

MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE



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CHAPTER 6

**ELECTRODEIONIZATION OF Li-CONTAINING SOLUTIONS USING
ION EXCHANGE MATERIAL BASED ON TiO₂-MnO₂**

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Abstract. *In this work the problem of selective extraction of Li⁺ ions from combined solutions by electromembrane method is being solved. Sorbent based on lithium-substituted titanium manganese oxide was used. It is established that the function of the sorbent in the membrane system is reduced to the turbulization of the solution flow, but under the influence of alkalization of the solution near the surface of the sorbent granules, its sorption capacity increases with an increase in voltage from 3 to 20 V.*

Keywords: *electrodialysis, electrodionization, ion-exchange membrane, lithium-titanium-manganese spinel.*

Introduction. Due to the ever-increasing production of electronic portable devices, particularly gadgets, raw materials needs for lithium-ion batteries rise. As a rule, lithium is extracted from minerals. A promising area is the processing of brines that are formed after desalination of seawater and mine waters [1], as well as directly from seawater, where its content reaches 0.17 mg dm⁻³ (0.024 mmol dm⁻³) [2]. In this case, it is advisable to use sorption [2] (TiO₂-MnO₂ oxide is the promising material for this purpose) or electromembrane [3] methods, combination of which, in contrast to the membrane methods, makes it possible to remove ionic components from solutions of very low concentration. The first stage of the process of extracting ions from the solution is their sorption by intermembrane filler, and the second one is the transfer of ions directly into the ion-exchanger phase affected by an electric field [4]. The advantage of the combined method comparing to sorption is reagentless continuous removal of species, since regeneration occurs due to the transfer of ions in the ion-exchanger bed and through the membranes.

Thus, the purpose of the work is to evaluate the possibility of using a double TiO₂-MnO₂ oxide for electromembrane extraction of Li⁺ ions from combined solutions.

Experimental. Composite titanium-manganese sorbents were synthesized according to the method [5]. Sorption of cations was investigated using the method described *ibid*.

For electrochemical studies, the sorbent was heated at 600 °C and following membranes were used: cation exchange (KM) Nafion-117 (DuPont) and anion exchange (AM) AMI-7001 (Membrane International). The electromembrane extraction of Li^+ and Na^+ ions was performed using a five-chamber cell. A 0.1 M KNO_3 solution was circulated through the cathode compartment (the first liquid line), through the concentration chamber (the second line), and through the anode compartment (the third line). The fourth line provided the passage of a model two-component solution through the desalination compartment under once-through operation. The composition of the model solution was (mmol dm^{-3}): $\text{Li}^+ - 3$; $\text{Na}^+ - 400$ $\text{K}^+ - 9$, chloride salt of these metals were used for the solution preparation. Sorbent or glass particles were located in the desalination compartment. The process was carried out under variation of voltage (3-20 V) or at 30 A m^{-2} . At the end of the experiment, the sorbent was regenerated and the eluate was analyzed.

In the next series of experiments, the sorbent was located in both concentration and desalination compartments. A model solution circulated through the cathode and concentration compartments (first liquid line), passed through the desalination compartment (second line). KNO_3 solution circulated through the anode compartment (third line).

Results and discussion. According to the data of the X-ray diffraction analysis, a sample of titanium manganese oxide treated at 500° C contains phases of TiO_2 (rutile) and MnO_2 in approximately equal amounts [5, 6]. A crystalline spinel $\text{Li}_{0.75}\text{Mn}_{0.25}\text{Ti}_2\text{O}_4$, which coexists with the rutile phase, is formed at 600-700°. Both phases determine the sorption properties of materials that are characterized by sufficiently developed surface (Table 6.1). It is worth noting that the values of a specific surface decrease with the increase in the temperature of heat treatment.

Table 6.1. Effect of heat treatment of sorbent on sorption of ions from seawater

Temperature of treatment, degrees C	Surface area, m^2g^{-1}	Sorption capacity, mmol g^{-1}				
		Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
500	126	0.009	0.217	0.026	0.153	0.073
600	122	0.026	0.109	0.026	0.074	0.042
700	86	0.024	0.109	0.015	0.014	0.027

Sorption of metal cations from seawater was studied. In the case of the sample obtained at 500° C, its sorption capacity towards Na^+ and Ca^{2+} ions are values of the same order. Regarding K^+ and Mg^{2+} ions, these values are smaller by one order of magnitude. The ratio of the content of Na^+ and Li^+ ions in the

sorbent reaches 25. The increase in the temperature of the heat treatment of the sorbent leads to an increase in the Li^+ capacity and to a decrease in this value for other ions. The ratio of the content of Na^+ and Li^+ in sorbents treated at 600 and 700 °C is 4.1 and 4.5, respectively.

