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Lithium Hydroxide Formation by Membrane Electrolysis

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Abstract

The production of high-purity lithium hydroxide (LiOH) solution by electrochemical conversion of soluble lithium salts (membrane electrolysis) was tested on semi-industrial scale. Stainless steel (cathode) and lead (anode) were used as electrode materials. Lithium sulphate solution was utilised as anolyte and water – as catholyte. During membrane electrolysis, water oxidation takes place in the anode compartment with the formation of gaseous oxygen and protons. Lithium ions permeate through the cationic membrane into the cathode compartment, where gaseous hydrogen and hydroxide ions are formed as the products of water decomposition on the cathode, so lithium hydroxide gets concentrated up to 33–36 g/dm^3 with respect to lithium oxide. Electrolysis efficiency is 50–55 % for one process cycle. Sulphuric acid formed in the anode compartment may be then neutralised by adding lithium carbonate, and the formed lithium sulphate may be re-used in membrane electrolysis, which means anolyte recycling. Five successive electrolysis cycles with recycled anolyte allow an increase in the degree of lithium ion transfer from the anode to cathode compartment to 95–98 %. It is established that, in addition to lithium, other metal ions (sodium, potassium, calcium, *etc*.) and sulphate ions migrate through the cation-exchange membrane into the cathode compartment from anolyte solution. To evaluate the quality of the obtained lithium hydroxide monohydrate ($LiOH \cdot H_2O$), lithium hydroxide solutions obtained both by membrane electrolysis and by the traditional lime causticisation process were evaporated. Comparison between the concentrations of impurity ions in lithium hydroxide monohydrate samples obtained using different methods shows that the product of better purity may be synthesized from lithium sulphate solution by membrane electrolysis.

Keywords: membrane electrolysis, lithium hydroxide, lithium sulphate

INTRODUCTION

Lithium hydroxide (LiOH) plays an essential part in modern industry because it is a basic component for manufacturing a number of products: alkaline rechargeable batteries, rocket propellants, greases with good waterproofing characteristics based on lithium stearate, catalysts for polymerization, *etc*. [1–4].

There are various methods to obtain lithium hydroxide, for example hydration of lithium oxide formed through thermochemical dissociation of lithium carbonate in vacuum. However, this method did not win broad application on the industrial scale because of the low rate of lithium carbonate decomposition [5].

It is possible to obtain LiOH with the help of exchange reactions between lithium salts and hydroxides of alkaline earth metals (barium or calcium) in aqueous solutions. The most widespread process, causticisation, based on the interaction of lithium carbonate with calcium hydroxide, forms the basis of the industrial method of obtaining crystal lithium hydroxide monohydrate ($LiOH \cdot H_2O$). An advantage of this method is the use of available and cheap initial reagents [6, 7],

while its drawback is the formation of diluted lithium hydroxide solutions (up 36 g/L with respect to LiOH) containing large amounts of extrinsic ions (sodium, potassium, calcium, *etc.*) that inter the solution from lithium carbonate and calcium hydroxide (lime) [8]. To achieve higher purity of the resulting $LiOH \cdot H_2O$, it has been proposed to use barium hydroxide instead of calcium hydroxide, but the cost of this reagent is much higher than that of lime, which causes a substantial increase in the cost of the obtained LiOH [5, 8].

At present, increasingly widespread are electrochemical methods for obtaining the hydroxides of alkaline metals with the help of ion exchange membranes [9–17]. For instance, one of the known methods of obtaining lithium hydroxide from lithium carbonate involves the process in a two-compartment electrolyser with a cation-exchange membrane, lead anode and iron cathode [13]. A method of obtaining lithium hydroxide from solid wastes containing lithium carbonate through their contact with water, followed by the separation of clarified liquid phase is described in [14]. The lithium-containing solution is passed through the central chamber of a three-chambered electrodialyser to obtain lithium hydroxide solution in the cathode space and a solution of the mixture of acids in the anode space [5, 14].

