

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2020.2518-1491.78>

Volume 5, Number 443 (2020), 38 – 45

UDC66.669.2

ICSTI44.41.29;53.37.35;61.31.51;53.01.91

**G.K. Bishimbayeva<sup>1</sup>, D.S. Zhumabayeva<sup>1</sup>, A.K. Zhanabayeva<sup>1,2</sup>,  
A.M. Nalibayeva<sup>1</sup>, E.N. Abdikalykov<sup>1</sup>, Zh.B. Bakenov<sup>3</sup>**

<sup>1</sup>D.V.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan;

<sup>2</sup>Department of Chemical Engineering, Kazakh-British Technical University, Almaty, Kazakhstan;

<sup>3</sup>School of Engineering of Nazarbayev University, Astana, Kazakhstan.

E-mail: [a.k.zhanabaeva@mail.ru](mailto:a.k.zhanabaeva@mail.ru), [bigauhar@mail.ru](mailto:bigauhar@mail.ru), [d.zhumabayeva@ifce.kz](mailto:d.zhumabayeva@ifce.kz), [aray77@mail.ru](mailto:aray77@mail.ru),  
[abdikalykov.yerlan@gmail.com](mailto:abdikalykov.yerlan@gmail.com), [zbakenov@nu.edu.kz](mailto:zbakenov@nu.edu.kz)

## PROSPECTS FOR CREATING A FULL CYCLE OF LITHIUM PRODUCTION IN KAZAKHSTAN – FROM ORE PROCESSING TO LITHIUM BATTERIES

**Abstract.** Today, lithium is becoming a new strategic material capable of influencing the sustainable development of the world economy. The results of developments in the production of innovative electrode materials from lithium carbonate on the basis of domestic lithium-containing raw materials with the creation of a full cycle of the technological line of lithium production: from ores to modern lithium batteries are presented. Analysis of the explored reserves, mineral and material composition of domestic spodumene raw materials and lithium-containing dumps of the Belogorsk GOK indicate the prospects and expediency of their development for the production of the ever-increasing needs of the world market for lithium materials. As a result, the sulfuric acid technology for obtaining high-grade lithium carbonate directly from spodumene was optimized, bypassing the stage of obtaining a technical grade product, in a single technological process for processing spodumene with a reduction in the number of technological operations, excluding the expensive operation of concentrating a lithium sulfate solution by stripping. An efficient technology of purification and post-treatment of technical lithium carbonate to battery quality of 99.95% has been developed, including the processes of causticization of technical lithium carbonate, ultrafiltration and ion-exchange sorption of a solution of lithium hydroxide, followed by precipitation of lithium carbonate by ammonium carbonate. Cathode materials - lithium iron-phosphate, obtained from high-purity lithium carbonate by aerosol pyrolysis (MAP) and the sol-gel method (SGM), showed good electrochemical characteristics. The end result is innovative electrode materials for modern LIBs with significantly increased capacity and stability. The practical implementation of a full cycle of technologies from lithium-containing raw materials to modern lithium batteries opens up prospects for the creation in Kazakhstan of a high-tech lithium cluster according to the Scheme: Spodumene ores → Lithium concentrate → Lithium carbonate → Lithium cathode materials → Batteries

**Keywords:** lithium, extraction, ore, spodumene, battery grade lithium carbonate, li-ion battery, method, purification, technology, recycling, cathode material, lithium iron phosphate.

**Introduction.** Lithium-ion batteries (LIB) lead the market among all available battery technologies. They are widely used in portable electronic devices and electric vehicles [1]. LIBs have the advantages of high energy density, high potential, long shelf life and wide operating temperature range. The main part in the cost of LIB is made up of lithium-containing components (anode, cathode and electrolyte salt). Therefore, intensive work is underway to find new materials with better performance and low cost. This demand and the rapid development of the market for battery-powered devices, especially electric and hybrid vehicles and renewable energy, over the past 10 years has led to a sharp demand for higher capacity materials for LIB [2]. These batteries are also in demand in the market for military and space technology, medicine, etc. The growing consumption of LIB in electronic equipment has increased the demand for metals, especially lithium and lithium products. Lithium carbonate  $\text{Li}_2\text{CO}_3$  is an important

lithium salt that is widely used for the synthesis of cathode LIB materials due to its electrochemical reactivity and other unique properties [3,4].

EV developers are constantly exploring new sources of lithium carbonate in order to reduce dependence on its main suppliers - Chile and China. Today, the prospect of an "explosion" in the world lithium market associated with the aggravated raw material issue is becoming real. Increased investor interest in lithium products has led to dramatic changes in the lithium materials market. In May 2016, lithium carbonate prices rose sharply and reached \$ 26.4/kg. Lithium metal prices also rose sharply from \$ 100/kg to \$ 400– \$ 500/kg [5].

