

O. Svietskina¹, Dr. Sc. (Tech.), Assoc. Prof.,
orcid.org/0000-0003-0857-8037,
V. Protsiv¹, Dr. Sc. (Tech.), Prof.,
orcid.org/0000-0002-2269-4993,
O. Bohdanov¹, Cand. Sc. (Tech.), Assoc. Prof.,
orcid.org/0000-0003-4790-2338,
K. Bas^{1,2}, Cand. Sc. (Tech.), Assoc. Prof.,
orcid.org/0000-0003-2918-3501

1 – National Mining University, Dnipro, Ukraine, e-mail:
svetkina.yelena@gmail.com; protsiv@ukr.net; bogdanov.alex-
sandr17@gmail.com

2 – National Transport University, Kyiv, Ukraine, e-mail:
k.m.bas.69@gmail.com

MECHANOCHEMICAL SYNTHESIS OF ADDITIVES FOR CATHODE MATERIAL OF LITHIUM-ION TRACTION BATTERIES

Purpose. To study the effect of mechanical activation on $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ system (in the form of minerals) to apply them as cathode material additives.

Methodology. Mechanochemical activation (MA) of materials was performed by means of a vertical vibration mill (VVM). Average size of the powdered particles was determined according to the data obtained with the help of laser analyzer SK LAZER MICRON SIZER PRO-700 (Japan). Formation of the activated state is closely connected with energy characteristics of the material. In this context, multipurpose technique to research energy characteristics of the materials was used; the technique involves potentiometric measurements within suspensions with indifferent electrode. “In situ” diffractograms were obtained using X-ray diffractometer ДРОН-2 (Burevestnik, Russia). Phase analysis of the materials was determined with the help of X-ray diffractometer ДРОН-3 (Burevestnik, Russia): Fe $K\alpha$ emission, high voltage 35 eV, and anode current 20 mA. Physical and chemical processes, taking place in the process of GH (Gas Hydrate) methane, were analyzed with the help of differential thermal analysis (DTA) and X-ray fluorescence analysis (RFA). A content of gaseous products was studied by means of a gas adsorption chromatography method using “LXM-2000-TM” chromatograph (*Elektra*, Russia).

Findings. Physical and chemical properties of the systems using $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--PE}$ in the form of minerals after their mechanochemical activation have been analyzed. It has been determined that after their activation within VVM, the additives intensify electronic conductivity owing to the formation of solid solutions in the process of the activation, on the one hand, and, on the other hand, owing to changes in crystal-chemical composition. It has been demonstrated that the activated minerals intensify electronic conductivity up to $10^{-2} \text{ Ohm}^{-1}\text{cm}^{-1}$.

Originality. It is in the fact that vibroimpulse activation involves changes in electric conductivity of minerals (in particular, rutile and oxidized quartzites) depending upon the formation of solid solutions or chemical compounds resulted from mechanochemical activation.

Practical value. A technique to intensify additives for cathode material of lithium-ion accumulators, where electronic conductivity grows, has been developed.

Keywords: *vibration machine, mechanical activation, cathode material, lithium-ion batteries, polyelectrolytes*

Introduction. Modern life is impossible without electric transport [1, 2]; it concerns particularly hybrid cars [3, 4] and completely electric cars [5, 6] as well as rail transport [7, 8]. In addition to internal-combustion engine, the vehicles should also have alternative power systems. The power systems have to be highly energetic, light, timeproof, safe, cheap, and reliable. Lithium-ion batteries (LIB), being efficient, light, and rechargeable power sources, are both current and potential energy-storage devices with high power density.

Thus, according to estimates by Research. Techart, in 2018 world market size of LIB may exceed 8.3 billion USD. Mainly, the growth will be stipulated by the production of electric cars and the necessity in stationary batteries. Today, hybrids and electric cars are on the verge of wide-scale commercialization. It is assumed that by 2018 the world fleet of electric cars will achieve 5.7 million pieces. In Ukraine, their share will be 5 to 10 % of a vehicle park. According to expert prognosis, a market of lithium-ion batteries will experience its more than 700 % expansion (i. e. from 2 billion USD in 2013 to 14.9 billion USD by 2018). As for the cost of the lith-

ium-ion batteries for electric cars, it will reduce drastically down to USD 523 per kWh. Basic demand (almost 50 %) will fall at Asian countries (first of all, China) followed by Europe (25 %) and the USA (21 %).

Panasonic/Sanyo (Japan), Samsung (Korea), Sony (Japan), BYD (China), LG Chem (China), BAK (China) and others are primary world producers of lithium-ion batteries. Overall participation share of the listed manufacturers is almost 80 % of the total number of the product. Cost of the battery involves several parameters (Fig. 1); in this context, share of cathode cost is 36 %.

Analysis of the recent research. Currently, the world is engaged intensively in the development of new advanced cathode materials [9]. The development of innovative batteries having high specific energy, capable of complete charging for several minutes, operating under high-density current, and being of state-of-the-art design is possible if only new electrode materials are used having high theoretical capacity as for the lithium incorporation. $\text{Li}_2\text{FeSiO}_4$ is considered to be the promising cathode material.

