

# Synthesis and modification of $\text{LiFePO}_4$ cathode materials for lithium-ion batteries by aerosol pyrolysis method

*G.K.Bishimbayeva*<sup>1</sup>, *A.K.Zhanabayeva*<sup>1,2</sup>, *I.Kurmanbayeva*<sup>3</sup>,  
*A.M.Nalibayeva*<sup>1</sup>, *D.S.Zhumabayeva*<sup>1</sup>, *Z.B.Bakenov*<sup>3</sup>

<sup>1</sup>D.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, 142  
D.Kunaev Str., 050010 Almaty, Kazakhstan

<sup>2</sup>Department of Chemical Engineering, Kazakh-British Technical  
University, 050000 Almaty, Kazakhstan

<sup>3</sup>Institute of Batteries LLP, 53 Kabanbay Batyr Ave., 010000 Nur-Sultan,  
Kazakhstan

*Received February 4, 2020*

The aerosol pyrolysis method was used to synthesize lithium-iron-phosphate ( $\text{LiFePO}_4$ ), a cathode material for lithium-ion batteries.  $\text{LiFePO}_4$  was synthesized from lithium carbonate, obtained from Kazakhstan spodumene, raw material. Modifying additives as the electrically conductive polymer polyaniline improve battery cycling.

**Keywords:** spray pyrolysis, lithium iron phosphate, modification, spodumene, lithium carbonate, polyaniline.

**Синтез і модифікація матеріалів катодів  $\text{LiFePO}_4$  для літій-іонних акумуляторів методом аерозольного піролізу.** *Г.К.Бішимбаєва, А.К.Жанабаєва, І.Курманбаєва, А.М.Налібаєва, Д.С.Жумабаєва, З.Б.Бакінов*

Методом аерозольного піролізу синтезовано літій-залізо-фосфат ( $\text{LiFePO}_4$ ), катодний матеріал для літій-іонних акумуляторів.  $\text{LiFePO}_4$  синтезований з карбонату літію, отриманого з казахстанської сподуменової сировини. Модифікуючі добавки, такі як електропровідний полімер поліанілін, покращують цикліруемість акумулятора.

Методом аерозольного піролізу синтезовано литий-железо-фосфат ( $\text{LiFePO}_4$ ) в качестве катодного материала для литий-ионных аккумуляторов.  $\text{LiFePO}_4$  синтезован из карбоната лития, полученного из казахстанского сподуменового сырья. Модифицирующие добавки, такие как электропроводящий полимер полианилин, улучшают циклируемость аккумулятора.

## 1. Introduction

The development of technologies in portable electronics and electric transport, has led to the fact that lithium is becoming a new strategic material that can influence the sustainable development of the global economy [1, 2]. This led to its high demand in the international market and to increase in its prices. It is predicted that lithium

demand will increase significantly over the coming years [3]. Global demand for lithium compounds in 2016 exceeded 150 thousand tons in terms of lithium carbonate; by 2020, it is expected to grow to 300–320 thousand tons, and by 2025 to 550 thousand tons. This will mainly happen due to the mass introduction of electric vehicles and hybrids [4, 5].

Lithium-ion batteries (LIBs) are currently the market leaders among all avail-

able battery technologies and are efficient, lightweight, rechargeable power supplies and energy storage devices for consumer electronics (laptop computers, digital cameras and cell phones). This is due to their high energy intensity (per unit and by volume). LIBs have much higher performance compared to other analogues — lead, Ni–Cd, and Ni–Mn, and are leaders in the market of portable electronics and electric vehicles [6]. The main part of the LIB cost are lithium-containing components (anode, cathode and electrolyte salt). Therefore, intensive work is underway to find new materials with the best performance and low cost. This led to the emergence of new cathode materials, for example,  $\text{LiFePO}_4$ ,  $\text{LiMnPO}_4$  and others and their derivatives [7], anode materials based on silicon, lithium titanate and alloys [8].

The main precursor of lithium electrode materials is lithium carbonate. Lithium producers are mainly focused on the lithium carbonate market for LIBs. On the basis of Kazakhstan spodumene raw material, an effective technology for producing lithium carbonate of the battery grade has been developed [9, 10].

To date, the most promising cathode material for lithium-ion batteries is lithium iron phosphate  $\text{LiFePO}_4$  with an olivine structure. It has a number of important features: high theoretical capacity (170 mAh/g), charge/discharge potential (3.4 V relative to the lithium electrode), resistance to high temperatures ( $\leq 80^\circ\text{C}$ ) during the charge/discharge, non-toxic and therefore is widely used on portable battery market [11].

