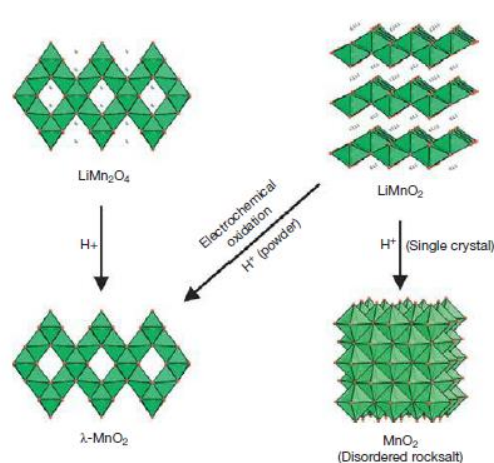
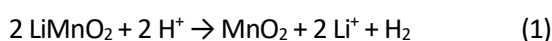
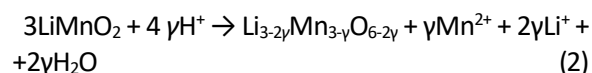


Figure 2 - Delithiation of LiMn_2O_4 and LiMnO_2 leads to the formation of new metastable polymorphs of MnO_2 [43].

In contrast, the reaction between powder samples of orthorhombic LiMnO_2 and acid proceeds via a combination of disproportionation and ion exchange as shown in reactions (2) and (3) [[43], [44]]:



In this case, the deintercalation reaction drives migration of the manganese cations so that they adopt the $\lambda\text{-MnO}_2$ network of delithiated LiMn_2O_4 , which shares a common oxide ion lattice with the rock salt structure.

Transformation of the orthorhombic LiMnO_2 to the spinel-type lithium manganese oxide has been explained by researchers in the works [[45], [46]]. A delithiated orthorhombic LiMnO_2 structure is unstable; lithium extraction from the zig-zag layers is accompanied by a migration of manganese cations into some of the octahedral sites left vacant by the extracted lithium to yield a stable spinel-type structure.

Lithium extraction from the zig-zag channels causes a displacement of 50% of the manganese ions into neighbouring octahedra left vacant by the extracted lithium ions. These displacements generate the 3:1 spinel ratio of manganese ions in alternate layers between the close-packed oxygen planes.

Thus, the obtained sorbent, represented according to XRD, spinel structure of MnO_2 , can have both $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ and $\lambda\text{-MnO}_2$ phases in its composition. Additional information can be obtained after saturation of the sorbent, which should result in lithium

intercalation with the formation of lithium-manganese phases.

The saturation of the sorbent with lithium was carried out by contacting it with a lithium-containing brine containing: 38,32 mg/dm³ Li; 10,14 g/dm³ Ca; 2,29 g/dm³ Mg; 27,26 g/dm³ Na; 0,824 g/dm³ K; 0,335 g/dm³ Al.

The saturation process of 4 g of sorbent was performed in four cycles while maintaining the following conditions in each cycle: T = 40°C; duration 24 hours; brine volume 2.8 dm³, brine pH 8.77. In this case, the total capacity of the sorbent for lithium for all cycles was 20.44 mg/g. The sorbent, after its saturation with lithium, was studied using instrumental analysis methods.

Study of the saturated sorbent composition. The manganese dioxide sorbent was studied by X-ray phase analysis after saturation by providing contact with brine. Figure 3 shows a diffraction pattern of a saturated sorbent.

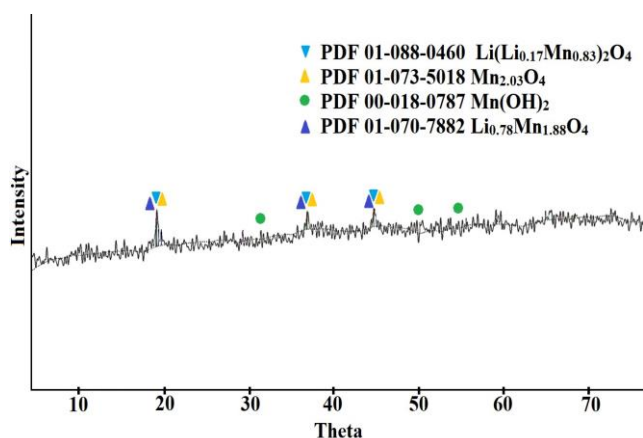


Figure 3 – Diffraction pattern of saturated sorbent

It can be seen according to the XRD data in Figure 3 that new lithium-containing oxide phases were formed on the sorbent during the sorption of lithium from brine, i.e., lithium-manganese oxides - mostly $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$, stoichiometrically equivalent to the $\text{Li}_{1.34}\text{Mn}_{1.66}\text{O}_4$, compound, and in slightly smaller quantities of $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$. Both phases have a cubic Fd3m crystal lattice structure with a lattice constant of 8.14 Å for $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ and 8.18 Å for $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$. The sample also contains oxide $\text{Mn}_{2.03}\text{O}_4$ and manganese hydroxide $\text{Mn}(\text{OH})_2$. It can be noted that the valence of manganese in the $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ phase is close to four, i.e., when this compound was formed during the interaction of the sorbent with lithium from the

