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Jiang-Fang Wu

Huazhong University of Science and Technology

Wei Kong Pang

University of Wollongong, wkpang@uow.edu.au

Vanessa K. Peterson

The Bragg Institute, Australian Nuclear Science And Technology Organisation, vep@ansto.gov.au

Lu Wei

University of Wollongong, lwei@uow.edu.au

Xin Guo

Huazhong University of Science and Technology

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Abstract

All-solid-state Li-ion batteries with metallic Li anodes and solid electrolytes could offer superior energy density and safety over conventional Li-ion batteries. However, compared with organic liquid electrolytes, the low conductivity of solid electrolytes and large electrolyte/electrode interfacial resistance impede their practical application. Garnet-type Li-ion conducting oxides are among the most promising electrolytes for all-solid-state Li-ion batteries. In this work, the large-radius Rb is doped at the La site of cubic $\text{Li}_6\text{.10Ga}_0\text{.30La}_3\text{Zr}_2\text{O}_{12}$ to enhance the Li-ion conductivity for the first time. The $\text{Li}_6\text{.20Ga}_0\text{.30La}_2\text{.95Rb}_0\text{.05Zr}_2\text{O}_{12}$ electrolyte exhibits a Li-ion conductivity of 1.62 mS cm^{-1} at room temperature, which is the highest conductivity reported until now. All-solid-state Li-ion batteries are constructed from the electrolyte, metallic Li anode, and LiFePO_4 active cathode. The addition of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ electrolytic salt in the cathode effectively reduces the interfacial resistance, allowing for a high initial discharge capacity of 152 mAh g^{-1} and good cycling stability with 110 mAh g^{-1} retained after 20 cycles at a charge/discharge rate of 0.05 C at 60°C .

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Garnet-type fast Li-ion conductors with high ionic conductivities for all-solid-state batteries

Jian-Fang Wu¹, Wei Kong Pang^{2, 3}, Vanessa K. Peterson^{2, 3}, Lu Wei^{1*}, and Xin Guo^{1*}

1. Laboratory of Solid State Ionics, School of Materials Science and Engineering,

Huazhong University of Science and Technology, Wuhan 430074, P.R. China

2. Australian Centre for Neutron Scattering, Australian Nuclear Science and

Technology Organisation, Locked Bag 2001, Kirrawee DC, New South Wales 2232,

Australia

3. Institute for Superconducting & Electronic Materials, Faculty of Engineering,

University of Wollongong, NSW 2522, Australia

** Author to whom correspondence should be addressed.*

Tel: +86-27-87559804; Fax: +86-27-87559804; E-mail: xguo@hust.edu.cn,

lwei@hust.edu.cn

Abstract

All-solid-state Li-ion batteries with metallic Li anodes and solid electrolytes could offer superior energy density and safety over conventional Li-ion batteries. However, compared with organic liquid electrolytes, the low conductivity of solid electrolytes and large electrolyte/electrode interfacial resistance impede their practical application. Garnet-type Li-ion conducting oxides are amongst the most promising electrolytes for all-solid-state Li-ion batteries. In this work, the large radius Rb is doped at the La site of cubic $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$ to enhance the Li-ion conductivity for the first time. The $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ electrolyte exhibits a Li-ion conductivity of 1.62 mS cm^{-1} at room temperature, which is the highest conductivity reported until now. All-solid-state Li-ion batteries are constructed from the electrolyte, metallic Li anode and LiFePO_4 active cathode. The addition of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ electrolytic salt in the cathode effectively reduces the interfacial resistance, allowing for a high initial discharge capacity of 152 mAh g^{-1} and good cycling stability with 110 mAh g^{-1} retained after 20 cycles at a charge/discharge rate of 0.05 C at 60 °C.