The rapid development of technologies in portable electronics (smartphones, laptops / tablets) and electric transport, led to the fact that lithium is becoming a new strategic material capable of influencing the sustainable development of the world economy [6, 7]. This led to its high demand in the international market and an increase in prices for it. Lithium demand is predicted to grow significantly over the coming years [8].

Currently, the sources for all commercial lithium production are mineral solutions and rich lithium ores. Solutions of continental origin are the largest resource (59%) in terms of lithium content, followed by hard rocks (25%). The largest known lithium deposits are found in Bolivia and Chile [9]. Australia and Chile are the leading producers and exporters of lithium ore materials. China and Chile have significant resources of lithium ore. Canada, Congo (Kinshasa), Russia and Serbia have lithium reserves of about 1 million tons each, while the same reserve for Brazil is 180,000 tons [10]. The distribution of lithium reserves in the world is uneven. Access to its reserves plays a significant role and influences technological development. Currently, lithium minerals are mined mainly from pegmatite. There are reserves of mineral raw materials containing mainly spodumene and petalite, which are intensively explored and mined in Canada, Finland and other countries. Spodumene is the main commercial lithium mineral containing about 8% lithium (in terms of Li<sub>2</sub>O oxide). About 50% of spodumene is mined in Australia and processed into lithium carbonate in China [11]. Another type of lithium deposits is the brines of some highly saline lakes. Chile and Argentina produce the largest part of the world's lithium from lake salts, together about 46% of all lithium production (companies FMC, Rockwood and S.Q.M.) [10, 11].

One of the main uses of spodumene is in the production of high purity lithium for lithium-ion batteries. Lithium obtained from spodumene has fewer impurities than lithium obtained from brines. These pollutants can degrade battery performance, making it the preferred raw material source for lithium battery. In this regard, there is currently growing interest in the development of lithium reserves concentrated in the pegmatite deposits of spodumene, the main lithium-containing mineral suitable for industrial processing. The problem of their development is the lack of efficient technologies for obtaining lithium concentrates, which can significantly reduce the cost of obtaining lithium carbonate [12].

The growth of areas and volumes of application of chemical power sources based on lithium compounds has led to the problem of developing a lithium raw material base due to the involvement of new, previously unused lithium sources.

Kazakhstan has large reserves of various rare earth metals and their accompanying lithium, mainly concentrated in Eastern Kazakhstan. According to the degree of readiness for development and development costs, the lithium deposits of the East Kazakhstan region can be divided into two groups.

The first group includes lithium mineral deposits in the East Kazakhstan region. The Akhmetkino deposit (vein 25), which has been explored and whose reserves have been approved, should be considered promising, and in which more than 23 thousand tons of lithium oxide and other useful components are concentrated [13, 14].

According to the US Geological Survey (USGS) at the beginning of 2013, the confirmed reserves of lithium in the subsoil of foreign countries show that even according to preliminary data of proven reserves, Kazakhstan is among the 10 world leaders.

The second group is represented by technogenic deposits, which are "tailings" formed due to the activities of the Belogorsk GOK during the Soviet period. This group of deposits requires the lowest development costs among the groups under consideration [15]. This group includes such concentrators as Belogorsk with tailings reserves of 1560.3 (lithium content 2800 g/t), BelogorskoeVerkhne-Baimurzinskoe with reserves of 4260 (lithium content 3200 g/t), Bakennoye with reserves of 1372

(lithium content 1500 g/t), Ak-Kezenskaya with reserves of 700 (lithium content 250 g/t), etc. In total, 15868 t of reserves with lithium content of 958.33 g/t. In total, for the Belogorsk GOK, there are more than 32 thousand tons of lithium in the dumps of the processing plants.

The purpose of this is to develop a technology for producing innovative electrode materials for modern lithium batteries with the creation of a full cycle of a technological production line from extracting lithium from domestic minerals and raw materials to science-intensive high-tech products - cathode and anode materials of modern lithium-ion batteries

#### **Methods and Materials.**

*Feedstock:* lithium-bearing, spodumene ore from the Ognevka deposit (East Kazakhstan region). Due to the fact that at present there is no production capacity for the production of spodumene concentrate from the ores of lithium deposits in the East Kazakhstan region, this work was carried out on the ore of manual disassembly. For this purpose, in the area of the exit of a powerful lithium-bearing, spodumene vein in the area of Ognevka (VKO), a technological sample weighing about 20 kg was taken. The processes of processing a technological sample for lithium carbonate were tested on the experimental laboratory equipment of the Central Scientific Research Laboratory of JSC Ulba Metallurgical Plant (UMP).

