Russian Journal of Applied Chemistry, Vol. 77, No. 6, 2004, pp. 915–920. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 6, 2004, pp. 929–934.
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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Synthesis and Ionic Conductivity of Lithium-conducting Titanium Phosphate Solid Electrolytes

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Received March 28, 2003; in final form, September 2003

Abstract—Solid electrolytes were synthesized in the systems $Li_2O–Al_2O_3–TiO_2–P_2O_5$ and $Li_2O–Al_2O_3–TiO_2–P_2O_5–H_2O–H_2O_2$. Their ionic conductivities were studied and compared. The possibility of obtaining a film of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid electrolyte on a sapphire substrate from an aqueous peroxide solution of a precursor was analyzed.

To be suitable for practical application in chemical power cells or secondary batteries, a solid electrolyte must primarily have the maximum ionic conductivity, so that potential drop across the internal resistance of a cell be much lower than its working voltage. Presently, only few lithium-based solid electrolytes with a room-temperature ionic conductivity on the order of 10^{-3} Cm cm^{-1} are known [1]. These are, in the first place, lithium analogues of nasicons, compounds based on double lithium and titanium phosphates, in which some Ti^{4+} cations are replaced with In^{3+}, Sc^{3+} or Al^{3+} cations.

An important requirement to the solid electrolytes of lithium power cells is their high chemical stability when in contact with cathode and anode materials. In this case, it is necessary to take into account that metallic lithium or lithium alloys used as anode are rather chemically active. The known solid electrolytes based on double lithium and titanium phosphates are chemically unstable at elevated temperatures because of the interaction of metallic lithium with titanium phosphate [2]. Hence follows that, to enhance the chemical stability of this type of solid electrolytes, it is necessary to decrease the content of titanium and phosphate groups in them.

Previously [3], $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid electrolytes have been synthesized by the ceramic method. However, this technique has some drawbacks limiting its application in the cases of increased requirements to the stability and reproducibility of properties of the materials. These drawbacks are due to the mechanism of solid-state reactions, which occur originally at the interface and then continue owing to the diffusion of atoms across a layer of the products formed. In the course of a reaction, the diffusion length increases and the reaction rate decreases. The ceramic process can commonly come to sufficiently full completion only in the case of an intermediate multiple grinding of the reaction mass. But even then, the required chemical and structural homogeneity of the product cannot be always achieved. To overcome the above difficulties, various modifications of the ceramic method, based on a number of procedures for preliminary homogenization down to the molecular level of the solid-phase reaction mixture, have been suggested. These are coprecipitation of components from solutions, drying of solutions by spraying, pulverization of the solutions into liquid nitrogen (cryochemical method), or sol–gel procedure. The sol–gel method shows promise for synthesis of lithium-based solid electrolytes [4].

The goal of this study was to search for ways to raise the ionic conductivity and chemical stability of phosphate lithium-conducting solid electrolytes in the solid-phase and sol–gel syntheses.

EXPERIMENTAL

As starting reagents were used Li_2CO_3 (special purity); $LiNO_3$ (analytically pure); $Al(NO)_3 \cdot 9H_2O$,

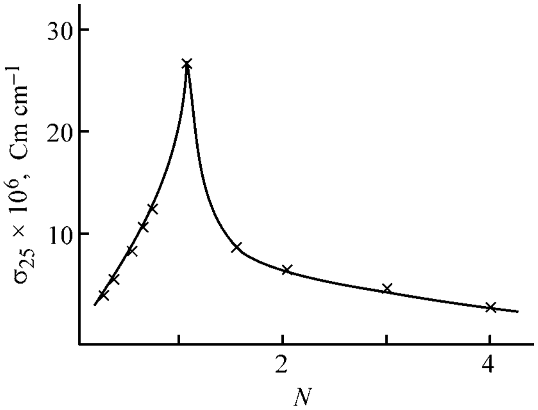


Fig. 1. Ionic conductivity σ_{25} of double lithium and titanium phosphates vs. Li_2O : TiO_2 molar ratio *N*.

