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SYNTHESIS OF $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ FILMS WITH NASICON STRUCTURE BY «TAPE CASTING» METHOD

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For the first time lithium aluminum titanium phosphate $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ thick films with NASICON structure have been obtained by "tape casting" method. A sol-gel method was used to synthesize nanopowder $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$. Film-forming solution was obtained based on previously synthesized nanoparticles and mixed with organic reagents. Films were deposited on the substrate of α-Al_2O_3 and were exposed to isostatic lamination. Sintering thick films were carried out at temperature of 1000 °C. Different regimes of heat treatment were studied to determine the optimal conditions of heat treatment. Investigation of structural and morphological characteristics has shown that the maximum dense film is achieved at low heating rate (20 °C/h) and by the action of isostatic lamination. Reducing of porosity positively affects electrical properties. Films after isostatic lamination are characterized by high values of Li-ion conductivity. Thus, the laminated film after low rate heating, which has the lowest porosity of 17 %, shows the highest values Li-ion conductivity – $5.6 \cdot 10^{-6}$ S/cm.

Keywords: lithium aluminum titanium phosphate $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, NASICON structure, "tape casting" method, thick films, isostatic lamination, sol-gel method

INTRODUCTION

Lithium-ion batteries are widely used as storage power generation and UPS systems due to high energy performance [1–3]. However, using of organic liquid or polymer electrolyte prevents the creation of completely safe device [4–6]. Replacement of the organic electrolyte with inorganic solid will not only significantly improve the safety of lithium-ion battery, but extend its life by reducing the degradation processes [7–10].

Interest in the creation of film batteries has appeared in recent years. This interest is associated with a trend of miniaturization of electronic equipment, and with certain specific categories of devices. Smart cards, implanted medical devices, microelectromechanical systems, memory blocks, various sensors, transducers, and special and military equipment are potential consumers of film batteries [11, 12].

Lithium aluminum titanium phosphate, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, with NASICON structure [13, 14] is a promising material for producing thick film electrolytes of solid-state batteries. Bulk samples are characterized by high bulk conductivity for lithium ions ($\sigma_{general} \sim 5 \cdot 10^{-5}$ S/cm) at room temperature, chemical resistance and mechanical stability [14–16]. These materials are widely studied in the form of glass ceramics, while there is a lack of information on the synthesis and study of their electrical properties as thick films. It should also be noted that the film materials always have much lower ion conductivity as compared with that of bulk samples.

The optimal method to obtain thick films with a thickness of more than 10 μm is the method of «tape casting» [17]. The pores and cracks in the films have a negative impact on their electrical properties. Therefore, it is necessary to find ways to increase the density of thick films at their synthesis. Using optimal heat reatment or by reducing the deformation of the surface (wet film lamination technology) can increase the density of films [17–19]. Isostatic lamination is one of the most important processes in multilayer ceramic technology that effect the quality of the three-dimensional structure.

Therefore, the aim of the work is to research the effect of different heat treatment conditions, isostatic lamination on the value of porosity, grain size and value of Li-ion conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ thick films with NASICON structure obtained by "tape casting" method.

EXPERIMENT

Nanopowder of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ was prepared by sol-gel method. For this aqueous

solutions of salts of lithium nitrate $LiNO_3$ and aluminum nitrate $Al(NO_3)_3$, titanium diisopropoxide bis(acetylacetonate) $C_{16}H_{28}O_6Ti$, phosphoric acid 85 % H_3PO_4, citric acid $C_6H_8O_7$ and ethylene glycol $C_2H_6O_2$ (all of high purity grade) were used as starting reagents. Citric acid was dissolved in ethylene glycol at a ratio of 1:4. The resulting solution was homogenised at 150 °C for 6 h to held esterification and polymerization between ethylene glycol and citric acid. Synthesized polymer additionally was heated for 12 h 100 °C to produce gels. Polymer fried on the sandy bath at 350±10 °C (5 h) to obtain precursor powder.

