A comparative Study of Physic-Chemical Properties of Certain Cerium Doped Li7La3-xCexZr2O12 Ceramic Oxides

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Research Article

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Abstract

Solid-state electrolytes have emerged as a promising alternative material for next-generation Li-ion batteries due to their safety and reliability. In this investigation, we report the synthesis of Cerium(Ce) doped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) ceramic oxide which has a garnet-like structure and in which Ce$^{3+}$ typically occupies La$^{3+}$ sites. The synthesised LLZO ceramic oxide is doped with various weight percentages of cerium(Ce$^{3+}$) by sol-gel method using oxalic acid as a complexing agent and ethane-1,2-diol as a surface-active agent. The synthesised Li$_7$La$_{3-x}$Ce$_x$Zr$_2$O$_{12}$ garnet is screened for surface morphology, chemical composition, and phase transition by various analytical techniques. The surface morphology and composition were analysed by HR-SEM with EDX analysis respectively. The cubic face formed was confirmed by XRD results. Thermogravimetric analysis indicates the thermal stability of the prepared materials. The effect of addition of various weight percentages of cerium with LLZO on ionic conductivity was analysed using ac impedance spectroscopy and compared. The maximum ionic conductivity measured was $6.34 \times 10^{-5}$ S cm$^{-1}$. The potential window was examined by cyclic voltammetry (CV), which showed that the lithium deposition and dissolution peak appeared around 0V. Li$^+/Li$ and no further reaction beyond 5.8V vs Li$^+/Li$. The results showed that these materials could be used as a potential alternative material in the fabrication of lithium-ion batteries.

1. Introduction

In recent years, solid-state lithium-ion batteries, with high energy density and efficiency, have received considerable attention due to the increasing demand. The solid-state conductors expected to address the safety concerns of the traditional liquid electrolytes system. Therefore, storage systems such as Li-ion batteries (LiBs) are actively investigated in the context of large-scale power plants, as well as portable applications such as electronic devices, electric vehicles, and growing popularity for military and aerospace applications[1].

The Solid inorganic lithium-ion conductor is one of the lithium garnet families being widely studied is Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) garnet like ceramic oxide has been investigated in detail due to its chemical stability, high lithium-ionic conductivity, and wide electrochemical window as well as high thermal and mechanical stability[2-5]. The extensive investigation of these materials is considered a promising source for the development of solid-state lithium ions batteries with enhanced efficiency. There are two types of garnets with crystal phase tetragonal, and cubic structures are reported[6]. Further, it is observed that Li-ion conductivity of the cubic phase system is approximately two orders higher than that of the tetragonal phase system and the cubic structure could not be obtained low sintering temperature [7]. Many researchers have carried out the preparation of LLZO doped with aliovalent cations stabilise the cubic phase at room temperature with low sintering temperature and reported the materials with the conductivity of about 1 mS cm$^{-1}$, which is comparable to that of liquid electrolytes [9-11]. Various doping methods were adopted such as Al$^{3+}$[12], Ga$^{3+}$[13] in Li$^+$ sites and Ta$^{5+}$[14], Nb$^{5+}$[15], Mo$^{6+}$[16], Sb$^{5+}$[17], Te$^{6+}$[18], W$^{6+}$[19], Y$^{3+}$[20], Mg$^{2+}$, Sc$^{3+}$[21] replacing Zr$^{4+}$ at the octahedrally coordinated position,
simultaneous substitution of Li$^+$ and Y$^{3+}$ for Zr$^{4+}$[22] and Ce$^{4+}$ in La$^{3+}$ [23]. The different synthesis methods for the doping were solid-state method, sol-gel method, modified Pechini sol-gel process, precipitation method, and wet chemical methods. Many of them reported on the cubic phase in the solid-state method with higher sintering temperature around 1000ºC above for 36 h in an alumina crucible. There are very few reports dealt with the cubic phase using a sol-gel method with low temperature[24]. Thus, developing a novel solid electrolyte system based on garnet based ceramic material with enhanced performances at room temperature is of great importance. Hence, we report on LLZO garnet doped with various weight percentage of cerium [Li$_7$La$_{3-x}$Zr$_2$Ce$_x$O$_{12}$,(x=0.1,0.25,0.5,0.75)] and their characterisation methods.