There are different methods for producing lithium iron phosphate: solid-phase and hydrothermal syntheses, mechanical activation, sol-gel method, microwave synthesis method, aerosol pyrolysis method, vapor deposition, microemulsion technology, etc. The difficulty in the synthesis of  $\text{LiFePO}_4$  is due to the oxidation of  $\text{Fe}^{2+}$  by atmospheric oxygen; therefore, preference is given to single-stage methods. Among these methods, aerosol pyrolysis is an effective one-step method for producing large quantities of materials in a short period of time and ensuring a homogeneous composition of the product particles.

The aim of this work is to synthesize the cathode material  $\text{LiFePO}_4$  (LFP) for the first time by an one-stage method of aerosol pyrolysis using lithium carbonate obtained from Kazakhstani spodumene raw materials. The surface of the obtained cathode material is modified by polyaniline in order to improve the electrochemical conductivity.

## 2. Experimental

$\text{LiFePO}_4$  was synthesized by a spray-pyrolysis method according to the earlier published [12]. Spray pyrolysis is the method for preparing nanostructured powders, which based on the generation of droplets from precursor colloids in a flow mode. The droplets are generated in a nebulizer and sprayed into a quartz cylindrical reactor by carrier gas. The temperature in the cylindrical reactor is determined based on the decomposition temperature of the precursor and its crystallization.

Lithium carbonate  $\text{Li}_2\text{CO}_3$ , iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), ammonium dihydroorthophosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) which served as sources of Li, Fe, P (in a molar ratio of 1:1:1) were dissolved in distilled water and mixed for 1 h. The pH of the solution was adjusted to 2 by adding nitric acid. Citric acid was used as a carbon source. The precursor solution was atomized at a frequency of 1.7 MHz by an ultrasonic nebulizer and is transferred to a heated reactor ( $350\text{--}600^\circ\text{C}$ ) by a gaseous mixture of  $\text{N}_2 + 5\%$   $\text{H}_2$  with a flow rate of 5 liter per min. At the outlet of the reactor, LFP powders were collected and subjected to a heat treatment in a muffle furnace at  $600^\circ\text{C}$  for 4 h in a  $\text{N}_2 + 5\%$   $\text{H}_2$  atmosphere.

To study the synthesized powders ( $\text{LiFePO}_4$ ), an X-ray diffraction method (determination of the phase composition) (Rigaku Smart Lab.) was used. The carbon content of  $\text{LiFePO}_4$  synthesized by aerosol pyrolysis was determined using chemical analysis (CHNS elemental analyzer, Elementar).

Electrode tests (recording of charge-discharge curves) were carried out in button cells of a CR2032 type with a lithium anode. As an electrolyte, a 1 M solution of  $\text{LiPF}_6$  in a mixture of ethylene carbonate, diethyl carbonate, methyl ethyl carbonate (1:1:1) was used.

The composite electrode was prepared by mixing 80 wt. % of  $\text{LiFePO}_4$ , 10 wt.% of polyvinylidene fluoride (Aldrich) as a binder and 10 wt.% acetylene black used as a conductive agent. The mixture was homogenized in an agate mortar with the addition of a small amount of solvent *n*-methylpyrrolidone (NMP). The resulting slurry was coated onto aluminum foil by doctor blade technique and dried in a vacuum oven at a temperature of  $60^\circ\text{C}$  for 3 h.

CR2032 type coin cells were assembled using a lithium foil as an anode, LFP as a cathode and 1 M  $\text{LiPF}_6$  in a mixture of eth-

Table 1. The dependence of the time of receipt of  $\text{LiFePO}_4$  on the concentration of the solution

Name	Concentration, mol/l	The volume of the original solution, ml	Time, h
LFP 1	0.01	1270	23
LFP 2	0.05	255	14
LFP 3	0.1	127	17
LFP 4	0.15	85	27

ylene carbonate, diethyl carbonate, methyl ethyl carbonate (1:1:1) as an electrolyte.