Synthesized nanoparticles of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ were homogenized with organic reagents: 22 wt. % acetylacetone and 2 wt. % isopropanol (solvents), 2 wt. % polymethylmethacrylate (a binder), 30 wt. % dibutylphthalate (a plasticizer), 9 wt. % dybutylphosfate, 5 wt. % hallotannine (dispersants). Ratio of organic reagents to the nanoparticles $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ was 70: 30 wt. %. Homogenization of components was performed using a planetary mill Fritsch Pulverisette 7 for 2 h at the rotational speed of 300 rev/min. For application of films an appliance Film Applicator and Drying Time Recorder Coatmaster 510 (Erichsen, Germany) was used. The rate of application of slurry of the substrate of polykore α-Al_2O_3 was 0.1 mm/s. After drying in air film thickness of 120 μm and an area of 15×15 mm subjected to heat treatment followed by lamination with different modes of heating and shutter 2 h at the temperature of 1000 °C.

$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ green films were subjected to degasification under vacuum to pressure of 0.1 MPa for 60 s at Original HENKELMAN vacuum system (jumbo 30). Then the evacuated films were subjected to lamination at an Isostatic Laminator system model IL-4008PC at 75 °C for 20 min, the pressure was 55.16 MPa.

Heat treatment of films was performed using different conditions: "slow heating" (the film was heated at 20 °C/h to 500 °C, then from 500 to 1000 °C at 60 °C/h); "heating with conventional speed" (the film was heated from room temperature to 1000 °C at 60 °C/h); and "thermal shock" (the film was placed in to the preheated oven to 500 °C, then heated from 500 to 1000 °C at 60 °C/h).

The products were identified by X-ray diffraction patterns recorded on a DRON-3M (CuK_α-radiation; Ni-filter). The voltage at the X-ray tube was 40 kV, current − 18 mA, the average rate of 10^4pulses/s; goniometer rotation speed of 0.5 deg/min. Shooting diffraction was performed in the range of angles $2\theta = 10 \div 150°$ a numerically adjustable step to $\pm 0.01°$; the exposure of each point was 1 °C. As external standards were used SiO_2 (standard 2θ) and NistSRM 1976 − Al_2O_3 (standard intensity). The relative error in calculating the pulses of X-rays did not exceed 0.5 %.

In electrical measurements, Pt electrodes (0.5 μm) were deposited by electron-beam evaporation. The impedance of our samples was measured from 100 Hz to 1 MHz using an impedance analyzer 1260A Impedance/Gain-Phase Analyzer (Solartron Analytical).

The microstructure of polycrystalline samples was examined with a scanning electron microscope (SEM JSM-6490-LV, JEOL, Japan) with integrated electron probe analysis INCA Energy + based energy and dispersive spectrometers (EDS + WDS, OXFORD, United Kingdom) detector HKL-Channal (OXFORD).

RESULTS

X-ray diffraction of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ thick films are presented in Figs. 1 *a* and 1 *b*. As shown in Fig. 1 *a,* obtained $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ film is single-phase at the temperature of 1000 °C. Increasing the sintering temperature of films to 1100 °C leads to an additional phase of TiO_2, that is caused by partial evaporation of lithium. Therefore sintering thick films were carried out at the temperature of 1000 °C. According to the results of XRD (Fig. 1 *b*), sintered at 1000 °C $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ films are single phase regardless of speed of heating.

Fig. 2 shows micrographs of the surface of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ films and the cross-section (inset), obtained after various speed of heating and with/without lamination. Films heated with speed of 60 °C/h ("heating with conventional speed") are characterized by a large number of pores (~80 %), cracks and delamination (Fig. 2 *a*). After heating with speed of 20 °C/h ("slow heating") films contain much less pores (~43 %) (Fig. 2 *b*). At the same time, they are characterized by irregular thickness from 64 to 85 μm (Fig. 2 *b*, inset), which may be due to irregular evaporation of organic components. Porosity of the film does not exceed 47 %, and

its thickness is uniform of ~30μm (Fig. 2 *c*, inset).