The indicated electrochemical methods of conversion have substantial advantages over the chemical methods because they allow the synthesis of high-purity lithium hydroxide according to a simplified scheme with a minimal loss of lithium ions. However, lithium carbonate is poorly soluble in water, which is a substantial disadvantage for the arrangement of production on the industrial scale due to low productivity and high energy consumption by the process [5, 12]. It is known that the efficiency of membrane electrolysis is to a high extent determined by the solubility of a salt in water, its specific electrical conductance, so it is necessary to use a well soluble salt, for example lithium sulphate or chloride, as anolyte in order to eliminate the disadvantages mentioned above [5, 17].

An advantage of lithium sulphate solution for use in electrolysis is in the evolution of oxygen at the anode, without any problems with utilization, and the formation of sulphuric acid, which may be later on neutralized by adding lithium carbonate, while the formed lithium sulphate may be re-used in membrane electrolysis, that is, anolyte recirculation will be implemented.

The objective of the work presented herein was to evaluate the possibility of high-purity lithium hydroxide production from lithium sulphate solution by membrane electrolysis and to determine the effect of the main process characteristics (reagents flow rate, current strength) on the yield and composition of the formed lithium hydroxide solution.

EXPERIMENTAL

Analysis of catholyte and anolyte solutions, lithium hydroxide monohydrate for the major component content and the concentrations of extrinsic ions was carried out with the help of atomic absorption spectrometer ICE 3300 (Thermo Fisher Scientific, USA) and atomic emission spectrometer with inductively coupled plasma ICAP 7400 Duo (Thermo Fisher Scientific, USA) with the relative error not more than 21 %.

Experiments on electrolysis were carried out using a pilot electrolyser MB-5/L-RE (ASET LLC, Russia) 18 dm^3 in volume, with a YuanBo membrane (China). An electrode made of stainless steel of AISI 304 grade was used as the cathode, while anode was an electrode made of S1 grade lead. The working area of the membrane was 15 dm^2, and electrodes – 30 dm^2.

The solution of lithium sulphate (Li_2SO_4) with the concentration 200 g/L, prepared from crystalline technical-grade Li_2SO_4 and technical-grade water, was used as the anolyte, while catholyte was technical-grade water. The concentrations of impurities in the initial catholyte and anolyte solutions are presented in Table 1.

The rate of initial components income was regulated with DLX-MA/MB20-3 pumps (Etatron, Italy), which came with the electrolyser. The voltage did not go higher than 5.0 V during electrolysis under variations of all process parameters.

TABLE 1
Impurities in the initial catholyte and anolyte solutions

Determined component	Impurity content, mg/L	
	Anolyte	Catholyte
Calcium	7.5	2.8
Sodium	26.6	1.3
Potassium	2.4	0.2
Aluminium	0.1	0.3
Iron	0.7	0.9
Silicon	77.6	1.5
Magnesium	0.7	1.1

The degree of lithium ion transfer from the anode compartment to the cathode one was assessed relying on the concentration of lithium hydroxide in the cathode compartment, it was calculated using equation:

$$R = \frac{V_K C_K}{V_A C_A} \cdot 100$$

where R is the degree of lithium ion transfer from the anode to cathode compartment, %; V_K is the obtained catholyte volume, L; V_A is the reacted anolyte volume, L; C_K and C_A are the concentrations of catholyte and anolyte, respectively, calculated for Li_2O, g/L.

The qualitative and quantitative composition of catholyte and anolyte solutions was monitored during electrolysis.

To determine the chemical composition and quantitative content of impurities in the final product (lithium hydroxide monohydrate), the catholyte solution was evaporated to the concentration of 220 g/L with respect to Li_2O in closed vessels under permanent heating. The resulting suspension was separated by filtering through a double layer of capron fabric with the help of a vacuum pump, and the resulting crystal precipitate was analysed for the major component content and the concentrations of impurities using atomic spectroscopy methods according to the standard procedure [18].