Lithium intercalation into carbon materials is a complex process whose mechanism and kinetics depend heavily on the carbon material nature and nature of electrolyte [10]. The limited specific capacity of carbon materials, used for the current Li-ion batteries as well as the stability problems of such materials in the cycling process, actuated intensive research intended to the search for alternative materials of negative electrode. Tendencies in the progress of electronics connected with electronic plate miniaturizing need voltage drop down to 3 V (and lower) provide conditions for the use of alternative materials. Nowadays, lithium titanate is considered to be promising anode material since it is of high theoretical capacity and excellent cycling by means of heavy current. Lithium titanate has three-dimensional crystalline lattice into which lithium ion may intercalate quite easily deintercalating from it without any structural deformations. It is common knowledge that lithium ion intercalation into two-dimensional crystalline lattice of graphite is followed by separation of layers; as a result, stresses within the lattice structure arise. However, lithium titanate has fundamental disadvantages, i. e. low values of specific electric conductivity and lithium diffusion coefficient [11]. The problems can be

solved by means of the following: decrease in particle size, development of a defect structure, particle surface coating with carbon, and metal doping. For smaller particles and within defect structures, diffusion paths of lithium ions shorten in solid phase and interphase surfaces extend. Covering titanate particles with carbon increases electronic conductivity of the material; its doping improves electrode stability while intensifying electronic conductivity and reducing polarization loss. Attaining the objectives involves such various synthesis techniques as solid state reaction, sol-gel synthesis, gel-emulsion process, hydrothermal synthesis, microwave synthesis, and their combinations [12]. Much attention is paid today to preprocessing of precursors: synthesis of lithium titanate has been implemented with the use of mechanical activation. The technique helps synthesize lithium titanate with the use of mechanical activation. The technique makes it possible to obtain compounds in a disperse state with sufficient structural disorder resulting in the improved stability while anode cycling [13]. Mechanical activation by means of high pressure facilities of Bridgman anvil type is one of the most efficient techniques to affect a solid body structure. Plastic deformation of multicomponent heterogeneous mixtures involves an intensive process of size reduction of heterogeneous compositions forming initial mixture. It has been demonstrated before that mechanical activation of precursor while using high pressure facilities of Bridgman anvil type can be applied successfully to synthesize fine cathode materials of lithium batteries [14].

Lithium cobaltate is the most popular industrial cathode material owing to high values of its specific capacity and discharge potential. However, future development is restricted due to its costliness and high toxicity. Lithium ferrophosphate (LiFePO_4)-based cathode material is quite attractive having a number of advantages such as low cost, hypotoxicity, and relatively high capacity [15]. However, it has serious disadvantages, i. e. low values of electronic and ionic conductivity resulting in significant electrochemical characteristics drop in terms of discharging current increase. Carbonaceous coating for lithium ferrophosphate is applied to improve electronic conductivity; ionic conductivity is improved while magnesium ions, titanium ions, and tungsten ions doping. Much attention is paid to the technological development of obtaining LiFePO_4 (i. e. temperature optimization of high-temperature synthesis; microwave synthesis; mechanochemical synthesis; and emulsion drying) to upgrade characteristics of electrodes manufactured on its basis. Mainly, electrode characteristics are upgraded owing to the production of nanodispersed powders [16]. The development of the mixed compositions of electrode materials consisting of two or more active components to use their advantages is one of upcoming tendencies [17]. Owing to the unique combination of properties, such electrodes have the following advantages: longer life; decrease in capacity losses while cycling; diminution in value; improved thermal stability; acceptable profiles of charging-discharging characteristics and others. Specifically, authors of [14] synthesized $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites with the use of mechanical activation in the process

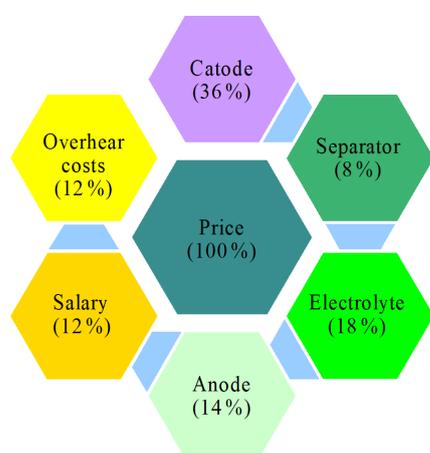


Fig. 1. Diagram of the battery cost

of simultaneous carbothermal reduction of Fe_2O_3 and V_2O_5 in a mixture with Li_2CO_3 and $(\text{NH}_4)_2\text{HPO}_4$. It has been demonstrated that the composite electrodes are characterized by more stable cycling within a wide range of current density to compare with separate components. Despite the fact that double lithium-titanium phosphate is somewhat behind LiFePO_4 in terms of discharge potential and theoretical specific capacitance, it is of high conductivity. Thus, $\text{LiFePO}_4/\text{LiTi}_2(\text{PO}_4)_3$ composite is considered to be rather challenging. Currently, it is topical to develop three-phase electrodes and lithium batteries on the basis of innovative high-electroconductive polymeric electrolytes; they are of high energy intensity, do not contain liquid electrolyte, and can take any shape [18].

Competition to charge electric cars and electronic gadgets sets a mission to develop innovative materials for rechargeable lithium-ion batteries with nickel as an integral component. Nickel-metal-hydride batteries dominate in the growing market of hybrid electric vehicles remaining to be advantageous for rechargeable batteries intended for domestic use. However, it is quite possible that the technique using innovative cathode material to make lithium-ion batteries more powerful, durable, and safe is the most challenging for accumulator batteries with nickel. Material, known as NCM or NMC (interchangeable names mention the presence of nickel oxides, cobalt oxides, and manganese oxides) was introduced a decade ago as an alternative to lithium-cobalt oxide used traditionally for lithium-ion batteries [19]. For instance, Sanyo Company produces NiMH batteries for Toyota Prius. 288 V battery package meant for 1.8 kW · h with complete system weight of 70 kg provides 38.8 kW power for electrical drive system.