Additional purification of lithium carbonate to the quality of a battery grade of carbonization-decarbonization in combination with sorption processes. For this purpose, ion-exchange resins from Purolite and the appearance of ion exchangers Purolite S 930 plus, Purolite S 940, and Purolite S 950 were studied.

To prepare the cathode material by spray pyrolysis and the sol-gel method, lithium-iron phosphate and its modifications were synthesized. Syntheses of electrode materials were carried out on special equipment of the Institute of Accumulators.

#### *Electrochemical cell preparation:*

The cathode suspension is uniformly applied to the carbon surface covered with aluminum foil (CC Al) using a Micrometer Adjustable Film Applicator 150 mm with a Doctor Blade. A two-electrode electrochemical cell of the "coin cell 2032" type, where the anode is metallic lithium and the cathode is the synthesized material, lithium iron phosphate is collected in the glove box of the MBraun company. After assembling the cell, it is pressed on a hydraulic machine. To prepare the anode part of the button cell, spot welding of the Spot Welder brand (Japan) is used.

X-ray diffraction analysis of a lithium-iron-phosphate sample is performed on a Rigaku Smart Lab diffractometer. For electrochemical studies: cyclic voltammetry (reaction reversibility) and galvanostatic charge / discharge curves (determination of the cell capacity and cyclability, a VMP3 multichannel galvanostatpotentiostat (Biologic) was used.

**Results.** The full cycle of technology for producing lithium materials from spodumene raw materials includes the following main processing stages:

1. *Sulfuric acid decomposition of spodumene concentrate and optimization of the technological process.*

The sulfuric acid method includes decryption of the spodumene raw material at a temperature of 1100 °C, which ensures the transfer of spodumene to the acid-soluble  $\beta$ -modification and the subsequent processing of these media with sulfuric acid at a temperature of 250-300 ° C to obtain lithium sulfate [12, 16, 17].



Treatment of the latter with a solution of soda ash makes it possible to obtain lithium carbonate as the final product [15].

The task of this stage is to develop a method for producing high-grade lithium carbonate by simplifying the process of purifying a lithium-containing solution from impurities. Optimization of sulfuric acid technology made it possible to obtain high-grade lithium carbonate directly from spodumene, bypassing the stage of obtaining a technical grade product, in a single technological process of processing spodumene with a reduction in the number of technological operations for purification from impurities, excluding the expensive operation of concentrating a solution of lithium sulfate by stripping.

A feature of the proposed technology is that the concentration of lithium is carried out by the membrane method of reverse osmosis, purification from impurities of metals and anions is carried out by the method of causticization of lithium sulfate, the precipitation of lithium carbonate is carried out with ammonium carbonate-UAS at a temperature of no more than 400 °C, followed by heating to 900 °C. Moreover, the concentration of lithium by the reverse osmosis method is carried out with the return of a part of the retentate stream to membrane filtration, and the proportion of the circulating retentate is calculated so that the total salt content of the lithium sulfate solution supplied to the membrane filtration does not exceed 35-40 g/l.

An essential feature of the method is the use of reverse osmosis membranes for concentrating a solution of lithium sulfate, which makes it possible to exclude from the technology a very laborious and expensive method of stripping off a solution of lithium sulfate. Concentration with the return of part of the retentate stream to membrane filtration leads to an increase in the degree of concentration of lithium in the retentate. Determination of the proportion of circulating retentate by the value of the salt content allows for optimal filtration modes by the reverse osmosis method. An increase in the salt content of the lithium sulfate solution supplied for filtration above 40 g/l is not advisable, since it will lead to a decrease in the membrane performance. The proposed method also differs in that the purification of metal impurities that form water-insoluble hydroxides and sulfate ion is carried out in one stage in the process of causticization - the conversion of lithium sulfate into lithium hydroxide. This technique allows further precipitation of lithium carbonate with a relatively cheap reagent, ammonium carbonate, and exclude the additional introduction of sodium ions into the technological process [17-18].

