Investigation of Li-In alloy application as anode for all-solid-state batteries

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Abstract. The problem of the interface optimization between solid electrolyte and anode must be resolved for all-solid-state power sources creation. In the presented work, it is proposed to use Li-In alloy as anode material instead of metallic lithium. The wettability of the composite solid electrolyte based on Li/La2Zr2O12 by In and Li-In alloy was investigated by high-temperature optical dilatometry. The symmetric cells with metallic lithium and Li-In alloy were assembled and their resistance was measured at room temperature. It was established that Li-In alloy application leads to a significant decrease in the resistance at the interface between anode and solid electrolyte (from 37.2 to 0.5 kΩ cm²). So, it can be concluded that using of Li-In alloy leads to the interface optimization between anode and composite electrolyte based on cubic Li/La2Zr2O12 and can be applied for all-solid-state power sources creation.

1. Introduction

Energy plays an important role in many aspects of our life. Electrochemical storage devices and energy converters, primarily batteries, are the most convenient way to store it. Batteries are characterized by high specific capacity and relatively low self-discharge. Currently, the development of all-solid-state lithium and lithium-ion power sources is under great demand [1, 2].

The Li1/2La2/3Zr2/3O12 (LLZO) compound obtained by Murugan R. et. al. [3] and electrolytes based on it are considered as one of the promising lithium-ion solid electrolytes for such batteries [4, 5]. Since these systems have high lithium-ion conductivity (10⁴ S/cm at 25 °C) and stability versus metallic lithium [3, 5]. Moreover, a large number of studies are currently devoted to the composite solid electrolytes based on Li1/2La2/3Zr2/3O12 [6-10]. The introduction of different sintering additives, including glasses, is carried out in order to reduce the final annealing temperature and time of the solid electrolyte, as well as to increase the lithium-ion conductivity of the initial compound. New composite electrolytes in the Li1/2La2/3Zr2/3O12 –x wt% 40.2Li2O·5.7Y2O3·54.1SiO2 (LYS) system with x = 1 – 10 were obtained in our previous work [10]. It was found that the introduction of 1 wt% LYS glass leads to the conductivity increase of cubic LLZO from 1.5·10⁻⁴ to 2.8·10⁻⁴ S/cm at 25 °C.

The electrolyte and electrodes are in a solid state in all-solid-state power sources, therefore the interface problems between solids can be observed [1-3, 11]. The surface of solid electrolytes based on Li1/2La2/3Zr2/3O12 is poorly wetted by metallic Li, as a result of which microscopic gaps are at the interface between anode and solid electrolyte. This leads to high interfacial resistance and non-uniform current distribution during cell operation. The problems associated with high interface resistance and lithium dendrite formation can be solved by using of lithium-based metal alloys as anode materials [12-15].
example, it was established in work [14] that the introduction of 10 at% Mg into lithium metal anode can effectively prevent the loss of contact between anode and solid electrolyte based on LLZO during electrochemical experiments. The use of the Li–Zn alloy also improved the contact between electrode and Li2.28Al0.24La0.9Zr0.12 solid electrolyte, and, as a consequence, led to decrease in the interface resistance [15].

In the presented work, it is proposed to consider an In-Li alloy as anode material, since it has a number of advantages: high electropositivity of lithium in relative to indium; a constant redox potential of about 0.6 V vs. Li+/Li; minimum capacity fade [12]. In addition, the Li-In alloy has an underestimated chemical activity in comparison with pure lithium and keeps high rates of the electrochemical reaction Li+y/Li+y, moreover, the introduction of less than 50 wt% Li does not lead to the compounds formation [16].

Thus, the wettability study of composite solid electrolyte based on Li3La0.8Zr0.2O12 by Li-In alloy and the possibility of Li-In alloy application as anode for all-solid-state power sources creation is the aim of this work.

2. Experimental

Li2CO3, La2O3, ZrO(NO3)2, 2H2O, Al(NO3)3·9H2O were used as initial reagents for the sol-gel synthesis of Li3La0.8Zr0.2O12 with the addition of 0.15 mol of Al (LLZO). Lanthanum were pre-dried at 1000 °C for 1 h to constant weight. The components were mixed in the stoichiometric ratio, except Li2CO3, which was taken with the excess of 10 wt% [3]. These reagents were dissolved in the mixture of diluted HNO3 and C6H5OH·H2O. The resulting mixture was evaporated. Then, the obtained gel was dried and heated at ~200 °C. The synthesis was performed by increasing the temperature stepwise (700 °C – 1 h; 800 °C – 1 h; 900 °C – 1 h) in Air atmosphere. Li2CO3, Y2O3 and SiO2 were used as the starting materials in order to obtain 40.2Li2O·5.7Y2O3·54.1SiO2 glass. The starting materials were taken in stoichiometric ratio and mixed. The mixture was heated in a platinum crucible for 1 h at 1500 °C. The samples were obtained by the conventional quenching method and were subsequently annealed below the glass transition temperature (Tg) [17].

LLZO with 1 wt% 40.2Li2O·5.7Y2O3·54.1SiO2 glass were ground and homogenized in a planetary mill (FRITSCH, Germany) with agate balls of 10 mm in diameter (the mass ratio between the balls and the product was 3:1). The grinding was performed in 5 ml of ethanol per 10 g of the product at a speed of 750 rpm during 30 min. Then the obtained powder was cold-pressed into pellets (diameter 10 mm and thickness ~1 mm) at 240 MPa. The pellets were covered with powder of the same composition and then sintered on a Pt substrate in Air atmosphere.