Many studies concern multidoping when simultaneous introduction of two or more addition elements including those combined with anionic substitution takes place. First of all, that relates to lithium-manganese spinel material. Many samples of the substituted spinel material are applied as cathode material (voltage range is 5 V). Much attention is also paid to nickel-manganese oxides with the addition of multidoping elements $\text{LiNi}_{1-x-y}\text{Mn}_x\text{M}_y\text{O}_2$ ($M = \text{Al, Ti, W, Cr, Mo, Mg, Ta, etc.}$) as well as to the mixed tertiary oxides $\text{LiNi}_{1-x-y}\text{Mn}_x\text{CoO}_2$ [20].

Currently, actual specific capacity of the materials is close to theoretical one; hence, energy intensity of a battery of LiCoO_2/C system achieved its limited range (150–160 Watt-hours/kg).

Despite the distinct advantages of the systems, they have a number of disadvantages: short cyclic life, fire- and explosive risk, high price, and toxicity. Hence, research aimed at the development of new and modernization of currently available cathode and anode materials for batteries of hybrid vehicles is a topical scientific and technical problem.

Objective is to study effect of mechanical activation on $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ system (in the form of minerals) to be used as cathode material additives.

Methodology. Mechanochemical activation (MA) of materials was performed by means of a vertical vibration

mill (VVM). Its basic advantage is as follows: cutting time for powder reducing, on the one hand, and vibroimpulsive activation involving surface activation of the material as well as disturbance of the internal structure of the particles, on the other hand. Thus, active zone penetrates deeper resulting in volumetric ionization of the activated material.

A technique to estimate the power grading on the specific surface was applied to determine dispersion constant since specific surface is accessible dispersion characteristic. The specific surface was determined according to filtration resistance of dilute gas. The technique relies upon a theory of dilute gas flow through the system of a system of solid globes when a path of gas molecules is much longer to compare with distance between the globes (Knudsen flow pattern). The theory has been developed by B. N. Deriagin. Error of the technique is 1 %.

Average size of the powdered particles was identified according to data by laser analyzer LAZER MICRON SIZER PRO-700 (Japan). Formation of the activated state is closely connected with energy characteristics of the material. For that matter, multipurpose technique to analyze energy characteristics of the materials was applied by means of potentiometric measurements within suspensions with indifferent electrode. The technique of potentiometric measurements makes it possible to calculate potential curve and total adsorption potential.

“In situ” diffractograms were obtained with the help of diffractometer ДРОН-2 (Burevestnik, Russia). Phase analysis of the materials was determined with the help of X-ray diffractometer ДРОН-3 (Burevestnik, Russia): $\text{Fe K}\alpha$ emission, high voltage 35 eV, and anode current 20 mA. Physical and chemical processes, taking place in the process of GG methane, were analyzed with the help of differential thermal analysis (DTA) and X-ray fluorescence analysis (RFA). A content of gaseous products was studied by means of a gas adsorption chromatography method using JIXM-2000-TM chromatograph (Elektra, Russia).

Results and discussions. Mechanical activation (MA) of the minerals was performed using a device being a laboratory vertical vibration mill (VVM) [21] designed and produced by the NMU experts. Experiments concerning MA of the minerals were carried out in continuous-wave mode and in periodic mode with the help of grinding chambers of different designs. In terms of continuous-wave mode, material is supplied from a feeding bin to a grinding chamber, travels over L distance being further directed to a receiving bin. The L , m value is determined by means of the grinding chamber height and the number of the material passes through it. In terms of a periodic mode, the material is supplied to the grinding chamber closing down hermetically; then, the material is being powdered during the predetermined time. Weight of a portion of the material being powdered is recorded.

In terms of a periodic mode, the material, being powdered, is supplied to the chamber in advance. To avoid environmental pollution, a chamber cover is closed hermetically. When the electric engine is energized, the grinding chamber performs rectilinear vibration motions within vertical plane with preset amplitude (7 mm) and frequency (16 Hz). While passing through the upper dead point and the lower one, grinding bodies interact with each other as

well as with the bottom of the grinding chamber and its cover. Description of the functional principle without the scheme is incorrect delivery of information.

Δ clearance between the upper layer of globes and the grinding chamber cover is the important factor affecting powdering process efficiency; it depends on the volume of globes filling the chamber. Preliminary tests helped identify that if diameters of the globes are 6 and 9 mm, then maximum energy intensity of technological loading takes place if the clearance amount is 9 to 20 mm depending insignificantly on the total height of a layer of globes within a chamber.

The laboratory tests took two stages. Stage one determined the most rational technological powdering parameters making it possible to obtain the best results as for the specific surface size. Diameter of grinding bodies and ratio between the weight of the material, being powdering, and technological loading varied during the experiment.

Globes of 6 and 9 mm were grinding bodies. In the context of all the experiments, a clearance between the globes and the chamber cover was 10 mm. Weight of the powdered material portions m_m was 1/20 and 1/40 of the weight of globes m_b . The powder was sampled at stated intervals to be observed through the microscope to analyze shape of the particles and to estimate grain-size distribution of the obtained material. In each case, the chambers were uncovered only after their cooling down to room indoor temperature. Then, the powder samples were placed to the chambers again for their further powdering. Thus, there was determined the globe diameter d_b for the most efficient material powdering. It turned out to be impossible to estimate visually the effect of m_m/m_b parameter on grain-size distribution of powdering product. To keep the data current, experiments were carried out with the use of technical methods of laboratory analysis.

