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Sol-gel synthesis and determination of optimal sintering conditions of the $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte

E A Il'ina¹, E D Lyalin^{1,2}, B D Antonov¹, A A Pankratov¹

¹ Institute of High-Temperature Electrochemistry of Ural Branch of the Russian Academy of Sciences, 20 Akademicheskaya st., 620137, Ekaterinburg, Russia

² Ural Federal University named after the first President of Russia B.N. Yeltsin, 19 Mira st., 620002, Ekaterinburg, Russia

Abstract. Solid electrolytes are widely used in electrochemical devices. Among these materials, electrolytes with the lithium-ion conductivity can be used in high-energy lithium and lithium-ion power sources. The perspective $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte was synthesized by modified sol-gel synthesis method using the sparingly soluble Nb_2O_5 as one of the initial compounds. The influence of pressure and final sintering temperature on phase composition, density and lithium-ion conductivity was studied. Solid electrolyte obtained at 1150°C was single phase and had a cubic structure with the space group *Ia-3d*. Thus in the presented work, the cubic modification of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ was obtained by thermal treatment for 1 h at 1150°C (versus 36 h at 1200°C in the literature). Moreover at this temperature the samples had the highest density and total lithium-ion conductivity ($3.9 \cdot 10^{-5} \text{ S cm}^{-1}$ at 25°C). According to the SEM study ceramic samples have a dense structure with a particle size ~1-3 μm. Solid electrolyte was also obtained by isostatic pressing at a pressure of 500 MPa but the values of density and total lithium-ion conductivity were comparable with that of the samples compressed statically.

1. Introduction

Energy has an important role in many aspects of human life. The increase in population and the aspiration for higher living standards leads to the growth in the necessity of high-energy power sources. Solid electrolytes with a garnet-like structure are promising electrolyte materials among lithium-conducting ones for using in high-energy lithium and lithium-ion power sources, including perspective all-solid-state batteries [1-4]. The $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ compounds (M = Ta, Nb) with a cubic structure and ionic conductivity of $\sim 10^{-6} \text{ S cm}^{-1}$ at 25°C are the first examples of superionic conductors having the garnet-like structure [5]. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) compound was synthesized by the Weppner's group [6] in 2007 and it has been actively studied during the last decade. The main advantages of the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ are the electrochemical stability versus metallic lithium and high lithium-ion conductivity of the cubic modification at room temperature ($\sim 10^{-4} \text{ S cm}^{-1}$) [6]. This compound also has a tetragonal modification, but its conductivity is much lower $\sim 10^{-6}$ - $10^{-7} \text{ S cm}^{-1}$ at 25°C [7]. The highly conductive cubic modification can be stabilized by doping LLZ with Al, Sc, Y, Nb or other elements [1]. The synthesis of electrolytes based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with the perspective addition of Nb is carried out using a solid-phase method with an exposure at high temperatures for a long time (for example, at 1200°C for 36 h [8]). It was established by S. Ohta et al [8] that $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte had the highest lithium-ion conductivity in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ – $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ system.



However it is widely known that the synthesis by the sol-gel method leads to the production of ceramics with a smaller particle size which allows to obtain a final product with higher values of electrical conductivity as well as to reduce the temperature and sintering time of ceramic membranes [9]. For example, in work [10], the sol-gel synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ doped with aluminum and molybdenum ions made it possible to effectively reduce the sintering temperature of ceramics, as well as increasing its ionic conductivity and density. In [11] an attempt of the sol-gel synthesis at low temperatures (700°C) of the solid electrolyte $\text{Li}_7\text{La}_3(\text{Zr}_{2-x}\text{Nb}_x)\text{O}_{12}$ using $\text{Nb}(\text{OC}_2\text{H}_5)_5$ was made, however, high conductivity values of ceramics were not achieved ($10^{-7} \text{ S cm}^{-1}$ at room temperature) and the conditions for its preparation were not selected. In this work the modified sol-gel synthesis method of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte using the sparingly soluble niobium oxide as one of the initial compounds was developed. Moreover, the optimal sintering conditions for dense ceramic membranes were studied.

2. Experimental

Li_2CO_3 , La_2O_3 , Nb_2O_5 and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were used as starting components for sol-gel synthesis of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$. Lanthanum and niobium oxides were pre-dried at 1000°C to constant weight. The reagents were mixed in the stoichiometric ratio, except Li_2CO_3 , which was used with a 10 wt.% excess, as in Murugan R. et al [6]. These components were dissolved in the mixture of the dilute nitric and citric acids. Then Nb_2O_5 was added to prepared solution. The resulting solution was evaporated at 80°C to transparent gel. Then the gel was dried and pyrolyzed at $\sim 200^\circ\text{C}$. The synthesis was performed by increasing the temperature stepwise (from 700 to 900°C for 3 h). After each stage of the synthesis, the mixture of reagents was thoroughly ground in an agate mortar. The powdered samples were pressed into pellets at 240 MPa. The pellets were covered with powder of the same composition and then sintered at different temperatures (1000 , 1100 and 1150°C) for 1 h in an Air atmosphere. The densities of the obtained electrolytes were determined from geometrical parameters and mass of studied samples.