Keywords: solid electrolyte, LLZO, garnet, lithium-ion conductivity, all-solid-state lithium batteries

1. Introduction

All-solid-state Li-ion batteries based on solid electrolytes offer the possibility to solve safety issues of traditional Li-ion batteries arising from the leakage of flammable organic liquid electrolytes. Therefore, intensive efforts are being enforced to advance all-solid-state batteries towards a safe and stable power source.^{1,2} Applications requiring power sources operating at high temperature and pressure in military, space exploration, mineral and fossil fuel exploitation, are particularly important; all-solid-state Li-ion batteries are considered as currently the best choice.³ Moreover, all-solid-state Li-ion batteries utilizing high voltage electrode and metallic Li with the highest specific capacity (3860 mAh g⁻¹) and the lowest negative electrochemical potential (~3.04 V vs. the standard hydrogen electrode), widen the operating voltage window and maximize the capacity density, therefore, enhance the energy density.^{4,5} However, compared with organic liquid electrolytes, the low Li-ion conductivity of solid electrolytes and large electrolyte/electrode interfacial resistance largely hamper the practical applications of all-solid-state Li-ion batteries.⁶⁻⁸

Several inorganic solid electrolytes have been proposed for use in all-solid-state Li-ion batteries, including sulfides,⁹⁻¹¹ nitrides¹² and oxides.¹³⁻¹⁵ The highest Li-ion conductivity of ~10 mS cm⁻¹ was achieved in sulfide-type electrolytes,⁹⁻¹¹ however, sulfides are unstable against metallic Li and can produce poisonous H₂S if exposed to moisture.¹⁶ Nitride-type electrolytes are stable against metallic Li only in a narrow electrochemical window below 2 V, beyond which they decompose or form an insulating layer.¹² Among the oxide electrolytes, NASICON (sodium superionic conductor) and perovskite electrolytes are also unstable against metallic Li.^{14,15}

Li₇La₃Zr₂O₁₂ (LLZO), a garnet-type oxide solid electrolyte, possesses a high Li-ion conductivity (~10⁻⁴ S cm⁻¹), high chemical stability against metallic Li, and high

electrochemical window above 5 V;¹³ therefore, it is one of the most promising solid electrolytes for all-solid-state Li-ion batteries. Murugan *et al.* first fabricated and characterized LLZO,¹³ and cubic and tetragonal phases were found.¹⁷ Cubic LLZO exhibits a Li-ion conductivity that is two orders of magnitude higher than that of tetragonal LLZO,¹⁷ since the structure greatly affects the Li-ion distribution and subsequent migration pathway.¹⁸ The tetragonal modification possesses an ordered Li-ion distribution, in contrast to the disordered distribution in the cubic phase, with the latter arising from the presence of vacancies. Pure LLZO is tetragonal at room temperature, however, the cubic phase can be stabilized by supervalent doping with Ta⁵⁺,¹⁹ Nb⁵⁺,²⁰ Te⁶⁺,²¹ and W⁶⁺²² at Zr⁴⁺ sites, or Al³⁺,¹³ and Ga³⁺²³⁻²⁹ substituting Li⁺. Doping leads to Li-ion deficiency, and the disordered Li sublattice, hence stabilizing the cubic phase. In contrast to supervalent doping, low valent doping leads to excess Li ions, de-stabilizing the cubic phase. However, it is predicted that doping at La sites with larger radius cations, such as Sr²⁺ (low valent doping), may enhance conductivity,^{30,31} although there has been little supporting evidence for this.

The electrolyte/electrode interfacial resistance also plays an important role in determining the performance of all-solid-state Li-ion batteries, and in solid-state thin film Li-ion batteries the interfacial resistance can be decreased.³²⁻³⁴ However, such a configuration limits capacity owing to the small quantity of electrode loaded in the film. Bulk synthesis techniques are considered promising for improving the capacity, which could lead to the high energy batteries. Hu *et al.*³⁵ demonstrated that coating an ultrathin layer of Al₂O₃ onto a garnet-type solid electrolyte (Nb and Ca codoped LLZO) could lower the electrolyte/Li electrode interfacial resistance. Guo *et al.*³⁶ and Hassoun *et al.*³⁷ proposed a simple yet effective method to construct high performance all-solid-state Li-ion batteries through the use of polymer electrolytes, such as

Li(CF₃SO₂)₂N in poly(vinylidene fluoride)³⁶ or LiCF₃SO₃ in poly(ethylene oxide) in the electrode,³⁷ which improves the Li-ion transportation and diffusion at the electrolyte/electrode interface and reduces the resistance.

