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Thin films of solid-phase amorphous electrolyte made from nitrogen-doped lithium metaphosphate with an increased ionic conductivity

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Thin ($1\,\mu$m) films of amorphous solid electrolyte were synthesized by anodic evaporation of $LiPO_3$ in Ar/N_2 plasma of a low-pressure (0.5 Pa) arc and vapor deposition on metal substrates at the rate of $0.5\,\mu$m/h under the conditions of a widely adjustable (from 0.1 to 0.9) fraction of free Li in vapor. Ionic conductivity of the films was shown to reach $1.7 \cdot 10^{-5}$ S/cm at room temperature.

Keywords: anodic evaporation, thin films, solid lithium-ion electrolyte.

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Lithium-ion electrolytes are widely used in up-to-date electrochemical devices because they possess a number of advantages, including a relatively wide range of operating voltages (0−8 V) and temperatures (from −20 to 300°C), high accumulated energy density (more than 250 W · h/kg), fast charging cycle (several A), low rate of charge dissipation ($\sim 5\%$ in the first 24 h and 1−3% within a month), high cyclic stability and resource ($\sim 10^4$ cycles) [1,2]. Transition from liquid electrolytes to an all-solid-state configuration allows overcoming a number of key problems induced by the growth of lithium dendrites, electrolyte corrosiveness, insufficient safety of the battery, and makes it possible to reduce the weight and size of devices. A great attention is attracted by amorphous films of solid-phase electrolytes having isotropic properties and characterized by the absence of porosity and grain-boundary resistance to ionic conductivity, low level of internal stress, and low cost. The main representative of this class of electrolytes is lithium phosphorus oxynitride (LiPON) obtainable by substituting with nitrogen a part of oxygen atoms in the Li_3PO_4 structure [3]. Despite the fact that LiPON has specific ionic conductivity ($\sim 2 \cdot 10^{-6}$ S/cm at 25°C) greater than that of its crystalline analogue, it is inferior in this characteristic to a number of perovskites, sulfides and electrolytes with the garnet structure [4]. To improve the properties of amorphous films, optimal synthesis conditions [5] and compositions ensuring high mobility of lithium ions are being searched for.

The goal of this study was to obtain thin films of solid amorphous lithium-conducting electrolyte with ionic conductivity exceeding that of LiPON. As the base material for synthesizing the films, there was chosen lithium metaphosphate ($LiPO_3$) having phosphate chains shorter than in the case of Li_3PO_4 [6] and polar structural chemical units [7] able to provide a higher diffusion rate of lithium ions; this is a prerequisite for obtaining thin films of solid electrolyte with a modified structure characterized by an increased ionic conductivity. As shown by theoretical analysis, nitridation of $LiPO_3$ is accompanied by an increase in ionic conductivity as in the case of LiPON [8].

Films of nitrogen-doped lithium metaphosphate (LiPO3N) were synthesized at a rate of $\sim 0.5\,\mu$m/h by anodic evaporation in a low-pressure arc [9] in a wide range of varying the free Li fraction in vapor. The vapor pressure (evaporator heating power) was kept constant, while the frequency of interaction with the electron vapor fed from the discharge plasma was controlled providing variations in the vapor dissociation degree. Schematic diagram of the film deposition device is presented in Fig. 1. The discharge was maintained between the self-heating hollow cathode (SHC) *1*, crucible *2* and rod electrodes *3* being under the anode potential. Working gas consisting of Ar and N_2 in the ratio of 1:5 was fed through the cathode hollow. The crucible heating by electrons accelerated in the layer of the anodic potential drop was accompanied by melting and evaporation of base compound $LiPO_3$. In the initial state, the weighed samples to be evaporated were glasses obtained by quenching the melt under laboratory conditions. Interaction of the $LiPO_3$ vapor with discharge plasma gives rise to free Li atoms. The highest-intensity line in the vapor-gas plasma optical emission spectra measured with a high-resolution spectrometer HR4000 (OceanOptic) is the Li I line (670.8 nm). No lines corresponding to O, P or their compounds were detected.

Previous studies have shown that properties of the LiPON solid electrolyte films obtained by anodic evaporation of Li_3PO_4 in the low-pressure arc depend significantly on the vapor decomposition degree[10]. In the experiments on synthesizing the LiPO3N films, the free lithium fraction in the vapor-gas plasma was controlled by varying the main discharge electron current in the crucible circuit from 0 to 12 A. Constancy of the crucible heating power was provided by controlling the auxiliary discharge current supported by emission of directly heated cathode *4* and isolated from the main discharge gap by screen *5*. To determine the free lithium fraction in vapor, the optical actinometry method was used[11].