RESULTS AND DISCUSSION

During membrane electrolysis with lithium sulphate as anolyte, electrochemical oxidation of water with the formation of gaseous oxygen and hydrogen ions takes place in the anode compartment:

$$H_2O - 2e^- \rightarrow 2H^+ + 1/2O_2\uparrow \quad (1)$$

Lithium ions pass through the cation-exchange membrane without hindrance into the cathode compartment, where hydrogen and hydroxide ions are formed due to water decomposition on the cathode, so lithium hydroxide concentrating occurs:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow \quad (2)$$

The overall equation of electrolysis is:

$$1/2Li_2SO_4 + 2H_2O \rightarrow LiOH + 1/2H_2SO_4 + H_2 + 1/2O_2\uparrow \quad (3)$$

So, the concentration of lithium hydroxide solution in the cathode compartment increases with time due to a decrease in lithium ion concentration in the anode compartment.

Sulphuric acid formed in the anode compartment may be later on neutralized by adding lithium carbonate, and the formed lithium sulphate may be re-used in membrane electrolysis, that is, anolyte recirculation will take place:

$$H_2SO_4 + Li_2CO_3 \rightarrow Li_2SO_4 + H_2O + CO_2 \quad (4)$$

The concentration of lithium hydroxide solution in the cathode compartment increases to 33–36 g/L with respect to Li_2O during the tests of the semi-industrial electrolysis installation.

It should be stressed that the lead anode decay under the action of electric current takes place during the operation, and lead(IV) oxide is formed as a result of electrochemical action.

To determine the effect of current strength on the yield of the catholyte, electrolysis was carried out under different current load values. The experiments revealed the absence of a linear dependence between current strength and the concentration of the resulting lithium hydroxide solution (Fig. 1 and 2). The maximal degree of lithium ion transfer from the anolyte to catholyte (60 %) was detected at the 100 $mA \cdot cm^2$ current density, and further increase in current density up to 130 $mA \cdot cm^2$ causes a decrease of this parameter to 51 %.

Several major processes take place during electrolysis: transport of Li^+ and H^+ ions through the membrane, electroosmotic water transport, and electrode processes. In our opinion, when current density exceeds an optimal value, the solution–membrane boundary gets lithium-depleted, and the fraction of water and hydrogen ion transfer increases. Under these conditions, the electrolytic decomposition of water becomes the major process, with accompanying passivation and destruction of the lead electrode, while the efficiency of the actual useful process decreases [16].

To determine the dependence of resulting alkali concentration on the rate of reagents feed, the process was carried out with variations of the flow rate of one component, with the constant feed of the other. Calculations of the consumption of electrolytes were carried out taking into account the area of the membrane. This approach will allow us to use the obtained data for an arbitrary membrane area.

An increase in anolyte consumption per unit membrane area from 1.3 to 2.7 $cm^3/(h \cdot cm^2)$ was accompanied by an increase in alkali concentration in the cathode compartment from 32 to 38 g/L calculated for Li_2O, however, the percentage of Li^+ ion transfer from the anolyte into the

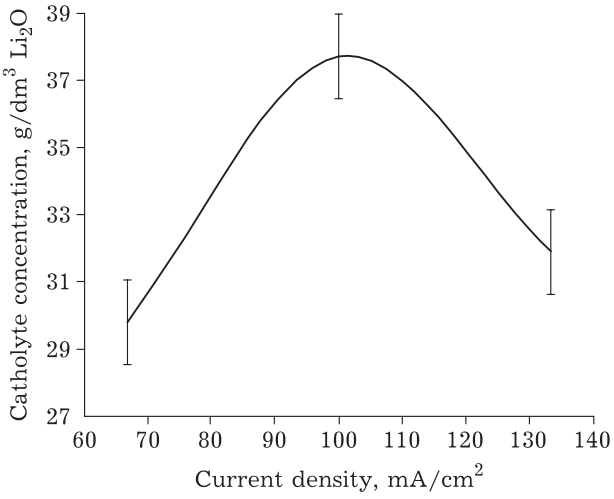

Fig. 1. Dependence of the concentration of resulting catholyte on current density.