2. Experimental

2.1 Materials

Lithium nitrate (LiNO$_3$) (Sigma–Aldrich), Lanthanum nitrate(La(NO$_3$)$_3$.6H$_2$O) (SigmaAldrich), and zirconium oxy nitrate(ZrO(NO$_3$)$_2$.xH$_2$O) (Sigma–Aldrich), Cerium nitrate(Ce(NO$_3$)$_3$.6H$_2$O) (Merck), and anhydrides Oxalic acid (COOH)$_2$(Merck) with Ethane 1,2 diols(Emplura) were used as precursor materials. During the synthesis procedure. Fig.1 shows the detailed procedure followed in this work. The required quantities of LiNO$_3$ (Sigma–Aldrich) (10 wt % excess was added to compensate for the expected Li loss during sintering at high temperature), La(NO$_3$)$_3$.6H$_2$O, and ZrO(NO3)$_2$.xH2O, Ce(NO3)$_3$.6H2O were dissolved in de-ionised water, and then oxalic acid and ethane-1,2-ol were added to the above clear solution with continuous stirring. The amount of oxalic acid added was twice the total moles of the cation in the precursor solution.

The solution was heated to 60ºC with stirring initially to remove the excess water. The solvent was then slowly evaporated, and white gel precipitate was formed. The resulting gel precursor was heated at 150ºC for an hour in a hot oven, and tiny flakes of light yellow precursor powder were obtained. Then the powder was finely grounded and heated at 850ºC for 6 hours, powder of ceramic material was obtained. The various weight percentage (x=0.1, 0.25, 0.5, and 0.75) of Ce doped garnet materials are designated as G11, G12, G13, and G14, respectively.

\[
7 \text{LiNO}_3(s) + 3-x\text{La(NO}_3)_3(s) + x\text{Ce(NO}_3)_3(s) + 2\text{ZrO(NO}_3)_2(s) \rightarrow \\
\text{Li}_7\text{La}_{3-x}\text{Ce}_x\text{Zr}_2\text{O}_{12}(s) + x\text{NO}_2(g) + x\text{O}_2(g)
\]

when x = concentration of cerium weight % 0.1, 0.25, 0.5, 0.75.

The surface morphology of ceramic oxide was analysed by a high-resolution scanning electron microscope (HRSEM; HITACH S-4800). The phase composition of the synthesised garnet powder was characterised with x-ray diffraction using cu kα radiation at 1.5406 Å, scanned over 2θ range of 10-60º at room temperature. Thermal analysis of the prepared materials was carried out by TG/DTA and
thermograms were recorded using SDTQ600 (T.A.) in nitrogen flow with a heating rate of 10ºC/min. The lithium-ion conductivity of the synthesised Ce doped LLZO was measured by using and thermograms were recorded using SDTQ600 (T.A.) in nitrogen flow with a heating rate of 10ºC electrochemical impedance spectroscopy (ESI, Bio-Logic SP200) the impedance of the fabricated cells was measured in the frequency range from 10 Hz to 7 MHz with a perturbation amplitude of 100 mV. The potential window was examined by cyclic voltammetry (CV), which showed lithium deposition.

3. Results And Discussion

3.1 HRSEM study

The fine powder of the prepared sample was pale yellow in colour. The intensity of colour gradually intensifies to dark yellow on continuous doping with various weight percentages of cerium (Li$_7$ La$_{3-x}$ Zr$_2$Ce$_x$ O$_{12}$). The HR-SEM image of the Ce doped LLZO ceramic oxide powder calcinated at 850 ºC is shown in Figure 2. The SEM images of ceramic oxide demonstrated that the materials have large size irregular spherical and well-defined cubic like structure. Figure 2(a) shows an irregular spherical structure with porosity in the surface of ceramic oxide, which results in high gain boundaries resistance may lead to low lithium ions conductivity. The surface morphology of irregular spherical pores in the ceramic electrolyte gradually decreases with the increasing content of x precursors (x= 0.1, 0.25, 0.5, 0.75 of Ce) and grains excellent contact with each other[13,23]. The SEM image of a ceramic oxide containing 0.5 weight percentage of Ce (Li$_7$ La$_{2.5}$ Zr$_2$Ce$_0.5$ O$_{12}$) shown in Figure 2(c) exhibited a large regular and homogeneous cubic morphology. Further, it is observed that the ceramic oxide with Ce concentration with above x=0.5, cubic morphology gradually reduced which may enhance the grain boundaries resistance and influence lithium-ions conductivity.