The taken diameter of the grinding bodies was used for further experiment when only ratio between weights of the material, being powdering, and technological loading varied. Visual observations were added by specific surface measuring. Optimum powder weight-globe weight ratio (i. e. m_m/m_b) was determined on the maximum value of specific surface value S_s .

Stage two used the determined optimum powdering mode. DTA and DPA physical and chemical analysis was carried out for mechanically activated samples.

Temporal dependence of electrical conductivity on the period of vibroimpulsive activation was studied experimentally in the process of rutile powdering.

Fig. 2 represents a dependence of rutile electrical conductivity on the period of vibroimpulsive loading.

As Fig. 2 demonstrates, the dependence is a function with one extremum. It can be explained by the increase in rutile mechanical activity resulting from its powdering, on the one hand, and decrease at the expense of oxygen adsorption as a result of the mineral vibroimpulsive activation, on the other hand.

In the context of MA, structural defects are formed; the defects are connected with formation of fissures and cracks in a solid body. In the neighbourhood of a fissure bottom, considerable stresses are formed resulting in fissures being deeper and sharper to compare with metallic

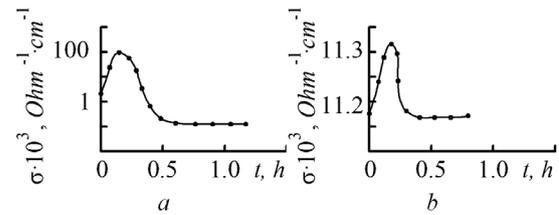


Fig. 2. Changes in rutile electrical conductivity in terms of vibroimpulsive activation:

a – polycrystalline sample; b – TiO_2 monocrystal

crystals. In this connection, activation of ceramic materials factors into the increased reactive capability not only at the boundaries of the grains but also in their volume.

Changes in electric conductivity of powder can prove that. Despite the fact that electrical conductivity of polycrystalline system is being determined by means of contact barriers, electronic state of crystallite volume remains to be dominating contribution.

Increase in electrical conductivity means the increase in quasisurface electrical conductivity, i. e. increase in the thickness of the “prepared” near-surface crystallite layer.

According to Morrison equation for conductivity, σ of powder-like semiconductor is $\sigma = \sigma_0 \exp[-(E_{CS} - E_F)/kT]$ where E_F is Fermi energy, E_{CS} is energy of a conductivity zone of the bottom at the surface; the near-surface conductivity under measurement contains information concerning the volume of the crystallite as well. In the context of the equation, $E_{CS} - E_F$ characterizes surface barrier stipulated by all surface states including contact ones.

Experiments were carried out for $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ system. They concerned comparison of electric characteristics and X-ray phase characteristics of complex spinel systems. Such systems are a result of MA in terms of simultaneous powdering of oxidized ores and hydrargillite.

Fig. 3 demonstrates dependence of electrical conductivity of oxidized quartzites-hydrargillite system on volumetric content and period of mechanical activation.

X-ray phase analysis has shown the following composition of phase areas:

I – $\text{Fe}_2\text{O}_3 + \beta$ goethite mixture;

II – solid solution FeAl_2O_4 in Fe_{1-x}O ;

III – spinel solution FeAl_2O_4 in magnetite;

IV – two solid solutions of normal spinel and inverted spinel FeAl_2O_4 ;

V – solid solution Al_2O_3 in tetragonal spinel FeAl_2O_4 ;

VI – solid solution FeAl_2O_4 in Al_2O_3 .

A feature of MA is the formation of different-nature solid solutions in the process of solid-phase synthesis being responsible for increase or decrease in electrical conductivity. Correlation between mechanical activity and electronic energy of the activated material has relied on the assumption that volumetric shift of Fermi level cannot change a system of surface levels.

From a practical viewpoint, substitution of ions within lattice sites for allogenetic ions of other valency (i. e. the development of “allogenetic defects” which, however, have no vital differences from defects resulting valency variation of proper lattice ions) is the most expedient

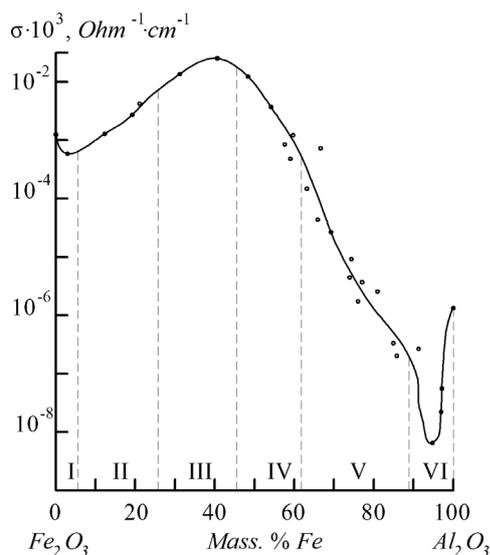


Fig. 3. Dependence of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ system electrical conductivity on volumetric composition determined with the help of X-rays

technique of a shift of volumetric Fermi level. Thus, according to a principle of the controlled valency, electrical conductivity will decrease consequently in the context of n -type semiconductor (electronic) and increase in the context of p -type semiconductor (acceptor-type).

