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================== APPLIED ELECTROCHEMISTRY ==================
AND CORROSION PROTECTION OF METALS

</div>

Preparation of High-Purity Lithium Hydroxide Monohydrate from Technical-Grade Lithium Carbonate by Membrane Electrolysis

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Abstract—A scheme for preparing high-purity lithium hydroxide monohydrate from technical-grade lithium carbonate is suggested.

The basic stage in preparation of $LiOH \cdot H_2O$ from Li_2CO_3 is transformation of solid Li_2CO_3 into a LiOH solution. In this case, the throughput of the conversion process and its energy consumption, as well as the concentration and purity of the resulting LiOH solution largely determine the quality of the product obtained, its production cost, and the efficiency of the method as a whole.

Of the known techniques for preparing LiOH from Li_2CO_3, the method based on the reaction of Li_2CO_3 with lime milk $Ca(OH)_2$ is mainly used in practice [1, 2]. Despite the simplicity of this method and use of low-cost and readily available raw materials, it has a number of important disadvantages. For example, to obtain high-quality $LiOH \cdot H_2O$, it is necessary to impose stringent requirements on the purity of the starting components. In view of the low solubility of $Ca(OH)_2$, the technique in question is also characterized by low yield of LiOH into solution and large loss of Li^+, associated with the necessity for washing and settling of voluminous precipitates of $CaCO_3$.

To raise the yield of LiOH and improve the purity of the $LiOH \cdot H_2O$ obtained, it has been suggested to use, instead of $Ca(OH)_2$, a more soluble compound, $Ba(OH)_2$ [2]. However, the given method is also largely characterized by the same disadvantages. Moreover, $Ba(OH)_2$ is more expensive than $Ca(OH)_2$.

A method for obtaining LiOH by hydration of its oxide formed in thermochemical dissociation of Li_2CO_3 in a vacuum was suggested in [2]. However, the low rate of Li_2CO_3 decomposition gives no way of using this technique in the industry.

In recent years, electrochemical methods using ion-exchange membranes have found wide use in manufacture of high-purity alkali metal hydroxides [3–9].

For example, a method is known for preparing LiOH from Li_2CO_3 in a two-chamber electrolyzer with a cation-exchange membrane, lead anode, and iron cathode [8].

In [9], it was suggested to prepare LiOH from solid Li_2CO_3-containing wastes by bringing them in contact with water and subsequent separation of the clarified liquid phase. A lithium-containing solution is passed through the central chamber of a three-chamber electrolyzer, and a LiOH solution is obtained in the cathode chambe, and a solution of a mixture of acids, in the anode chamber. The circulation of the starting solution leads to desalting of the liquid in the central chamber, and this liquid is recycled into the dissolution stage.

The above-mentioned electrochemical methods for conversion of Li_2CO_3 into LiOH exhibit important advantages over chemical production techniques, because they make it possible to directly obtain high-purity LiOH at lower loss of Li^+. Therefore, development of a process for obtaining high-purity $LiOH \cdot H_2O$ by membrane electrolysis shows promise. However, the low output capacity and high energy consumption by electrochemical conversion, which is due to low solubility of Li_2CO_3 in water, is an important disadvantage in setting up a large-scale production.

The above disadvantages can be eliminated by preliminarily converting Li_2CO_3 into a well-soluble lithium salt. In this case, the solubility of the salt in water, electrical conductivity of its solution, and the nature of anodic reactions and products formed will

largely determine the efficiency of membrane electrolysis.

The most suitable salt is Li_2SO_4, which is due not only to its high solubility, but, to a considerable extent, also to specificity of the anodic processes that occur in electrolysis of a Li_2SO_4 solution.

The main anodic reaction in electrolysis of the sulfate solution proceeds to give O_2 and H_2SO_4 as products, which makes it possible to use readily available and inexpensive lead anodes. In addition, the evolving O_2 presents no problems with its utilization, and H_2SO_4 generated in the anolyte is easily neutralized with Li_2CO_3, with its conversion into Li_2SO_4.

In addition to the electromembrane conversion of Li_2CO_3 into a LiOH solution, it is necessary to solve, in developing a process for production of high-purity $LiOH \cdot H_2O$, the problem of removal of Na, Ca, Mg, Al (halides and sulfates) impurities, and also SiO_3^{2-} ions, contained in Li_2CO_3. Solving this problem required a number of experimental studies and predetermined the goals of this work. Among the issues studied were the following: electrochemical conversion $Li_2SO_4 \rightarrow LiOH$ with determining the main technical and economical characteristics of the process and factors affecting the yield and qualitative composition of the conversion-produced LiOH; evaporation of the conversion-produced LiOH solution, crystallization of $LiOH \cdot H_2O$ from this solution, distribution of impurities among the liquid and solid phases, and washing of the resulting $LiOH \cdot H_2O$ crystals to remove mother liquor; and carbonation of mother liquors after evaporation as applied to utilization of Li^+ from these solutions.