*2. Additional purification of lithium carbonate to the quality of a battery grade of at least 99.5% of the content of the main component.*

The technical problem posed is achieved due to the fact that in order to obtain high-purity lithium carbonate, the purification of technical lithium carbonate from impurities is carried out by converting it into lithium hydroxide monohydrate by the causticization method, since during the causticization process there is a partial purification of most of the normalized impurities, primarily calcium, magnesium, strontium, iron, due to the formation of poorly soluble hydroxides or carbonates of these elements at  $\text{pH} > 14$ . The total degree of purification from the analyzed impurities is 96.3%. However, in order to achieve the requirements of the quality specification of battery grade lithium carbonate, it is necessary to reduce the total content of impurities by about 2.7 times, for which finer methods of purification should be used - ion exchange sorption and / or ultrafiltration. The ultrafiltration method makes it possible to selectively remove most of the contaminants dissolved in it from the solution, to purify a larger number of impurities, and to reduce the load on sorption operations on synthetic cation-exchange resins based on phosphonic compounds, sulfonic acids, or complex chelate compounds. Further purification goes through the stages of ultrafiltration, ion-exchange sorption of a solution of lithium hydroxide and precipitation with ammonium carbonate (UAS) of purified lithium carbonate, the suspension of which is treated with carbon dioxide, and then after de-carbonization at a temperature of 75-900 °C, filtration and drying of the resulting precipitate of lithium carbonate, we obtain high-purity 99, 95% lithium carbonate. The bicarbonation is carried out at a pressure of 0.3 atm, which allows the use of conventional equipment that is not designed to work under pressure, which simplifies and reduces the cost of the process and the final product.

The technical result of the developed post-treatment technology is the production of high-purity lithium carbonate with a basic substance content of 99.95% [19].

*3. Obtaining innovative electrode materials for LIB from battery-grade lithium carbonate based on domestic spodumene and technogenic raw materials*

To date, the most promising cathode material for lithium-ion batteries is lithium iron phosphate  $\text{LiFePO}_4$  with the olivine structure (hereinafter LFP). It has a number of important features: high theoretical capacity (170 mAh/g), charge/discharge potential (3.4 V relative to the lithium electrode), resistant to high temperatures ( $\leq 80$  °C) during charge/discharge, non-toxic and therefore widely used in the portable battery market. To obtain lithium iron phosphate by the sol-gel method, as well as by the spray pyrolysis method, powders of high-purity lithium carbonate ( $\text{Li}_2\text{CO}_3$ , obtained on the basis of the Kazakh mineral deposit Ognevka), 9-aqueous nitrate of iron (III)  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were taken as starting materials, ammonium dihydrogen phosphate  $\text{NH}_4\text{H}_2\text{PO}_4$ , which served as sources of Li, Fe, P (0.5:1:1 or 1:1:1 in a molar ratio) with stirring in distilled water. Citric acid is then added to form a homogeneous

suspension. Citric acid was used as a carbon source. The acidity of the solution, equal to pH 2, was maintained by the addition of nitric acid. Then the solution is heated at 80 °C with constant stirring until a gel is formed. The resulting gel is dried at 100 °C overnight. Finally, it is annealed at 720 °C for 12 hours in an Ar/H<sub>2</sub> atmosphere (95:5) to obtain lithium iron phosphate.

To study the synthesized powders (LiFePO<sub>4</sub>), the methods of X-ray diffraction (determination of the phase composition) and scanning electron microscopy (determination of morphology) were used. To select the optimal temperature regime, synthesized samples were synthesized by spray pyrolysis at temperatures of 500, 550, 600 °C and the results of X-ray diffraction are shown in figure 10. For comparison, the X-ray diffraction pattern of a commercial LiFePO<sub>4</sub> sample is presented.

#### 4. Electrochemical characteristics of a battery with a synthesized cathode material.

When studying the electrochemical properties of the synthesized materials, the following methods were used: cyclic voltammetry (VA) (reaction reversibility) and galvanostatic charge / discharge curves (determination of the cell capacity and cyclability).

Studies of the Li/LiFePO<sub>4</sub> system showed a stable potential for lithium deintercalation from the LiFePO<sub>4</sub> structure at 3.6 V and intercalation at 3.3 V for charge/discharge. No additional peaks were found, indicating the absence of impurities in the synthesized material. Based on the results of cyclic voltammetry, further galvanostatic testing was carried out within the voltage range of 2.5 - 4.2 V.

When analyzing the obtained charge-discharge curves, the initial discharge and charge capacities are about 145 and 138 mAhg<sup>-1</sup>, respectively. Material capacity is over 81% of theoretical capacity. In addition, the sample has identical curves both during charging and discharging, which indicates a good reversibility of the reaction and the ability to deliver all the accumulated energy during the LIB discharge [20, 21].

**Conclusion.** Thus, a technology has been developed for obtaining innovative electrode materials for modern lithium batteries with the creation of a full cycle of a technological production line from extracting lithium from domestic mineral raw materials to science-intensive high-tech products - cathode and anode materials of modern lithium-ion batteries.