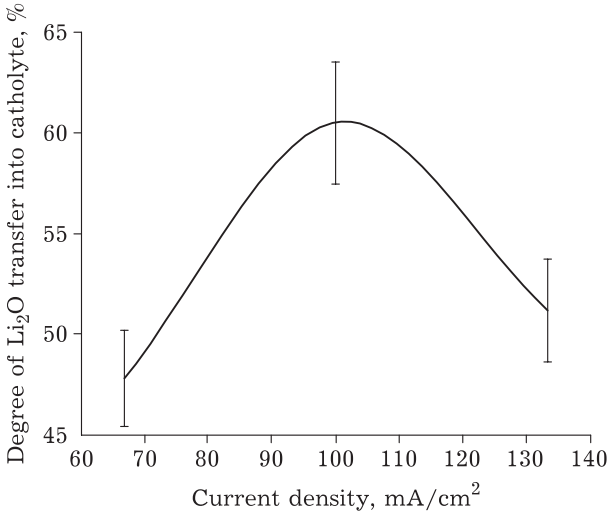

Fig. 2. Dependence of the degree of lithium transfer from the anode to cathode compartment on current density.

catholyte decreased (Fig. 3 and 4, curve *1*). In turn, as increase in the rate of technical-grade water income into the cathode compartment from 1.3 to 2.7 cm^3/(h · cm^2) caused an increase in the degree of Li^+ ion transfer from the anolyte into the catholyte, but the concentration of the formed lithium hydroxide solution decreased from 25.3 to 18.1 g/L calculated for Li_2O (see Fig. 3 and 4, curve *2*).

It has been established on the basis of the obtained results that the optimal rate of both catholyte and anolyte income under the given conditions (300 A, anolyte concentration 200 g/L with respect to Li_2SO_4) is 1.3 cm^3/(h · cm^2).

During electrolysis, in addition to lithium ions, other cations (potassium, sodium, calcium, *etc.*) and sulphate anions also migrate through the cation-exchange membrane from the anolyte solution (Table 2).

It is worth noting that current density increase insignificantly changes the concentrations of calcium, potassium and iron ions in the acquired alkaline solution, while the concentrations of magnesium, sodium, silicon and sulphate ions increase. The composition of lithium hydroxide solution is of prime importance for the Public Joint-Stock Company Chemical-Metallurgical Plant because this solution is used to ob-

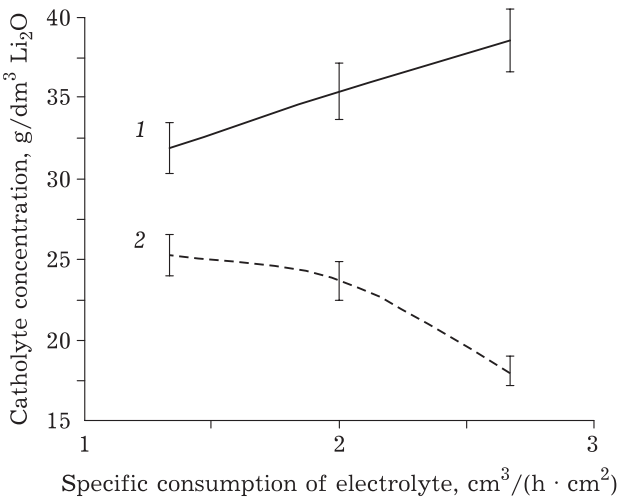

Fig. 3. Dependence of the concentration of resulting catholyte on the specific rate of solution consumption per unit membrane area under changes of the rate of anolyte (*1*) and catholyte (*2*) income.

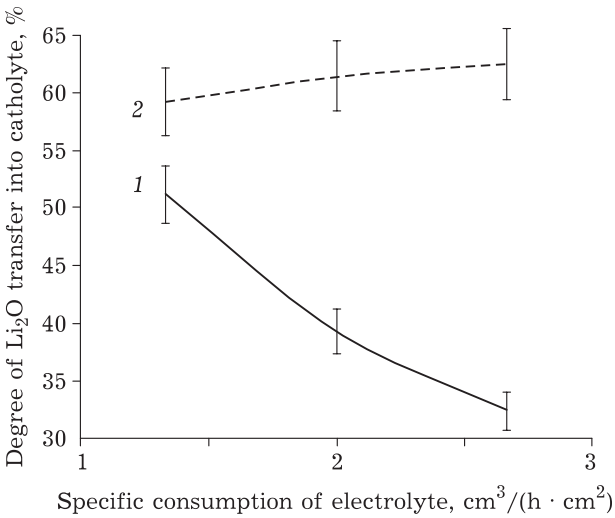

Fig. 4. Dependence of the degree of lithium transfer from the anode to cathode compartment on the specific consumption of solutions per unit membrane area under changing rates of anolyte (*1*) and catholyte (*2*) income.