EXPERIMENTAL

In the study was used technical-grade Li_2CO_3 manufactured by the SQM company (Chile) and containing about 1% impurities. The starting Li_2CO_3 solution was prepared from chemically pure grade crystalline lithium sulfate and distilled water.

The electrochemical conversion was studied in a galvanostatic mode on a laboratory setup whose main part is a membrane electrolyzer in the form of a filter-press apparatus with a stainless steel cathode and lead anode. The interelectrode space of the electrolyzer is separated by an MK-40 cation-exchange membrane into the anode and cathode chambers. The working area of the membrane and electrodes was the same and equal to 0.78 dm^2.

The rate of solution circulation in all the experiments was 0.15 $l \, min^{-1}$. The thickness of the elec-

trode chambers was varied from 2 to 16 min, and the concentration of H_2SO_4 in the anolyte, from 0 to 87 $g \, l^{-1}$. The concentration of the resulting LiOH was in the range from 10 to 85 $g \, l^{-1}$, and the current density, from 5.2 to 15.4 $A \, dm^{-2}$. The process temperature depended on the current load and varied in the range $30-40°C$.

In the experiments, the main parameters of the electrolysis process (transfer of Li^+ ions into the cathode chamber, current efficiency, electrolyzer voltage, and specific electric power consumption) were determined. In addition, the qualitative and quantitative composition of the conversion-produced LiOH and the influence exerted on these parameters by the anolyte composition were found.

The rate of transfer of Li^+ ions into the cathode chamber, ΔP_{Li^+}, ($g \, Li \, h^{-1} \, dm^{-2}$), was determined from changes in the concentration of Li^+ ions, or in the equivalent concentration of OH^- ions in the catholyte (the negligible content of impurity ions in the catholyte was disregarded), and from changes in its volume in unit time, using the formula

$$\Delta P_{Li^+} = \frac{\Delta V_c \, \Delta c_{Li^+}}{\tau \, S_m} \times 0.292,$$

where ΔV_c is the change in the catholyte volume in a time τ (l); Δc_{Li^+}, the change in the concentration of LiOH in the time τ ($g \, l^{-1}$); τ, the time of electrolysis (h); S_m, the membrane area (dm^2); and 0.292, the recalculation factor.

The current efficiency η (%) was calculated by the formula

$$\eta = \frac{\Delta P_{Li^+} F}{j \, E_{Li^+}} \times 100,$$

where j is the current density ($A \, dm^{-2}$); $F = 26.8$, the Faraday constant (A h); and $E_{Li^+} = 7$, the chemical equivalent of lithium (g).

The specific energy expenditure was determined using the formula

$$W = \frac{Uj}{\Delta P_{Li^+}},$$

where W is the specific expenditure of electric power ($W \, h \, g^{-1}$ Li), and U is the electrolyzer voltage (V).

The crystallization of $LiOH \cdot H_2O$, including the stage of its washing, was studied with conversion

solutions of LiOH. A solution was evaporated to a LiOH concentration in solution of $170\text{--}180$ g l^{-1}. Then, the evaporated solution was cooled in a closed flask to room temperature and the crystals formed were rapidly filtered off. The product was dried in a desiccator at room temperature and then analyzed for the content of impurities and subjected to washing.

The mother liquor, which is a saturated solution of LiOH with impurities, was recycled into the stage of evaporation and crystallization, and so on. This yielded, each time, crystals and mother liquors increasingly contaminated with impurities. A total of five different samples were obtained.

The resulting $LiOH \cdot H_2O$ samples were, each separately, washed to remove impurities with a pure saturated solution of LiOH in accordance with a scheme of three-stage batch washing with phase mixing; the l : s ratio was 1 : 1 for each stage.

The washed $LiOH \cdot H_2O$ samples were dried, and the residual content of impurities in them was determined.

A mother liquor formed after crystallization, which is a saturated LiOH solution contaminated with Na, K, and Ca ions, was placed in a vessel for carbonation, into which CO_2 was fed from a cylinder at a rate of 0.3 l min^{-1} through a gas-distribution unit. The carbonation was performed in the bubbling mode to pH 12.3 to prevent formation of lithium hydrocarbonate.

The resulting suspension was separated by filtration, after which the precipitate was washed on the filter with a threefold volume of distilled water, dried in a desiccator, and analyzed for the content of impurities.

