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INFLUENCE OF STRUCTURAL CHARACTERISTICS ON SORPTION PROPERTIES OF LITHIUM-SELECTIVE COMPOSITE MATERIALS BASED ON TiO₂ AND MnO₂

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Novel composite materials with equimolar ratio of TiO₂ to MnO₂ have been synthesized. Using the low-temperature N₂ adsorption method their structural characteristics were calculated; and their influence on selectivity and kinetics of lithium sorption was shown. It was proved that sorption characteristics of the obtained materials are determined by conditions of heat treatment during the synthesis. Higher temperatures provoke agglomeration of sorbent and decrease in its kinetic characteristics. At the same time, more lithium-selective sorption sites are formed and the selectivity of sorption increases. By the proposed synthesis method a highly selective to lithium ion-exchange material was obtained.

Keywords: titanium dioxide, manganese dioxide, lithium, ion exchange selectivity

INTRODUCTION

Interest to the sources of lithium raw materials is increasing due to widespread use of this metal in lithium power sources and other areas. The deposits of lithium mineral resources do not satisfy the growing market demand. In this regard, technologies of lithium ions recovery from aqueous media - sea water, geothermal waters, and brines – are in demand [1]. Ion exchange recovery methods with the use of selective inorganic ion exchangers appear to be the most promising for these purposes. Inorganic ion exchangers have a number of significant advantages over organic resins. They are resistant to high temperatures, ionizing radiation, and contamination with organic substances. Furthermore, the synthesis of these materials is easy. Everything mentioned suggests the possibility of using lithium-selective inorganic ion exchangers in industrial processes to recovery lithium ions from aqueous media of varying salinity.

Modification of existing sorbents in order to obtain selectivity to lithium ions may be performed by directional thermal synthesis. According to this method, ion exchangers are saturated with desired cations and calcinated. During the calcination, these cations become surrounded by negatively charged elements of the matrix and the ion exchanger obtains crystalline structure where the added cations are included. The directional thermal

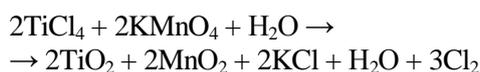
synthesis leads to increasing of the low-radius canals fraction and to the formation of a spinel oxide structure, where lithium ions are localized in tetrahedral cavities accessible only for lithium [2, 3]. As a result of heat treatment, the materials obtain ion sieve properties due to directional structuring caused by condensation processes. However, the complete condensation of polymer matrix elements is not achieved; thereby a part of charge of the resultant frame is compensated by lithium counterions allocated in tetrahedral cavities of the spinel structure; its cavities are not available for other ions due to the size. Removal of lithium ions from such materials gives rise to the selectivity to these ions in the subsequent adsorption.

An increase in specific selectivity for lithium ions can be achieved by introduction of highly selective ion exchanger component. In this work, manganese dioxide was selected as such component; it was introduced during the synthesis in titanium dioxide followed by directional heat treatment of the obtained binary material. Increasing the ratio of Li/Mn in the resulted sorption material leads to higher values of capacitance. It should be noted that in the case of using only manganese dioxide Mn³⁺ ions in LiMn₂O₄ are subjected to the disproportionation under acid treatment to Mn⁴⁺ and Mn²⁺ (Mn³⁺ → ½ Mn⁴⁺ + ½ Mn²⁺) [4]. Mn⁴⁺ ions remain

in the spinel lattice and Mn^{2+} are washed out into solution what eventually leads to the gradual destruction of the spinel structure. When using the binary material, the effect of these processes is greatly reduced.

EXPERIMENTAL

Synthesis of titanium-manganese composite sorbents was performed through a redox reaction between titanium chloride and potassium permanganate in aqueous solution. In this process solid potassium permanganate was gradually added to 1 M solution of titanium chloride until a molar ratio $TiCl_4:KMnO_4 = 1:1$. As it is known, during hydrolysis of $TiCl_4$, an excess of Cl^- ions is formed, which can reduce $Mn(VII)$ to $Mn(II)$ in acidic medium. In the presence of chloride ions the obtained $Mn(II)$ ions react with $Mn(VII)$ with the formation of manganese dioxide. In the overall reaction



gel consisting of hydrated oxides of $Ti(IV)$ and $Mn(IV)$ is formed. Control of the reaction speed is provided by $KMnO_4$ low solubility in water when added to a solution of $TiCl_4$, which ensures slowdown of excess acidity neutralization and leads to gelation of the mixed oxide.

This process is accompanied by intense elimination of chlorine at the initial stages of the synthesis and ends with the formation of durable dark brown gel. The gel was broken into pieces, washed with distilled water to the absence of MnO_4^- and Mn^{2+} ions in washing waters, and air dried. The resulting inorganic material was in the form of strong black granules of irregular shape with metallic luster on fracture.