All operations for assembling button batteries were carried out in a glove box (MBraun) in an inert atmosphere. The content of water and oxygen vapors in the atmosphere of the box did not exceed 5 ppm. The cathode and anode parts were separated by Celgard separators. The assembled batteries were galvanostatically tested by a NEWARE battery tester (Neware Co, Ltd, China), the cyclic voltammetry (CV) was carried out with a VMP3 potentiostat/galvanostat (Bio-Logic Science Instrument Co., France).

The LFP surface was modified in the following way: for polymerization of an aqueous solution of aniline and ammonium, the peroxydisulfate agent was degassed with nitrogen for 1 h at room temperature. The polymerization was carried out at 65°C for 24 h in a nitrogen atmosphere. PANI was dried at 40°C for 4 h. Then LFP was mixed with 15 ml of a PANI solution and heat-treated at 700°C for 3 h.

### 3. Results and discussion

#### 3.1. Synthesis of $\text{LiFePO}_4$ by aerosol pyrolysis

To determine the optimal ratio of the initial precursors, solutions were prepared on the basis of obtaining 2 g of  $\text{LiFePO}_4$  at the outlet. Table 1 shows the data on the time taken to obtain  $\text{LiFePO}_4$  as a function of the concentration of the initial solution in the spray pyrolysis unit. At the lowest (0.01 M) concentration of the solution, aerosol spraying of particles takes a long time (23 h), which was associated with high dilution. An increase in the concentration of the solution to 0.05 M made it possible to obtain the cathode material in 14 h. With a further increase in the concentration to 0.1 M and 0.15 M, an increase in the time spent (17 and 27 h, respectively) for obtaining the specified material was observed, which was caused by an increase in the viscosity of the solution, and, conse-

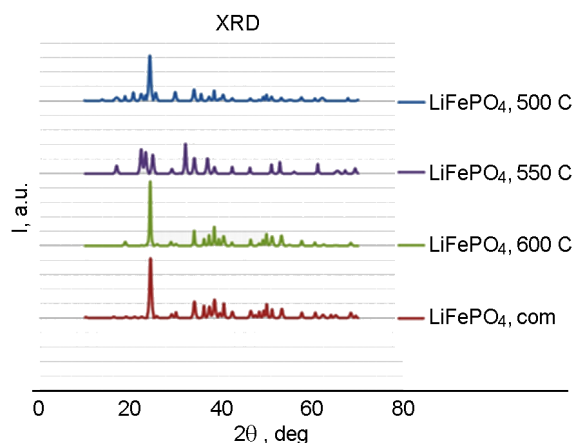


Fig. 1. X-ray diffraction patterns of synthesized  $\text{LiFePO}_4$  at various temperatures.

quently, difficulty in aerosol spraying on the Omron nebulizer.

Based on the results obtained, further studies were carried out at a concentration of the initial solution of 0.05 M. Initially, the feed rate of the material varied in the range of 3–7 l/min, and the optimal flow value of 5 l/min was determined experimentally.

In order to select the optimal temperature regime, samples were prepared at temperatures of 500, 550 and 600°C by the spray pyrolysis method and analyzed by XRD. The resulted X-ray diffraction patterns are presented in Fig. 1. For comparison, an X-ray diffraction pattern of a commercial  $\text{LiFePO}_4$  sample is shown. It is seen from the Fig. 1, that all LFP samples have a crystal structure. Peaks of the sample synthesized at 600°C, fully correspond to the spectra of commercial  $\text{LiFePO}_4$ . However, samples obtained at 500°C and 550°C show additional peaks in the angle range from 20 to 25 deg, which are related to impurities. For this reason, a spray pyrolysis reactor mode of 600°C was selected for the further experiments.

The carbon content in the  $\text{LiFePO}_4$  synthesized by the spray pyrolysis method, depending on temperature, varies in the range of 7–9 % (Table 2).

#### 3.2. Electrochemical properties of LIB with synthesized cathode material

Cyclic voltammetry (CV) studies of the Li/ $\text{LiFePO}_4$  system showed a stable potential for lithium deintercalation from the  $\text{LiFePO}_4$  structure at 3.6 V and intercalation at 3.3 V for charge/discharge, respectively. No additional peaks were detected, indicating the absence of impurities in the synthesized material.