Creation of scientific and technological foundations for the development in Kazakhstan of a high-tech lithium cluster for the production of products with a high degree of readiness for the end user according to the scheme: Spodumene ores → Lithium concentrate → Lithium carbonate → Lithium cathode materials → Batteries. A business plan for the creation of a cluster-oriented lithium production was developed

**Acknowledgement.** This research has been funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP05135814).

Г.К. Бишимбаева<sup>1</sup>, Д.С. Жумабаева<sup>1</sup>,  
А. К. Жанабаева<sup>1,2</sup>, А.М. Налибаева<sup>1</sup>, Е. Н. Абдикалыков<sup>1</sup>, Ж.Б. Бакенов<sup>3</sup>

<sup>1</sup>«Д.В. Сокольский атындағы Жанармай, катализ және электрохимия институты» АҚ,  
Алматы, Қазақстан;

<sup>2</sup>«Химиялық инженерия» ғылыми білім беру орталығы,  
Қазақстан-Британ техникалық университеті, Алматы, Қазақстан;

<sup>3</sup> «Аккумуляторлар институты» ЖШС, Нұр-Сұлтан, Қазақстан

### ҚАЗАҚСТАНДА ЛИТИЙ ӨНДІРІСІНІҢ КЕН ӨНДІРУДЕН ЛИТИЙ БАТАРЕЯЛАРҒА ДЕЙІНГІ – ТОЛЫҚ ЦИКЛІН ЖАСАУ ПЕРСПЕКТИВАЛАРЫ

**Аннотация.** Бүгінде литий әлемдік экономиканың тұрақты дамуына әсер етуге қабілетті жаңа стратегиялық материалға айналды. Литий-ионды батареялар (ЛИБ) қолданыстағы батарея технологиялары арасында нарықта көш бастап келеді. ЛИБ жоғары энергия тығыздығы, жоғары потенциал, ұзақ сақтау мерзімі және жұмыс температурасының ауқымы сияқты артықшылықтары бар. Электрондық жабдықтағы ЛИБ тұтынудың өсімі металдарға, әсіресе, литий мен литий өнімдеріне деген сұранысты арттырды. Литий карбонаты Li<sub>2</sub>CO<sub>3</sub> – электрохимиялық реактивтілігі және басқа да ерекше қасиеттері арқасында ЛИБ катодты материалдарды синтездеу үшін кеңінен қолданылатын маңызды литий тұзы. Қазіргі кезде литийдің барлық өндірістік көзі минералды ерітінділері мен литий бай кен болып саналады. Литий минералдары негізінен пегматиттен өндіріледі. Құрамында сподумен және петалит бар минералды шикізат қоры бар. Сподумен – негізгі тауарлық литий минералы, құрамында (Li<sub>2</sub>O оксиді бойынша) 8% литий бар. Литий шөгінділерінің