brine, the valence of manganese did not change. It indicates that the process of lithium sorption mainly occurred through the ion exchange mechanism in this case, and not with the participation of valence forces due to the exchange of electrons between the sorbent and the brine [47]. Chitrakar et al. built a phase diagram containing of lithium manganese oxides and their delithiated products [42] (Figure 4). The diagram shows a compound of $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ composition, and it is almost similar to the $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ phase obtained in a saturated sorbent composition. According to the diagram, the reactions of lithium extraction and incorporation to form the delithiated oxide product $\text{MnO}_2 \cdot 0.31\text{H}_2\text{O}$ and lithium-manganese oxide $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, respectively, can occur in both directions.

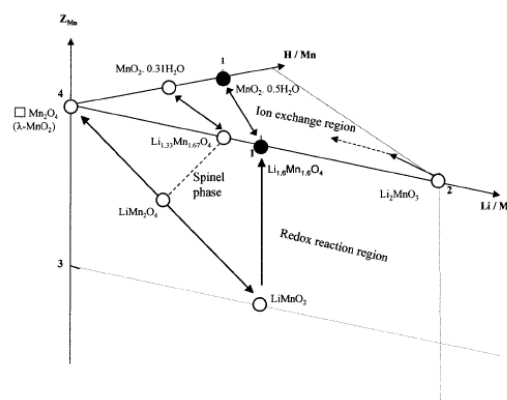
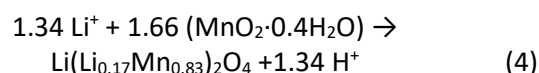


Figure 4 – Phase diagram of lithium manganese oxides and their delithiated products [42]

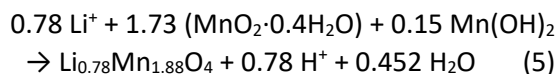
However, the formation of the $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ phase obtained as a result of saturation can be represented under the expected reaction:



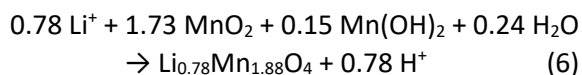
In this case, the expected composition of the sorbent before its saturation with lithium, calculated by equation (4), can be represented as $\text{MnO}_2 \cdot 0.4\text{H}_2\text{O}$. A sorbent of similar composition was obtained by the authors of from a precursor with the composition of $\text{Li}_4\text{Mn}_5\text{O}_{12}$, i.e. from $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ [48].

Lithium sorption from brine also partially occurs with the formation of the $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$ phase. The $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$ phase has manganese with both valence +4 and +3. The formation of this compound may be influenced by the presence of the $\text{Mn}(\text{OH})_2$ phase in the sorbent. Its presence led to the

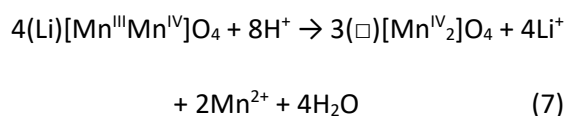
formation of lithium-manganese oxide, accompanied by a coproportionation reaction. The expected reaction can be imagined:



or



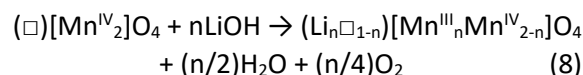
At the same time, the $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$ phase is close in composition to the LiMn_2O_4 spinel with a cubic crystal structure belonging to the $\text{Fd}3\text{m}$ space group. Lithium ions occupy position 8a of tetrahedra in this structure. Mn^{3+} and Mn^{4+} ions are randomly distributed over the positions of 16d octahedra with a molar ratio of 1:1, and oxygen anions occupy positions of 32e face-centred cubes [43]. The approximately cubic, close-packed array of oxide ions includes an MnO_6 octahedron connected in three dimensions by common edges. On the other hand, the unit cell of LiMn_2O_4 can be considered a complex cubic structure: 32 oxygen atoms and 16 manganese atoms occupy half-positions of the octahedral interstitial site (16d), and the remaining half-positions (16c) are free. Here, 8 lithium atoms occupy 1/8 of the tetrahedral interstitial site (8a). Li^+ can be intercalated/deintercalated in the three-dimensional network of vacant octahedra and octahedral interstices along the 8a-16c-8a-16c channel, which is the structural basis of Li^+ intercalation/deintercalation in LiMn_2O_4 spinel [49]. Hunter in his work proposed a redox mechanism for the topotactic extraction of lithium from LiMn_2O_4 and defined the resulting spinel-type manganese oxide as $\lambda\text{-MnO}_2$ [50]:



where () are tetrahedral positions 8a; [] – octahedral positions 16d; \square – vacant positions.

