

Design and Analysis of the Electrical Properties of a Solid-State Lithium-Boron-Phosphate Electrolyte

V.E. Volkovitskiy, V.A. Spiridonov, L.V. Azina and D.I. Panov

ITMO University, Kronverkskiy pr., 49, lit. A, Saint Petersburg, 197101, Russia

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Abstract. In this article, we report on the fabrication of a solid-state lithium-boron-phosphate electrolyte and the study of the dependence of its electrical properties on electrode materials and heat treatment. Impedance spectroscopy was used to analyze the solid-state electrolyte. The values of conductivity of samples heat-treated at 850 °C and 900 °C have been found as $2.02 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and $4.28 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, respectively.

1. INTRODUCTION: A SHORT OVERVIEW ON SOLID-STATE ELECTROLYTES

Over the past two hundred years, most of the research in the field of electric batteries has focused on systems with liquid electrolytes [1]. On the one hand liquid electrolytes have such properties as high conductivity and good contact between electrolyte and electrodes due to wetting of electrode surface, at the same time there are also disadvantages of liquid electrolyte batteries such as electrochemical and thermal instability, low ion selectivity, which can result in problems with the safety of such batteries [2]. The replacement of liquid electrolytes with solid-state electrolytes will help not only to overcome the existing problems of liquid electrolyte batteries, but also open new opportunities for the search of more effective chemicals for electric charge transport and storage in batteries [3]. Solid-state electrolyte (SSE) is used to fabricate batteries that can operate under adverse conditions because it has high elastic modulus, good thermal and chemical stability, wide electrochemical window, high ionic conductivity and low electronic conductivity [4]. Due to such advantages, there is a rapidly growing trend to use

solid electrolytes in batteries. Interest in the development of solid electrolytes is caused by the emergence of new high-performance materials, strict safety rules, and new application areas. Nowadays, several classes of solid electrolytes with different chemical properties achieved ionic conductivity at room temperature about $1 \text{ mS} \cdot \text{cm}^{-1}$ that is comparable to the results known for liquid electrolytes.

The market demands for electrical energy storage (EES) technology are permanently growing in transportation, smart grids, and residential backup power systems. The challenge here is no longer in the use of small, mostly isolated devices, but in the exploration of rather large systems consisting of many energy-intensive EES components located in close proximity to each other and to the human living environment. This increase in scale places more stringent regulatory requirements on EES components and devices, as well as on system-wide safety [5]. It can be assumed that growing safety concerns will be a serious threat to the currently dominant EES technologies on the market, including lithium-ion batteries that use liquid electrolytes, which can lead to cell ignitions.

SSE technologies allow batteries to be stacked in a single case using bipolar electrodes, which reduces

Corresponding author: D.I. Panov, e-mail: dmitriipnv@gmail.com

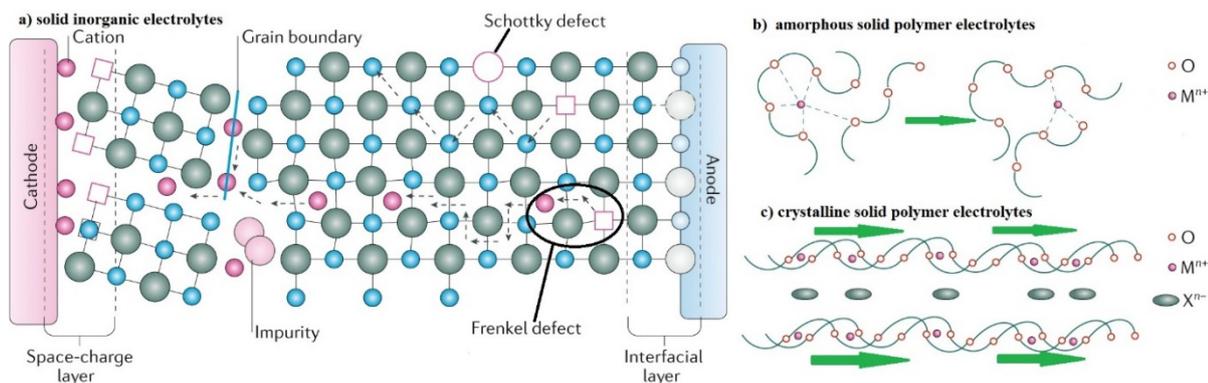


Fig. 1. Mechanisms of ion transport in solid inorganic electrolytes (SIEs) – (a) and solid polymer electrolytes (SPEs) – (b, c), adapted from Ref. [12].

the volume of the case and increases energy density. This trend is facilitated by the emergence of portable technology; for example, fully autonomous robotics requires batteries that not only integrate easily (in terms of fit, comfort and functionality) into clothing, but also meet more stringent active material content and safety standards than currently possible ones with liquid electrolytes. The use of SSE in such applications brings into focus the following requirements for solid electrolytes: cost and weight reduction, as well as increased efficiency of interfacial ion transport, environmental stability and long-term chemical, structural and mechanical stability in contact with active electrode materials.