тағы бір түрі – кейбір көл тұзы. Сподуменнің негізгі қолданысының бірі литий-ионды батареялар үшін жоғары таза литий өндірісі болып саналады. Қазақстанда әртүрлі сирек кездесетін металдардың және оларда ілеспе литийдің үлкен қоры кездеседі, негізінен қорлар Шығыс Қазақстанда шоғырланған. Бұл сақтау жүйелері мен энергия көзінің, жаңартылатын энергияның, электрониканың әлемдік нарығында маңызды орынға ие болу үшін Қазақстанда жаңа литий индустриясын құруға мүмкіндік тудырады. Бұл жұмыста литий өндірісінің кеннен қазіргі заманғы литий батареяларына дейінгі технологиялық желісінің толық циклын құра отырып, құрамында литий бар отандық минералды және техногенді шикізат негізінде литий карбонатынан инновациялық электродты материалдарды алудың өндіріс нәтижелері көрсетілген. Литий материалдарына әлемдік нарық сұранысын қанағаттандыру үшін отандық сподумен шикізатының және құрамында литий бар Белогор ГОК үйінділердің барланған қорларының минералды және материалды құрамының анализі олардың даму перспективалары мен мақсаттылығын көрсетеді. Нәтижесінде қымбат тұратын литий сульфаты ерітіндісін буландыру арқылы концентрациялау операциясын жойып, технологиялық операциялар санын азайту арқылы сподуменді қайта өңдеудің бірыңғай технологиялық процесінде жоғары сапалы литий карбонатын сподуменнен өндірудің күкірт қышқылы технологиясы оңтайландырылды. Техникалық литий карбонатын каустиктендіру, литий гидроксидінің ерітіндісін ультрафилтрациялау және ион алмастыру сорбциясы, содан кейін литий карбонатының аммоний карбонатымен тұндыру процестерінен тұратын техникалық литий карбонатын 99,95% батарея сапасына дейін тазарту және кейінгі өңдеудің тиімді технологиясы әзірленді. Аэрозольды пиролиз (МАП) және золь-гель әдісімен (SGM) тазалығы жоғары литий карбонатынан алынған катодты материалдар – литий темір фосфаты және оның модификациялары жақсы электрохимиялық сипаттамаларды көрсетті. Түпкілікті нәтиже – қуаттылығы мен тұрақтылығы едәуір артқан заманауи ЛИВ арналған инновациялық электродты материалдар болып саналады. Құрамында литий бар шикізаттан қазіргі заманғы литий батареяларына дейінгі технологиялардың толық циклін іс жүзінде жүзеге асыру схемасы бойынша соңғы пайдаланушыға дайындық деңгейі жоғары өнім өндіру үшін Қазақстанда жоғары технологиялық литий кластерін құру перспективаларын көрсетеді. Соңғы тұтынушыға дайындық деңгейі жоғары өнім өндіру үшін құрамында литий бар шикізаттан қазіргі заманғы литий батареяларына дейінгі технологиялардың толық циклін келесі сызба-нұсқа бойынша көрсетіледі: Сподумен кендері → Литий концентраты → Литий карбонаты → Литий катодының материалдары → Батареяларды іс жүзінде жүзеге асыру жұмыстары Қазақстанда жоғары технологиялық литий кластерін құрудың келешегін қалыптастырады.

**Түйін сөздер:** литий, экстракция, кен, сподумен, аккумуляторлы сапалы литий карбонаты, литий-ионды аккумулятор, әдіс, тазалау, технология, қайта өңдеу, катодты материал, литий темір-фосфаты.

Г.К. Бишимбаева<sup>1</sup>, Д.С. Жумабаева<sup>1</sup>,  
А. К. Жанбаева<sup>1,2</sup>, А.М. Налибаева<sup>1</sup>, Е. Н. Абдикалыков<sup>1</sup>, Ж.Б. Бакенов<sup>3</sup>

<sup>1</sup>Институт топлива, катализа и электрохимии имени Д.В. Сокольского, Алматы, Казахстан;

<sup>2</sup>Научно-образовательный центр «Химическая инженерия», Казахстано-Британский технический университет, Алматы, Казахстан;

<sup>3</sup>ТОО «Институт аккумуляторов», Нур-Султан, Казахстан

### ПЕРСПЕКТИВЫ СОЗДАНИЯ ПОЛНОГО ЦИКЛА ПРОИЗВОДСТВА ЛИТИЯ В КАЗАХСТАНЕ – ОТ ПЕРЕРАБОТКИ РУД ДО ЛИТИЕВЫХ БАТАРЕЙ

**Аннотация.** Сегодня литий становится новым стратегическим материалом, способным влиять на устойчивое развитие мировой экономики. Литий-ионные батареи (ЛИВ) лидируют на рынке среди всех доступных аккумуляторных технологий. ЛИВ обладают такими преимуществами, как высокая плотность энергии, высокий потенциал, длительный срок хранения и широкий диапазон рабочих температур. Растущее потребление ЛИВ в электронном оборудовании увеличило спрос на металлы, особенно на литий и литиевые продукты. Карбонат лития  $\text{Li}_2\text{CO}_3$  является важной литиевой солью, которая широко используется для синтеза катодных материалов ЛИВ из-за ее электрохимической реакционной способности и других уникальных свойств. В настоящее время источниками для всего коммерческого производства лития являются минеральные растворы и богатые литиевые руды. Литиевые минералы добываются в основном из пегматита. Сподумен - основной коммерческий литиевый минерал, содержит около 8% лития (в пересчете на оксид  $\text{Li}_2\text{O}$ ). Одним из основных применений сподумена является производство лития с высокой степенью чистоты для литий-ионных батарей. Казахстан имеет большие запасы различных редкоземельных металлов и сопутствующего им лития, в основном сосредоточенные в Восточном Казахстане. Это дает возможность создать в Казахстане новую литиевую отрасль, чтобы стать важным игроком на мировом рынке систем