Additional isostatic lamination of films considerably affects the porosity of the film before the heat treatment. The film does not contain cracks and porosity does not exceed 17 % (Fig. 2 *d*) after lamination and heating with speed of 20 °C/h ("slow heating"). The porosity of the film is 27 % (Fig. 2 *e*) after lamination and heat "thermal shock".
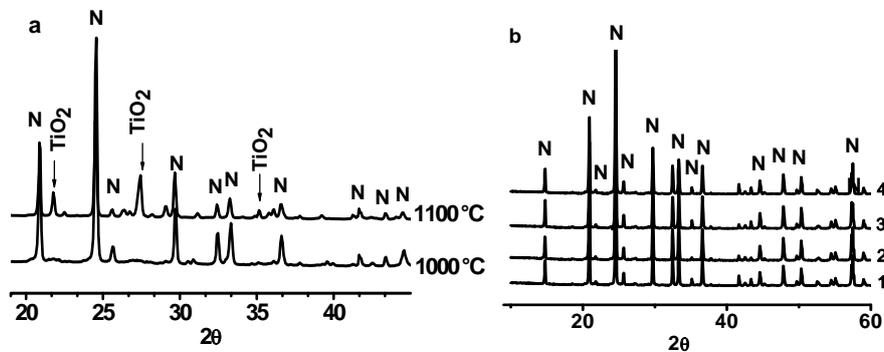
Fig. 1. XRD patterns of Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ thick films: *a* – "heating with conventional speed" and sintering at different temperatures; *b* – different speed of heating of films: *1* – at 20 °C/h ("slow heating"); *2* – "thermal shock"; *3* – lamination of film and "slow heating"; *4* – lamination of film and "thermal shock". (N – phase of NASICON)
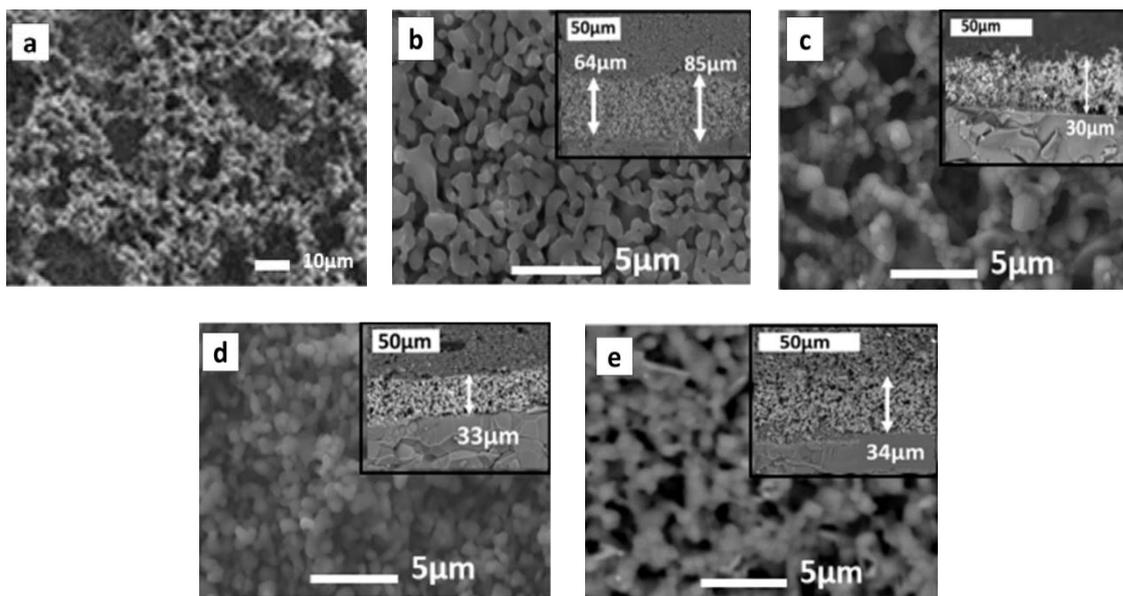
Fig. 2. The microstructure of the surface films and of the cross section (inset) obtained ba treating under different conditions: *a* – speed of heating at 60 °C/h ("heating with conventional speed"); *b* – speed of heating at 20 °C/h ("slow heating"); *c* – "thermal shock"; *d* – lamination and "slowheating"; *e* – lamination and "thermal shock"