The conventional analytical techniques were used in the study. The concentration of Li, K, and Na ions was determined by the spectral method on a Philips AAS-SP-9 atomic-absorption spectrophotometer [10]; that of calcium and magnesium ions, by EDTA titration [11]; that of OH^- and H^+ ions, by titration with a 0.1 N solution of HCl or KOH, respectively [12]; and that of chloride ions, by mercurimetric titration, with nitroprusside as indicator [13]. Sulfate ions were determined in solutions with their concentration exceeding 1 g l^{-1} by volumetric EDTA titration [14], and in cases when the concentration of these ions was lower than 1 g l^{-1}, by the nephelometric method on a KFK-1 photocolorimeter [12]. The accuracy of determination was 5%. The formation of PbO_2 in the system under study was monitored as follows. The precipitate was filtered off and then boiled, together with the filter, in a mixture of HNO_3 with H_2O_2, with

the whole amount of PbO_2 quantitatively dissolved. The concentration of lead in solution was determined by EDTA titration, with Xylenol Orange as indicator, at pH 5.5 [15]. The concentrations of Cl_2 and O_3 in the gas phase were determined by photocolorimetry on a KFK-2MP instrument [16].
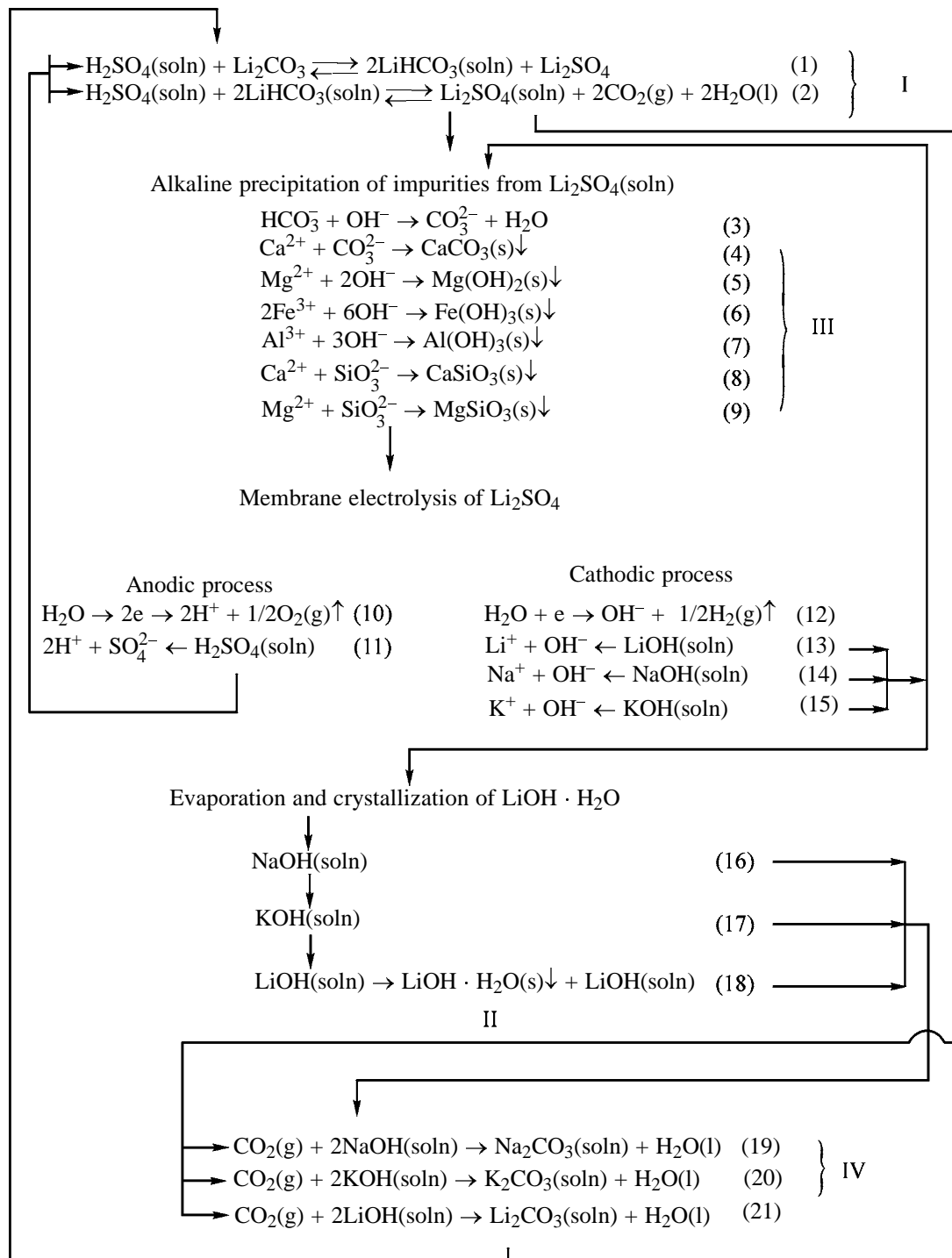
The procedure for obtaining high-purity $LiOH \cdot H_2O$ from technical-grade Li_2CO_3 is shown in Scheme 1.

