

PROMISING SOLID AMORPHOUS ELECTROLYTE WITH LITHIUM-ION CONDUCTIVITY BASED ON $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3$ SYSTEMS

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Solid electrolytes with the structure of glasses in the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3$ are well-studied [1,2]. At the same time electrolyte ion conductivity in the system is investigated only for the composition comprising 30 and more mol. % of boron anhydride [2]. Results of the NMR system analysis have shown that with the content of 70 and more mol. % of R_2O ($\text{R}=\text{Li, K, Na}$) in their compositions boron cations are only in a three-coordination state [3]. Alkali metal cations in such glasses are connected with non-bridge oxygen anion, i.e. they are in a dissociate state. Taking into account this fact we can suppose that the glasses in the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3$ comprising less than 30 mol. % B_2O_3 should have increased lithium ion conductivity. However, stabilization of a glassy state of these glasses is a complicated technological problem.

Necessity of this investigation was caused by lack of the information about the properties of solid electrolytes in the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3$ since in the earlier works the following problems have not been studied:

1) Technological peculiarities of the synthesis of glasses with Li_2O content up to 70 mol. % (composition of raw materials, medium, etc);

2) Ion and electronic conductivity of solid electrolytes with the structure of glasses with a high content of lithium oxide (up to 70 mol. %) at room temperature (in [1] there is a remark only about the conductivity values of such electrolytes at the temperature at least 180°C) and its interconnection with the chemical composition of glasses.

The work is aimed at the development of solid electrolyte based on the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3$ with a high content of lithium oxide, which is characterized by a high workability and maximum lithium ion conductivity at room temperature.

Experimental

Solid electrolytes have been synthesized by a specially developed technology. The synthesis was carried out at $900\text{-}1000^\circ\text{C}$ for 0.5 h. Melts were manufactured by the method of rolling through massive metal rolls.

Ion conductivity of solid amorphous electrolytes was determined by the method of impedance spectroscopy in a solid-state cell with aluminum electrodes.

The impedance characteristics of a solid electrolyte cell at different temperatures are presented in Fig.1. Character of the impedance characteristics of solid-electrolyte cell shows mainly the ion conductivity of electrolyte.

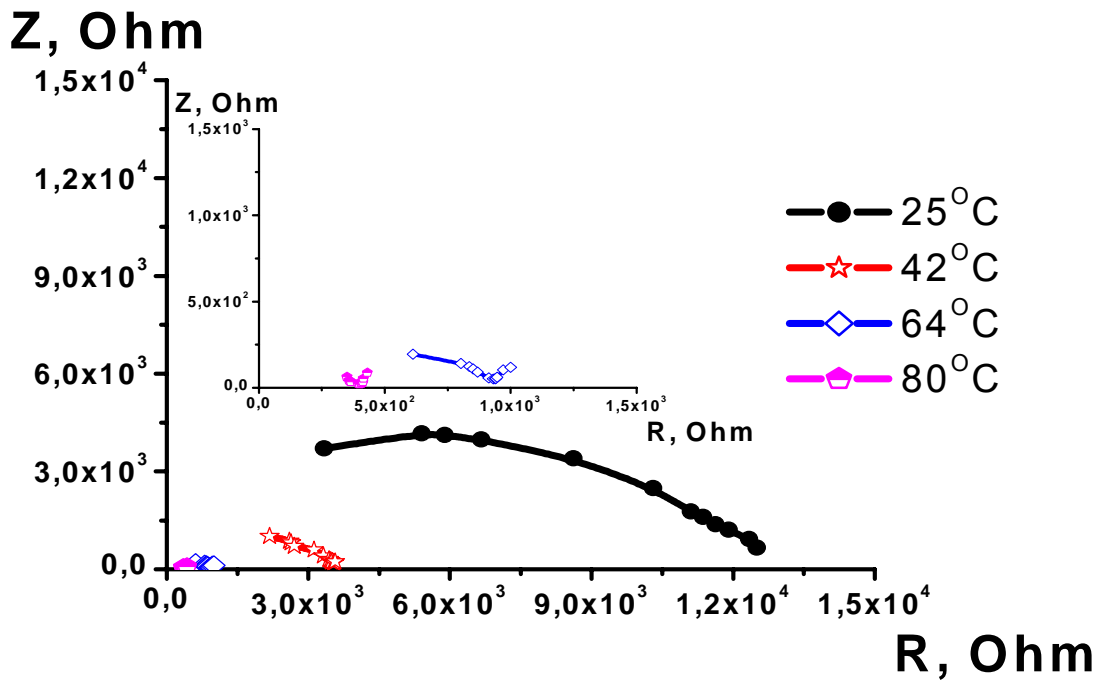


Fig.1. Impedance characteristics of the solid-electrolyte cell $Al/xLi_2O-yLi_2SO_4-zB_2O_3/Al$ at different temperature. Electrolyte dimensions: $730 \mu m, 3.05 cm^2$