DISCUSSION

It is known that the heat treatment should be carried out in several stages [20], where the first stage is necessary to remove organic components (annealing of film), and the second - for sintering grains (sintering of films). The first stage is particularly important. Annealing of the films is characterized by two processes: 1) organic bunch evaporation from the surface of the film; 2) diffusion of the organic bunch from volume to the film surface. Diffusion is a limiting factor in this. Ideally, the rate of organic bunch evaporation from the surface should be equal to the rate of diffusion $v_{ev.} = v_{diff}$, but when $v_{ev} > v_{diff}$, at the surface of the film a thick crust begins to form. The presence of crust, which prevents uniform evaporation of the

organic bunch volume porosity leads to the resulting film observed in the case of films obtained after "heating with an average speed" (Fig. 2 *a*). Film gradually shifts from liquid (inorganic particles in a polymer matrix and solvent) in a gel-like state (inorganic particles in a polymer matrix) and solid (inorganic particles) during heat treatment.

Organic solvents (isopropanol and acetylacetone) evaporate uniformly, and diffusion of the solvent occurs from bulk of the film to surface. It is accompanied by a gradual degradation of the polymer matrix and does not cause cracks in the surface film at "slow heating" with speed 10–20 °C/h. The presence of large grains ~1.5 μm (Fig. 2 *d*) may be due to the fact that the low heating at 20 °C/h solvent evaporation and degradation of the polymer matrix is uniform, resulting in shrinkage of the film due to capillary phenomena. Inorganic particles that form the polymer matrix frame gradually converge and sintered due to coalescent mechanism [21].

Decomposition of organic matrix takes place at the "thermal shock" (fast heating) (based on differential thermal analysis, it is 500 °C). Once pyrolysis of organic components is at thermal shock, bypassing the stage of evaporation [23, 24]. Inorganic carcasus is completely preserved due to the rapid pyrolysis of organic components, which leads to a porous structure. Because the particles are far away from each other, they becom e larger and their average size is 0.6–1 μm (Fig. 2 *c*).

The influence of lamination on the microstructure shows that the porosity of the films is significantly reduced (Fig. 2 *d, e*). Reducing porosity of films due to creating residual compressive stresses in the outer layers due to lamination [24]. During heating the polymer matrix under pressure carcasus of inorganic particles can be partially destroyed, and the share will be closer together, so grains become larger. Analysis of the microstructure of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ laminated films after "slow heating" and "thermal shock" (Fig. 2 *d, e*) shows that the impact of isostatic lamination only enhances the effect of evaporation rate (pyrolysis) on the microstructure. Sealing of inorganic frame happen is due to compression of the frame by reducing pore size under pressure, and by capillary recovery after sintering with speed at 20 °C/h ("slow heating") (Fig. 2 *d*). Analysis of the morphology of the grains shows that the maximum grain size of 2 microns is observed for laminated films after sintering at the speed of heating of

20 °C/h ("slow heating") (Fig. 2 *d*). This is quite logical, since the frame with inorganic particles are most dense after drying the film in this sample, and by sintering grains become larger.

The fact should be noted that the size of the grains in the film dried at a "slow heating" without isostatic lamination (Fig. 2 *b*) and the films after lamination and "thermal shock" (Fig. 2 *d*) are almost identical of 1–1.5 μm. This suggests that the isostatic lamination does not affect the grain size and regime drying affects on the porosity of the film.