In turn, the authors proposed a redox mechanism for the introduction of Li^+ into the dioxide structure when they studied the adsorption

properties of $\lambda\text{-MnO}_2$ with the extraction of lithium from the aqueous phase [51]:



Besides, the author found during the study that spinels have 2 types of Li^+ extraction/incorporation reaction centres - redox-type centers and ion-exchange-type centres [51]. The proportions of each type can be assumed from the values of the Li/Mn molar ratio and the total valence of manganese in spinel. Ion exchange-type centres are predominantly formed at temperatures below 500 °C, while redox-type centres are formed at higher temperatures. Extraction/incorporation reactions of Li^+ occur predominantly with ion-exchange-type centres.

As it can be seen from equation (8), the reaction proceeds by interaction with LiOH; the extraction of lithium for manganese dioxide took place from a chloride-type brine upon saturation of the resulting sorbent in this study. At the same time, the pH of the brine was slightly alkaline and amounted to 8.77, and the brine contained hydroxyl ions in the composition of LiOH required for the possible occurrence of this reaction.

However, the researchers indicate that centres of the redox type are formed predominantly at temperatures of 500 °C and above [51]. The precursors were calcined at 450 °C in the present study, as noted above, and the $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$ phase was present in a small amount according to the XRD of the saturated sorbent. Its formation could also be influenced by the presence of $\text{Mn}(\text{OH})_2$ (reaction 5 or 6).

A thermal analysis of the saturated sorbent was performed; the thermograms are presented in Figure 5. As can be seen from the results of the above studies, an exothermic effect with a peak at 471.4 °C appeared on the DTA curve; well-pronounced endothermic effects with maximum development at 1084.2 °C and 1155.3 °C can also be noted. The dDTA curve recorded additional endothermic effects with extremes at 386.9 °C, 513.1 °C, 602.6 °C, 835.2 °C, 943.6 °C. Minima can be noted at 526.2 °C, 584.5 °C, 1011 °C on the DTG curve.