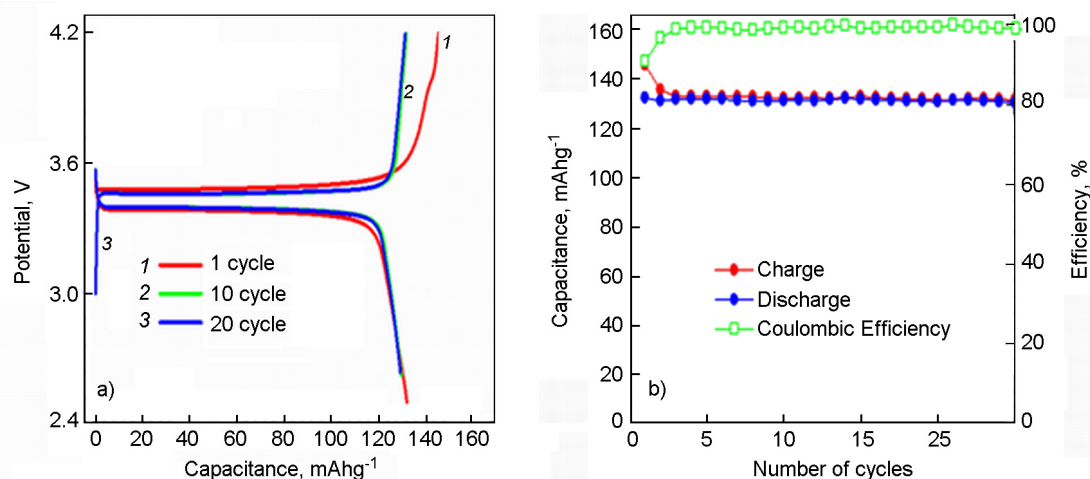


Fig. 2. (a) Charge/Discharge curves of  $\text{LiFePO}_4/\text{C}$  between 2.5 and 4.2 V at  $0.2^\circ\text{C}$  and (b) Specific Charge/Discharge Capacity vs. number of cycles.

Based on the results of cyclic voltammetry, further galvanostatic testing was carried out within the voltage range of 2.5–4.2 V (Fig. 2).

When analyzing the obtained charging-discharge curves, the initial discharging and charging capacity is about 145 and 138  $\text{mAh}^{-1}$ , respectively. The capacity of the material is more than 81 % of the theoretical capacity. In addition, the sample has identical curves both during charging and discharging, which indicates good reversibility of the reaction and the ability to release all the stored energy during the LIB discharging.

### 3.3. Surface modification of materials

$\text{LiFePO}_4$  as a cathode material for LIB has a high theoretical capacity, stability and environmental friendly. However, its main disadvantages are the low electronic and ionic conductivity, which can be improved by surface modification. Polyaniline is one of conductive polymers, the most widely studied and used for a variety of applications due to unique conduction mechanism. To increase the electrical conductivity of the synthesized material, the surface of  $\text{LiFePO}_4$  was covered with a layer of polyaniline (PANI). PANI macromolecules form a polyconjugation system as a

result of strict alternation of benzene rings and nitrogen atoms in the main polymer chain. Charge carriers-positive polarons are introduced into the polymer by its chemical or electrochemical oxidation. Delocalization of charge carriers and an increase in electrical conductivity occurs as a result of stabilization of polarons by strong acids. The reaction takes place in a strongly acidic environment; ammonium peroxodisulfate is used as an oxidizing agent. Figure 3 shows TEM images of synthesized LFP and LFP with polyaniline — modified surface (PANI@LFP).

It could be found from Fig. 3b that there is a large amount of PANI wrapping and connecting the  $\text{LiFePO}_4$  particles. Thereby it could ensure good electrical continuity between  $\text{LiFePO}_4$  particles. Micrographs show a uniform polyaniline coating over the entire surface of  $\text{LiFePO}_4$  particles (Fig. 3, b); this helps to reduce surface imperfection and porosity compared to the initial  $\text{LiFePO}_4$  cathode material (Fig. 3, a). As a conductive polymer, PANI also acts as a binder on the surface of  $\text{LiFePO}_4$  to make the surface of the PANI@LFP electrode smoother and with stand prolonged cyclic work. Therefore, surface modification of  $\text{LiFePO}_4$  with polyaniline not only leads to increased electrical conductivity, but also serves as an adhesive to improve the bonding of particles on the electrode and, thus, improves the electrochemical characteristics for the LFP/PANI composite (Fig. 3). Both LFP and PANI@LFP materials were assembled and electrochemically tested in the structure of coin cells. The results are shown in Fig. 4.