In crystalline solid materials, ion transport usually depends on the concentration and distribution of defects. Ion diffusion mechanisms based on Schottky and Frenkel point defects include either a simple vacancy mechanism or relatively complex atomic processes, such as the divacancy formation, the interstitial-substitution exchange, and the collective atom rearrangement [6]. However, some materials with special structures can achieve high ionic conductivity without a high concentration of defects. Such structures usually consist of two sublattices: a crystal framework consisting of immobile ions and a sublattice of mobile species. To achieve fast ionic conductivity, three minimum criteria must be met for this type of structure [7]: the number of equivalent (or nearly equivalent) sites that can be occupied by mobile ions must be much larger than the number of mobile species; the migration barrier energy between adjacent accessible sites must be low enough so that the ions can easily jump from one node to another; and these accessible sites must be connected to form a continuous path.

Similar to the diffusion process in a crystal structure, ion transport in glassy materials starts with ions at local sites being excited to have a possibility to

move to neighboring sites and then collectively to migrate on a macroscopic scale [8]. For most glassy materials, order at short and intermediate distances still exists in the amorphous structure. In such conditions, the interaction between the charge carriers and the structural framework cannot be neglected [9].

In polymer electrolytes, microscopic ion transport is associated with the segmental motion of polymer chains above the glass transition temperature [10]. Segmental motion of the chains can create free volumes for lithium ions to jump, which are coordinated with polar groups. The lithium ion can jump from one coordination site to another coordination site, accompanying the segmental motion of the polymer chains [11,12]. In an electric field, long-range transport is accomplished by continuous hopping. The number of free ions depends on the dissociation ability of the lithium salt in the polymer.

Figure 1 shows schematics for the mechanisms of ion transport in solid inorganic electrolytes (SIEs) and solid polymer electrolytes (SPEs) [12]. The transport of lithium ions in SIEs is facilitated by the free space at the grain boundaries as well as by Schottky and Frenkel defects (Fig. 1a). The interfacial layer is formed when two materials with different chemical potentials come into contact and/or two materials react. This layer can retard or accelerate the transport of ions across the interface, depending on operating conditions. Ionic conductivity in SPEs is thought to occur through amorphous and crystalline phases. In the amorphous phase, the segmental motion of the polymer chains promotes the migration and jumping of alkali metal (M^{n+}) ions from one coordination site to the other (Fig. 1b). In contrast, in the crystalline phase, conduction occurs through ordered domains formed by folded polymer chains, and anions (X^{n-}) migrate outside these tunnels (Fig. 1c).

In this article, we report about development and optimization of composition and synthesis of solid

