Structure and lithium-ion conductivity investigation of the \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) solid electrolytes

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Abstract. Currently solid electrolytes with high values of lithium-ion conductivity are required for creation high-energy lithium and lithium-ion power sources, including all-solid-state batteries. Compounds with a garnet structure based on \( \text{Li}_3\text{La}_3\text{Zr}_2\text{O}_{12} \) are promising solid electrolytes for such power sources. In presented work solid electrolytes in the \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) system were synthesised using the sol-gel method in a wide concentration range of tantalum from \( x=0 \) to \( x=2.0 \). According to X-ray diffraction analysis, compounds with \( x>0 \) has a cubic modification with the space group \( \text{Ia}-3\text{d} \). The electrical resistance of the obtained solid electrolytes was measured by the complex impedance method in the temperature range of 25–210 °C, and the values of total lithium-ion conductivity were calculated. It was found that \( \text{Li}_3\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12} \) has the maximum values of lithium-ion conductivity in studied system – \( 1.4 \cdot 10^{-4} \text{ S/cm at 25 °C} \). The Density Functional Theory modeling confirms that moderate Ta-doping is most suitable for enhancing Li diffusion.

1. Introduction

Solid electrolytes are widely used in different devices for high-temperature electrochemical energetics. The compounds with lithium-ion conductivity have a special place among these materials, because they are necessary for creation lithium power sources, which surpassing all known electrochemical systems in energy capacity. Moreover lithium-conducting solid electrolytes are promising for use in low-temperature all-solid-state and medium-temperature power sources with a molten lithium anode, as well as a lithium-conducting thickener phase for molten salt electrolyte of lithium thermal power sources.

According to the literature data [1-3], compounds with a garnet structure, which have been firstly obtained by Hayashi and Noguchi in 1986 [4, 5], are considered to be one of the most promising lithium-conducting electrolytes. Trangadurai V. and Weppner W. drew attention to the \( \text{Li}_3\text{La}_3\text{M}_2\text{O}_{12} \) (\( M = \text{Ta}, \text{Nb} \)) garnets as new highly conductive lithium-ion solid electrolytes (~\( 10^{-6} \) S/cm at 25 °C) with structural disorder in 2003 year [6]. Later, the group of Murugan R. obtained the \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) (LLZO) compound, which has a high lithium-ion conductivity (~\( 10^{-4} \) S/cm at 25 °C) in combination with stability to metallic lithium [7]. LLZO has the garnet structure and two crystal modifications: cubic and tetragonal.
It was established that the conductivity of cubic LLZO at room temperature is several orders of magnitude higher than that of tetragonal one; however, the stabilization of the cubic phase requires the introduction of some dopant [8]. The replacement of some ions in the zirconium sublattice by Ta$^+$ is one of the promising doping [8]. Since it leads to the stabilization of highly conductive cubic modification of LLZO without deprivation of such an important property as stability of the solid electrolyte to one of the most promising anode materials – metallic lithium.

From the analysis of the presented in the literature data, it can be seen that there are conflicting information about the composition with the highest value of lithium-ion conductivity in the Li$_{1-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ system. Thus, the maximum conductivity was observed for compounds with different tantalum content equal to 0.25 [9], 0.3 [10], 0.4 [11], 0.5 [12], 0.6 [13], and 1.0 [14]. Moreover, the total conductivity of the obtained solid electrolytes varies from $10^{-5}$ to $10^{-3}$ S/cm at room temperature because of different synthesis methods (sol-gel and solid-state methods) and sintering conditions for ceramic membranes. The total conductivity values of solid electrolytes based on LLZO, obtained by solid-state synthesis, without any additionally introduced dopants are equal $\sim 10^{-5}$ S/cm [12]. While sintering ceramics at high temperatures (above 1150 °C) for a long time in Al$_2$O$_3$ crucibles leads to uncontrollable incorporation of aluminum into the structure of solid electrolytes and, as a consequence, to higher values of lithium-ion conductivity [11, 13].

The structure and conductivity investigation of Li$_{1-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ solid electrolytes, obtained by the sol-gel method, is the aim of this study. Additionally, we have performed the modeling of lithium ion diffusion in the cubic LLZO, both in the pristine and doped states by using of the Density Functional Theory (DFT) approach [15, 16]. We have evaluated the migration energy barriers and vacancy formation energy to find the most promising variants of Ta-doping.