хранения и источников энергии, возобновляемой энергетики, электроники. В настоящей работе представлены результаты разработок получения инновационных электродных материалов из карбоната лития на основе отечественного литийсодержащего минерального и техногенного сырья с созданием полного цикла технологической линии литиевого производства: от руды до современных литиевых батарей. Анализ разведанных запасов, минерального и вещественного состава отечественного сподуменового сырья и литийсодержащих отвалов Белогорского ГОК свидетельствуют о перспективности и целесообразности их освоения для производства всевозрастающих потребностей мирового рынка в литиевых материалах. В результате оптимизирована сернокислотная технология получения высокосортного карбоната лития непосредственно из сподумена, минуя стадию получения продукта технического сорта, в едином технологическом процессе переработки сподумена с сокращением числа технологических операций, исключением дорогостоящей операции концентрирования раствора сульфата лития методом упарки. Разработана эффективная технология очистки и доочистки технического карбоната лития до аккумуляторного качества 99,95%, включающая процессы каустификации технического карбоната лития, ультрафильтрации и ионообменной сорбции раствора гидроксида лития, с последующим осаждением углеаммонийной солькарбоната лития. Катодные материалы - фосфат лития, железа и его модификации, полученные из высокочистого карбоната лития аэрозольным пиролизом (МАП) и золь-гель методом (ЗГМ), показали хорошие электрохимические характеристики. Конечным результатом являются инновационные электродные материалы для современных LIB со значительно увеличенной емкостью и стабильностью. Практическое внедрение полного цикла технологий от литийсодержащего сырья до современных литиевых аккумуляторов открывает перспективы создания в Казахстане высокотехнологичного литиевого кластера для производства продукции с высокой степенью готовности для конечного потребителя по Схеме: Сподуменовые руды → Литиевый концентрат → Карбонат лития → Литиевые катодные материалы → Аккумуляторы.

**Ключевые слова:** литий, извлечение, руда, сподумен, карбонат лития аккумуляторного сорта, литий-ионный аккумулятор, метод, очистка, технология, переработка, катодный материал, литий-железо фосфат.

#### Information about the authors:

Bishimbayeva Gaukhar Kozykееvna, Doctor of Technical Sciences, Professor, Chief Scientific Researcher, D.V. Sokol'skii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, [bigauhar@mail.ru](mailto:bigauhar@mail.ru), <https://orcid.org/0000-0002-8243-1124>

Zhumabayeva Dinara Sarsenovna, Doctor of Engineering, PhD, Senior Researcher, D.V. Sokol'skii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, [d.zhumabayeva@ifce.kz](mailto:d.zhumabayeva@ifce.kz), <https://orcid.org/0000-0002-6843-1056> (author for correspondence)

Zhanabaeva Asem Kaldybekkyzy, PhD student of Kazakh-British Technical University, Engineer, D.V. Sokol'skii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, [a.k.zhanabaeva@mail.ru](mailto:a.k.zhanabaeva@mail.ru), <https://orcid.org/0000-0002-4738-9012>

Nalibayeva Arailym Muratovna, Scientific Researcher, D.V. Sokol'skii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, [aray77@mail.ru](mailto:aray77@mail.ru), <https://orcid.org/0000-0003-3976-5134>

Abdikalykov Yerlan Nurzhanuly, Undergraduate of al-Farabi Kazakh National University, Engineer, D.V. Sokol'skii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, [abdikalykov.yerlan@gmail.com](mailto:abdikalykov.yerlan@gmail.com), <https://orcid.org/0000-0003-0502-942X>

Bakenov Zhumabay Bekbolatovich, Doctor of Engineering, PhD, Professor, Nazarbayev University, Director of CEAMS, National Laboratory Astana, CEO at Institute of Batteries LLC, Nur-Sultan, Kazakhstan, [zbakenov@nu.edu.kz](mailto:zbakenov@nu.edu.kz), <https://orcid.org/0000-0003-2781-4955>