3.2 Energy dispersive X-ray spectroscopy

The EDX spectrum of Ce doped LLZO ceramic materials was recorded to analyse the elemental composition of the synthesised materials. The EDX spectrum of figure 3, 4, 5, 6 shows the elemental composition of x=0.1, 0.25, 0.5, 0.75 weight percentage of Ce doped ceramic oxide, LLZO, (Li$_7$La$_3$Ce$_x$Zr$_2$O$_{12}$). The presence of oxygen(O), Lanthanum(La), Zirconium(Zr), and Cerium(Ce) present in Ce doped LLZO showed in the spectrum.

3.3 X-ray Diffraction Analysis

The x-ray diffractograms of ceramic garnet containing various weight percentages of (x= 0.1 to 0.75 of Ce) having the formula Li$_7$ La$_{3-x}$ Ce$_x$Zr$_2$ O$_{12}$ are shown in figure 7. First, it is clear that the addition of super valent cation stabilises the cubic LLZO phase, which may increase the Li$^+$ mobility due to the structural modification around the lithium sites[25-26]. The decrease in the intensity of peak doublet decrease as the weight percentage of cerium increases shown in figure 8, indicated that the addition of Ce results in the transformation of structure from tetragonal to cubic in cerium doped LLZO [23]. When the
concentration of doped cerium is 0.1 weight percentage (x=0.1 of Ce), tetragonal with cubic structure is formed, and its respective formula is Li$_7$La$_{2.9}$Zr$_2$Ce$_{0.1}$O$_{12}$. The intensity of peak doublet significantly decreases above 0.1 weight percentage of Ce and samples shows a peak at 2$\theta$ = 27.98° which indicated the presence of La$_2$Zr$_2$O$_7$ in both samples [27-28] and the XRD peak at 2$\theta$ = 27.38°, 32.41°, and 47.58° due to the CeO$_2$ in the samples.

3.4 Thermal analysis

The thermal behaviour of the synthesised ceramic oxide materials was studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA and DTA thermograms recorded in the temperature range from 30°C to 1000°C in a nitrogen atmosphere for the synthesised Li$_7$La$_{3-x}$Zr$_2$Ce$_x$O$_{12}$ ceramic material were presented in the Figure.8 and Figure.9 respectively. The TG. curves in figure 9 showed that there are three stages of weight loss in the ranges of 50–120°C, 280–370°C, and 850–980°C. Similarly, there are three corresponding inflections recorded DTA curves in the ranges 76–148°C, 310–418°C and 870–980°C shown in figure 10. The first stage of weight loss was observed in the range 50–120°C of TG. curves were due to the evaporation of adsorbed water on the prepared sample. The significant weight loss observed in the range 280–370°C, attributed to the decomposition of organic solvent present in the sample. The final weight loss observed in the range 870–980°C was identified as a result of the removal of leftover carbon and initiation of the formation of the cubic phase in the ceramic materials.

3.5 Conductivity Study of Ce doped ceramic oxide

The ionic conductivity property of the synthesised ceramic oxide material was characterised using electrochemical impedance spectroscopy. The synthesised samples calcined at 850°C and the conductivity is measured at room temperature, for various weight percentage of cerium doped LLZO materials. The A.C. impedance spectra of Li$_7$La$_{3-x}$Ce$_x$Zr$_2$O$_{12}$ fitted through an equivalent circuit to obtain the ionic conductivities, as shown in Figure 11, and the plot can be well-resolved into bulk, grain-boundary, and electrode resistances. The high-frequency semicircle can be attributed to the bulk resistance of La$_{2.9}$Ce$_{0.1}$(G11), while the semicircle in the low frequency range correlates with the grain-boundary resistance[29]. From Fig. 11 and Table 1, several observations can be made. First, the observations showed that the addition of various weight percentages of Ce concentration increases in LLZO decreases the total resistance of ceramic electrolytes , and hence, the total conductivity increases. Secondly, the conductivity of the Li$_7$La$_{2.5}$Ce$_{0.5}$Zr$_2$O$_{12}$ (6.34×10$^{-5}$Scm$^{-1}$) specimen is slightly higher compared to the conductivity of the Li$_7$La$_{2.5}$Zr$_2$Ce$_{0.75}$O$_{12}$ (3.06×10$^{-5}$Scm$^{-1}$) specimen. The plot of La$_{2.5}$Ce$_{0.5}$ concentration possesses a smaller semicircle compared to La$_{2.9}$Ce$_{0.1}$, La$_{2.75}$Ce$_{0.25}$, and La$_{2.25}$Ce$_{0.75}$ ceramic electrolytes because there is less CeO$_2$ present in the material, which increases the grain boundary resistance.