Upon that the granulated sorbent was treated with 1 M $LiOH$ solution for 48 h with the volume ratio of sorbent to solution 1:100, washed from the hydroxide with excess of water, air dried, heat treated at various temperatures (in the range of 300–700 °C), then washed with 1 M HNO_3 solution and dried in air.

Isotherms of nitrogen adsorption and desorption from the samples were recorded using an automatic gas adsorption surface area and porosity analyzer Autosorb-iQ equipped with automated systems of the experiment and the processing of results. Texture parameters of the test samples were calculated from the obtained isotherms: specific surface area (S_{sp}) – by BET

method, and distribution of pore volume (V_s) – by equivalent diameters according to the BJH (Barret-Joyner-Halenda) method from the nitrogen desorption branch.

Scanning Electron Microscope Tescan Mira 3 LMU was used to determine the structure of the materials and the elemental composition (Ti, Mn).

For the sorption capacity study the samples of materials were submersed in $LiCl$ solutions of various concentrations – from 0.0001 to 0.1 mol/l. The sorbent to solution ratio was 1:500 g/cm^3 , contact time – 24 h. Lithium content in the equilibrium solutions was determined by atomic absorption method. The pH was adjusted by addition of 0.1 M $LiOH$ and measured with the ionomer.

Sorption kinetics was studied using a limited volume method with sample fractions of 0.16–0.25 mm. Volume ratio of the ion exchanger to the solution was 1:400. After certain time the contact of the solution with the ion exchanger was interrupted, adsorbed ions were desorbed with acid, and the eluate was analyzed by atomic absorption method. As it was found, the pH of the equilibrium solution during almost all the sorption time was within 3.2–3.5.

Study of selective absorption of Li^+ ions was carried out from solutions containing different amounts of $LiCl$ with 0.5M $NaCl$ as background. All the experiments were carried out under static conditions with the ratio solution : sorbent = 100 and the contact time of 24 h to reach sorption equilibrium.

Analysis of the adsorbed ions was done from the equilibrium solution according to

$$A = ((C_o - C)V)/m,$$

where C_o – initial ion concentration, mmol/l, C – equilibrium ion concentration, mmol/l, V – solution volume, l, m – sorbent sample weight, g; or by desorption of adsorbed ions with 1M HNO_3 and following analysis of desorption solution.

RESULTS AND DISCUSSION

Studies of sorption-structural characteristics of the materials provided by low-temperature nitrogen adsorption showed that for all samples the nature of adsorption-desorption curves corresponded to type IV of BET classification with respective hysteresis loops. The results indicate a significant contribution of the mesopores to the pore structure together with micropores.

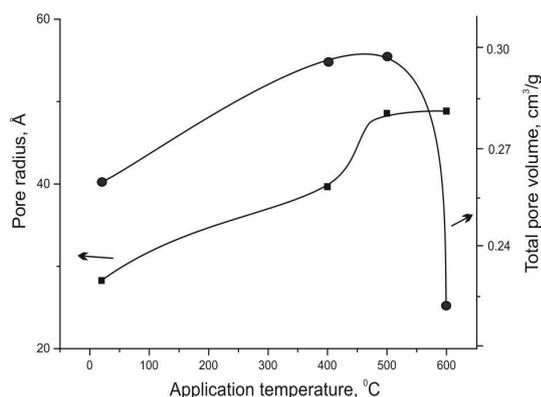


Fig. 1. Influence of the heat treatment temperature on the average pore radius and total pore volume for $\text{TiO}_2\text{-MnO}_2$ materials

From the dependences shown in Fig. 1 it can be seen that the increase of application temperature leads to an increase in the average pore radius with a general decrease in amount of micropores. It should be noted that increasing of the processing temperature over 500 °C brings a sharp decrease in the total pore volume due to shrinkage and contraction of the sorption material.

The results of SEM study of the binary material comparing to the material based on pure titanium dioxide (Fig. 2) show that appending of manganese provides obtainment of smaller sorbent granules, what is reflected on the sorption properties [5]. And by comparing images of two samples calcinated at different temperatures, it is possible to draw conclusions about the presence of nanoscale material particles that are agglomerated during the heat treatment process. The sorbent treated at 700 °C is characterized by tighter structure of the aggregates as compared with the material treated at 500 °C (Fig. 3). As the temperature increases, the structural rebuild with formation of spinel structure and rutile takes place in the material.