Al_2O_3, and $(NH_4)_2HPO_4$ (all chemically pure); TiO_2 (special purity); and $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (chemically pure). Freshly precipitated titanium(IV) hydroxide was obtained by dissolving a weighed portion of titanium(IV) oxide of the anatase modification in hydrofluoric acid. The resulting acid fluoride solution was heated to 50–60°C and added in small portions to a 25% solution of ammonium hydroxide under vigorous agitation. The precipitated amorphous titanium(IV) hydroxide was washed with a 5% NH_4OH solution to remove fluoride ions by repulping. The content of the F^{-1} ions was controlled potentiometrically using a Kh-F-001 fluoride-selective electrode. The content of the F^{-1} ions in the washing water from the final repulping was 10 mg l^{-1} and less.

The method for determining the ionic conductivity σ_{25} (at 25°C) of the samples of lithium-conducting solid electrolytes has been described in detail previously [5]. The measurements were done on an E7-12 digital LCR-meter at a frequency of 1 MHz in a cell with graphite electrodes on several pellets of different heights. For samples of the same composition, the σ_{25} values were reproduced to within ±5%.

Table 1. Ionic conductivity of $Li_{2+x}Al_xTi_{1-x}(PO_4)_2$ and $Li_{2-3x}Al_xTi_{1-x}(PO_4)_2$ solid solutions

Solution	Composition	σ_{25}, Cm cm^{-1}
(I)	$Li_2Ti(PO_4)_2$	2.7×10^{-5}
	$Li_{2.1}Al_{0.1}Ti_{0.9}(PO_4)_2$	1.3×10^{-4}
	$Li_{2.2}Al_{0.2}Ti_{0.8}(PO_4)_2$	3×10^{-5}
	$Li_{2.3}Al_{0.3}Ti_{0.7}(PO_4)_2$	2.3×10^{-5}
(II)	$Li_2Ti(PO_4)_2$	2.7×10^{-5}
	$Li_{1.7}Al_{0.1}Ti(PO_4)_2$	2.7×10^{-4}
	$Li_{1.4}Al_{0.2}Ti(PO_4)_2$	5.4×10^{-4}
	$Li_{1.1}Al_{0.3}Ti(PO_4)_2$	5.6×10^{-4}
	$Li_{0.8}Al_{0.4}Ti(PO_4)_2$	2.5×10^{-4}

The electronic conductivity σ_e was determined by the polarization Wagner method in a cell with irreversible graphite electrodes. A voltage lower than the voltage of electrolyte decomposition was applied to the measuring cell and the current in the circuit was measured with a U5-11 charge amplifier [6].

The phase composition of the products synthesized was studied by X-ray phase analysis (DRON-2 diffractometer, Cu_{K_α} radiation, graphite monochromator).

The base component of the known lithium-conducting solid electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ is double phosphate $LiTi_2(PO_4)_3$ with the molar ratio Li_2O : TiO_2 = 1 : 4. No data for double lithium and titanium(IV) phosphates with other molar ratios are available.

The synthesis of double lithium and titanium(IV) phosphates and the measurement of their ionic conductivity were performed at the Li_2O : TiO_2 ratio in the range from 1 : 4 to 4 : 1. These compounds were synthesized by the ceramic method [3] at the temperature of the final sintering stage equal to 800–1000°C, depending on composition. The results obtained in a study of σ_{25} of the samples obtained are presented in Fig. 1. It can be seen that the optimal composition is obtained at Li_2O : TiO_2 = 1 : 1 and corresponds to chemical formula $Li_2Ti(PO_4)_2$. The generally accepted composition $LiTi_2(PO_4)_3$ is unremarkable.