Table 1 Ionic conductivity of synthesised Ce-LLZO
### Table of Ionic Conductivity

| Sample | Primary face                  | Ionic Conductivity \( \text{Scm}^{-1} \) |
|--------|-------------------------------|------------------------------------------|
| Reported | Tetragonal                  | \( 3.12\times10^{-7} \) (30)          |
| G11    | Tetragonal and cubic        | \( 1.34\times10^{-5} \)                |
| G12    | Cubic                        | \( 2.04\times10^{-5} \)                |
| G13    | Cubic                        | \( 6.34\times10^{-5} \)                |
| G14    | Cubic                        | \( 3.06\times10^{-5} \)                |

#### 3.6 Cyclic Voltammetry

The electrical conductivity of the synthesised ceramic oxide was estimated by assessing by cyclic voltammetry (CV) using a potentio-galvanostat (solaron 1480) at a scanning rate of \( 1\text{mvs}^{-1} \) at room temperature between -0.5 to 5.8 \( \text{v(Li}^+/\text{Li}) \). The cyclic voltogram of figure6 shows the Ce doped LLZO with stainless-steel and Li metal as working and counter electrode, respectively. The deposition and dissolution peaks are near to 0V vs \( \text{Li}^+/\text{Li} \), and no peak has appeared beyond 5.9V\[31\]. Thus, it indicates that \( \text{Li}_7\text{La}_{2.5}\text{Zr}_2\text{Ce}_{0.5}\text{O}_{12} \) has a wide electrochemical window.

#### 4. Conclusion

The garnet structured solid electrolytes were prepared according to the formula \( \text{Li}_7\text{La}_{3-x}\text{Zr}_2\text{Ce}_x\text{O}_{12} \) with different Ce content was successfully synthesised by a sol-gel method and calcinated at 850°C for 6 hours. It was noted that the addition of Cerium in LLZO could induce significant transformation of the structure from tetragonal to cubic phase and hence, increases ionic conductivity. It is, also, observed that single the cubic face phase was observed in the composition \( X \geq 0.25 \) to 0.75, which is confirmed by XRD results. The ac impedance of \( \text{Li}_7\text{La}_{3-x}\text{Zr}_2\text{Ce}_x\text{O}_{12} \) has been investigated at room temperature and exhibits the highest ionic conductivity \( 6.34\times10^{-5} \) \( \text{Scm}^{-1} \) for \( \text{Li}_7\text{La}_{2.5}\text{Zr}_2\text{Ce}_{0.5}\text{O}_{12} \). The HR-SEM images revealed that cerium concentration influences the size and the density of the cubic phase. The cubic phase with relatively dense morphology expected to show better ionic conductivity. The cyclic voltammogram of lithium deposition and dissolution peaks near 0V vs \( \text{Li}^+/\text{Li} \) and indicated that there is no other peak beyond 5.9V vs. \( \text{Li}^+/\text{Li} \), demonstrated that \( \text{Li}_7\text{La}_{3}\text{Zr}_{1.55}\text{Ce}_{0.5}\text{O}_{12} \) has a wide potential window. The materials prepared showed that they possess optimal conductivity for the fabrication of batteries.

#### Declarations
Conflict of interest

Authors do not have any conflict of interest.

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References

[1] Ballon, Massie Santos "Electrovaya, Tata Motors to make electric Indica". cleantech.com. Archived from the original on 9 May 2011. Retrieved 11 June 2010.

[2] R. Murugan, V. Thangadurai, W. Weppner, Fast Lithium Ion Conduction in Garnet-Type Li(7)La(3)Zr(2)O(12), Chem. Int. 2007;46:7778–7781.

[3] Yunsung Kim, Aeri Yoo, Robert Schmidt, Asma Sharafi, Heechul Lee, Jeff Wolfenstine and Jeff Sakamoto, Electrochemical Stability of Li_{6.5}La_{3}Zr_{1.5}M_{0.5}O_{12} (M = Nb or Ta) against Metallic Lithium, frontiers in energy research. 2016; (4) 20.