According to the scheme suggested, a Li_2SO_4 solution is obtained from H_2SO_4 and Li_2CO_3 [reactions (1), (2)]. In the process, impurities of Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, SiO_3^{2-}, and Cl^- ions will also pass into solution from technical-grade Li_2CO_3. Some of these impurities can impair the quality of the resulting LiOH solution and disturb the course of electrolysis to the point of its complete termination. This primarily refers to cations that tend to form poorly soluble compounds on coming in contact with alkali formed in the cathode chamber. Therefore, prior to delivering the Li_2SO_4 solution to electrochemical conversion, it should be alkalized to pH 11–12 in order to precipitate these impurities in the form of poorly soluble compounds [reactions (4)–(9)]. The purified Li_2SO_4 solution is fed into the anode chamber of the electrolyzer. In the course of electrolysis, water is oxidized electrochemically at the anode to give gaseous O_2 and H^+ ions by reaction (10).

The cathode space is filled with a dilute LiOH solution, with the electrochemical reduction of water occurring at the cathode to give gaseous H_2 and OH^- ions by reaction (12). The cation-exchange membrane separating the cathode and anode spaces of the electrolyzer ensures free transfer of cations (mainly Li^+) from the anode space of the electrolyzer into its cathode space under the action of an electric field and precludes transfer of anions. As a result, a fairly pure LiOH solution concentrates in the cathode chamber [reaction (13)]. The main ingredients that contaminate LiOH will be Na^+ and K^+, which are present in the anolyte and cannot be removed from the anolyte in the stage of its alkaline purification preceding the electrolysis. Therefore, these cations will also freely pass, together with Li^+ cations, into the cathode chamber and thereby contaminate the product [reactions (14), (15)].

The thus obtained LiOH solution containing a certain amount of Ba^+ and K^+ impurities is delivered to the stage of evaporation and crystallization of $LiOH \cdot H_2O$ and is, in part, used to alkalize the Li_2SO_4 solution before the electrochemical conversion.

Scheme 1

$$H_2SO_4(soln) + Li_2CO_3 \rightleftharpoons 2LiHCO_3(soln) + Li_2SO_4 \qquad (1)$$
$$H_2SO_4(soln) + 2LiHCO_3(soln) \rightleftharpoons Li_2SO_4(soln) + 2CO_2(g) + 2H_2O(l) \quad (2)$$

I

Alkaline precipitation of impurities from $Li_2SO_4(soln)$

$$HCO_3^- + OH^- \to CO_3^{2-} + H_2O \qquad (3)$$
$$Ca^{2+} + CO_3^{2-} \to CaCO_3(s)\downarrow \qquad (4)$$
$$Mg^{2+} + 2OH^- \to Mg(OH)_2(s)\downarrow \qquad (5)$$
$$2Fe^{3+} + 6OH^- \to Fe(OH)_3(s)\downarrow \qquad (6)$$
$$Al^{3+} + 3OH^- \to Al(OH)_3(s)\downarrow \qquad (7)$$
$$Ca^{2+} + SiO_3^{2-} \to CaSiO_3(s)\downarrow \qquad (8)$$
$$Mg^{2+} + SiO_3^{2-} \to MgSiO_3(s)\downarrow \qquad (9)$$

III

Membrane electrolysis of Li_2SO_4

Anodic process

$$H_2O \to 2e \to 2H^+ + 1/2O_2(g)\uparrow \quad (10)$$
$$2H^+ + SO_4^{2-} \leftarrow H_2SO_4(soln) \qquad (11)$$

Cathodic process

$$H_2O + e \to OH^- + 1/2H_2(g)\uparrow \quad (12)$$
$$Li^+ + OH^- \leftarrow LiOH(soln) \qquad (13) \longrightarrow$$
$$Na^+ + OH^- \leftarrow NaOH(soln) \qquad (14) \longrightarrow$$
$$K^+ + OH^- \leftarrow KOH(soln) \qquad (15) \longrightarrow$$

Evaporation and crystallization of $LiOH \cdot H_2O$

$$NaOH(soln) \qquad (16) \longrightarrow$$

$$KOH(soln) \qquad (17) \longrightarrow$$

$$LiOH(soln) \to LiOH \cdot H_2O(s)\downarrow + LiOH(soln) \quad (18) \longrightarrow$$

II

$$CO_2(g) + 2NaOH(soln) \to Na_2CO_3(soln) + H_2O(l) \quad (19)$$
$$CO_2(g) + 2KOH(soln) \to K_2CO_3(soln) + H_2O(l) \qquad (20)$$
$$CO_2(g) + 2LiOH(soln) \to Li_2CO_3(soln) + H_2O(l) \qquad (21)$$

IV

Chemical reactions that occur in preparing high-purity $LiOH \cdot H_2O$ from technical-grade lithium carbonate.