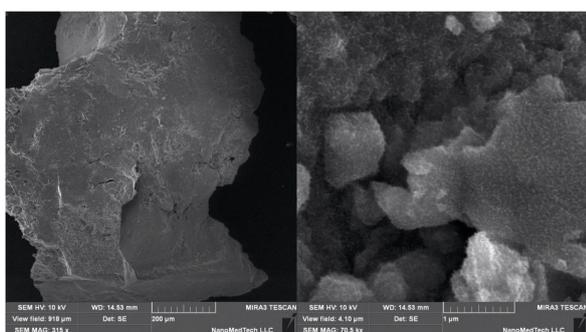


Fig. 2. SEM photos of ion exchange material based on TiO_2 calcinated at 500 °C with different amplification

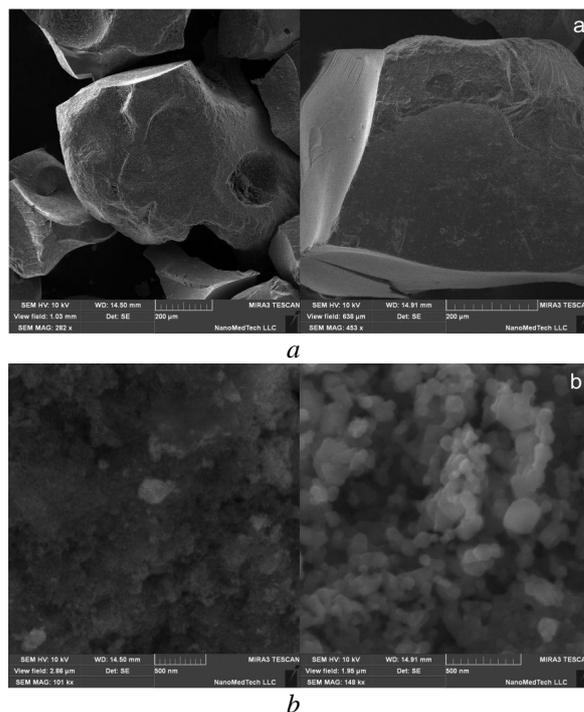


Fig. 3. SEM photos of ion exchange materials based on $\text{TiO}_2\text{-MnO}_2$, calcinated at 500 °C (on the left), 700 °C (on the right) with different amplification

According to the data obtained by electron microscopy, the molar ratio of titanium and manganese in the prepared sorbent is 3:2, although the initial ratio was 1:1. The obtained information is confirmed by other methods of material composition determination. Thus, we can talk about the loss of manganese in the synthesis process.

To study the acidity of surface sorption sites, the method of potentiometric titration was used (Fig. 4). The obtained dependences are typical for weakly acidic cation exchangers; stepped shape of the curves shows that the materials synthesized at 600 °C have several sites of sorption with different pK, while sorption centers of the ion exchanger treated at 700 °C are almost uniform.

Conclusions drawn from the dependences shown in Fig. 1 and Fig. 4 are confirmed by the results of sorption properties study. Thus, an increase in application temperature leads to a decrease in sorption capacity, but significantly increases the selectivity of adsorption of lithium ions from the solution with sodium ions on the background. Fig. 5 shows the dependences of capacitance on application temperature for sorption from solutions of 0.02M LiCl + 0.5M NaCl + LiOH (added to create the desired pH). It can be seen that, despite the considerable saline background,

lithium sorption by the synthesized materials increases as the treatment temperature raises due to the higher amount of formed selective sorption sites, whereas the total ion exchange capacity of the material decreases. Lack of capacity increasing at higher synthesis temperatures can be attributed to sintering of the material and growth of nonexchangeable lithium fraction, which is remaining in the bulk of ion exchanger.

Results of the study of thermal application influence on the sorption-kinetic properties of obtained materials are listed in the Table. Lithium ions diffusion coefficients during the sorption from solutions of pH 8 and pH 12 indicate that increasing the temperature of treatment results in a fall of this kinetic parameter, despite the rise of transport mesopores fraction. A probable cause of this is the formation of selective sorption sites

located in the channels of the crystal structure, the diffusion of ions to them being difficult.

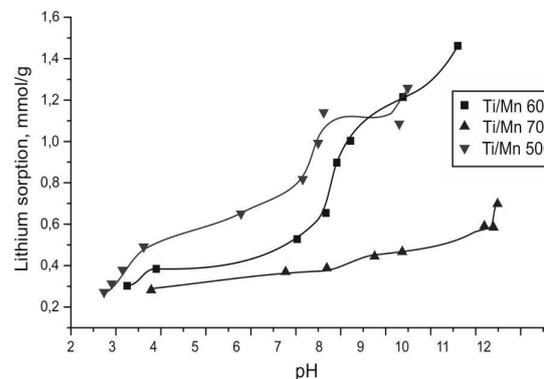


Fig. 4. Dependence of sorption capacity on pH of the solution for the materials calcinated at different temperatures