In this work, we dope the relatively large radius cation Rb⁺ at the La³⁺ site in cubic Li_{6.10}Ga_{0.30}La₃Zr₂O₁₂ to improve the Li-ion conductivity. This strategic doping leads to the highest ionic conductivity of 1.62 mS cm⁻¹ at room temperature, and 4.56 mS cm⁻¹ at 60 °C. All-solid-state Li-ion batteries were constructed from the Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂ electrolyte, metallic Li anode and LiFePO₄ active cathode. To reduce the electrolyte/cathode interfacial resistance, Li(CF₃SO₂)₂N electrolytic salt was added into the cathode; adding Li(CF₃SO₂)₂N electrolytic salt in the cathode can promote the Li-ion transportation and diffusion at the electrolyte/cathode interface. Benefiting from the high Li-ion conductivity of the LLZO solid electrolyte and the improved garnet/cathode interface, the fabricated all-solid-state Li-ion batteries exhibit good electrochemical performances.

2. Experimental

2.1 Preparation of solid electrolytes

Li_{6.10+2y}Ga_{0.30}La_{3-y}Rb_yZr₂O₁₂ (y = 0.05, 0.10, 0.15, and 0.20) ceramic samples were fabricated through a solid-state reaction using Li₂CO₃, Rb₂CO₃, La₂O₃, ZrO₂, and Ga₂O₃ powders, with 10 mol.% excess Li₂CO₃ used for compensating Li volatilization in high temperature calcination processes. The mixed powders were firstly ball-milled for 15 h with isopropanol and calcined at 900 °C for 6 h in air, followed by another 15 h's ball-milling. Ceramic pellets were obtained by cold isostatic pressing the powders at 250 MPa and sintering at 1100 °C for 24 h in air. To avoid Al³⁺ incorporation caused by the alumina crucible, we put LLZO pellets with the same composition

between the crucible and the samples during the sintering process. Moreover, mother powders were used to cover the samples to decrease Li loss. Finally, the obtained ceramic pellets were polished to ~1 mm thickness and cut into disks with a diameter of 12 mm. Then they were stored in an Ar filled glovebox ($O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm) for later use.

2.2 Composition and structure analyses

The crystalline phase of the samples were analyzed by X-ray diffraction (XRD) using a XRD-7000S (Japan Shimadzu Corporation). The relative densities of the samples were measured by the Archimedes method using water. Neutron powder diffraction (NPD) was conducted on the samples using the high-resolution neutron powder diffractometer (ECHIDNA) at the Australian Nuclear Science and Technology Organisation (ANSTO).³⁸ The neutron beam wavelength was determined to be 0.162172(5) nm using the $La^{11}B_6$ NIST standard reference material (SRM) 660b. GSAS-II was used for structural refinements.³⁹ A field emission scanning electron microscope (FE-SEM, Sirion 200, Holland FEI Corporation) equipped with an energy dispersive X-ray detector (EDX) was used to investigate the microstructure and elemental distribution within the samples.

2.3 Conductivity measurements

Alternating current (AC) impedance measurements were undertaken using a Solartron 1260 impedance and gain-phase analyzer in the frequency range of 1 to 5×10^6 Hz at an amplitude of 50 mV at temperatures from -60 to 60 °C in an environmental test chamber. Li-ion blocking Ag electrodes were used for the tests. The sample was kept at the desired temperature for an hour before each measurement. The electronic conductivity was determined by the DC polarization method using an electrochemical station under an applied DC voltage of 0.1 V.