Taken the data of Table 1 into consideration, the optimum calcination temperature of the sorbent is 600 °C: while maintaining a sorption high rate of Li^+ ions, a considerable selectivity of the sorbent to these ions is achieved. Consequently, for the electromembrane removal of these ions from the model solution, the material obtained under these conditions was applied.

In a five-chamber cell, the scheme of transfer of ions under the conditions, which provide lower current than limiting value, looks as shown in Figure 6.1. Water is decomposed in the cathode compartment, the solution is alkalized. OH^- and NO_3^- anions migrate through the AM to the concentration compartment that is closer to cathode. Here cations of alkaline metals are transported from the desalination compartment. Cl^- anions are removed from the same compartment to the concentration chamber, which is located closer to anode. The solution in the anode compartment is acidified. H^+ and K^+ ions are transported to the concentration chamber. The concentrate is gradually saturated with KNO_3 , its pH remains at the level of 7, since H^+ ions are neutralized with OH^- anions.

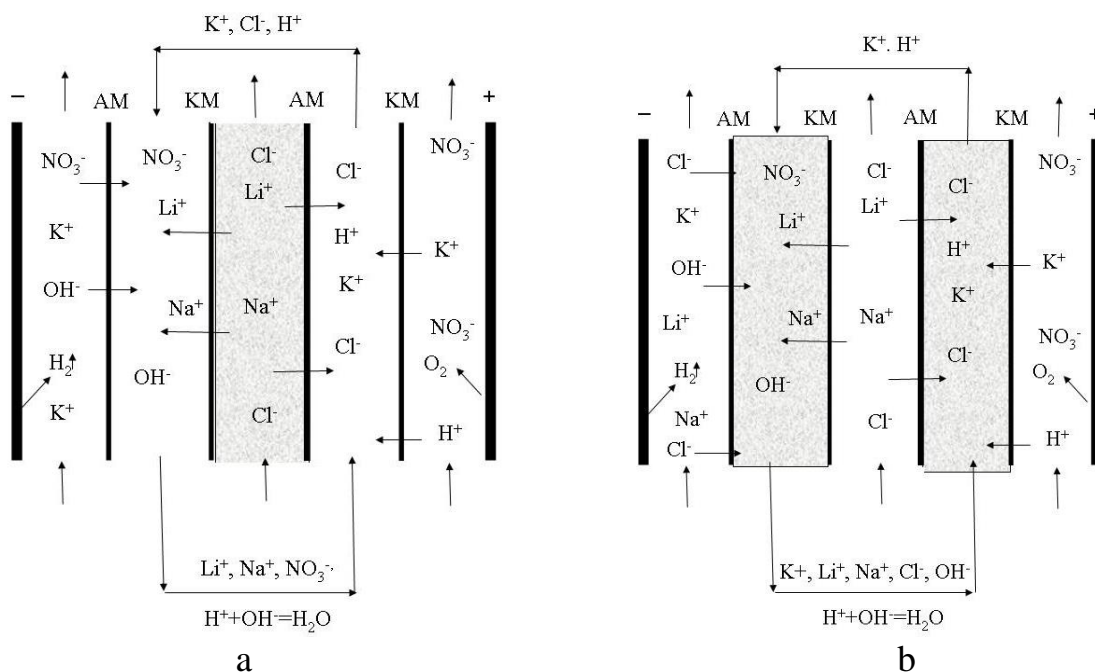


Fig. 6.1. Schemes for the transfer of ions in the membrane system, consisting of two KM and two AM (a, b): the sorbent is located in the desalting compartment (a) and in the concentration compartment (b).