Table 2. The percentage of carbon in samples of  $\text{LiFePO}_4$  cathode composites synthesized by spray pyrolysis

Temperature of spray pyrolysis/heat treatment, $^\circ\text{C}$	Carbon content, at. %
500	8.5
550	7.48
600	7.12

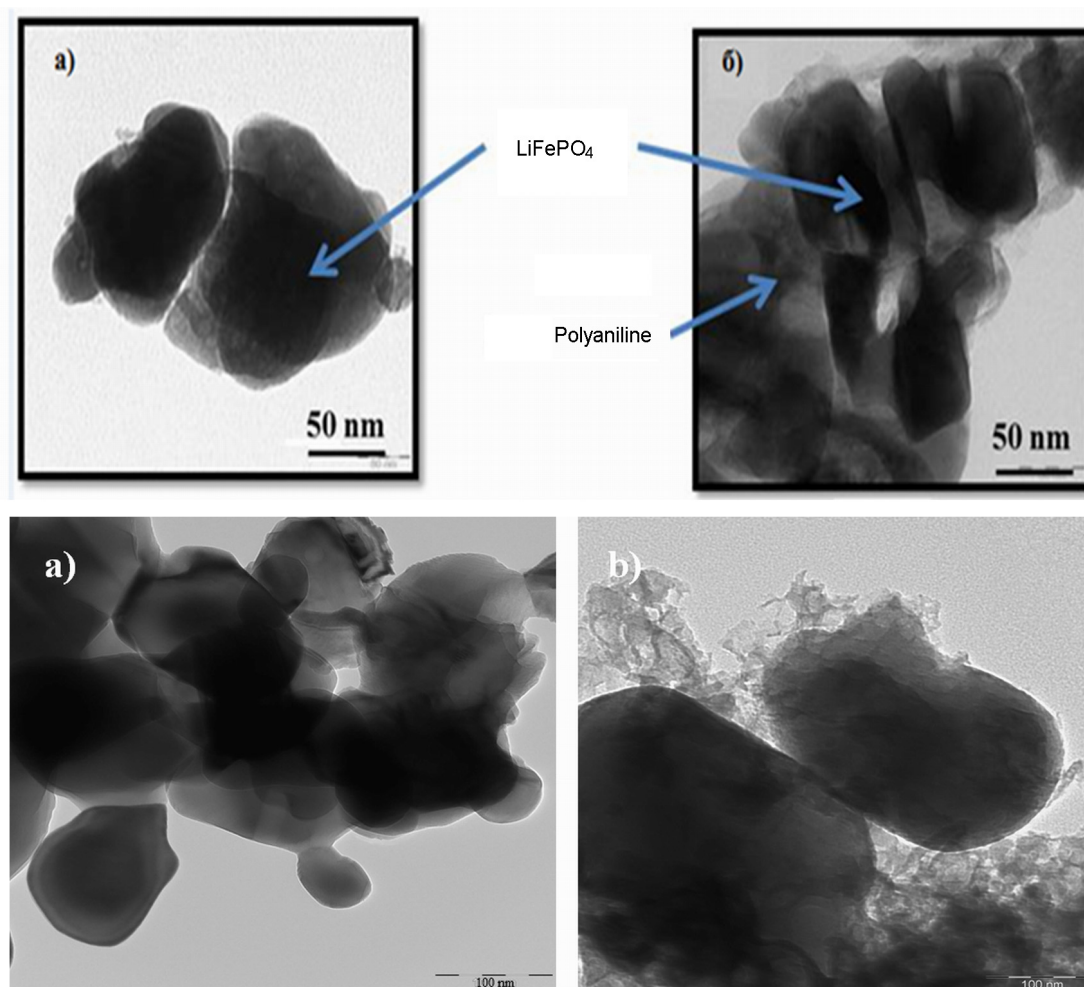


Fig. 3. TEM images (a)  $\text{LiFePO}_4$ , (b)  $\text{PANI@LiFePO}_4$ .