2.4 Fabrication of all-solid-state Li-ion batteries

The fabrication of all-solid-state Li-ion batteries was carried out in an Ar filled glovebox. One electrode was fabricated by mixing carbon-coated LiFePO₄ powder (Hefei Kejing Materials Technology CO.), Ketjen black, poly(vinylidene fluoride) (PVDF), Li(CF₃SO₂)₂N (LiTFSI) and N-methyl-2 pyrrolidon (NMP) in an agate mortar with a mass ratio of 7.5:1.5:1:6:150. The obtained slurry was coated on one side of the electrolyte pellet. After being pressed with a stainless steel plate, the solid electrolyte with electrode coating was dried in a vacuum oven at 80 °C for 12 h to remove NMP and trace moisture. The loading mass of the electrode was ~ 2.2 mg. Afterwards, lithium metal was attached on the other side of the electrolyte pellet by a 10 N pressure after removing the oxide layer. Finally, a laminated all-solid-state battery was assembled into a coin cell for electrochemical tests.

2.5 Electrochemical measurements

Galvanostatic charge and discharge performances of LFPO/doped-LLZO/Li all-solid-state batteries were investigated using a LANHE CT2001A charge/discharge system (Wuhan LAND Electronics Co.) in the potential range of 4.0 to 2.8 V at 60 °C. Before the charge/discharge, the battery was heated at 100 °C for 3 h and then at 60 °C for 24 h to increase adhesion between the metallic Li and electrolyte. The current density is normalized to the mass of LiFePO₄, *i.e.* 1 C being 170 mA g⁻¹. Moreover, Li/doped-LLZO/Li batteries were also assembled, and the DC cycling performance was characterized at 60 °C with a current density of 5 μA cm⁻².

3. Results and Discussion

Cubic Li_{6.10+2y}Ga_{0.30}La_{3-y}Rb_yZr₂O₁₂ garnets were prepared following the preparation method presented in Figure 1a. A ceramic pellet and the cubic garnet crystal structure

are shown in Figure 1b and c, respectively. The Rb doping facilitates the densification of the garnet at a relatively low sintering temperature. More importantly, the larger ionic radius of Rb^+ (0.148 nm), compared with that of La^{3+} (0.106 nm), offers the possibility to enlarge migration pathway for Li ions (Figure 1d).^{30,31}

The garnet structure was confirmed by X-ray diffraction (XRD) analysis as shown in Figure 2a. Data for $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$ ($y = 0$), $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ ($y = 0.05$), and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$ ($y = 0.10$) are all indexed to the cubic phase. In addition to the cubic phase, XRD data for $\text{Li}_{6.40}\text{Ga}_{0.30}\text{La}_{2.85}\text{Rb}_{0.15}\text{Zr}_2\text{O}_{12}$ ($y = 0.15$) and $\text{Li}_{6.50}\text{Ga}_{0.30}\text{La}_{2.80}\text{Rb}_{0.20}\text{Zr}_2\text{O}_{12}$ ($y = 0.20$) exhibit peaks characteristic of an impurity phase Li_2ZrO_3 .

Neutron powder diffraction (NPD) was employed to investigate the substitution of Rb^+ at the La site in $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$. Rietveld refinement of structural models from Wang *et al.*⁴⁰ and Chen *et al.*⁴¹ against the NDP data were performed with the results shown in Figure 2b and c, and corresponding structural parameters are summarized in Table 1. Li occupies 24d (tetrahedral) and 96h (octahedral) sites (Figure 1c), with 96h sites deviating from the octahedral center (48g), Ga occupies Li (24d) sites,²⁶ and Rb is at the La-site; such a structure is consistent with the theoretical prediction of Miara *et al.*⁴²

The microstructure of $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples with different Rb contents are presented in Figure 3. All samples exhibit high densification, being consistent with the relative densities measured by the Archimedes method in Table 2. Energy dispersive X-ray spectroscopy (EDS) mapping of the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ sample shown in Figure 3 reveals that Ga, La, Rb, Zr, and O are homogeneously distributed.