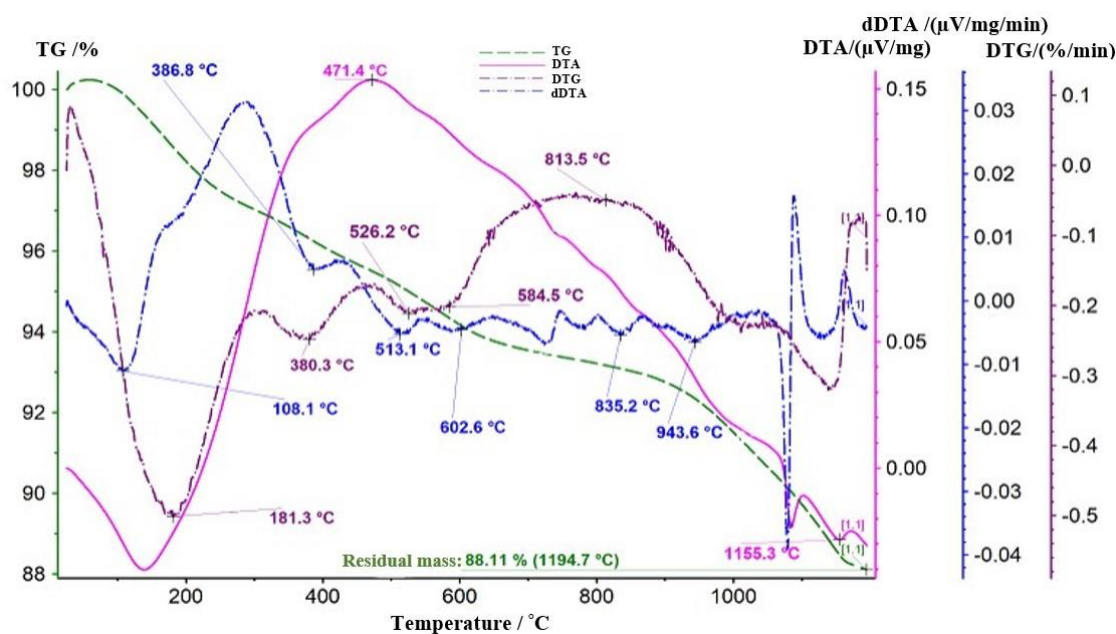


Figure 5 – Thermogram of the sorbent sample after saturation

The exothermic effect with a peak at 471.4 °C in the DTA curve may be a manifestation of the crystallization of the synthesized manganese dioxide gel. The combination of endothermic effects with extremes at 386.9 °C and 943.6 °C on the dDTA curve and an endothermic effect with maximum development at 1,155.3 °C on the DTA curve may reflect the presence of manganite - MnOOH. The first effect is associated with dehydration and the formation of pyrolusite or β -kurnakite (β -Mn₂O₃). Pyrolusite can transform into β -Mn₂O₃ in the region of 500 – 600 °C. In the region of the development of the second effect (943.6 °C), β -Mn₂O₃ decomposes with the formation of β -Mn₃O₄. The latter effect reflects the reversible polymorphic transformation of β -Mn₃O₄ into γ -Mn₃O₄. Considering separately the peaks of 1,084.2 °C and 1,155.3 °C on the DTA curve, we can assume the presence of α -Mn₃O₄. The first peak reflects the transition of α -Mn₃O₄ into β -Mn₃O₄, the second – the reversible polymorphic transformation of β -Mn₃O₄ into γ -Mn₃O₄.

Buzanov provides thermograms of LiMn₂O₄, Li_{1,3}Mn₂O₄ [52]. It can be assumed that the endothermic effect with an extremum at 835.2 °C reflects the decomposition of the LiMn₂O₄ phase. The peak of decomposition was recorded at 846 °C in the source. In superposition, with a stretch, a combination of the endothermic effect with an extremum at 602.6 °C on the dDTA curve (on the DTG curve it corresponds to a minimum at 584.5 °C) with the above-mentioned endothermic effect

835.2 °C (on the DTG curve it corresponds to a very weak minimum at 813.5 °C) may be a manifestation of the decomposition of Li_{1,3}Mn₂O₄. The thesis indicates temperatures of 613 °C and 823 °C.

It is not possible to unambiguously state the presence of γ -MnO₂ in a sample. The combination of endothermic effects at 602.6 °C, 943.6 °C on the dDTA curve and 1155.3 °C on the DTA curve can be interpreted as both a manifestation of β -MnO₂ and a manifestation of γ -MnO₂.

As the results of thermal analysis show, the presence of phases of lithium-manganese oxides - LiMn₂O₄ and Li_{1,3}Mn₂O₄ is assumed in a sample of a saturated sorbent, in addition to the possible phases of manganite MnOOH, α -Mn₃O₄, β -MnO₂ or γ -MnO₂. The detection of LMO phases indicates the sorption of lithium from brine with intercalation of lithium into the composition of the synthesized manganese-oxide spinels with the formation of these compounds.

Conclusions

The results of the studies showed that the sorption of lithium from brine on a synthesized manganese-oxide sorbent occurs with the formation of new lithium-containing phases. X-ray phase analysis showed the presence of phases in the sorbent after its saturation with lithium of Li(Li_{0.17}Mn_{0.83})₂O₄ and Li_{0.78}Mn_{1.88}O₄. The formation of the first phase occurs without a change in the

valence of manganese. It may indicate the ion-exchange nature of the interaction during the sorption of lithium from brine. And the formation of the second phase that occurs with a change in the valence of part of the manganese, indicates the redox nature of the interaction during sorption. The possibility of the presence of LiMn_2O_4 and $\text{Li}_{1,3}\text{Mn}_2\text{O}_4$, phases in the sorbent after saturation, formed due to redox reactions, is also indicated by the results of thermal analysis. In general, an ion exchange interaction takes place between a lithium ion from the brine and a proton from the manganese oxide spinel composition during sorption. All lithium intercalation reactions proceed topotactically without significant changes in the main structure of the original sorbent.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

CRedit author statement: **Z. Karshyga:** Conceptualization, Visualization, Writing draft preparation, Investigation, Methodology. **R. Abdulvaliyev:** Supervision. **A. Yersaiynova:** Reviewing and Editing, Investigation, Methodology, Data curation. **A. Yessengaziyev:** Validation. **B. Orynbayev:** Software. **M. Kvyatkovskaya:** Methodology.

Acknowledgements. This work was supported by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (No. BR18574018).