[4] A.A. Trofimov, C. Li, K.S. Brinkman, L.G. Jacobsohn. Luminescence investigation of Ce incorporation in garnet-type Li_{7}La_{3}Zr_{2}O_{12}. Elsevier, Optical Materials. xxx 2016; 1-4.

[5] Martin Bitzer, Tim Van Gestel, Sven Uhlenbruck, Hans-Peter-Buchkremer. Sol-gel synthesis of thin solid Li7La3Zr2O12 electrolyte films for Li-ion batteries. Elsevier Thin Solid Films. 2016; 615: 128 –134.

[6] Frederieke Langera, Jens Glenneberga, Ingo Bardenhagenb, Robert Kuna. Synthesis of single phase cubic Al-substituted Li7La3Zr2O12 by solid state lithiation of mixed hydroxides. Elsevier journal of allows and compound. 2015;0925-8388.

[7] Hui Xie a, Yutao Li a,b, John B. Goodenough. Low-temperature synthesis of Li7La3Zr2O12 with cubic garnet-type structure. Elsevier Materials Research Bulletin. 2012; 47: 1229–1232.

[8] Ramaswamy Murugan, Dr. Venkataraman Thangadurai Prof., Werner Weppner Prof. Dr. Fast Lithium Ion Conduction in Garnet-Type Li_{7}La_{3}Zr_{2}O_{12}. Angew. Chem. Int. Ed. 2007; 46: 7778 –778.

[9] E. Rangasamy, J. Wolfenstine, J. Sakamoto. The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition Li7La3Zr2O12. Solid State Ionics 2016;28–32.

[10] S. Ohta, T. Kobayashi, T. Asaoka, High lithium ionic conductivity in the garnet-type oxide Li_{7-x}La_{3}(Zr_{2-x}, Nb_{x})O_{12} (X=0–2), Elsevier J. Power Sources. 2011;196 (6):3342–3345.
[11] V. Thangadurai, S. Narayanan, D. Pinzaru. Garnet-type solid-state fast Li ion conductors for Li batteries: critical review. Chem. Soc. Rev. 43 2014;13, 4714–4727.

[12] Hany El-Shinawi, Gary W. Paterson, Donald A., Edmund J. Cussen and Serena A. Corr. Low-temperature densification of Al-doped Li7La3Zr2O12: a reliable and controllable synthesis of fast-ion conducting garnets, Journal of Materials Chemistry A. 2017;5 319-329.

[13] Shuqiao Hu, You-Fen Li, Ru Yang, Zijian Yang, Lege Wang, Structure and ionic conductivity of Li7La3Zr2−xGexO12 garnet-like solid electrolyte for all solid state lithium ion batteries. Elsevier Ceramics International 2018; 44:6614–6618.

[14] Ting Liua,b, Yibo Zhanga, Xue Zhanga, Lei Wangc, Shi-Xi Zhaob, Yuan-Hua Lin. Enhanced electrochemical performance of bulk type oxide ceramic lithium. RAC Journal of Materials Chemistry.2017;01 1-27.

[15] K. Ishiguro, Y. Nakata, M. Matsui, I. Uechi, Y. Takeda, O. Yamamoto, z and N. Imanishi. Stability of Nb-Doped Cubic Li7La3Zr2O12 with Lithium Metal, Journal of The Electrochemical Society, 2013;160 (10): A1690-A1693.

[16] Daniel Rettenwander, Andreas Welzl, Lei Cheng, Jürgen Fleig, Maurizio Musso. Synthesis, Crystal Chemistry, and Electrochemical Properties of Li7−2xLa3Zr2−xMoxO12 (x = 0.1–0.4): Stabilisation of the Cubic Garnet Polymorph via Substitution of Zr4+ by Mo6+. Inorganic chemistry. 2015.

[17] Sampathkumar Ramkumar, Ramasamy Murugan, Structure and Li+ Dynamics of Sb-Doped Li7La3Zr2O12 Fast Lithium Ion Conductors, RAC Phys. Chem. 2013;21:16:43.