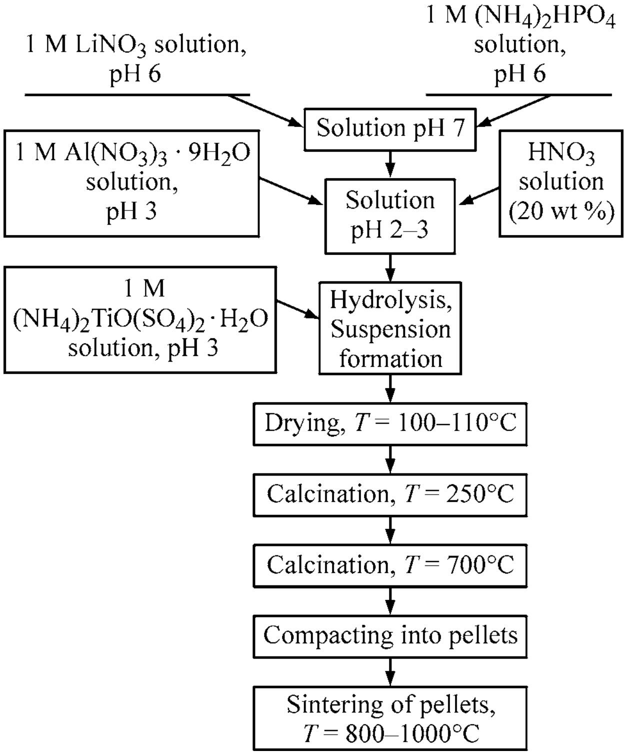
To study the influence exerted on the ionic conductivity by the $Ti^{4+} \rightarrow Al^{3+} + Li^+$ heterocharge substitution, experiments on the synthesis of $Li_{2+x}Al_xTi_{1-x}(PO_4)_2$ solid solutions were performed. The results presented in Table 1 show that such a substitution results in an increase in the ionic conductivity only at $x = 0.1$.

Because the composition $Li_2Ti(PO_4)_2$ is characterized by relatively high concentration of lithium ions, it was appropriate to perform the heterocharge substitution $3Li^+ \rightarrow Al^{3+}$. The data of Table 1 show that this type of heterocharge substitution considerably increases the ionic conductivity in the range $0.1 \le x \le 0.4$, with the ionic conductivity of the composition $Li_{1.1}Al_{0.3}Ti(PO_4)_2$ being the highest.

The results of experiments with mixed heterocharge substitution, i.e, with joint occurrence of $Ti^{4+} \rightarrow Al^{3+} +$

Li^+ and $3Li^+ \rightarrow Al^{3+}$ processes, are listed in Table 2. It can be seen that the composition $Li_{1.4}Al_{0.2}Ti(PO_4)_2$, in which the Ti : Li and PO_4^{-3} ratios are 0.71 and 1.43, respectively, is the most promising from the standpoint of chemical stability. At the same time, for the generally accepted composition $Li_{1.3}Al_{0.3}Ti(PO_4)_2$, these ratios are 1.3 and 2.31.

The room-temperature electronic conductivity of $Li_{1.4}Al_{0.2}Ti(PO_4)_2$ is 3×10^{-8} Cm cm^{-1}. Its ionic conductivity linearly increases in the range 25–100°C from 5.4×10^{-4} to 8.1×10^{-4} Cm cm^{-1}.



Scheme of the sol–gel process.

The sol–gel synthesis of lithium-conducting phosphate solid electrolytes was performed using 1 M aqueous solutions of the starting reagents, $LiNO_3$, $Al(NO_3)_3$, $(NH_4)_2HPO_4$, and $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$, taken in stoichiometric amounts in accordance with the formula $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$. The process by which the solid electrolyte was synthesized is illustrated by the scheme. A neutral solution of $LiNO_3$ (pH 6) and a weakly alkaline solution of $(NH_4)_2HPO_4$ (pH 8) were poured together, and the acidity of the resulting solution was adjusted to pH 2–3 with a 20% solution of HNO_3. Then, $Al(NO_3)_3$ (pH 3) and $(NH_4)_2TiO(SO_4)_2$ (pH 1) solutions were successively poured-in under vigorous agitation. As a result, a white suspension was formed. The necessary condition was that the pH value was preliminarily adjusted to pH 2–3. Otherwise, crystalline quick-settling precipitate appeared in the solution instead of a suspension. The suspension obtained was poured onto a fluoroplastic pan, evaporated, and dried at 100–110°C for 8 h. As a result, a precursor of the solid electrolyte was formed as a loose bulky powder.

Table 2. Ionic conductivity of $Li_2Ti(PO_4)_2$-based solid solutions with a mixed heterocharge substitution

Composition	σ_{25}, Cm cm^{-1}
$Li_{0.9}Al_{0.1}Ti_{1.2}(PO_4)_2$	1.4×10^{-4}
$Li_{1.0}Al_{0.2}Ti_{1.1}(PO_4)_2$	6.2×10^{-4}
$Li_{1.1}Al_{0.3}Ti(PO_4)_2$	5.6×10^{-4}
$Li_{1.2}Al_{0.4}Ti_{0.9}(PO_4)_2$	2.4×10^{-4}
$Li_{1.3}Al_{0.1}Ti_{1.1}(PO_4)_2$	4.2×10^{-4}
$Li_{1.4}Al_{0.2}Ti(PO_4)_2$	5.4×10^{-4}
$Li_{1.5}Al_{0.3}Ti_{0.9}(PO_4)_2$	1.4×10^{-4}
$Li_{1.8}Al_{0.2}Ti_{0.9}(PO_4)_2$	1.1×10^{-4}