The required degree of purification of the final product to remove Na^+ and K^+ can be achieved by crystallization of $LiOH \cdot H_2O$ from an evaporated LiOH solution [reactions (16)–(18)]. In the crystallization of $LiOH \cdot H_2O$, Na^+ and K^+ ions must mainly remain in the mother liquor because of the higher solubility of NaOH and KOH and, up to their certain content in the solution being evaporated, must not affect the purity of the $LiOH \cdot H_2O$ crystals obtained. In this case, the resulting $LiOH \cdot H_2O$ crystals should
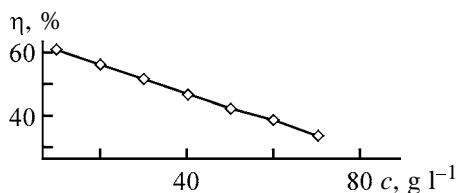
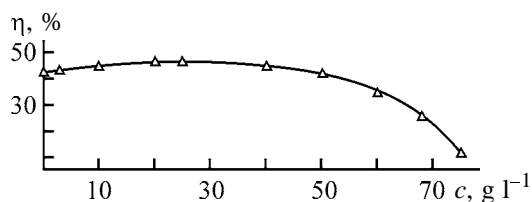**Fig. 1.** Current efficiency η vs. LiOH concentration c.

Fig. 2. Current efficiency η by conversion LiOH vs. the H_2SO_4 concentration c in the anolyte.

be washed with the condensate for more complete removal of the mother liquor from their surface.

In order to prevent the loss of Li^+, it is advisable to treat spent washing solutions and mother liquors with carbon dioxide evolved in reaction (2). It is necessary to separate the poorly soluble Li_2CO_3 from the liquid phase, which contains mostly Na_2CO_3 and K_2CO_3 [reactions (19)–(21)]. The carbonate mother liquors formed after separation of Li_2CO_3 can be used in the industry, e.g., for neutralization of wastewater, or in installations for water softening.

The main characteristic of any process is the specific energy expenditure necessary for obtaining the target product. The specific energy expenditure in electrolysis is determined by the electrolyzer voltage and current efficiency by the target product. The electrolyzer voltage is largely determined by the electrical conductivity of the electrolyte, which, as a rule, depends on its concentration. In studying the electrochemical conversion of Li_2SO_4 into LiOH, the optimal Li_2SO_4 concentration in the solution delivered to the conversion stage was determined to be 180–230 g l^{-1} [17]. To this concentration corresponds the maximum electrical conductivity of approximately 0.09 S cm^{-1}, which, combined with the relatively low viscosity, ensures the minimum energy expenditure for overcoming the ohmic and hydrodynamic resistances in the given process. It was established experimentally that changing the thickness of chambers of the electrolysis cell in the range 2–8 mm has virtually no effect on the loss of voltage in electrolysis of a Li_2SO_4 solution with a concentration of 200 g l^{-1} in the current density range studied. In the elementary cell, the chamber thickness was taken to be 4 mm, which enables one, on the one hand, to simplify to the

maximum possible extent the fabrication of an electrolyzer of the filter-press type, and, on the other, to construct apparatus with a high output capacity and relatively small dimensions.

The concentration of LiOH in the cathode chamber affects the loss of voltage in an elementary cell of the electrolyzer only at LiOH concentrations of up to 40–45 g l^{-1}.

A much stronger influence is exerted by the concentration of LiOH obtained on the current efficiency by LiOH, whose value directly determines the specific energy expenditure.

The dependence of the current efficiency on the concentration of the LiOH being obtained, shown in Fig. 1, indicates that the transfer of Li^+ ions linearly decreases as the content of Li^+ ions in the catholyte becomes higher. This leads to a proportional rise in the specific expenditure of electric power. The minimum specific expenditure of electric power for electrochemical conversion corresponds to concentrations of LiOH obtained equal to 20–25 g l^{-1}. However, obtaining a more concentrated LiOH solution is advantageous as regards energy saving in evaporation of a solution of conversion LiOH in production of LiOH·H_2O.

Rough feasibility studies demonstrated that, as regards lowering to the maximum possible extent the total energy expenditure for obtaining LiOH·H_2O as a commercial product, the optimal concentration of conversion LiOH is 40–50 g l^{-1}. In this case, the concentration of the acid in the anolyte does not exert, in a rather wide range (up to 50 g l^{-1} of H_2SO_4), any noticeable influence on the cathode current efficiency by LiOH (Fig. 2). A moderate increase in the acidity even improves the process parameters because of a certain enhancement of the transfer of Li^+ ions and the corresponding increase in the current efficiency (by approximately 5%). The possible reason is that, when the acidity of the anolyte increases, H^+ ions neutralize OH^- ions in the membrane or in the near-membrane layer on the anode side to give water. The reaction between H^+ and OH^- ions, which are charge carriers, is compensated for by an increase in the fraction of current transported by Li^+ ions. The optimal concentration of H_2SO_4 in the anolyte in production of LiOH is in the range 15–40 g l^{-1}. Impurity ions constantly delivered into the anolyte with Li_2CO_3 in the neutralization of the acid cannot affect the process parameters to any noticeable extent because of their insignificant content in the anolyte.