[18] Brahma Prakash Dubey a, Asit Sahoo, Venkataraman Thangadurai b, Yogesh Sharma. Morphological, dielectric and transport properties of garnet-tyLi6.25+yAl0.25La3Zr2yMnyO12 (y = 0, 0.05, 0.1, and 0.2). Elsevier solid state ionics. 2020; 351, 115339.

[19] Dhivy L.; Janani N.; Palanivel B.; Murugan R., Li+ transport properties of W substituted Li7La3Zr2O12 cubic lithium garnets. AIP Adv. 2013; 3 082115.

[20] Murugan R.; Ramakumar S.; Janani N. High conductive yttrium doped Li7La3Zr2O12 cubic lithium garnet, Electrochem Commun. 2011; 13, 1373–1375.

[21] Yue Jiang, Xiaohong Zhu, Shiyong Qin, Ming’en Ling, Jiliang Zhu. Investigation of Mg2+, Sc3+ and Zn2+ doping effects on densification and ionic conductivity of low-temperaturesintered Li7La3Zr2O12 garnets. Elsevier, Solid state ionics. 2017; 300:73-77.

[22] C. Deviannapoorani, L. Dhivy, S. Ramakumar R. Murugan, Synthesis of garnet structured Li7+xLa3YxZr2−xO12 (x 5 0–0.4) by modified sol−gel method, J Sol-Gel Sci Technol, 2012
[23] Ezhiylmurugan Rangasamy, Jeff Wolfenstine, Jan Allen, Jeff Sakamoto. The effect of 24c-site (A) cation substitution on the tetragonal cubic phase transition in Li$_{7-x}$La$_{3x}$A$_x$Zr$_2$O$_{12}$ garnet-based ceramic electrolyte. Elsevier, Journal of Power Sources. 2013; 230:261-266.

[24] Junhao Li, Zhongqi Liu, Wen Ma, Hongying Dong, Kefu Zhang, Ruigang Wang. Low temperature synthesis of cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$ via sol-gel and ball milling induced phase transition, Elsevier journal of power source. 2019; 412: 189-196.

[25] Reinhard Wagner, Günther J. Redhammer, Daniel Rettenwander, Anatoliy Senyshyn, Walter Schmidt, Martin Wilkening, and Georg Amthauer. Crystal Structure of Garnet-Related Li-Ion Conductor Li$_{7-3x}$Ga$_x$La$_3$Zr$_2$O$_{12}$: Fast Li-Ion Conduction Caused by a Different Cubic Modification?, ACS, Chem. Mater. 2016; 28, 1861-1871.

[26] Weijie Lan, Hongyang Fan, Vincent Wing-hei Lau, Jiliang Zhang, Jiafeng Zhang, Ruirui Zhao and Hongyu Chen. Realising Li$_7$La$_3$Zr$_2$O$_{12}$ garnets with high Li$^+$ conductivity and dense microstructures by Ga/Nb dual substitution for lithium solid-state battery applications. ACS, Sustainable Energy & Fuels. 2020, 4, 1812-1821

[27] Ryohei Takano, kiyaoharu, Akitoshi Hayashi, Masahiro Tatsumisago. Low temperature synthesis of Al-doped Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolyte by a sol-gel process. Elsevier, solid state ionics. 2014; 255: 104-107.

[28] Reinhard Wagner, Daniel Rettenwander, Günther J. Redhammer,† Gerold Tippelt, Synthesis, Crystal Structure, and Stability of Cubic Li$_{7-x}$La$_3$Zr$_{2-x}$Bi$_x$O$_{12}$, 2016, 5 55(23): 122112219.

[29] A.A. Raskovalov, E.A. Il’ina, B.D. Antonov, structure and transport properties of Li$_7$La$_3$Zr$_2$-0.75xAlxO$_{12}$ superionic solid electrolytes, Journal of Power Sources 238 (2013) 48e52.

[30] I. Kokal, M. Somer, P.H.L. Notten, H.T. Hintzen, Sol–gel synthesis and lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ with garnet-related type structure, Solid state ionics 2011, 185, 42-46.

[31] Ryoji Inada, Satoshi Yasuda, Masaru Tojo, Keiji Tsuritani, Tomohiro Tojo and Yoji Sakurai. Development of Lithium-Stuffed Garnet-Type Oxide Solid Electrolytes with High Ionic Conductivity for Application to All-Solid-State Batteries. Frontiers in Energy Research. 2016; 4: 28.