Linear correlations of conductivity activation energy with power parameters of reactions of solid solution formation in the context of semiconductor compounds, containing similar metals, shaping spinel structures (i.e. transition of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ type) are of interest.

Hence, activity-electrical conductivity correlation connects origination the activated state within a solid body with electronic changes, i.e. with transitions of metal-insulator or metal-semiconductor types.

Fig. 4 demonstrates such dependence for a system of aluminosilicates and oxidized quartzites.

In terms of vibroimpulsive loading and as a result of activation, recombination of oxygen atoms takes place; it occurs on $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ ($\text{M} = \text{Cu}, \text{Cd}, \text{and Ti}$) ferrites with maximum velocity within compositions with $x = 0.4\text{--}0.6$ being of metallic conductivity nature.

Scientific sources do not describe changes in mechanochemical activity of minerals resulting from vibroimpulsive

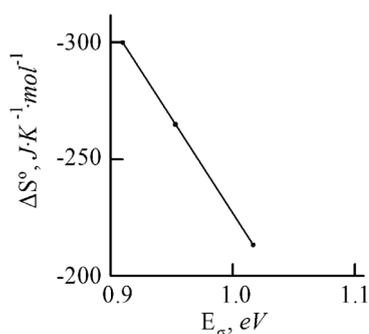
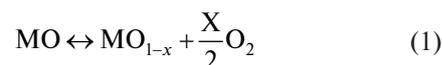


Fig. 4. Ratio between activation entropy and activation energy of conductivity

loading and connection of the parameters with changes in the mineral electrical conductivity. Thus, $\text{TiO}_2\text{-SiO}_2$ system is of utmost interest since its components do not interact, i.e. they just dilute each other mechanically in the limit. However, in the process of component data processing within MVV specific resistance varies.

Features of the system can be explained at the expense of the mineral lattice disorder. In particular, under standard conditions the minerals, including metallic oxides, always involve nonstoichiometric point defects which origination depends upon removal or consumption of certain hyperstoichiometric amount of oxygen. Then, it is possible to formulate for oxides losing oxygen (semiconductors of n -type) that



In this context, most commonly charged defects are formed; in this case either cations in interstices (i.e. Frenkel defects) or anion vacancies (i.e. Schottky defects). On the fundamental principle of electroneutrality of a crystal, the extra charges, localized within the defects, are balanced out by the occurrence of quasifree charge carriers in the crystal, i.e. e electrons (in the context of oxygen deficiency) or p holes (in the context of oxygen excess). Hence, changes in oxygen partial pressure will vary disorder degree and, consequently, electrical conductivity of the oxide. Nature of electrical conductivity dependence on oxygen pressure P_{O_2} will be determined by means of the defect charge. For instance, as for the TiO_2 , formation of interstitial cations (i.e. defects singly charged with TiO) is possible.

Dynamics of synthesis of new compounds within the vertical vibration mill belongs to a type of quasiexplosive processes since two periods are observed clearly on the kinetic curves: induction period and synthesis as such. No phase growth is seen during the whole induction period. In the process of vibroimpulsive ore activation in a vertical vibration mill of continuous-wave mode, clusters are formed which is demonstrated evidently by X-ray structural spectra.

Organic bond was used to intensify mechanical adhesion of particles of active electrode material. On the one hand, the bond strengthens adhesive power of the electrode materials; on the other hand, it improves stability of specific characteristics.

Parameters of crystalline lattice vary in the context of MA. Thus, molecules of reacting agents diffuse inside a crystal of inorganic salt; hence, the process of ore-reacting agent interaction involves all its inner atoms.

Clusters are formed in the process of mechanochemical activation which is demonstrated evidently by X-ray structural spectra. Results of potentiometric analysis (i.e. changes in the potential of titration of azodien saline solutions; composition calculation on Sillen method with the use of Bodländer equation; and stability calculation on the method of Leden) show that adducts of non-permanent composition are formed within the solution.

Composition and stability constants of the adducts, being formed, depend upon concentration of source

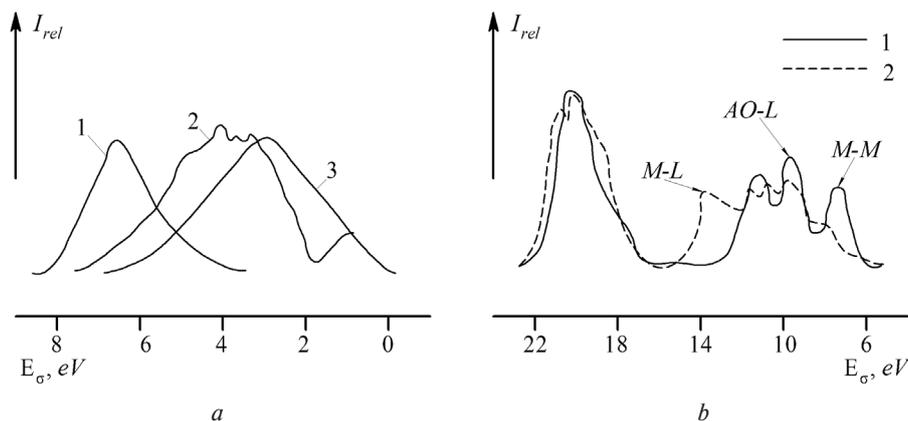


Fig. 5. Stitching scheme and energy-stitched X-ray emission spectra $\text{O}(\text{Cl})\text{K}_{\beta 1,3}$ (1), $\text{FeL}_{\beta 2}$ (3) (a) and X-ray electronic spectrum of a valence band of ferrum cluster after vibration loading (2) (b)

components distinguishing them from polynuclear complexes and confirming their cluster nature. If azodien molecules are introduced into $\text{Azodien} \times (\text{MeX}_2)_n$ clusters, a degree of the system aggrezation, owing to fixing of $(\text{MeX}_2)_n$ complexes (where $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{O}^-$, etc.), increases resulting in changes in physical/chemical properties of the solution (i.e. electrical conductivity, viscosity).