Figure 6.2 illustrates the dependence of the content of Li^+ and Na^+ (n) ions in the concentrate on the time of electrodialysis at 30 A m^{-2} , which corresponds to the limiting current of cations. Each value of n shown in the graphs represents the difference between the value of n , which is reached for a certain period of

time, and the initial value ($\tau=0$). When the desalination compartment was filled with glass particles, linear $n-\tau$ dependences were obtained. The flux of Na^+ ions through the cation exchange membrane was $3.01 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$, while it is $8.06 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ for Li^+ ions. The ratio of the fluxes is 373, the ratio of the initial concentrations is 133. Thus, predominantly Na^+ ions pass through the membrane. The current efficiency for ions is 2.6 % (Li^+) and 96% (Na^+).

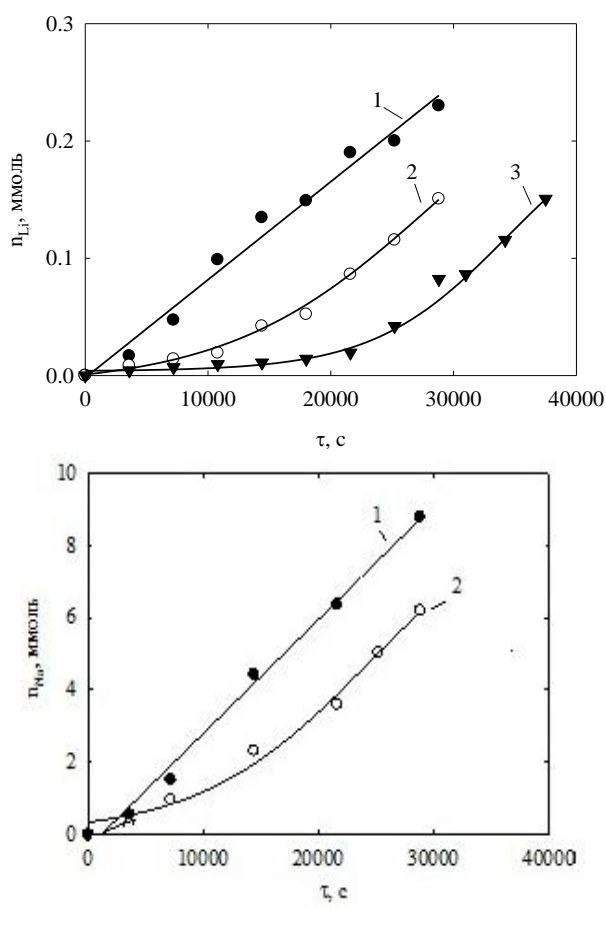


Fig. 6.2. The content of Li^+ (a) and Na^+ (b) ions in the concentrate as a function of time. The desalination compartment was filled with glass (1, 3) or sorbent (2), and the concentration compartment remained empty (1, 2) or was filled with sorbent (3).

When the membrane system included a sorbent in the desalination compartment, the $n-\tau$ curves show the regions of slow (corresponds to the sorbent saturation) and the rapid growth of the content of ions in the concentrate. The region of the rapid growth is parallel to the line obtained for inert glass. This means that the function of the sorbent is turbulization of the fluid, and the transfer of ions occurs mainly through the solution. Indeed, Li^+ and Na^+ ions in the sorbent are moving slowly: the order of magnitude of the diffusion coefficient of sorbed ions has been found to reach only 10^{-13} - $10^{-12} \text{ m}^2 \text{ s}^{-1}$.

When the concentration chamber is filled with the ion exchanger, a longer period of time is required to achieve a steady flux of Li^+ ions than in the case when the ion exchanger is in the desalination department. This is due to larger

amount of sorbent in the membrane system. A similar dependence on Na^+ ions was impossible due to their high initial content in the concentrate.

With an increase in voltage from 3 to 5 V, a slight increase in the electrical resistance of the membrane system is observed, indicating an approximation of the current, corresponding to the transfer of cations, to the limiting value (Figure 6.1a). The growth of the resistance is explained by the depletion of the hydrodynamically immobile layer of the solution near the surface of the cation exchange membrane from the side of the desalination compartment (concentration polarization) [4]. In the future, the near-surface layer of the solution collapses, as a result of which the resistance decreases – the transfer of cations and anions occurs due to overlimiting current.

At the end of the electrodialysis, the ion content in the intermembrane filler was determined and its sorption capacity was calculated. In all cases there is an increase in the capacity with voltage (Figure 6.3b). This, of course, is due to the dissociation of water on the surface of sorbent [4]. Hydrogen ions are involved into ion transport in the sorbent phase, and the OH^- ions remain in the near-surface layer of the solution near the granules. This additional factor promotes the solution alkalization. As a result, the equilibrium of sorption is shifted towards the formation of the substituted forms of sorbent. In all cases, sorbents exhibit the largest capacity of Li^+ ions, despite the Na^+ ions dominated in the solution. It was found that the smallest capacity is achieved for K^+ ions.