In addition to the parameters described above,

those affecting the feasibility of electrolysis include the current density, which determines the specific output capacity of the process. The dependences in Figs. 3 and 4 clearly demonstrate that raising the current density leads to an increase in the electrolyzer voltage (Figs. 3, 4) and to the corresponding rise in the specific energy expenditure (Fig. 4, straight line 2). At the same time, raising the current density leads to a proportional increase in the rate of transfer of Li^+ ions, ΔP_{Li^+}, i.e., in the specific output capacity of the process (Fig. 4, straight line 1). For example, a threefold increase in the current density leads to an identical increase in the specific output capacity of the process, whereas the energy expenditures grows by only 36.6%. It was also established that the current density does not affect significantly the qualitative composition of the LiOH obtained. The electrolysis is more efficient at higher current densities, because the component of the production cost, associated with the capital cost and running expenses, decreases in this case. This conclusion is also supported by the fact that the concentration polarization of the electrodes and membranes, which makes shorter their service life, is not observed at the current densities studied. This is indicated by the stable current efficiency by LiOH and by the sufficiently high chemical and corrosion resistance of the membranes and electrodes, observed in the course of the study.

The main disadvantage of MK-40 membranes is their high permeability to OH^- ions, which leads to low current efficiency. At the same time, these membranes enable production of LiOH that is virtually free of any foreign anions. The main impurities that pass from Li_2CO_3 into a LiOH solution in electrochemical conversion are Na^+ and Ca^{2+} ions, whose concentrations in the 2 M LiOH solution obtained in a stationary electrolysis mode are 35–40 and 12–15 mg l^{-1}, respectively. A decrease or increase in the concentration of LiOH does not affect their relative concentration in solution. The study performed demonstrated that, as expected, the concentration of Ca^{2+} ions in alkali can be diminished to 2–4 mg l^{-1} by purifying the anolyte by the carbonate–alkaline method. No transfer of lead ions into the LiOH solution was observed in the course of electrolysis.

The parameters characterizing the purification of $LiOH \cdot H_2O$ by evaporation, crystallization, and washing of the crystals obtained to remove the remainder of contaminated mother liquor are listed in Tables 1 and 2.

Table 2 shows that the maximum content of Na^+ ions in the $LiOH \cdot H_2O$ samples obtained, at which
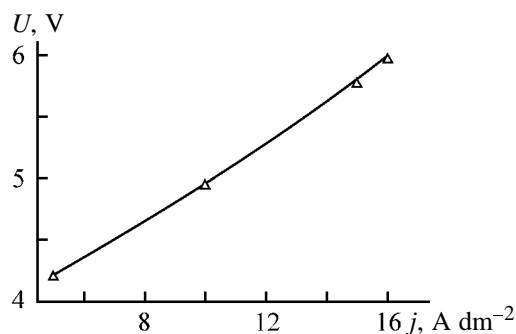

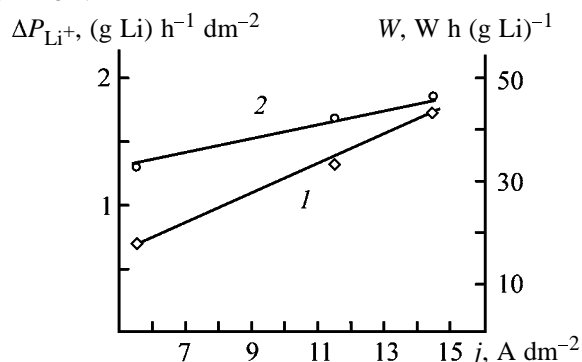**Fig. 3.** Voltage U vs. the current density j in production of LiOH.

Fig. 4. (1) Rate of transfer of Li^+ ions and (2) specific energy expenditure W vs. the current density j in production of a LiOH solution. (ΔP_{Li^+}) Specific transfer of Li^+ ions to the cathode chamber.

high-purity $LiOH \cdot H_2O$ can be obtained by their washing to remove mother liquor (residual content of $Na^+ \leq 0.002$ wt %), is about 0.06 wt %. As seen from Table 1, the concentration of Na^+ ions in a LiOH solution from which $LiOH \cdot H_2O$ with a residual sodium content $c \leq 0.06$ wt % can be obtained should not exceed 1.4 g l^{-1}.

As expected, Ca^{2+} is removed by washing to a considerably lesser extent than Na^+, and, therefore, the maximum content of Ca^{2+} impurity in the $LiOH \cdot H_2O$ samples delivered to the washing stage should not exceed 0.003 wt % for $LiOH \cdot H_2O$ of required purity as regards Ca^{2+} ions (residual content of Ca^{2+} $c \leq 0.001$ wt %) to be obtained. In this case, the concentration of Ca^{2+} in a LiOH solution from which $LiOH \cdot H_2O$ with a residual content of Ca^{2+} $c \leq 0.003$ wt % can be obtained should not exceed 0.05 g l^{-1}. Provided that the concentration of Ca^{2+} in the starting solution of conversion LiOH is lowered to 2–4 mg l^{-1} by its alkaline–carbonate removal from the anolyte delivered to electrolysis, it may be stated that Ca^{2+} is not an impurity component that determines the quality of $LiOH \cdot H_2O$ produced by the technique suggested.