LiPO3N films were deposited on polished substrates *6* $20 \times 20 \times 2$ mm in size made from steel 12X18H10T. The substrates were cleaned with acetone in an ultrasonic bath and placed in a vacuum chamber evacuated to ~ 1 mPa. Ion etching of the substrate surfaces was performed in the Ar-plasma of discharge maintained between SHC and rod anodes with the current density of 1ṁA/cm^2 and ion energy of -500 eV. The crucible was heated to operating temperatures in the auxiliary discharge plasma, shutter *7* being closed. The films were deposited during 2 h at the gas pressure of 0.5 Pa and discharge current between the SHC and rod anodes of 10 A. Those parameters were fitted empirically and provided the optimal film deposition mode ensuring a uniform microstructure and high ionic conductivity of the films. The ionic conductivity was evaluated by impedance spectroscopy in symmetrical electrochemical cells. The top contact layers made from steel 12X18H10T were applied on the LiPO3N film surfaces by magnetron sputtering. The measurements were performed by using potentiostat/galvanostat R-45X (Electro Chemical Instruments) in the frequency range of 1 Hz$-$0.3 MHz at the voltage amplitude of 0.15 V. Nyquist diagrams were analyzed using the ZView code.

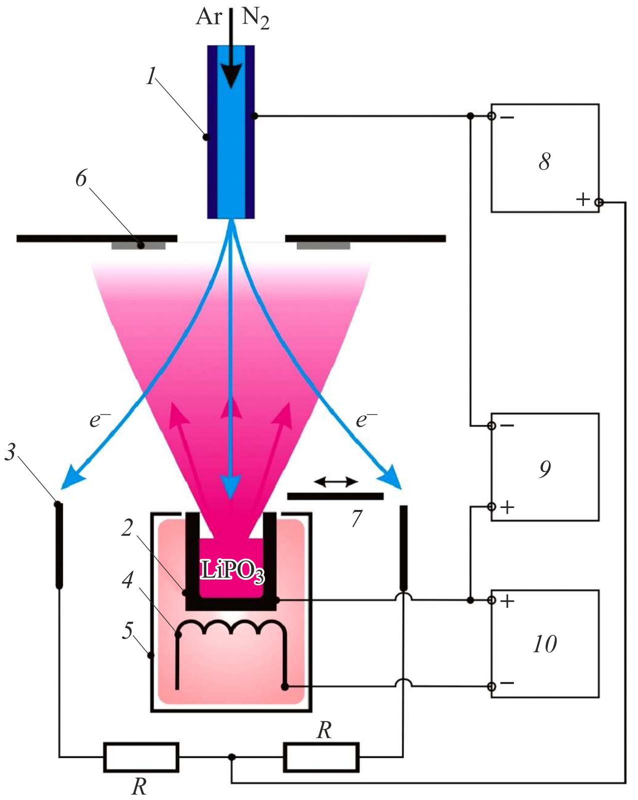

Figure 1. Schematic diagram of the film-deposition setup. *1* — self-heating hollow cathode, *2* — crucible, *3* — rod anodes, *4* — directly-heated cathode, *it 5* — screen, *6* — substrates, *7* — shutter, *8–10* — power supplies.

Fig. 2, *a* presents the Nyquist diagram for a $\sim 1\,\mu$m thick sample of the LiPO3N film. The semicircle in the high— and medium-frequency region represents the response from the electrolyte whose resistance R_e is determined by the point of the semicircle intersection with the axis of real impedance component Z'. The low-frequency linear section is due to the presence of a double electrical layer that gets formed on the interface between the electrolyte and contact electrode and is characterized by high values of electrical capacitance and active resistance. Room-temperature LiPO3N film ionic conductivity determined via relation $\sigma = l/(R_e A)$ (where l is the electrolyte thickness, A is the contact area) was $\sim 1.7 \cdot 10^{-5}$ S/cm. Resistance of the 1 mm thick glassy sample of initial compound LiPO$_3$ was $\sim 3.5 \cdot 10^7\,\Omega$ (Fig. 2, *b*), which matched the ionic conductivity of $\sim 10^{-9}$ S/cm.

The results of studying the effect of the free Li fraction in vapor on ionic conductivity of the LiP(O,N)$_3$ films are demonstrated in Fig. 3. An increase in the main discharge electron current to the crucible from 0 to 7 A was accompanied by an increase in the free Li fraction from ~ 0.1 to 0.9. The further increase in the current does not induce significant variations in the free Li fraction. The maximum in film ionic conductivity dependence on the main discharge current to the crucible takes place at the greatest free Li fraction in vapor. Films obtained by deposition from a vapor-gas medium with the lowest free Li fraction (~ 0.1) had ionic conductivity of $0.6 \cdot 10^{-5}$ S/cm, while the maximum ionic conductivity $\sim 1.7 \cdot 10^{-5}$ S/cm got reached at the current of 7.5 A.