To obtain the final product, the precursor was calcined. The temperature mode and calcination time were determined from the results of thermal and X-ray phase analyses. According to the thermal analysis, the weak endothermic effects exhibited by the electrolyte precursor (Fig. 2) at temperatures of up to 158°C are due to removal of water. The exothermic effect at 254–293°C is associated with the interaction of $LiNO_3$ and $(NH_4)_2HPO_4$, with evolution of nitrogen oxides and $NH_3 \cdot (NH_4)_2TiO(SO_4)_2$ decomposes within the range 400–700°C. At higher temperatures, no thermal effects or mass loss was observed. There-

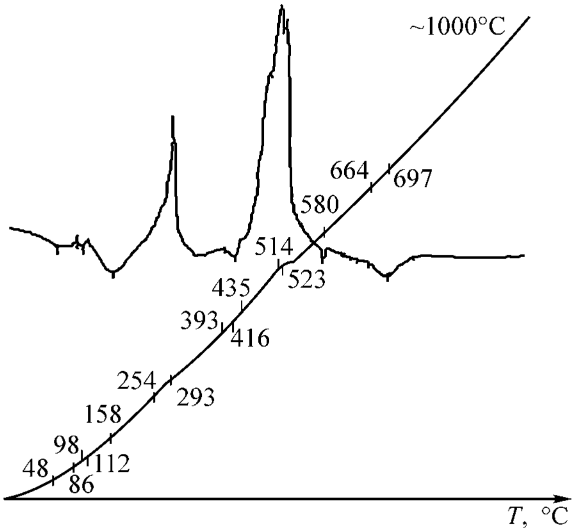


Fig 2. Thermogram for a precursor of lithium-conducting solid electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$. ($T$) Temperature.