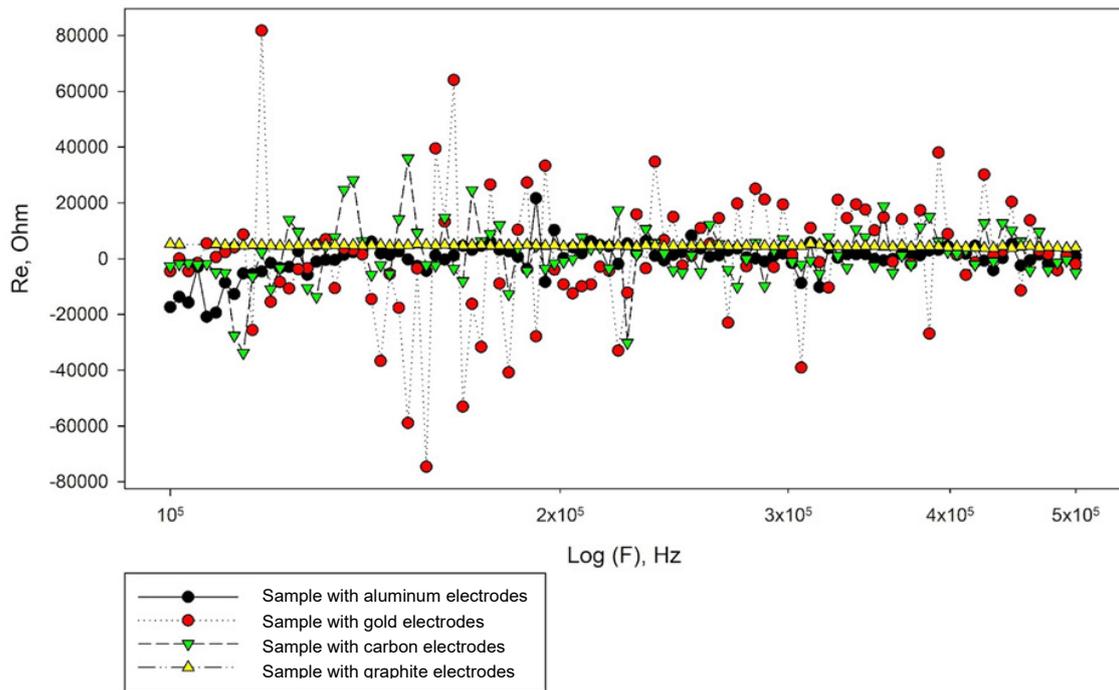


Fig. 2. The frequency dependences of resistance of samples with aluminum, gold, amorphous carbon and graphite electrodes.

electrolytes, improvement of methods of synthesis and processing of solid electrolytes, optimization of regimes of thermal treatment of samples and measurement of the electrophysical characteristics of the fabricated solid electrolytes by impedance spectroscopy.

2. EXPERIMENTAL SETUP AND METHODOLOGY

The basis of the ceramic electrolyte $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3-\text{K}_2\text{O}$ was lithium boron phosphate glass-ceramic. The initial components used were: Li_2CO_3 , Al_2O_3 , H_3PO_4 , H_3BO_3 , and K_2CO_3 . The combined goal of all stages of the electrolyte fabrication was to obtain a homogeneous glass melt, which does not include all kinds of heterogeneities in chemical composition and density.

Glass melting was carried out in glass furnace «TK.13.1500.SH.1F» using corundum crucibles with aluminum content not less than 98%. Corundum rods were used for stirring the melt. The synthesis was carried out on air. Buehler Isomet 1000 high-precision saw was used for cutting flat-parallel samples. The samples were ground using an aqueous suspension of aluminum oxide Al_2O_3 with a grain size of 5–10 μm , and then polished on a polishing machine using an aqueous suspension of aluminum oxide Al_2O_3 with a grain size of 1–2 μm .

The electrodes were applied to the test samples using a Quorum Q150ES universal sampler. Gold (Au/SSE/Au) and amorphous Carbon (C/SSE/C) films with a thickness of 30 nm were applied to the samples. Graphite electrodes (C/SSE/C) were applied to the samples by rubbing a piece of graphite on the planes of the solid electrolyte. The impedance was measured at 500 °C in an air atmosphere by applying 100 mV in a frequency range 100–100000 Hz using a potentiostat-galvanostat Electrochemical Instruments P45-X.

3. RESULTS AND DISCUSSION

3.1 Effect of the electrode material applied to the sample on conductivity

The electrodes for the study were selected according to the following principle: electrodes were applied to samples of the same composition and thickness, their resistance was measured and converted into conductivity. The obtained values were compared and, in this way, the electrode material that provided the maximum value of conductivity was selected, all other conditions being equal. Thin films of gold and amorphous carbon, as well as graphite were studied as electrode materials. Figure 2 shows the frequency dependences of the resistance of pure sample (samples were

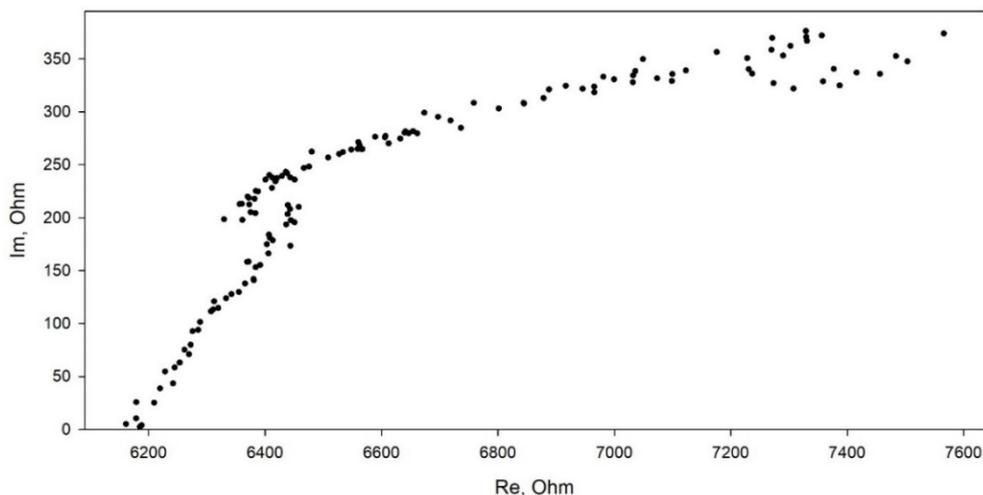


Fig. 3. The impedance specter of solid-state electrolyte heat-treated at 850 °C.