Cite this article as: Abdulvaliyev RA, Karshyga ZB, Yersaiynova AA, Yessengaziyev AM, Orynbayev BM, Kvyatkovskaya MN. Physical and chemical study of manganese dioxide sorbent after sorption of lithium from brines. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources.* 2025; 334(3):59-69. <https://doi.org/10.31643/2025/6445.28>

Тұзды ерітінділерден литийді сорбциялағаннан кейін алынған марганец диоксиді сорбентін физика-химиялық зерттеу

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<p>Мақала келді: 30 мамыр 2024 Сараптамадан өтті: 23 маусым 2024 Қабылданды: 15 шілде 2024</p>	<p>ТҮЙІНДЕМЕ Мақалада марганец диоксиді негізінде синтезделген сорбенттің тұзды ерітіндідегі литиймен қаныққаннан кейінгі зерттеу нәтижелері берілген. Алдын ала дайындалған сорбент: марганец оксиді қосылыстары мен литий гидроксидін 125 °С температурада ылғалды күйде ұстаудан, оларды 450 °С күйдіруден және одан әрі сұйылтылған тұз қышқылымен прекурсорды қышқылдық өңдеуден тұрады. Сорбентті литиймен қанықтыру процесі рН 8,77 литий бар тұзды ерітіндімен 24 сағат бойы қанықтыру арқылы жүргізілді, қанығудан кейінгі сорбент рентгендік фаза және термиялық талдау әдістері көмегімен зерттелді. Рентгендік фазалық талдау нәтижесінде $\text{Li}(\text{Li}_{0,17}\text{Mn}_{0,83})_2\text{O}_4$ и $\text{Li}_{0,78}\text{Mn}_{1,88}\text{O}_4$ құрамында литий бар фаза қосылыстары анықталды. Термиялық талдау нәтижелері қаныққаннан кейін сорбентте LiMn_2O_4 және $\text{Li}_{1,3}\text{Mn}_2\text{O}_4$ фазаларының болатындығын көрсетті. Зерттеу нәтижелері бойынша сорбция кезінде тұзды ерітіндідегі литий ионы мен марганец-оксидті шпинельді құрамның протоны арасында ион алмасу әрекеттесуінің көбірек болатынын көрсетті. Сонымен қатар, литий сорбциясы кезінде әрекеттесудің тотығу-тотықсыздану сипаты бар. Литийдің барлық интеркаляция реакциялары бастапқы сорбенттің негізгі құрылымында елеулі өзгерістерсіз топотактикалық түрде жүреді.</p>
	<p>Түйін сөздер: литий, тұзды ерітінді, сорбент, марганец диоксиді, сорбция, алмасу көлемі.</p>
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Физико-химическое исследование сорбента диоксида марганца после сорбции лития из рассолов

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<p>Поступила: 30 мая 2024 Рецензирование: 23 июня 2024 Принята в печать: 15 июля 2024</p>	<p>АННОТАЦИЯ В статье представлены результаты исследований по изучению синтезированного сорбента диоксида марганца после насыщения его литием из рассола. Предварительно был подготовлен сорбент, что заключалось в выдержке смеси оксидных соединений марганца с гидроксидом лития во влажном состоянии при 125 °С, прокаливании при 450 °С и дальнейшей кислотной обработке прекурсора разбавленной соляной кислотой. Процесс насыщения сорбента литием проводился посредством его контактирования в четыре цикла с литийсодержащим рассолом с pH 8,77 при T = 40°С, продолжительности 24 ч. Сорбент после насыщения был изучен с применением рентгенофазового и термического методов анализа. Рентгенофазовый анализ показал, что литийсодержащие фазы представлены соединениями $\text{Li}(\text{Li}_{0.17}\text{Mn}_{0.83})_2\text{O}_4$ и $\text{Li}_{0.78}\text{Mn}_{1.88}\text{O}_4$. Результаты термического анализа указывают на возможность присутствия в сорбенте после насыщения фаз LiMn_2O_4 и $\text{Li}_{1.3}\text{Mn}_2\text{O}_4$. Результаты исследований показали, что в большей степени при сорбции имеет место ионообменное взаимодействие между ионом лития из рассола и протоном из состава марганцево-оксидной шпинели. Помимо этого, присутствует при сорбции лития окислительно-восстановительный характер взаимодействия. Все реакции интеркаляции лития протекают топотактически без существенных изменений основной структуры исходного сорбента.</p> <p>Ключевые слова: литий, рассол, сорбент, диоксид марганца, сорбция, обменная емкость.</p>
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