TABLE 2

Impurities in the conversion alkaline solution at different current density values

Determined component	Current density, mA · cm^2		
	67	100	133
Lithium oxide, g/L	38.(0)	34.(0)	32.(0)
Calcium, mg/L	7.(0)	8.(0)	8.(0)
Sodium, mg/L	27.(0)	30.(0)	30.(0)
Potassium, mg/L	2.(0)	3.(0)	3.(0)
Aluminium, mg/L	1.2	0.6	0.4
Magnesium, mg/L	5.(0)	6.(0)	6.(0)
Iron, mg/L	0.5	0.5	0.5
Silicon, mg/L	3.(0)	4.(0)	4.(0)
Sulphate ions, mg/L	13(00)	14(00)	16(00)

Note. Number positions beyond the confidence interval of component content determination are shown in brackets.

tain crystalline $LiOH \cdot H_2O$ – one of the main products. The concentrations of extrinsic ions were assessed by evaporating the obtained alkaline solutions (Table 3); for comparison, the qualitative and quantitative composition of $LiOH \cdot H_2O$ obtained by causticisation was determined under the same conditions [19].

Comparison between the concentrations of impurity ions in lithium hydroxide monohydrate synthesized using different methods shows that the membrane electrolysis of lithium sulphate solution gives the product with higher purity than the conventional method does.

CONCLUSION

It has been shown in the set of experiments that lithium hydroxide monohydrate may be successfully obtained by membrane electrolysis on the industrial scale by electrochemical conversion of lithium salts with the following advantages over the traditional method:

1) the obtained lithium hydroxide solutions contained a smaller amount of impurity ions than LiOH solutions obtained through causticisation;

2) a minimal amount of reagents is necessary for the process to be carried out;

3) sulphuric acid that is formed in the anode compartment may be later neutralized by adding lithium carbonate, so that the formed lithium sulphate may be used in membrane electrolysis, that is, anolyte recirculation will take place, which will allow an increase in the degree of lithium ion transfer from the anode to cathode compartment up to 95–98 %;

4) the process includes less stages, compared to the technology based on causticisation, it excludes the use of additional units of equipment for washing and settling calcium carbonate precipitates.

It has also been demonstrated that the yield and quality of the formed alkali solution may be controlled by varying the major parameters of electrolysis.

TABLE 3

Results of the analysis of lithium hydroxide monohydrate obtained as a result of membrane electrolysis (experiment 1) and causticisation (experiment 2)

Determined component, wt. %	Impurities in lithium hydroxide monohydrate			
	obtained by membrane electrolysis			obtained by causticisation [19]
	Experiment 1	Experiment 2	Experiment 2 after washing	
LiOH	52.4	49.9	51.9	42.7
CO_2	0.600	0.600	0.100	0.300
Sulphate ions	0.009	0.004	0.002	0.030
Chloride ions	<0.002	<0.002	<0.002	0.002
Aluminium	0.006	0.003	0.002	0.002
Calcium	0.001	0.002	0.002	0.007
Iron	0.002	0.001	0.001	0.005
Potassium	<0.001	<0.001	<0.001	0.005
Sodium	0.003	0.002	0.001	0.005
Magnesium	0.003	0.003	0.001	0.002
Silicon	0.01	0.02	0.01	0.02

Note. Experiments 1 and 2 were carried out in parallel under identical conditions; the sample obtained in experiment 2 was washed with distilled water at room temperature (22 °C) at the S/L = 1 : 1.

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