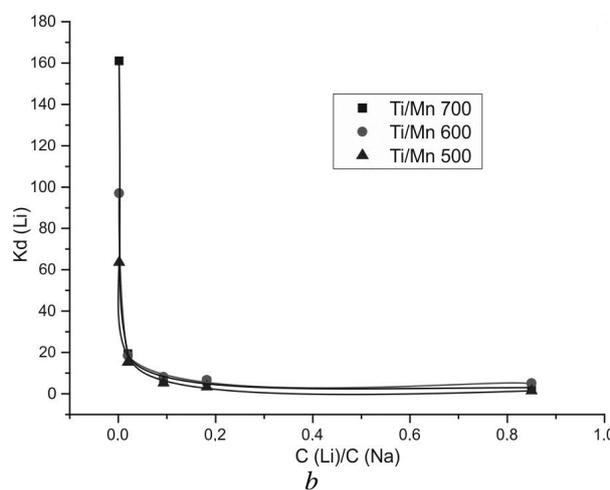
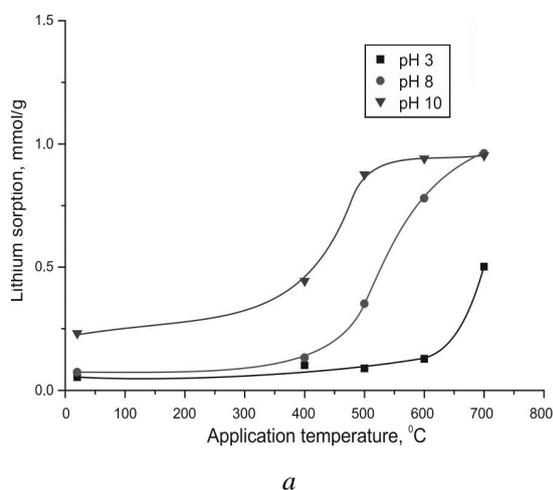


Fig. 5. Dependence of sorption capacity of synthesized materials on the application temperature for different pH of adsorbate solution (a) and dependence of lithium distribution coefficient on the molar ratio Li/Na in the solution (b)

Table. Lithium diffusion coefficients for TiO₂-MnO₂ materials

Ion exchanger	Lithium diffusion coefficient, m ² /s	
	at pH 8	at pH 12
TiO ₂ -MnO ₂ 500 °C	1.5·10 ⁻¹²	1.4·10 ⁻¹²
TiO ₂ -MnO ₂ 600 °C	3.9·10 ⁻¹³	1.2·10 ⁻¹²
TiO ₂ -MnO ₂ 700 °C	5.8·10 ⁻¹⁴	1.1·10 ⁻¹³

CONCLUSION

The results obtained confirm that the ion exchangers based on TiO₂-MnO₂ synthesized by the proposed method of thermal application exhibit high selectivity for the absorption of lithium ions from the solutions with high content of other cations. Increasing of the treatment temperature in the range of up to 700 °C leads to contraction of the material structure and reduces the kinetic

characteristics; however the formation of more lithium-selective sorption sites occurs, which positively affects the sorption capacity and lithium ion distribution in the system of ion exchanger-solution. This synthesis method allows us to obtain mesoporous materials with high distribution coefficients of lithium (up to K_d = 162) and the diffusion coefficient common to inorganic sorption materials (10⁻¹²-10⁻¹⁴ m²/s).

Вплив структурних характеристик на сорбційні властивості літій-селективних композиційних матеріалів на основі TiO_2 та MnO_2

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Синтезовано нові композиційні матеріали з еквімолярним співвідношенням TiO_2 та MnO_2 . Методом низькотемпературної адсорбції азоту досліджено структурні властивості і показано їхній вплив на селективність та кінетику сорбції літію. Сорбційні характеристики отриманих матеріалів визначаються умовами термічної обробки на стадії синтезу. Вищі температури синтезу призводять до агломерації сорбента та зниження його кінетичних характеристик, але водночас утворюється більша кількість літій-селективних центрів і вибірковість сорбції зростає. За допомогою запропонованого методу синтезу отримано високоселективні щодо літію іонообмінні матеріали.

Ключові слова: діоксид титану, діоксид мангану, літій, іонообмінна селективність

Влияние структурных характеристик на сорбционные свойства литий-селективных композиционных материалов на основе TiO_2 и MnO_2

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Синтезированы новые композиционные материалы с эквимольным соотношением TiO_2 и MnO_2 . Методом низкотемпературной адсорбции азота исследованы структурные свойства и показано их влияние на селективность и кинетику сорбции лития. Сорбционные характеристики полученных материалов определяются условиями термической обработки на стадии синтеза. Более высокие температуры синтеза приводят к агломерации сорбента и снижению его кинетических характеристик, но в то же время происходит образование большего количества литий-селективных центров и избирательность сорбции возрастает. С помощью предложенного метода синтеза получены высокоселективные по отношению к литию ионообменные материалы.

Ключевые слова: диоксид титана, диоксид марганца, литий, ионообменная селективность

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