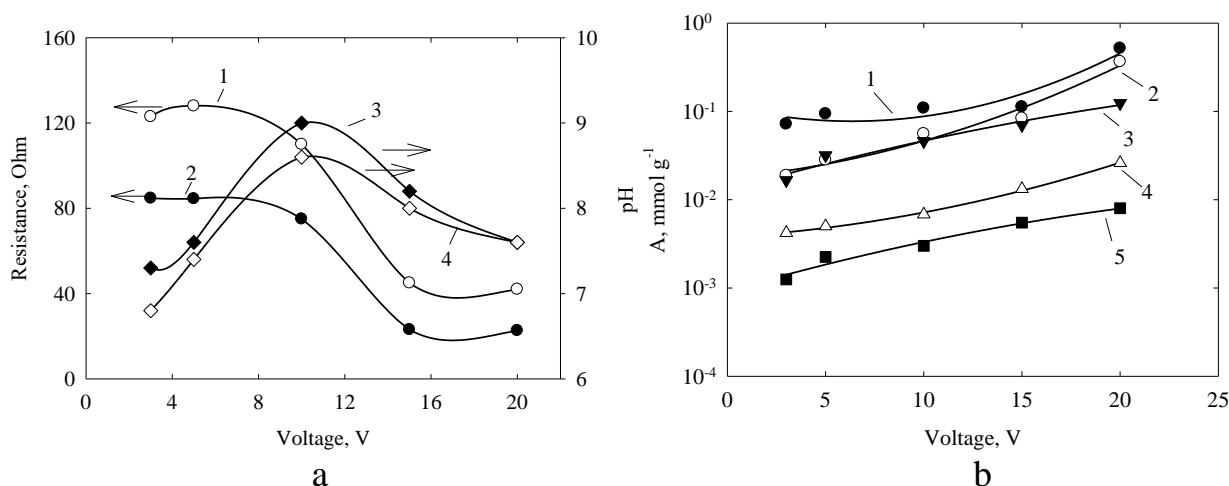


Fig. 6.3. Resistance of membrane system (a1, a2), pH of the solution at the outlet of desalination compartment (a3, a4), sorbent capacity towards Li^+ (b1, b3), Na^+ (b2, b4) and K^+ (b5) ions. Sorbent was placed in desalination (a1, b1, b2, b5) and concentration (a2, a4, b2, b4) compartments.

Thus, under conditions of electromembrane separation, the sorption capacity of materials based on titanium-manganese oxides increases. After treatment of the sorbent with a 1 M HNO_3 solution (mass ratio of sorbent and liquid was 1:5) followed by neutralization of the eluate with a Na_2CO_3 solution, a precipitate of Li_2CO_3 was obtained.

Conclusions. It should be noted that the purposeful recovery of lithium ions from seawater using the electromembrane method is economically unprofitable, but lithium salt can be obtained as a by-product during the electrodialytic desalination of seawater. Sorbent can be used as spacers for turbulization of the solution flow through the desalination compartments. In order to prevent the formation of a sediment of insoluble inorganic compounds in the membrane system and the competing influence of hardness ions upon precipitation of lithium carbonate, preliminary water softening with the use of nanofiltration method is recommended.

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ЕЛЕКТРОДЕІОНІЗАЦІЯ ЛІТІЙ-ВМІСНИХ РОЗЧИНІВ З ВИКОРИСТАННЯМ ІОНІТУ НА ОСНОВІ $\text{TiO}_2\text{-MnO}_2$

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Резюме. У роботі вирішується проблема селективного вилучення іонів Li^+ з комбінованих розчинів електромембранним методом. Використовували сорбент на основі літій-заміщеної форми титан-марганцевого оксиду. Встановлено, що у мембранній системі функція сорбенту зводиться до турбулізації потоку розчину. Проте під впливом підключення розчину біля поверхні гранул сорбенту, його сорбційна ємність зростає при збільшенні напруги з 3 до 20 В.

Ключові слова: електродіаліз, електродеіонізація, іонообмінна мембрана, літій-титан-марганцева шпінель.