2. Experimental

Li$_2$CO$_3$, La$_2$O$_3$, ZrO(NO$_3$)$_2$·2H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Ta$_2$O$_5$ were used as initial reagents for the sol-gel synthesis of Li$_{1-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x=0.0–2.0$) solid electrolytes. Lanthanum and tantalum oxides were pre-dried at 1000 °C for 1 h to constant weight. The components were mixed in the stoichiometric ratio, except Li$_2$CO$_3$, which was taken with the excess of 10 wt% [7]. These reagents were dissolved in the mixture of diluted HNO$_3$ and C$_6$H$_5$OH·H$_2$O, after that Ta$_2$O$_5$ powder was added to the prepared solution. The resulting mixture was evaporated at 80 °C. Then, the obtained gel was dried and heated at $\sim 200$ °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. 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 to avoid uncontrollable incorporation of aluminum from Al$_2$O$_3$ crucible in Air atmosphere. Annealing was carried at 1150 °C for 1 h.

The phase composition of the synthesized solid electrolytes was examined by X-ray diffraction method (XRD). The characterization of the ceramics was carried out using a Rigaku D/MAX-2200VL/PC diffractometer (Rigaku, Japan) with monochromate CuKα radiation at room temperature. The data were collected over a 20 range of 15–60°.

The electrical resistance of the Li$_{1-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ solid electrolytes was measured by electrochemical impedance spectroscopy using an immittance meter E7-25 (MNIP, Belarus). A gallium-silver paste was deposited on both sides of the studied samples and used as blocking electrodes. The conductivity measurements were conducted in a two-probe cell with Ag electrodes over a wide range of frequencies (0.025–1000 kHz) and in the temperature range of 25–201 °C in Air atmosphere. The conductivity of the obtained solid electrolytes was calculated considering the geometric dimensions and resistance of the ceramic samples.

The migration energies of the Li$^+$ ions $E_m$ were calculated within the DFT approach using the Nudged Elastic Band (NEB) method as implemented in VASP package [17]. The Generalized Gradient Approximation (GGA) exchange-correlation functional in the form of Perdew-Burke-Ernzerhof (PBE) [18] was used for the calculations. Full relaxation was allowed, the convergence thresholds for structure relaxation were set to $10^{-6}$ eV and $10^{-5}$ eV/Å for total energy and ionic forces, respectively. The energy cut-off for plane-waves of 600 eV and G-centred k-point mesh with the
resolution $2\pi \times 0.025$ Å$^{-1}$ was set in all cases. A further increase of the cut-off energy or the k-grid led to negligible changes in the results.

To take into account atomic disordering in the both pristine and Ta-doped LLZO structure, we have constructed 10 different lowest-energy configuration (i.e. with the minimal electrostatic energy) that fulfil charge neutrality and stoichiometry restrictions using the SUPERCELL software [19]. Then, all configurations were optimized by DFT and the structure with the lowest total energy was chosen for the subsequent analysis of Li diffusion.

The input files for the NEB calculations were prepared using the PATHFINDER script (http://batterymaterials.info/downloads) as follows: the shape and volume of the cell are fixed to the optimized geometry, seven images for each migration path were generated, the convergence criterion of the force was set to 0.02 eV/Å. The vacancy formation energies were roughly calculated according to the formula:

$$E_v(Li) = E_{\text{defect}} + E_{Li} - E_{\text{bulk}},$$

where $E_{\text{bulk}}$ and $E_{\text{defect}}$ are the total energies of the bulk structure and the structure with an introduced vacancy (one neutral Li per cell was removed), while $E_{Li}$ represents the total energy of a Li atom in the bulk metal.

3. Result and discussion

The XRD patterns of the Li$_{1-x}$La$_x$Zr$_2$-xTa$_x$O$_{12}$ solid electrolytes are demonstrated at figure 1. It should be noted that even a small amount of Ta$^{5+}$ ($x = 0.1$) leads to the transition from the tetragonal modification of LLZO to the cubic one; however, a small impurity peak of lanthanum zirconate (La$_2$Zr$_2$O$_7$) was also observed. While solid electrolytes in Li$_{1-x}$La$_x$Zr$_2$-xTa$_x$O$_{12}$ system with the cubic structure were obtained by solid-state synthesis only at tantalum content of $x \geq 0.2$ [10]. Solid electrolytes with $x > 0.2$ are single-phase and has the cubic modification with a space group Ia-3d, which is typical for compounds with the garnet-like structure [7]. Using X-ray diffraction analysis, it was found that the lattice parameter gradually decreases from 12.9903 (4) for $x = 0.1$ to 12.8126 (3) for $x = 2.0$ upon substitution of zirconium ions by tantalum in the Li$_{1-x}$La$_x$Zr$_2$-xTa$_x$O$_{12}$ system.