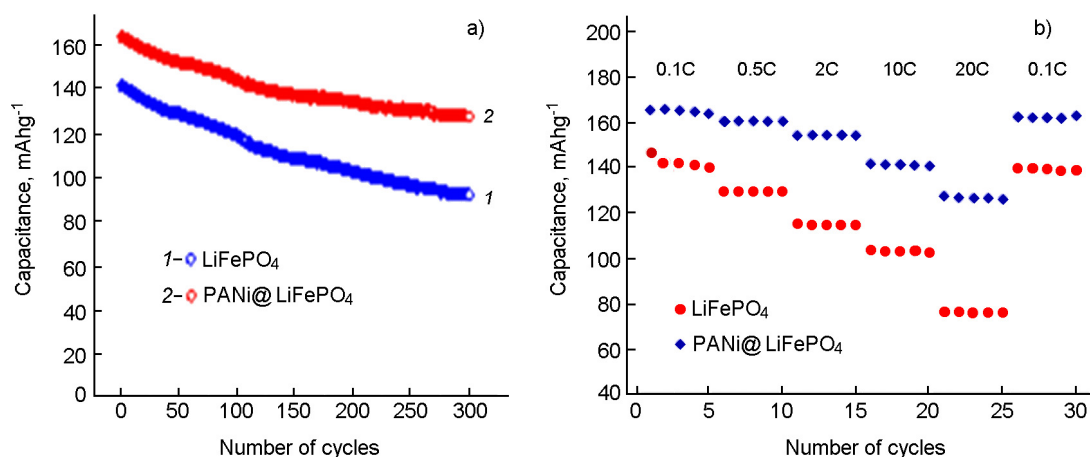


Fig. 4. Battery cycling with  $\text{LiFePO}_4$  and  $\text{PANI@LiFePO}_4$  at  $0.5^\circ\text{C}$  (a) and the ability to work at different current densities (b).

From the data on the cyclability of a battery with  $\text{LiFePO}_4$  and  $\text{PANI@LiFePO}_4$  at a current density of 0.5 C (Fig. 4a) and the results of measuring the capacitance of the discharge stage at different current densities

(Fig. 4b), it can be seen that a battery with  $\text{PANI@LiFePO}_4$  shows a cycling similar to the cycling of unmodified  $\text{LiFePO}_4$ , but with a slight increase in capacity.  $\text{PANI}$ -modified  $\text{LiFePO}_4$  reaches over

110 mAh<sup>-1</sup> capacity, even after 300 charge/discharge cycles. Also, a system with a PANI-coated cathode shows a high ability to operate at higher current densities: even at 20°C, the energy density is about 120 mAh<sup>-1</sup>. After decreasing the current density to 0.5°C, the system completely restores the high capacity of 160 mAh<sup>-1</sup>.

#### 4. Conclusions

The lithium iron phosphate cathode material (LFP) was synthesized by the aerosol pyrolysis method from lithium carbonate on the basis of Kazakhstan spodumene raw materials and showed quite satisfactory electrochemical properties. In order to improve the conductivity, the surface of the LFP was modified by a conductive polymer polyaniline. The modified LFP was electrochemically tested and compared with bare LiFePO<sub>4</sub>. It has been found that modification of LiFePO<sub>4</sub> surface improves battery performance.

*Acknowledgements.* This work was conducted under research grant project of AP05135814 "Development of full cycle technology for preparation of innovative electrode materials for lithium batteries from domestic raw materials". The authors would like to place on record their sincere

gratitude to the Ministry of Science and Education of the Republic of Kazakhstan for financial support.

#### References

1. G.B.Cho, J.P.Noh, H.J.Sung et al., *Microelectron. Eng.*, **89**, 104 (2012).
2. N.Dudney, *J. Electrochem. Soc. Interface*, **17**, 44 (2008).
3. J.Chen, *Materials*, **6**, 156 (2013).
4. IRENA. Battery Storage for Renewables Market Status and Technology Outlook, International Renewable Energy Agency (2015).
5. C.Pillot, Main Trends for Rechargeable Battery Market 2009-2020, Cannes, 248 (2010).
6. J.M.Tarascon, M.Armand, *Nature*, **414**, 359 (2001).
7. Z.Bakenov, M.Nakayama, M.Wakihara, *Electrochem. Solid-State Lett.*, **10**, 208 (2007).
8. Z.Bakenov, I.Taniguchi, *J. Electrochem. Soc.*, **157**, 430 (2010).
9. G.Bishimbayeva, D.Zhumabayeva, N.Zhandayev et al., *Oriental J. Chemistry*, **34**, 2762 (2018).
10. RK Patent 3, 33675 (2019).
11. M.Armand, J.-M.Tarascon, *Nature*, **451**, 652 (2008).
12. I.Taniguchi, Z.Bakenov, *Powder Technology*, **159**, 55 (2005). <https://doi.org/10.1016/j.powtec.2005.07.002>