Table 1. Characteristics of starting solutions and crystalline $LiOH \cdot H_2O$ samples obtained from these solutions

Sample no.	LiOH solution	Solution volume, l	c_{LiOH} in solution, g l^{-1}	Na$^+$ content		Ca^{2+} content	
				in solution, g l^{-1}	in LiOH·H$_2$O, wt %	in solution, g l^{-1}	in LiOH·H$_2$O, wt %
1	Starting	7.00	45.5	0.070	0.008	0.015	0.003
2	Mother liquor after crystallization:						
	first	1.25	Saturated solution, ~120 g l^{-1}	0.520	0.017	0.051	0.004
3	second	0.75	"	0.784	0.057	0.056	0.006
4	third	0.42	"	1.435	0.061	0.078	0.012
5	fourth	0.23	"	2.200	0.092	0.088	0.036
6	fifth	0.11	"	3.560	–	0.084	–

Note: The concentration of K$^+$ ions in all the samples and solutions studied is an order of magnitude lower than that of Na$^+$ ions.

Table 2. Results of a comparative analysis of $LiOH \cdot H_2O$ samples for the content of impurities after washing to remove mother liquor

Sample no.	Content of Na$^+$, wt %		Content of Ca^{2+}, wt %	
	before washing	after washing	before washing	after washing
1	0.008	0.0006	<0.003	<0.001
2	0.017	0.0020	<0.004	<0.002
3	0.057	0.0024	<0.006	<0.003
4	0.061	0.0022	0.012	<0.006
5	0.092	0.0103	0.036	0.020

In order to test the process on an enlarged scale, a pilot batch of the product was prepared from lithium carbonate of Chilean manufacture.

In the process, 8.5 l of a conversion solution of

Table 3. Composition of Li_2CO_3 manufactured by SQM (Chile) and of $LiOH \cdot H_2O$ obtained

Main substance and impurities	Content, wt %	
	Li$_2$CO$_3$	LiOH·H$_2$O
Li$_2$CO$_3$	99.0	0.6*
Cl$^-$	0.02	0.1×10^{-3}
Na$^+$	0.12	2×10^{-3}
K$^+$	0.05	0.2×10^{-3}
Ca^{2+}	0.04	$\leq 4 \times 10^{-3}$
Mg^{2+}	0.011	$\leq 1 \times 10^{-3}$
SO$_4^{2-}$	0.1	$\leq 0.1 \times 10^{-3}$
Fe$_2$O$_3$	0.03	$\leq 1 \times 10^{-3}$
Insolubles	0.02	–
Pb	–	–

* The product contains a CO$_3^{2-}$ impurity because of its storage conditions.

LiOH with an average concentration of 45 g l^{-1} was obtained. The average concentrations of the main impurities in the resulting solution are as follows (mg l^{-1}): Na$^+$ 70, Ca^{2+} 15, CO$_3^{2-}$ 300. The contents of other impurities (Pb, Fe^{2+}, Mg^{2+}, SO$_4^{2-}$, Cl$^-$) were either an order of magnitude lower than that of Na$^+$ and Ca^{2+}, or these impurities could not be detected at all by the analytical methods used.

It follows from Table 3 that the quality of LiOH·H$_2$O satisfies the requirements of GOST (State Standard) 8595–83 (LGO-1 brand) in all the parameters except the content of Ca^{2+}.

The increased content of Ca^{2+} (~0.004 wt % against 0.001 wt % required by GOST) can be brought to satisfactory values by preliminary alkaline–carbonate purification of the anolyte delivered to electrolysis.

A study of the carbonation of alkaline mother liquors obtained after evaporation and crystallization, which cannot be used to produce commercial LiOH·H$_2$O because of the high content of impurities, demonstrated sufficiently high efficiency of this process for utilization of Li$^+$. Li$_2$CO$_3$ obtained by carbonation