Electrochemical impedance spectroscopy (EIS) was used to determine the

conductivity. Figure 4a shows impedance spectra of the $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples at 25 °C. All spectra exhibit a semi-circle at high to medium frequencies and an almost vertical line at low frequencies. The semi-circle diameter represents the total (bulk and grain boundary) resistance of the sample, and the vertical line can be attributed to the Li-ion transfer resistance between the electrolyte and the Ag electrode.¹³ It can be seen that the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ sample shows the smallest semi-circle diameter, and therefore the lowest total resistance. The total conductivity (σ_{total}) of the samples calculated from the EIS measurements at 25 °C are given in Table 2. The σ_{total} of $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ reaches 1.62 mS cm^{-1} , which is the highest conductivity amongst all LLZO electrolytes reported in literatures, and even higher than the samples prepared by hot-pressing and sparking plasma sintering (Table 3).^{19,26,29,36,43,44} With increasing Rb content from 0 to 0.20 per formula unit, the conductivity increases from 1.12 to 1.62 mS cm^{-1} , then decreases to 1.04 mS cm^{-1} . The conductivity increase maybe correlated with a structural change upon Rb doping (Figure 1d) and a higher Li^+ concentration, while the conductivity decrease at higher Rb contents is due to the presence of the low conductive Li_2ZrO_3 phase and a decrease of available vacancies. We also measured EIS data for $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ at different temperatures (Figure 4b). At -60 °C, the spectrum exhibits a large semi-circle, and on increasing temperature to 60 °C, the semi-circle gradually reduces and disappears, with σ_{total} for the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ sample reaching 4.56 mS cm^{-1} at 60 °C.

The Arrhenius plots of $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ are presented in Figure 4c, with calculated activation energies (E_a) given in Table 2. The activation energy E_a is low, in the range of 0.25 to 0.28 eV ; a low activation energy for the Li-ion conduction plays an important role in the high performance of all-solid-state Li-ion batteries over

a wide temperature range.

An ideal solid electrolyte should be a pure ionic conductor, since the electronic conduction causes short-circuit in the battery. To determine the electronic conductivity, direct current (DC) polarization method was employed, and the results are summarized in Table 2. The electronic conductivity is on the order of $10^{-7} \text{ S cm}^{-1}$, about 4 orders of magnitude lower than the total conductivity, demonstrating that the electronic conduction can be ignored, and that the transference number of Li^+ ions in the $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ electrolytes is approximately unity.

To derive information on the Li-ion conduction in doped-LLZO electrolytes, complex modulus formalism was employed, where the complex electric modulus (M^*) is related to the complex impedance (Z^*) through the relationship: $M^*(\omega) = i\omega C_0 Z^* = M'(\omega) + iM''(\omega)$, where C_0 is the geometrical capacitance, M' is the real part of the modulus, and M'' the imaginary part. Figure 5a and b show the relationship of M'' with frequency for $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$ at different temperatures. The arising of peaks in the modulus spectra is a signal for the conductivity relaxation; Li ions hop over long distances at the frequencies below the peak frequencies (f_{max}), however, at frequencies above f_{max} , Li ions travel over short distances.^{45,46} The value of f_{max} also shows an Arrhenius-type temperature dependence (Figure 5c). The activation energies, as determined from Figure 5c for $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$, are 0.25 and 0.28 eV, respectively, which are close to those deduced from the conductivity data (0.26 eV, Figure 4c), therefore, the ionic conduction originates from the long distance hopping of Li ions (Figure 1e).^{45,46}

All-solid-state Li-ion batteries were constructed from the solid electrolyte with the highest conductivity, $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$. Firstly, symmetric

Li/Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂/Li batteries were constructed to check the stability of the Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂ electrolyte against metallic Li dendrites. Figure 6a shows the DC charge/discharge cycling performance of the battery at a current density of 5 $\mu\text{A cm}^{-2}$ at 60 °C. It can be seen that the battery voltage stabilizes, indicating that the Li/Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂/Li battery does not get short-circuited and that penetrable Li dendrites are not formed.⁴⁷ Voltage drops are observed in the first several circles, which may arise from the formation of a Li film on the Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂ surface during the Li plating/stripping process. Therefore, the Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂ electrolyte is stable with metallic Li.