The synthesized samples were examined by X-ray diffraction method (XRD) with a Rigaku D-MAX-2200V diffractometer at the room temperature. A curved graphite crystal was used to monochromate $\text{Cu } K_\alpha$ -radiation. The data were collected over a 2θ range of 10 - 55° in continuous mode at a scan rate of 3° min^{-1} . The sample surface was investigated with a MIRA3 FEG scanning electron microscope (Tescan, USA).

Both sides of the annealed samples were painted with a gallium-silver paste as an electrode to conduct an AC impedance study. The impedance measurements were performed in air over a temperature range of 25 - 210°C and a frequency range of 0.025 - 1000 kHz using an immittance meter E7-25 (MNIPI, Belarus). This set-up used a two-probe cell with silver electrodes. The conductivity measurements were performed on several sets of samples to check the reproducibility of the results.

3. Result and discussion

The $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte was obtained at different sintering temperatures (1000 - 1150°C). According to the XRD analysis, the pattern reflections of the obtained electrolytes after their annealing at different temperatures corresponded to the cubic modification of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with the space group $Ia\bar{3}d$ [6] (figure 1). Samples obtained at 1000 and 1100°C have impurity $\text{La}_2\text{Zr}_2\text{O}_7$, while solid electrolyte synthesized at 1150°C is single phase. The increase in the sintering temperature from 1000 to 1150°C led to growth in the samples density from 3.1 to 3.8 g cm^{-3} .

The surface of the $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte obtained at 1150°C was studied by scanning electron microscopy (figure 2). It can be seen that the ceramic sample has a dense structure and consists of particles with an average size ~ 1 - $3 \text{ }\mu\text{m}$.

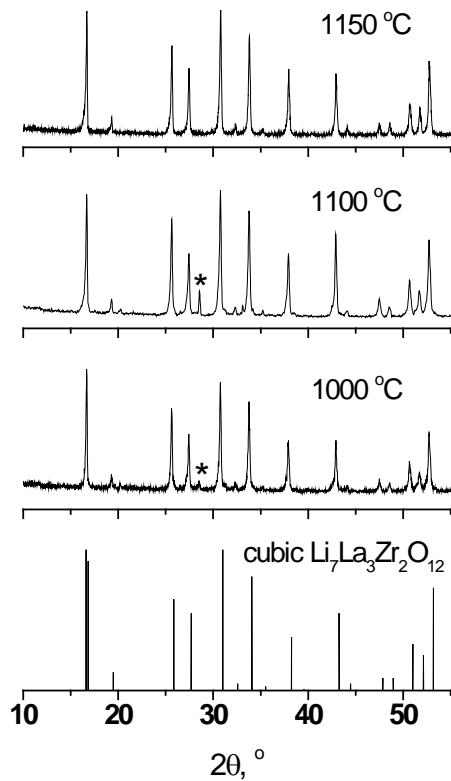


Figure 1. XRD patterns of the $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ obtained at different sintering temperatures. * — $\text{La}_2\text{Zr}_2\text{O}_7$.

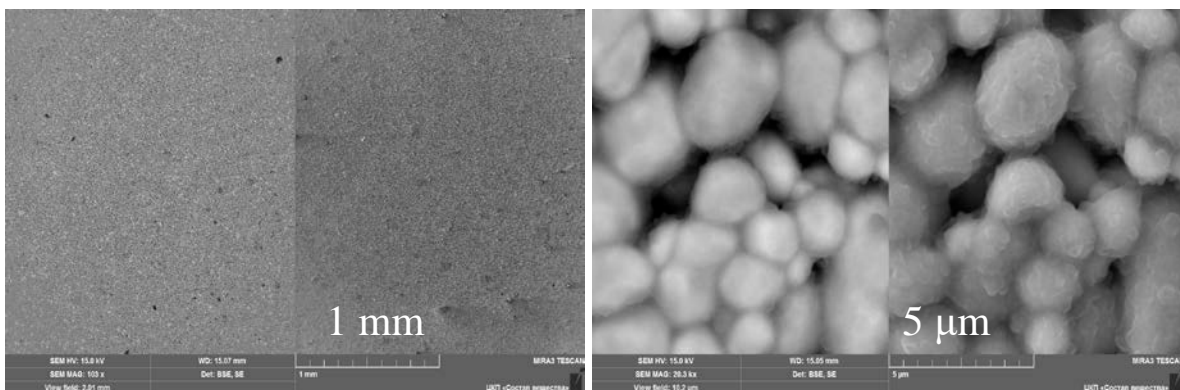


Figure 2. SEM micrographs of the surface of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte synthesized at 1150 °C.