Fig. 5 shows formation of a cluster group (at the expense of metal-metal connections) within the oxide structure provoking specific changes in ESCA spectrum.

The formed cluster structures are of higher adsorption potential owing to higher ionization energy at the surface of a powder [22]. The cluster is of electron-deficient nature.

The cluster formation process can be considered as a particular case of polymeranalogic transformation – reaction of inorganic salt cluster $(\text{MeX}_2)_n$ on energetically advantageous centres formed while activating, on the one hand, and on the double diene bonds, on the other hand.

A new (metal+silicium, MS) organic cluster is the interaction product. Thus, a surface clustering simplifies the reaction process; i.e. the higher the reaction velocity is, the more intensive the MS cluster formation is. The process determines possibility to form new compounds connected with the structure changes. While switching from structure to properties of clusters, it should be mentioned that they depend on the number of particles within the cluster. It is quite obvious that changes in properties depending upon size should be sharp for small clusters where addition of one particle means significant relative increase in the group.

Addition of azodiens to electrode materials results in the formation of quasi-one-dimensional metalorganic conductors. They consist of loosely bound circuits and molecules; moreover, they are of high electric conductivity along the circuits. Such compounds have metallic properties if atoms and molecules are along a circuit at regular intervals. Thus, equal distances between active centres should involve insignificant amounts of polyelectrolytes.

However, quasi-one-dimensional metallic circuits are mostly unstable due to lattice distortion (Peierls instability). In this connection, certain metals will form dimers, trimers, tetramers and so forth depending upon their electronic structure and distortion degree of a lattice in the context of vibroimpulse loading. The com-

pounds, resulting from the processing of the activated materials, are conductors. Such compounds with the distorted circuits but located regularly along the circuit, generate energy gap at Fermi characteristic energy level in electronic spectrum. Thus, electric properties will depend upon the structure of a circuit.

Fig. 6 represents dependence curves of specific conductivity of $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--PE}$ system on temperature depending upon MA.

Hence, in the context of vibroimpulsive loading, specific barrier layers are formed which are responsible for changes in physical and chemical nature of the material being crushed.

Conclusions.

1. Physical and chemical properties of systems have been analyzed relying upon $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--PE}$ in the form of minerals after mechanochemical activation.

2. It has been determined that additives after activation using MVV improve electronic conductivity owing to the formation of solid solutions during activation, on the one hand, and owing to changes in crystal-chemical composition, on the other hand.

3. Electric conductivity with the use of direct current has been studied (as well as with the use of low-frequency alternative current being about kilohertz); that has made it possible to sense near-surface layers of the activated material grains.

4. It has been demonstrated that the activated materials improve electronic conductivity up to $10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$.

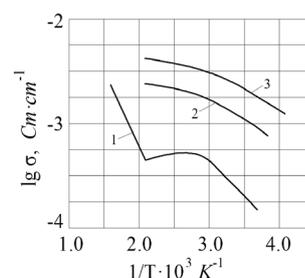


Fig. 6. Temperature dependence of electrolytic compound:

1 – before MA; 2 and 3 – MA during 5 minutes and 10 minutes respectively

References.