![Figure 1. XRD patterns of the Li$_{1-x}$La$_x$Zr$_2$-xTa$_x$O$_{12}$ (x=0.1–2.0) solid electrolytes. * - La$_2$Zr$_2$O$_7$.](image)

The temperature dependences of the total conductivity of studied solid electrolytes in Arrhenius coordinates are presented at figure 2. The growth of the lithium-ion conductivity is observed for ceramic membranes with Ta content increasing from $x = 0.1$ to $x = 0.6$. And the solid electrolyte with $x = 0.6$ possess the maximum value of lithium-ion conductivity at room temperature – 1.4·10$^{-4}$ S/cm. While further doping of zirconium sublattice leads to a decrease in the total conductivity of the ceramics to ~ 10$^{-5}$ S/cm. An increase in lithium-ion conductivity in the Li$_{1-x}$La$_x$Zr$_2$-xTa$_x$O$_{12}$ system can
be associated with an increase in the mobility of charge carriers in the structure of the studied solid electrolyte for the composition with \( x = 0.6 \); this assumption can be confirmed by modeling the structure of the studied solid electrolytes and diffusion of lithium ions in them.

Figure 2. Arrhenius plots for total conductivity of the \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) solid electrolytes.

The results of DFT modeling of \( \text{Li}^+ \) ion diffusion in the pristine LLZO structure are presented at figure 3. We have found eight non-equivalent paths which are suitable for \( \text{Li}^+ \) ion diffusion and form 3D migration map [20]. The migration energy for these channels did not exceed 0.26 eV/ion (figure 3b).

The vacancy formation energy \( E_V \) was calculated for six different stoichiometry of \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \). Here we observe a following tendency: vacancy formation energy smoothly decreases while Ta doping level increases in the \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) up to the level \( x \sim 1.25 \), the higher level of Ta-doping leads to increasing \( E_V \) (see Table 1 for details). Qualitatively it is in line with experimental observations: moderate Ta-doping is most suitable for enhancing of Li diffusion, but more precise modeling is desirable. It is the subject of future work.

Table 1. The vacancy formation energy \( E_V \) for six different stoichiometries \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \).

| Formula                  | \( E_V \) (eV) |
|--------------------------|----------------|
| \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) | 3.58           |
| \( \text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12} \) | 3.49           |
| \( \text{Li}_{5.75}\text{La}_3\text{Zr}_{0.75}\text{Ta}_{1.25}\text{O}_{12} \) | 3.31           |
| \( \text{Li}_5\text{La}_3\text{Zr}_0\text{Ta}_{1.5}\text{O}_{12} \) | 3.46           |
| \( \text{Li}_{5.25}\text{La}_3\text{Zr}_{0.25}\text{Ta}_{1.75}\text{O}_{12} \) | 3.47           |
| \( \text{Li}_7\text{La}_3\text{Ta}_2\text{O}_{12} \) | 3.57           |

Figure 3. The scheme of Li diffusion channels in the pristine LLZO structure (a) and the corresponding migration energy barriers for each channel (b) according to the DFT-NEB methodology.
4. Conclusions

The sol-gel method was used to synthesize Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ solid electrolytes in the wide concentration range of x (0.0–2.0). It was found that the introduction of the small amount of tantalum (x=0.1) leads to the stabilization of the cubic modification of Li$_7$La$_3$Zr$_2$O$_{12}$. The resistances of the obtained solid electrolytes were determined by the complex impedance method, it was found that Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ solid electrolyte has the maximum values of total conductivity (1.4·10$^{-4}$ S/cm at 25 ºC) in Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ system. The modeling of lithium ion diffusion in the cubic LLZO and Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ compounds was performed by using of the Density Functional Theory. It was established that moderate Ta-doping is most suitable for enhancing Li diffusion in LLZO structure.

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