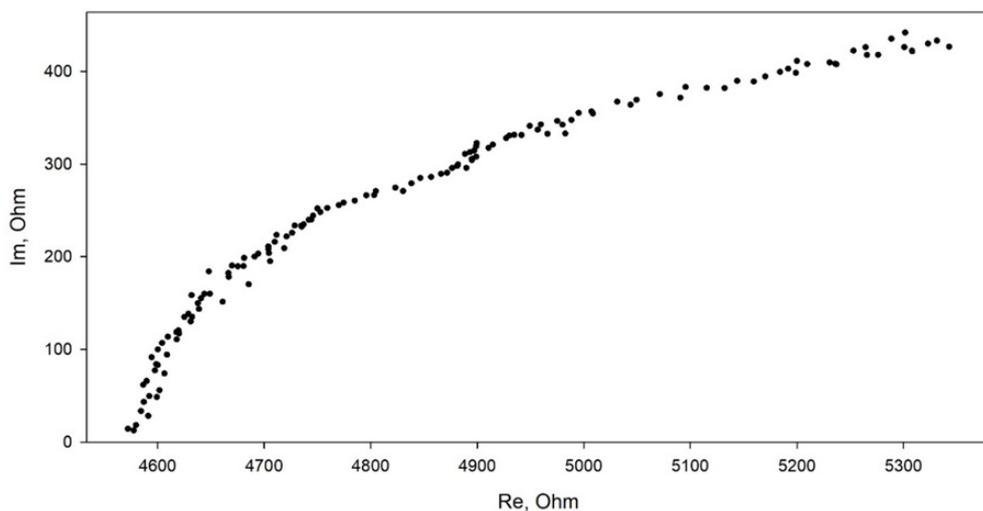


Fig. 4. The impedance specter of solid-state electrolyte heat-treated at 900 °C.

measured using pressure aluminum contacts (aluminum electrodes) and samples with gold, amorphous carbon and graphite electrodes. One can conclude that the graphite electrodes provide more stable resistance values, which is demonstrated in Fig. 2. In addition, the resistance of the sample with graphite electrodes is obviously lower. Thus, graphite electrodes were chosen for further analysis.

3.2 Effect of sample heat treatment regime on conductivity

Heat treatment of samples is a necessary operation stage that should be carefully controlled in the synthesis of solid-state electrolyte. This is because of glass crystallization during heat treatment. Accordingly, defects appear, including grain boundaries that affect the change in conductivity of the material. In addition, the grain size itself also affects the conductivity. The

larger the grain size, the lower the resistance of the grain boundaries.

In this work, the heat treatment of the samples was carried out at 850 °C and 900 °C. This temperature range was chosen because the samples heat-treated below 850 °C did not show significant changes compared to the original ones, and at 950 °C the samples already melt. To determine more correctly the optimal temperature treatment regime, it was necessary to consider impedance spectra and determine the conductivity of the sample from them. The impedance spectra for the studied samples are shown in Figs. 3 and 4. The following method was used to calculate the conductivity of solid electrolyte. The impedance spectra from the side of maximum frequency are extended to the intersection with the Re axis. The obtained value is substituted into formula:

$$\sigma = \frac{l}{RS}, \quad (1)$$

Table 1. Characteristics of the tested samples (a , b are geometric dimensions of the samples).

T , °C	a , mm	b , mm	l , mm	R , Ohm	σ , S·cm ⁻¹
850	16.81	12.65	2.65	6161	$2.02 \cdot 10^{-4}$
900	13.25	10.11	2.63	4577	$4.28 \cdot 10^{-4}$

where l is the distance between the electrodes (sample thickness), R is the sample resistance, S is the sample area. As it follows from Table 1, this formula can be used to estimate approximately the conductivity of the electrolyte under study.

According to the calculations in Table 1, heat treatment of samples at 900 °C provides the best conductivity values.

4. SUMMARY AND CONCLUSIONS

In this study, samples of solid-state lithium-boron-phosphate electrolyte have been synthesized, their electrophysical characteristics have been studied, as well as the influence of various parameters, such as electrode materials and heat treatment mode have been analyzed.

According to the results of the study, graphite turned out to be the most suitable electrode material for impedance measurements. Unlike lithium, which is an ideal electrode for lithium-conducting systems, using graphite does not imply creating special conditions, such as vacuum or inert gas atmosphere. The optimum regime of heat treatment has been determined. The values of conductivity of samples heat-treated at 850 °C and 900 °C have been found as $2.02 \cdot 10^{-4}$ S·cm⁻¹ and $4.28 \cdot 10^{-4}$ S·cm⁻¹, respectively.

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