Scheme 2
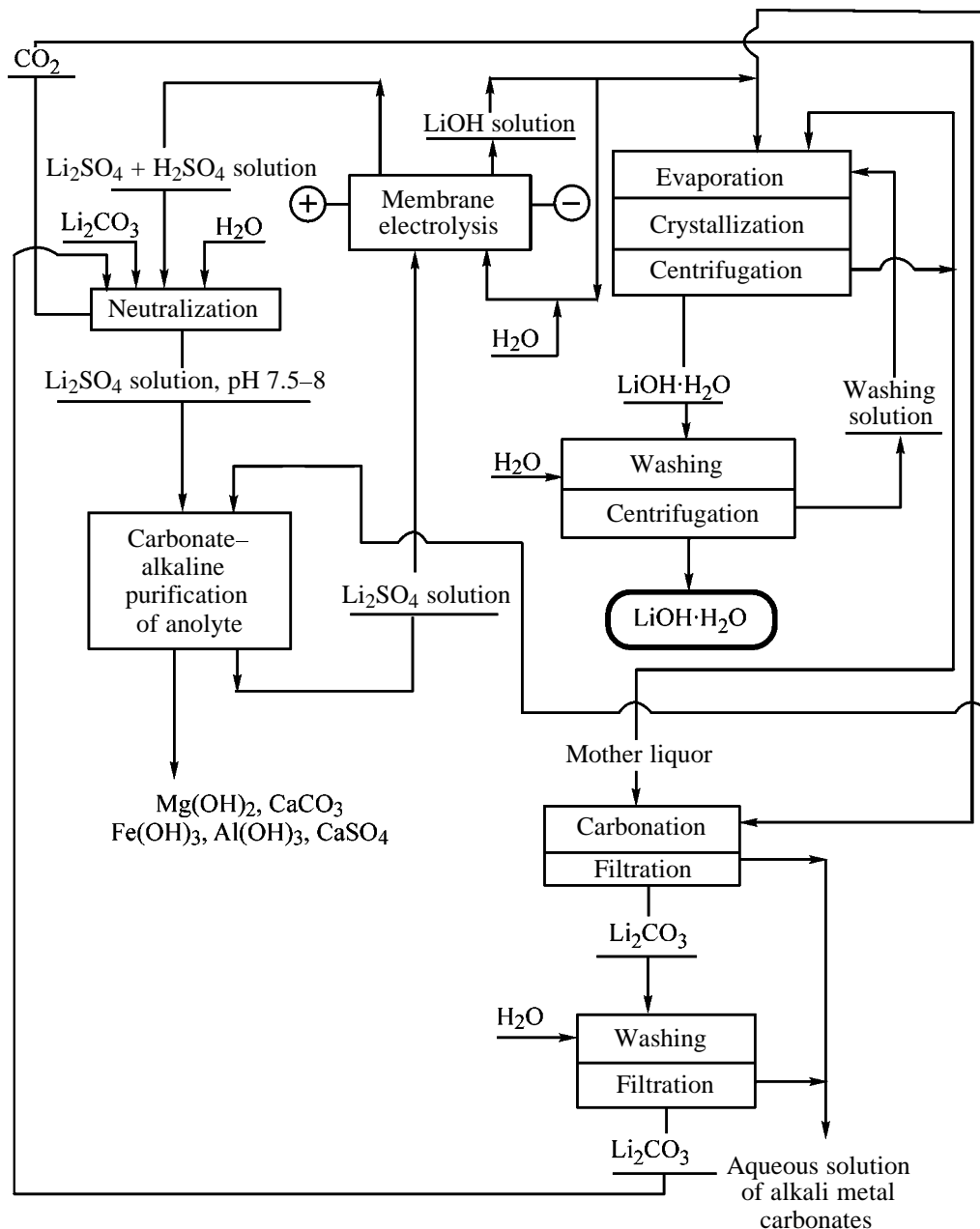
Flowsheet for production of high-purity $LiOH \cdot H_2O$.

contains only 0.007 wt % Na^+ and 0.043 wt % Ca^{2+}, which allows its recycling into the stage of electrochemical conversion. It was established that the main part of Ca^{2+} passes into the solid phase of Li_2CO_3 and cannot be removed by subsequent washing. Part of Na^+ ions (88%) remains in solution, and 12% Na^+ coprecipitates with Li_2CO_3, and this Na^+ can be completely removed by washing.

A calculation of the conversion of Li_2CO_3 into $LiOH \cdot H_2O$ of LGO-1 brand demonstrated that the loss of Li^+ without utilization from mother liquors formed in crystallization of $LiOH \cdot H_2O$ is 5.4%. With utilization of Li^+ from mother liquors by their carbonation and recycling of Li_2CO_3, the loss of Li^+ is about 1%.

The results obtained were used to develop a technique for manufacture of high-purity $LiOH \cdot H_2O$ from Li_2CO_3 by membrane electrolysis (Scheme 2). The technique was patented in the Russian Federation [18].

CONCLUSIONS

(1) The experimental study of production of LiOH·H_2O from technical-grade Li_2CO_3 by membrane electrolysis via Li_2SO_4 demonstrated that the use of a sulfate solution of Li^+ makes it possible to perform the process in an intensive mode at high current densities and allows use of lead anodes and MK-40 cation-exchange membranes of domestic manufacture.

(2) The use of these materials in a practical implementation of the process of electrochemical conversion demonstrated their high stability and efficiency. The technique is distinguished by an integrated approach to solution of the problem of use of technical-grade Li_2CO_3 and, in particular, that of Chilean manufacture. It yields high-purity LiOH·H_2O with a minimum amount of reagents used and does not produce any toxic waste.

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