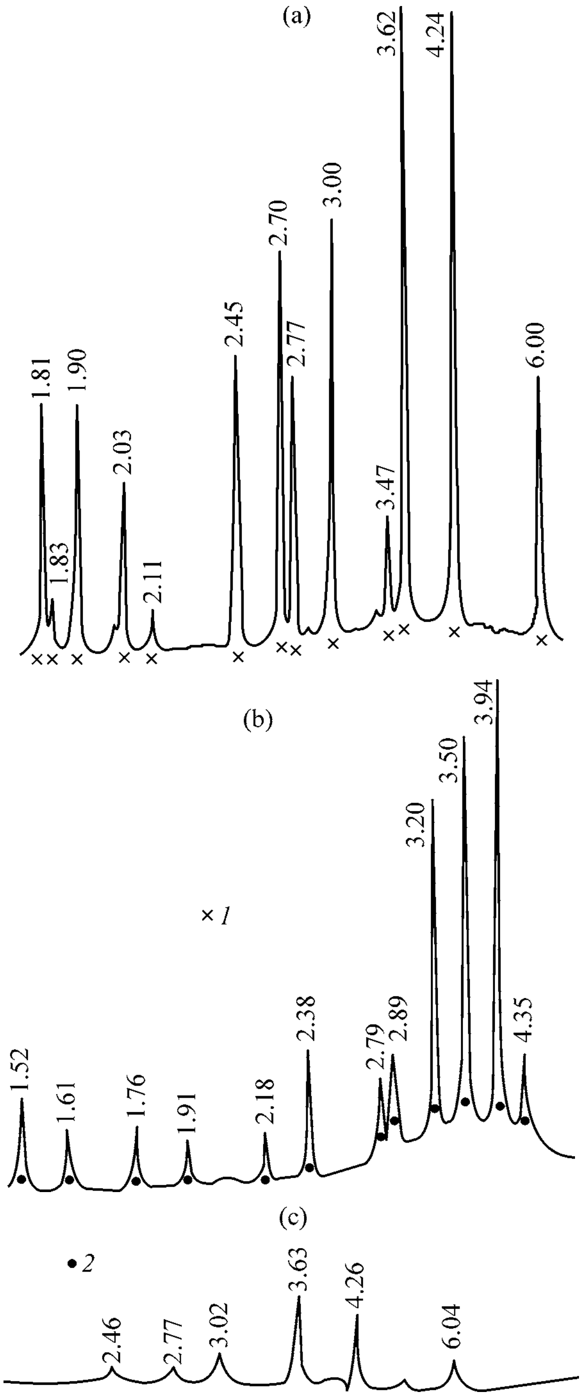


Fig. 3. Diffraction patterns of (a) lithium-conducting solid electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, (b) product of a synthesis of solid electrolyte with a 1.5-fold excess of H_3PO_4, and (c) $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ film on a sapphire substrate. (*1*) $LiTi_2(PO_4)_3$ and (*2*) TiP_2O_7.

fore, the temperature was raised stepwise to 700°C. The precursor powder was kept at 250°C for 1 h (till gas evolution stopped) in the first stage and at 700°C for 2 h in the second. The product obtained (bulky, loose, and easily disintegrating) was compacted into pellets 12 mm in diameter and 2–3 mm thick and sintered at 800–1000°C. The sintered pellets frequently separated into layers, cracked, and deformed. To improve sintering and avoid deformation of the pellets, a C_2H_5OH binder was introduced into the powder before compaction. The diffraction patterns of the electrolyte samples sintered at $T > 800°C$ contain only reflections associated with $LiTi_2(PO_4)_3$ (Fig. 3a). As follows from Table 3, the highest ionic conductivity $\sigma_{25} = 5 \times 10^{-4}$ Cm cm^{-1} is observed for the electrolyte sample sintered at 1000°C for a long time (7h).

In preliminary studies, we established that freshly precipitated titanium(IV) hydroxide satisfactorily dissolves in the form of a peroxide complex in an acid medium. To synthesize lithium-conducting solid electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, a freshly precipitated titanium(IV) hydroxide was dissolved in initial experiments in a mixture containing 40 vol % H_3PO_4 (acid concentration 85 wt %) and 60 vol % H_2O_2 (peroxide concentration 30 wt %). After stoichiometric amounts of aqueous solutions of $LiNO_3$ and $Al(NO_3)_3$ were added to the resulting titanium(IV) peroxide solution, a transparent solution (pH 0.7) of intense ruby color was formed. After evaporation of this solution at 150–160°C and subsequent drying of the precipitate at 300°C, a white powder was formed. The powder was compacted into pellets and sintered at 900°C for 1 h, with a mass loss of 35%. The sintered pellets were porous and could be easily broken. To obtain high-density pellets, sintering was performed at 1000°C for 1 h. It was found that the ionic conductivity is about 1×10^{-7} Cm cm^{-1}, i.e., is lower by three orders of magnitude than the predicted value. Additional sintering at 1200°C did not affect σ. According to XPA, the diffraction pattern of the product synthesized contains no reflections corresponding to $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (Fig. 3b), with the main reflections belonging to titanium diphosphate TiP_2O_7. Apparently, titanium(IV) polyphosphates, which do not decompose even at high temperature, are formed owing to excess content of H_3PO_4 in the initial solution.

In this connection, HNO_3 was used for obtaining an acid medium in dissolution of a freshly precipitated titanium(IV) hydroxide. The freshly precipitated titanium(IV) hydroxide was dissolved in a mixture containing 70 vol % HNO_3 (65 wt % concentration) and 30 vol % H_2O_2 (30 wt % concentration). To the resulting solution, stoichiometric amounts of aqueous solutions of $LiNO_3$, $Al(NO_3)_3$, and H_3PO_4 were added under agitation. The resulting aqueous peroxide solution of ruby color was transparent and contained 160–170 g l^{-1} of the final product. Evaporating the solution in a desiccator at 150–160°C yielded a white powder, which was sintered at 900°C for 1 h with a mass loss of 31%. The powder was compacted into pellets and sintered at 1000°C for 1 h. The ionic conductivity of the sintered pellets was 6×10^{-4} Cm cm^{-1}, which coincides with the conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ samples obtained by the solid-phase synthesis. The electronic conductivity did not exceed 2×10^{-8} Cm cm^{-1}.