The phase composition of the synthesized solid electrolyte was examined by X-ray diffraction method (XRD). The characterization of the composite solid electrolyte was carried out using a Rigaku D/MAX-2200VL/PC diffractometer (Rigaku, Japan) with monochromate CuKα radiation over a 20 range of 10 – 60° at room temperature.

The preparation of In-Li alloy with 18 at% Li was carried out by melting at a temperature of ~300 °C. Firstly, metallic In was melted in a beryllium crucible on a heated plate C-MAG HP 7 (IKA, Germany), then the required weighed amount of lithium metal was added. The resulting melt was heated in a furnace to 700 °C with holding for 1 h to homogenize the alloy. Then the obtained melt was cooled to room temperature.

The wettability investigation of the composite solid electrolyte based on Li3La0.8Zr0.2O12 by In and Li-In alloy was carried out using a high-temperature optical dilatometer ODP 868 (TA Instruments, USA) in the temperature range of 20 – 200 °C in air.

Metallic Li and Li-In alloy was rolled to the foil, electrodes were cut out from obtained foil and adpressed by rolling to both surfaces of the sample (the diameter of electrodes are equal ~5 mm). The symmetric cells were assembled in a dry argon box M-BROWN (H2O concentration < 1 ppm). The electrical resistance of the studied cells was measured by electrochemical impedance spectroscopy using an immittance meter E7-25 (MNIP, Belarus) over a wide range of frequencies (0.025 – 1000 kHz) at 25 °C.
3. Result and discussion

According to XRD data the LLZO + 1 wt% LYS composite solid electrolyte after annealing at 1150 °C had cubic structure with space group Ia-3d and did not contain additional impurities.

The wettability of the composite solid electrolyte surface by metallic indium and the obtained Li-In alloy was investigated. From figure 1 it can be seen that metallic indium after melting wets the surface of the studied sample; the calculated contact angle is equal 57 °. However, Li-In alloy wets ceramic electrolyte worse than metallic indium (figure 2); the contact angle is equal 112 °. The softening of indium occurred at a temperature of about 124 °C, while the process of softening of the alloy with 18 at% Li was observed at a higher temperature of ~140 °C.

![Figure 1](image1.png)

**Figure 1.** Wettability of the LLZO + 1 wt% 40.2Li₂O·5.7Y₂O₃·54.1SiO₂ solid electrolyte by metallic In, at 25 (a) and 150 °C (b).

![Figure 2](image2.png)

**Figure 2.** Wettability of the LLZO + 1 wt% 40.2Li₂O·5.7Y₂O₃·54.1SiO₂ solid electrolyte by Li-In alloy, at 25 (a) and 150 °C (b).

The impedance plots of symmetric cells with metallic Li and Li-In alloy at room temperature are shown in figure 3. According to an equivalent circuit the total resistance of Li | LLZO+1 wt% LYS | Li cell is the sum of the electrolyte resistance (Rₑ) and the resistance at the interface between the electrodes and solid electrolyte (Rᵢ), figure 3a. It should be noted that the resistance of composite solid electrolyte is only a few hundred Ω, while the interface resistance between the solid electrolyte and lithium metal is equal ~37.2 kΩ cm². According to figure 3b, the use of Li-In alloy reduces the resistance at the anode | solid electrolyte interface to ~0.5 kΩ cm². The impedance plots of Li-In | LLZO+1 wt% LYS | Li-In symmetric cells, according to the equivalent circuit, has, in addition to Rₑ, two CR elements, which presumably related to processes at the Li-In | LLZO + 1 wt% LYS interface. The average resistance of studied cells does not change significantly for 14 days. It is also should be noted that Li-In alloy is a sufficiently ductile material that is well applied to ceramics. It was found that the alloy has good adhesion to the solid electrolyte based on LLZO and its removal from its surface is problematic.
4. Conclusions

In the presented work, the composite solid electrolyte based on Li$_3$La$_2$Zr$_2$O$_12$ with 40.2Li$_2$O·5.7Y$_2$O$_3$·54.1SiO$_2$ glass addition was synthesized, and Li-In alloy with 18 at% Li was obtained by melting. The wettability of the composite solid electrolyte by metallic In and Li-In alloy was studied by the high-temperature optical dilatometry in the temperature range of 20 – 200 °C. It was found that metallic indium wets ceramics better than lithium-indium alloy; however, Li-In alloy is the rather ductile material and has good adhesion to the composite solid electrolyte. Li | LLZO + 1 wt% LYS | Li and Li-In | LLZO + 1 wt% LYS | Li-In symmetrical cells were assembled and their resistance was measured by the electrochemical impedance method at room temperature. It was established that the use of Li-In alloy as an anode significantly reduces the total resistance of the studied cells. The replacing of Li with Li-In alloy leads to decrease in interface resistance between anode and solid electrolyte from 37.2 to 0.5 kΩ cm$^2$. Thus, it was shown that using of lithium-indium alloy leads to the interface optimization between anode and composite electrolyte based on Li$_3$La$_2$Zr$_2$O$_12$ and can be applied for all-solid-state power sources creation.

5. Reference

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Acknowledgments
The reported study was funded by the grant of the President of the Russian Federation according to the research project № MK-4015.2021.1.3. The research has been carried out with the equipment of the Shared Access Center “Composition of Compounds” of the Institute of High-Temperature Electrochemistry of Ural Branch of RAS, Yekaterinburg, Russian Federation.