Reduction of porosity and grain size influences the electrical properties (Fig. 3). Films are characterized by high values of Li-ion conductivity after isostatic lamination. Laminated film, which has the lowest porosity of 17 %, shows the highest values of Li-ion conductivity – $5.6 \cdot 10^{-6}$ S/cm after heating with speed of 20 °C/h ("slow heating"). Conductivity increased almost 2.5 times (from $2.3 \cdot 10^{-6}$ to $5.6 \cdot 10^{-6}$ S/cm) compared with non-laminated film (porosity of 43 %). Li-ion conductivity is of $2.8 \cdot 10^{-6}$ S/cm for film after isostatic lamination and "thermal shock", which is 2 times more than that for non-laminated film – $1.3 \cdot 10^{-6}$ S/cm.
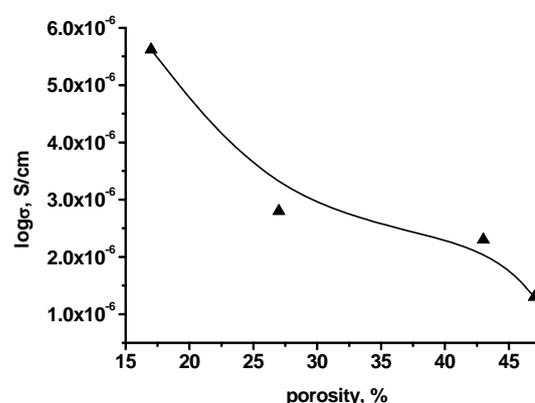
Fig. 3. The dependence of the ionic conductivity on the porosity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ film

CONCLUSIONS

$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ thick films were obtained by "tape casting" based on pre-synthesized nanoparticles and organic components. The speed of heating and isostatic lamination affect the porosity of the films. It is shown that the lowest porosity (17 %), respectively, the highest Li-ionconductivity at room temperature are achieved in the film, which is subjected to isostatic lamination and heat treating with speed of 20 °C/h.

Синтез плівок Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ зі структурою NASICON методом «tape casting»

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Вперше методом «tape casting» були синтезовані товсті плівки Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$, які кристалізуються в структуру NASICON. Плівкоутворюючий розчин був отриманий на основі попередньо синтезованих золь-гель методом наночастинок, які змішували з органічними реагентами. Плівки наносили на підкладки з α-Al$_2$O$_3$, піддавали їх ізостатичному пресуванню з наступною термообробкою. Дослідження структурних та морфологічних характеристик показало, що максимально щільна плівка досягається при малій швидкості нагріву (20 °C/год) та при дії ізостатичного ламінування, і її Li-йонна провідність становить 5.6·10^{-6} Ом$^{-1}$·см$^{-1}$.

Ключові слова: фосфат титану-алюмінію-літію Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$, структура NASICON, метод «tape casting», товсті плівки, ізостатичне ламінування, золь-гель метод

Синтез пленок Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ со структурой NASICON методом «tape casting»

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Впервые методом «tape casting» были синтезированы толстые пленки Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$, которые кристаллизуются в структуру NASICON. Пленкообразующий раствор был получен на основе предварительно синтезированных золь-гель методом наночастиц, которые смешивали с органическими реагентами. Пленки наносили на подложки из α-Al$_2$O$_3$, подвергали их изостатическому прессованию с последующей термообработкой. Исследование структурных и морфологических характеристик показало, что максимально плотная пленка достигается при малой скорости нагрева (20 °C/ч) и при воздействии изостатического ламинирования, и ее Li-ионная проводимость составляет 5.6·10^{-6} Ом$^{-1}$·см$^{-1}$.

Ключевые слова: фосфат титана-алюминия-лития Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$, структура NASICON, метод "tape casting", толстые пленки, изостатическое ламинирование, золь-гель метод

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