During work execution the lithium ion conductivity of the solid electrolytes of different composition in the system $Li_2O -Li_2SO_4-B_2O_3$ with B_2O_3 content up to 30 mol. % as well as glassy $2Li_2O-B_2O_3$ has been measured. Ion conductivity was determined by the method of impedance spectroscopy followed by the mathematical treatment of data according to [5]. The experimental results were plotted on the $1000/T-\lg(\sigma)$ coordinates and the activation energy of ion conductivity was determined by “Arrhenius” law.

On the basis of the experimental data obtained the correlation between ion conductivity (1), the energy of its activation (2) and chemical composition of glasses (mol. %) has been established.

$$\lg \sigma = -0.020 \cdot C_{Li_2O} - 0.084 \cdot C_{Li_2SO_4} - 0.135 \cdot C_{B_2O_3}, S \cdot cm^{-1} (1)$$

$$E_a = 6.25 \cdot 10^{-3} \cdot C_{Li_2O} + 6.74 \cdot 10^{-3} \cdot C_{Li_2SO_4} + 9.98 \cdot 10^{-5} \cdot C_{B_2O_3}, eV(2)$$

Coefficient of multiple correlation for the derived equations is $R(1)=0.982$ and $R(2) =0.895$, respectively.

Mathematical treatment of the model (1) has enabled establishment of the optimal solid electrolyte composition with 20 mol. % B_2O_3 content. The X-ray amorphous material synthesized under the above conditions at room temperature was characterized by the high ion conductivity $3.1 \cdot 10^{-6} S \cdot cm^{-1}$ which activation energy was 0.5 eV. Electronic conductivity of the glass was determined by the procedure described in [4]. Electronic conductivity is $2.4 \cdot 10^{-12} S \cdot cm^{-1}$ at $25^\circ C$. Thus, share of electronic conductivity is $7.65 \cdot 10^{-5} \%$ under these conditions.

Conclusions.

On the basis of the experimental measurement results of solid electrolyte conductivity in the system $Li_2O-Li_2SO_4-B_2O_3$ comprising B_2O_3 up to 30 mol. % a model has been designed. The model well describes the dependence between ion conductivity of the materials and their chemical composition. It has been established that in the investigated field of the system in a series $B_2O_3 \rightarrow Li_2SO_4 \rightarrow Li_2O$ one can observe the decrease of component content effect on solid electrolyte ion conductivity.

Activation energy for the investigated glasses, on the average, is $40\text{-}50\text{ kJ}\cdot\text{mol}^{-1}$ that is well agree with the literature data [2]. Analysis of the model connecting the activation energy of glass conductivity with their composition has shown that in a series of $\text{Li}_2\text{SO}_4 \approx \text{Li}_2\text{O} \rightarrow \text{B}_2\text{O}_3$ decrease in the influence degree on the activation energy is observed.

Production technology of glassy solid electrolyte in the system $\text{Li}_2\text{O}-\text{Li}_2\text{SO}_4-\text{B}_2\text{O}_3$ with the B_2O_3 content of only 20 mol. % which ion conductivity is 2.6 times higher than with glassy $2\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3$ one has been developed. High conductivity of such a material ($3.1\cdot 10^{-6}\text{ S}\cdot\text{cm}^{-1}$ at 25°C) is conditioned by both the positive effect of sulfate groups $[\text{SO}_4^{-2}]$ "loosening" [1] material structure and the structure position of lithium cations.

References

1. Solid-state batteries: materials design and optimization. / Edited by Julien C. u Nazri G.A. - Kluwer Academic publishers, 1994. – 625 p.
2. P.R. Gandhi, V.K. Deshpande, K. Singh // Solid State Ionics. 1989. Vol.36, #1. P. 97-102.
3. Němeč L. O struktuře boritých skel. – Silikaty, 1971, sv. 15, #1, s. 75-97.
4. M. Menetrier, A. Lavasseur and P. Hagenmuller // J. Electrochem. Soc. - 1984, #9. - p. 1971-1973.
5. A. Karthikeyan, P. Vinatier and A. Levasseur // Bull. Mater. Sci. –2000. - Vol.23, #3, June. - p. 179-183.