The scheme described was used to synthesize $Li_2Ti(PO_4)_2$ solid electrolyte and a number of electrolytes on its basis. The ionic conductivities of the samples synthesized are listed in Table 4.

It can be seen that the ionic conductivities of the samples obtained by two methods are virtually the same.

The main advantage of the method developed for preparing stable aqueous peroxide solutions in the $Li_2O–Al_2O_3–TiO_2–P_2O_5–H_2O–H_2O_2$ system consists in the possibility of using such solutions for obtaining thin films of solid electrolytes. Aqueous peroxide solution of a precursor of the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ electrolyte, which contained glycerol as a film-forming agent, was used to deposit films onto substrates by "dipping" method.

A solution containing (per 100 ml) 12 g of a precursor of the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid electrolyte and 5 ml of glycerol was stable (i.e., retained transparency and homogeneity) for seven days. To apply a film, the substrate was dipped into a solution and then withdrawn at a rate of 0.6 cm min^{-1}, dried in air, annealed at 450°C for 15 min, and cooled to room temperature. Then the solution was applied to the substrate again, only with the sample annealed at 850°C for 30 min this time. The existence of the film was confirmed by visual observation under a Neophot-2 microscope (magnification 200). An X-ray phase analysis showed that four relatively weak reflections (6.04, 4.26, 3.63, and 3.02 Å), which are characteristic of a powder-like electrolyte, are present in the diffraction pattern of the film obtained (Fig. 3c). The study performed demonstrated that dipping is a suitable method for obtaining on appropriate substrates films of lithium-conducting titanium phosphate solid electrolytes, which are promising for fabrication of thin-film chemical power cells.

CONCLUSIONS

(1) A study of the ionic conductivity of solid electrolytes obtained by the solid-phase method in the $Li_3PO_4–Ti_3(PO_4)_4$ system established that the maximum conductivity ($\sigma_{25} = 2.7 \times 10^{-5}$ Cm cm^{-1}) is observed for the composition $Li_2Ti(PO_4)_2$. The $Li_{1.4}Al_{0.2}Ti(PO_4)_2$ solid electrolyte with $\sigma_{25} = 5.4 \times 10^{-4}$ Cm cm^{-1} and the Ti : Li and PO_4^{3-} : Li molar ratios of 0.71 and 1.43, respectively, was obtained upon heterocharge substitution of some Li^+ ions for Al^{3+} ions in this compound. The same ratios for the generally accepted composition $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ are 1.3 and 2.31.

Table 3. Ionic conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ at different conditions of pellet sintering

T_{sin}, °C	τ_{sin}, h	h_{tab}, cm	σ_{25}, Cm cm^{-1}
800	2	0.227	4×10^{-5}
	4	0.181	1.1×10^{-4}
900	2	0.130	3.9×10^{-4}
	7	0.118	3.8×10^{-4}
1000	2	0.428	3.8×10^{-4}
	7	0.427	5.0×10^{-4}

Table 4. Ionic conductivity of $Li_2Ti(PO_4)_2$-based solid electrolytes

Composition	σ_{25},* Cm cm^{-1}
$Li_{1.1}Al_{0.3}Ti(PO_4)_2$	4.8×10^{-4} (5.6×10^{-4})*
$Li_{1.4}Al_{0.2}Ti(PO_4)_2$	4.5×10^{-4} (5.4×10^{-4})
$Li_{1.6}Al_{0.2}Ti(PO_4)_2$	2×10^{-4}
$Li_2Ti(PO_4)_2$	1×10^{-4} (1×10^{-4})

* The σ_{25} values for samples obtained by solid-phase method are given in parentheses.

(2) A method for obtaining stable aqueous peroxide solutions of precursors of solid electrolytes in the $Li_2O–Al_2O_3–TiO_2–P_2O_5–H_2O–H_2O_2$ system was developed. It was established that the solid electrolytes obtained from these solutions compare well in the ionic conductivity with electrolytes synthesized by the solid-phase method.

(3) It was shown that aqueous peroxide solutions of precursors are suitable for obtaining films of lithium-conducting titanium phosphate solid electrolytes on appropriate supports, which are promising for fabrication of thin-film chemical power cells.

ACKNOWLEDGMENTS

The study was financially supported in part by the "New Principles and Methods of the Development and Directional Synthesis of Substances with Prescribed Properties" Integrated Program of the Presidium of the Russian Academy of Sciences.

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