- Glebov, V. V., Klimov, V. F. and Volosnikov, S. A., 2017. Assessment of the Possibility to Use Hybrid Electromechanical Transmission in Combat Tracked Platforms. *Mechanics, Materials Science & Engineering*, 8, pp. 99–105.
- Protsiv, V. V. and Monya, A. G., 2003. Experimental determination of characteristics of clutch of mine locomotive under the braking conditions. *Metallurgicheskaya i Gornorudnaya Promyshlennost* [online], 2, pp. 95–97. Available at: <https://www.researchgate.net/publication/293546988_Experimental_determination_of_characteristics_of_clutch_of_mine_locomotive_under_the_braking_conditions> [Accessed 20 January 2017].
- Ziborov, K., Bas, K., Kravets, V., Fedoriachenko, D., Krivda, V., Fedoriachenko, S. and Kornilenko, K., 2016. Mathematical Models of Hybrid Vehicle Powertrain Performance. *Mechanics, Materials Science & Engineering Journal*, 7, pp. 153–164.
- Franchuk, V. P., Ziborov, K. A., Fedoriachenko, S. A. and Krivda, V. V., 2017. On wheel rolling along the rail regime with longitudinal load. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, 3, pp. 75–80.
- Sudakov, A. K., Khomenko, O. Ye., Isakova, M. L. and Sudakova, D. A., 2016. Concept of numerical experiment of isolation of absorptive horizons by thermoplastic materials. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, 5(155), pp. 12–16.
- Ziborov, K. A., Protsiv, V. V., Blokhin, S. Ye. and Fedoriachenko, S. O., 2014. Applicability of computer simulation while designing mechanical systems of mining rolling stock. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, 6, pp. 55–59.
- Kyrychenko, Y., Samusia, V., Kyrychenko, V. and Goman, O., 2012. Experimental investigation of aeroelastic and hydroelastic instability parameters of a marine pipeline. *Geomechanical Processes During Underground Mining – Proceedings of the School of Underground Mining* [online], pp. 163–167. Available at: <<http://www.crcnetbase.com/doi/abs/10.1201/b13157-28>> [Accessed 1 May 2017].
- Taran, I. and Klymenko, I., 2017. Analysis of hydrostatic mechanical transmission efficiency in the process of wheeled vehicle braking. *Transport Problems*, 12 (Special Edition), pp. 45–56. DOI: 10.20858/tp. 12. se. 4.
- Blomgren, G., 2017. The Development and Future of Lithium Ion Batteries. *J. Electrochem. Soc.* [pdf], 164, pp. A5019–A5025. Available at: <<http://jes.ecsdl.org/content/164/1/A5019.full.pdf>> [Accessed 30 October 2017].
- Safronov, D. V., Novikova, S. A., Skundin, A. M. and Yaroslavtsev, A. B., 2012. Lithium intercalation and deintercalation processes in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 . *Neorganicheskie Materialy*, 48(1), pp. 63–68. DOI: 10.1134/S0020168512010141.
- Fedotov, S., Khasanova, N. R., Samarin, A. Sh., Drozhzhin, O. A., Batuk, D., Karakulina, O. M., Hadermann, J., Abakumov, A. M. and Antipov, E. V., 2016. AVPO_4F (A = Li, K): A 4 V Cathode Material for High-Power Rechargeable Batteries. *Chem. Mater.*, 28(2), pp. 411–415. DOI: 10.1021/acs.chemmater.5b04065.
- Berbenni, V., Milanese, C., Bruni, G., Marini, A. and Naturforsch, Z., 2010. Mechano-thermally Activated Solid-state Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Spinel from $\text{Li}_2\text{CO}_3\text{--TiO}_2$ Mixtures. *A Journal of Chemical Sciences*, 65(1), pp. 23–26. DOI: 10.1515/znb-2010-0105.
- Kulova, T. L., 2013. New electrode materials for lithium-ion batteries (Review). *Russian Journal of Electrochemistry*, 49(1), pp. 1–25. DOI: 10.7868/S0424857013010118.
- Kosova, N. V., Rezepova, D., Petrov, S. and Slobodyuk, A., 2017. Electrochemical and chemical Na^+/Li^+ ion exchange in Na-based cathode materials: $\text{Na}_{1.22}\text{P}_2\text{O}_7$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. *Journal of the Electrochemical Society*, (164), pp. A6192–A6200. DOI: 10.1149/2.0301701jes.
- Yan, L., Rui, X., Chen, G., Xu, W., Zou, G. and Luo, H., 2016. Recent advances in nanostructured Nb-based oxides for electrochemical energy storage. *Nanoscale*, 8(16), pp. 8443–8465. DOI: 10.1039/c6nr01340f.
- Sloovere, D., Marchal, W., Ulu, F., Vranken, T., Verheijen, M., Van Bael, M. K. and Hardy, A., 2017. Combustion synthesis as a low temperature route to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ based powders for lithium ion battery anodes. *RSC Adv.*, 7, pp. 18745–18754. DOI: 10.1039/C7RA02503C.
- Yegorov, A., Putsylov, I., Smirnov, S. and Fateiev, S., 2016. Effect of mechanical activation on electrode characteristics on the basis of fluorated carbon nanotubes. *Journal of Applied Chemistry*, 89(3), pp. 400–403.
- Vaganova, E. S., Davydova, O. A., Buzaeva, M. V., Klimov, E. S., Frolov, I. V., Sergeev, V. A., Fomin, A. N. and Svetukhin, V. V., 2016. Hange of Surface of Polymeric Composites, Reinforced by Carbon Nanotubes. *Bulletin of the South Ural State University. Ser. Chemistry*, 8(3), pp. 35–41. DOI: 10.14529/chem160305.
- Pikul, J. H., Zhang, H. G., Cho, J., Braun, P. V. and King, W. P., 2013. High-power lithium ion microbatteries from interdigitated three-dimensional bicontinuous nanoporous electrodes. *Nature Communications*, 4(1732), pp. 1–5. DOI: 10.1038/ncomms2747.
- Mustyatsa, O. and Katerinko, I., 2012. Electric conductance and ratios of contributions in conductivity of sulfide and telurid of lithium in liquid and crystal conditions. *Visnyk NTU (Natsionalnoho Transportnoho Universytetu)* [pdf], 26, pp. 595–600. Available at: <http://publications.ntu.edu.ua/visnyk/26_2_2013/595-600.pdf> [Accessed 11 September 2017].
- Franchuk, V., Antsyferov, O. and Duganets, V., 2016. The drive force in the vertical vibratory mill. *Heotekhnichna mekhanika*, 131, pp. 100–107.
- Svetkina, O., 2012. Monitoring of quality of mineral by method of conductivity. *School of Underground Mining*, pp. 141–147. DOI: 10.1201/b13157-35.

**Механохімічний синтез добавок
для катодного матеріалу літій-іонних
тягових акумуляторних батарей**

О. Ю. Светкіна¹, В. В. Проців¹, О. О. Богданов¹,
К. М. Бас^{1,2}

1 – Державний вищий навчальний заклад „Національний гірничий університет“, м. Дніпро, Україна, e-mail: svetkina.yelena@gmail.com; protsiv@ukr.net; bogdanov.aleksandr17@gmail.com

2 – Національний транспортний університет, м. Київ, Україна, e-mail: k.m.bas.69@gmail.com

Мета. Вивчення впливу механоактивації на систему $TiO_2-SiO_2-Al_2O_3$ (у вигляді мінералів) з метою їх застосування як добавок катодного матеріалу.