Thus, using the method of anodic evaporation of lithium metaphosphate in the low-pressure arc Ar/N$_2$ plasma, there have been obtained thin films of a solid electrolyte whose ionic conductivity is an order of magnitude higher than that of the nitrogen-doped lithium orthophosphate (LiPON) films [2,10]. Estimates made by using the method given in [12] demonstrate that variation in ionic conductivity depending on the main discharge current to the crucible correlates with variation in the Li cations concentration, while the ion mobility decreases monotonically. Results of theoretical research [13] show that ionic conductivity of lithium phosphorus-oxynitrides is most significantly affected by the following factors: 1) nitrogen concentration in bridge bonds between phosphate structural and chemical units reducing electrostatic interaction of Li$^+$ with anions; 2) excess Li causing not only an increase in the number of mobile charge carriers, but also an increase in the number of short-distance Li$-$Li interactions, which can promote an increase in energy of Li positions as well as in ion mobility; 3) emergence of isolated O^{2-} anions as a result of oxygen substitution with nitrogen and introduction of excess Li. The last factor has a negative effect on the mobility of Li cations and contributes to a decrease in ionic conductivity of films synthesized at elevated nitrogen pressures and excess Li concentration in the flow of deposited particles. The complex character of variations in ionic conductivity of the LiPO3N films synthesized in this work indicates complex structural modifications of the electrolyte.

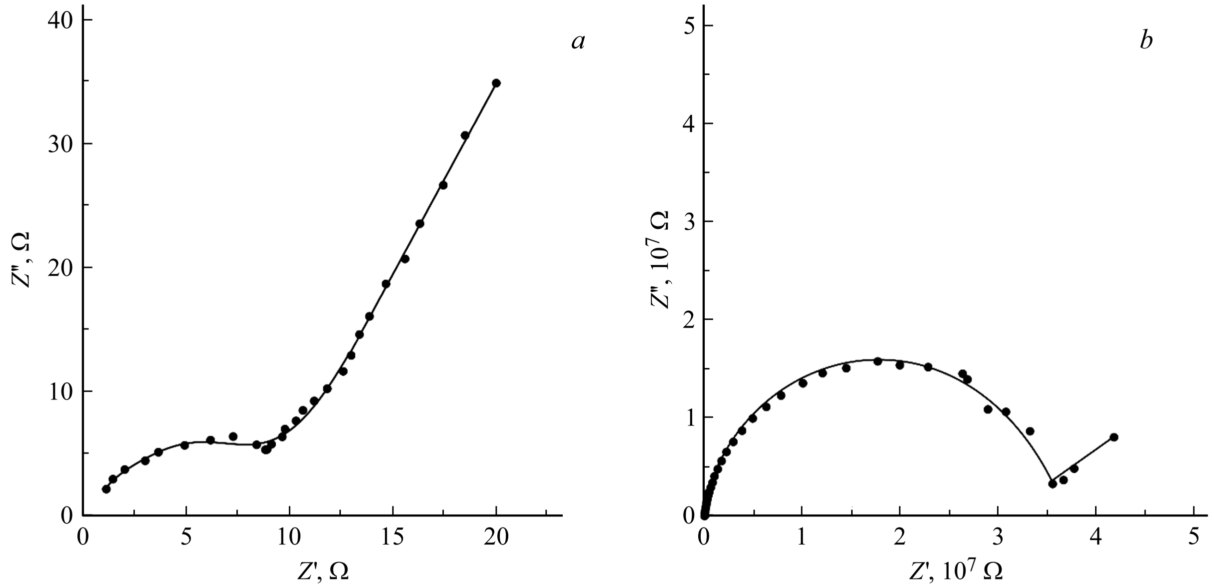

Figure 2. Nyquist diagrams of the LiPO3N (*a*) and glass $LiPO_3$ (*b*) films.

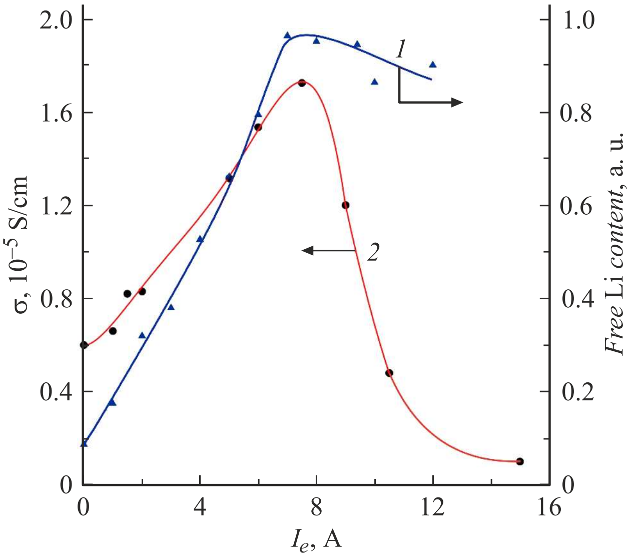

Figure 3. Free lithium fraction in vapor (*1*) and ionic conductivity of the $LiP(O,N)_3$ films (*2*) versus the main discharge current to the crucible.

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Conflict of interests

The authors declare that they have no conflict of interests.

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