The conductivity of the synthesized electrolyte was measured using impedance spectroscopy. The typical impedance plots of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte synthesized at different temperatures are presented in figure 3a. The impedance spectrum at room temperature may be separated into two semicircles. According [6], the high-frequency semicircle can be attributed to the bulk resistance R_b of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$, and the semicircle in the low-frequency range correlates with the grain-boundary resistance R_{gb} . The values of bulk and grain-boundary resistances and conductivities at 25 °C of studied solid electrolyte synthesized at different temperatures are presented in Table 1. It can be seen that the bulk σ_b and grain-boundary σ_{gb} conductivity increases with the growth of sintering temperature approximately one order of magnitude. Figure 3b shows the temperature dependences of the total conductivity in Arrhenius coordinates. In the examined

temperature range, the plots are linear. It can be seen that increasing in sintering temperature leads to total conductivity growth of studied solid electrolyte. The $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte obtained at 1150°C has the highest total conductivity — $3.9 \cdot 10^{-5} \text{ S cm}^{-1}$ at 25°C .

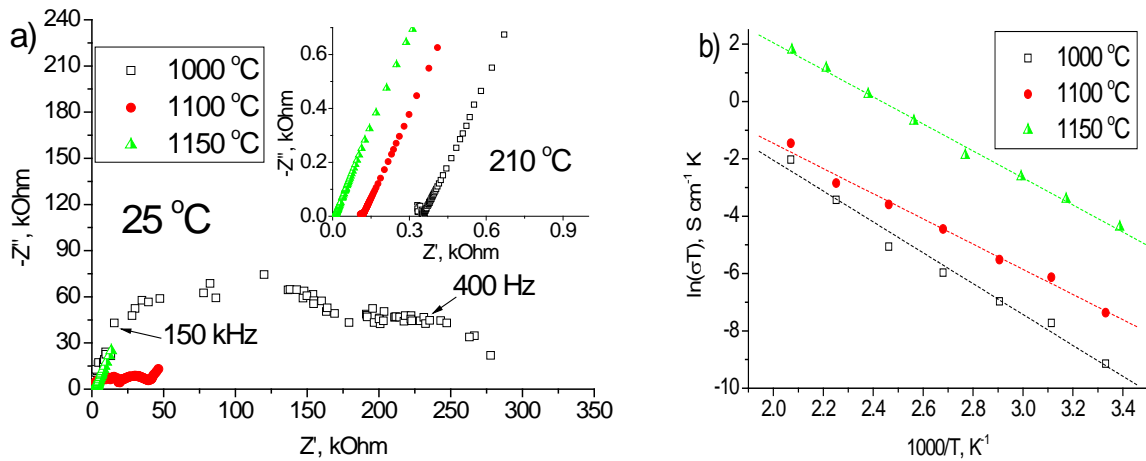


Figure 3. Impedance plots (a) and Arrhenius plots for total conductivity (b) of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolytes obtained at different temperatures.

Table 1. Bulk and grain-boundary resistance R_b , R_{gb} and conductivity σ_b , σ_{gb} at 25°C of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolytes obtained at different temperatures

$T, ^\circ\text{C}$	R_b, Ohm	R_{gb}, Ohm	$\sigma_b, \text{S cm}^{-1}$	$\sigma_{gb}, \text{S cm}^{-1}$
1000	183400	116600	$5.8 \cdot 10^{-7}$	$9.1 \cdot 10^{-7}$
1100	43200	36800	$3.9 \cdot 10^{-6}$	$4.6 \cdot 10^{-6}$
1150	1920	1400	$6.6 \cdot 10^{-5}$	$9.1 \cdot 10^{-5}$

The $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ was also obtained by isostatic pressing at a pressure of 500 MPa as optimal for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [12]. The obtained solid electrolytes were sintered at 1150°C because at this temperature the samples had the highest density and total conductivity. However, the density and total conductivity of the sample obtained by isostatic pressing is comparable with that of the sample compressed statically.

4. Conclusions

In this work the modified sol-gel synthesis method of solid electrolytes based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ using the sparingly soluble niobium oxide as one of the initial compounds was developed.

The obtained $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte synthesized at 1150°C had cubic structure $Ia-3d$ and was single phase. The total lithium-ion conductivity growth for $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ solid electrolyte from $3.6 \cdot 10^{-7}$ to $3.9 \cdot 10^{-5} \text{ S cm}^{-1}$ at 25°C sintered for 1 h at 1000 and 1150°C respectively was observed.

The $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ was also obtained by isostatic pressing at the pressure of 500 MPa but the density and conductivity of the solid electrolyte obtained by isostatic pressing is not change significantly.

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