Методика. Механохімічну активацію (МА) матеріалів проводять у вертикальній вібраційній дільниці (МВВ). Середній розмір подріблених часток визначали за даними, отриманими на лазерному аналізаторі SK LAZER MICRON SIZER PRO-700 (Японія). Утворення активованого стану щільно пов'язане з енергетичними характеристиками матеріалу. У зв'язку з цим був використаний універсальний спосіб дослідження енергетичних характеристик матеріалів шляхом потенціометричних вимірювань у суспензіях з індеферентним електродом. Дифрактограми „in situ“ отримували на рентгенівському дифрактометрі ДРОН-2 („Буревестник“, Росія). Фазовий аналіз матеріалів визначали на рентгенівському дифрактометрі ДРОН-3: випромінювання Fe $K\alpha$, висока напруга 35 еВ, анодний струм 20 мА. Фізико-хімічні процеси, що відбуваються при отриманні ГГ (газових гідратів) метану, вивчаються за допомогою методів диференціального термічного аналізу (ДТА) та рентгенофлуоресцентного аналізу (РФА). Склад газоподібних продуктів був досліджений методом газоадсорбційної хроматографії на хроматографі „ЛХМ-2000-ТМ“ („Електро“, Росія).

Результати. Вивчені фізико-хімічні властивості систем на основі $TiO_2-SiO_2-Al_2O_3-P\Theta$ у вигляді мінералів після механохімічної активації. Встановлено, що добавки після активації у МВВ підвищують електронну провідність за рахунок утворення у процесі активації твердих розчинів, з одного боку, а з іншого — за рахунок зміни кристалохімічного складу. Показано, що активовані мінерали підвищують електронну провідність до $10^{-2} \text{ Ом}^{-1}\text{см}^{-1}$.

Наукова новизна. Полягає в тому, що при віброударній активації відбувається зміна електропровідності мінералів (зокрема, рутил і окислених кварцитів), пов'язана з утворенням твердих розчинів або хімічних сполук у результаті механохімічної активації.

Практична значимість. Розроблений спосіб підвищення активності добавок для катодних матеріалів літій-іонних акумуляторів, за яким відбувається підвищення електронної провідності.

Ключові слова: *вібраційна машина, механоактивація, катодний матеріал, літій-іонні акумулятори, поліелектроліти*

Механохімічний синтез добавок для катодного матеріалу литий-іонних тягових акумуляторних батарей

Е. Ю. Светкина¹, В. В. Протсів¹, А. А. Богданов¹,
К. М. Басс^{1,2}

1 — Государственное высшее учебное заведение „Национальный горный университет“, г. Днепр, Украина, e-mail: svetkina.yelena@gmail.com; protsiv@ukr.net; bogdanov.aleksandr17@gmail.com

2 — Национальный транспортный университет, г. Киев, Украина, e-mail: k.m.bas.69@gmail.com

Цель. Изучение влияния механоактивации на систему $TiO_2-SiO_2-Al_2O_3$ (в виде минералов) с целью применения их в качестве добавок катодного материала.

Методика. Механохимическую активацию (МА) материалов проводили в вертикальной вибрационной мельнице (МВВ). Средний размер измельченных частиц определяли по данным, полученным на лазерном анализаторе SK LAZER MICRON SIZER PRO-700 (Япония). Образование активированного состояния тесно связано с энергетическими характеристиками материала. В связи с этим был использован универсальный способ исследования энергетических характеристик материалов путем потенциометрических измерений в суспензиях с индеферентным электродом. Дифрактограммы „in situ“ получали на рентгеновском дифрактометре ДРОН-2 („Буревестник“, Россия). Фазовый анализ материалов определяли на рентгеновском дифрактометре ДРОН-3: излучение Fe $K\alpha$, высокое напряжение 35 эВ, анодный ток 20 мА. Физико-химические процессы, происходящие при получении ГГ (газовых гидратов) метана, изучали с помощью методов дифференциального термического анализа (ДТА) и рентгенофлуоресцентного анализа (РФА). Состав газообразных продуктов был исследован методом газо-адсорбционной хроматографии на хроматографе „ЛХМ-2000-ТМ“ („Электро“, Россия).

Результаты. Изучены физико-химические свойства систем на основе $TiO_2-SiO_2-Al_2O_3-P\Theta$ в виде минералов после механохимической активации. Установлено, что добавки после активации в МВВ повышают электронную проводимость, за счет образования в ходе активации твердых растворов, с одной стороны, а с другой — за счет изменения кристаллохимического состава. Показано, что активированные минералы повышают электронную проводимость до $10^{-2} \text{ Ом}^{-1}\text{см}^{-1}$.

Научная новизна. Заключается в том, что при виброударной активации происходит изменение электропроводности минералов (в частности, рутила и окисленных кварцитов), связанное с образованием твердых растворов или химических соединений в результате механохимической активации.

Практическая значимость. Разработан способ повышения активности добавок для катодных материалов литий-іонних акумуляторів, при котором происходит повышение электронной проводимости.

Ключевые слова: *вибрационная машина, механоактивация, катодный материал, литий-іонные акумулятори, поліелектроліти*

Рекомендовано до публікації докт. техн. наук В. В. Кравцем. Дата надходження рукопису 13.11.17.