#### REFERENCES

- [1] Swain B. (2017) Recovery and recycling of lithium: a review. Separation and Purification Technol. 172:388-403. DOI: 10.1016/j.seppur.2016.08.031 (In Eng.).
- [2] Pillot C. (2010) Main trends for rechargeable battery market 2009-2020, Cannes, 248. (In Eng.).
- [3] Scrosati B., Garche J. (2010) Lithium batteries: status, prospects and future. J Power Sources. 195(9):2419-2430. DOI: 10.1016/j.jpowsour.2009.11.048 (In Eng.).
- [4] Linneen N., Bhave R., Woerner D. (2018) Purification of industrial grade lithium chloride for the recovery of high purity battery grade lithium carbonate. Separation and Purification Technology. 214:168-173. DOI: 10.1016/j.seppur.2018.05.020 (In Eng.).
- [5] Industry. (2016) Lithium 101. Deutsche Bank. Markets Research. (In Eng.).
- [6] Dudney N. (2008) J. Electrochem. Soc. Interface. 17. 44-48 (In Eng.).
- [7] Chen J. (2013) Recent Progress in Advanced Materials for Lithium Ion Batteries. Materials 6(1):156-183. DOI: 10.3390/ma6010156 (In Eng.).
- [8] Jaskula, B.W. (2012). Mineral commodity summaries - Lithium. US Geological Survey (USGS) (In Eng.).
- [9] Kudryavcev P.G., Kudryavcev N.P. (2018) Lithium: Resources, Production and World Market Development Prospects. Alternative energy and ecology (ISJAEE). (10-12):20-81 [Litij: Resursy, Dobycha i perspektivy razvitiya mirovogo rynka. Alternativnaya energetika i ekologiya]. (In Russian).
- [10] Jaskula, B.W. (2015). Mineral commodity summaries - Lithium. US Geological Survey (USGS) (In Eng.).

- [11] Meshram P., Pandey, B.D., Mankhand T.R. (2014) Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy*. 150: 192-208. DOI: 10.1016/j.hydromet.2014.10.012 (In Eng.).
- [12] Margarido F., Vieceli N., Durão F., Guimarães C., Nogueira C.A. (2014) Minerometallurgical processes for lithium recovery from pegmatitic ores. *Comun. Geol.* 101: 795–798. (In Eng.).
- [13] Research Report. (2011) Research on the processing of technogenic mineral formations in order to extract lithium and gold [Issledovaniya po pererabotke tekhnogennykh mineral'nykh obrazovaniy s cel'yu izvlecheniya litiya i zolota], Almaty, 2011. (In Russian).
- [14] Research Report. (2014) Technical and economic considerations (TEP) on the feasibility of exploration and industrial development of lithium deposits in the East Kazakhstan region of the Republic of Kazakhstan [Tekhniko-ekonomicheskie soobrazheniya (TES) o celesoobraznosti razvedki i promyshlennogo osvoeniya mestorozhdeniy litiya v Vostochno-Kazahstanskoj oblasti Respubliki Kazahstan], Almaty. (In Russian).
- [15] Averill W.A.; Olson D.L. (1978) A review of extractive processes for lithium recovery from ores and brines. *Energy*. 3: 305–313. (In Eng.).
- [16] Choubey, P.K.; Kim, M.; Srivastava, R.R.; Lee, J.-C.; Lee, J.-Y. (2016) Advance review on the exploitation of the prominent energy-storage element: lithium. Part I: From mineral and brine resources. *Miner. Eng.* 89: 119–137. DOI: 10.1016/j.mineng.2016.01.010 (In Eng.).
- [17] Bishimbayeva G., Zhumabayeva D., Zhandayev N., Nalibayeva A., Shestakov K., Levanevsky I., Zhanabayeva A. (2018) Technological improvement lithium recovery methods from primary resources. *Oriental Journal of Chemistry*. 34(6):2762-2769. DOI: 10.13005/ojc/340611 (In Eng.).
- [18] Levanevskij I.O, Stolbova E.F., Shestakov K.A., Shulgin K.L., Zhandayev N.M., Bishimbayeva G.K., Zhumabayeva D.S. (2019) Method of obtaining high-grade lithium carbonate from spodumene concentrate [Sposob polucheniya vysokosortnogo karbonata litiya iz spodumenovogo koncentrata]. (In Russian).
- [19] Bishimbayeva G.K., Zhumabayeva D.S., Nalibayeva A.M., Zhanabayeva A.K. (2020) The method of producing high purity lithium carbonate [Sposob polucheniya vysokochistogo karbonata litiya]. (In Russian).
- [20] Bishimbayeva G.K., Zhumabayeva D.S. (2016) Technological methods for obtaining new components of cathode materials by direct sulfurization of industrial polymers. *NAN RK. – Ser. Him. i tekhnologiya*. 5: 28-38. [Tekhnologichnye metody polucheniya novykh komponentov katodnykh materialov pryamym oserneniem promyshlennykh polimerov]
- [21] Zhanabayeva A., Nalibayeva A., Zhumabayeva D., Korzhynbayeva K., Abdykhalykov E., Bakenov Zh., Bishimbayeva G. (2019) Innovative electrode materials for LIB from lithium battery-grade lithium carbonate based on Kazakhstan's spodumene raw materials. The 7th International Conference on Nanomaterials and Advanced Energy Storage Systems (INESS-2019), Almaty, 7-9 August 2019. Almaty c. 75.