All-solid-state Li-ion batteries were also constructed from Li_{6.20}Ga_{0.30}La_{2.95}Rb_{0.05}Zr₂O₁₂, metallic Li and LiFePO₄ active electrodes. To reduce the electrolyte/electrode interfacial resistance, Li(CF₃SO₂)₂N electrolytic salt was added into the cathode. The battery structure is shown in Figure 6b. The all-solid-state Li-ion battery underwent long charge/discharge cycling testing between 2.8 and 4.0 V at 0.05 C at 60 °C, with results being given in Figure 6c. It is clear that in the first charge/discharge cycle, the charge and discharge plateau change significantly as a result of polarization, which improves in subsequent cycles. The Li(CF₃SO₂)₂N electrolytic salt with PVDF, serving as a Li-ion conducting medium in the cathode, can improve Li-ion transportation and diffusion at the electrolyte/electrode interface, decreasing interfacial resistance (Figure 6d) and contributing to the better electrochemical performance.^{36,37} The battery delivers a specific capacity of 152 mAh g⁻¹ in the first cycle, which reaches 88% of the theoretical capacity of LiFePO₄, and the battery maintains a specific capacity of 110 mAh g⁻¹ after 20 cycles. The capacity decrease can be attributed to the unstable contact between the electrodes and the electrolyte after several cycles. Despite this, compared with the other all-solid-state

Li-ion batteries based on garnet electrolytes (Table 3),^{36,48-54} the battery constructed with the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ electrolyte shows high capacity and good cyclability.

4. Conclusions

Cubic $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ garnets ($y \leq 0.10$ Rb per formula unit) were successfully synthesized by substituting Rb at the La site of $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$. The doping leads to a Li-ion conductivity of 1.62 mS cm^{-1} at room temperature and 4.56 mS cm^{-1} at 60°C for $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$. However, with increasing Rb content ($y \geq 0.15$ Rb per formula unit), the low conductive impurity phase Li_2ZrO_3 is generated, which decreases the Li-ion conductivity. Importantly, the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ electrolyte exhibits a good stability against metallic Li, and bulk-type all-solid-state Li-ion batteries, constructed from $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$, metallic Li and LiFePO_4 with the addition of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ electrolytic salt, exhibit good electrochemical performances, including a high initial discharge capacity of 152 mAh g^{-1} with good capacity retention of 110 mAh g^{-1} after 20 charge/discharge cycles. Therefore, the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ garnet is a promising solid electrolyte for all-solid-state Li-ion batteries.

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References

1. Armand, M.; Tarascon, J. M., Building Better Batteries. *Nature* **2008**, *451*, 652-657.
2. Goodenough, J. B.; Kim, Y., Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587-603.
3. Kalaga, K.; Rodrigues, M.-T. F.; Gullapalli, H.; Babu, G.; Arava, L. M. R.; Ajayan, P. M., Quasi-Solid Electrolytes for High Temperature Lithium Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 25777-25783.
4. Zhang, J.; Zhao, N.; Zhang, M.; Li, Y.; Chu, P. K.; Guo, X.; Di, Z.; Wang, X.; Li, H., Flexible and Ion-Conducting Membrane Electrolytes for Solid-State Lithium Batteries. *Nano Energy* **2016**, *28*, 447-454.
5. Fua, K. K.; Gong, Y.; Daib, J.; Gong, A.; Han, X.; Yao, Y.; Wang, C.; Wang, Y.; Chen, Y.; Yan, C.; Li, Y.; Wachsman, E. D.; Hu, L., Flexible, Solid-state, Ion-conducting Membrane with 3D Garnet Nanofiber Networks for Lithium Batteries. *PNAS* **2016**, *113*, 7094-7099.
6. Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H. H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Lupart, S.; Lamp, P.; Giordano, L.; Shao-Horn, Y., Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction. *Chem. Rev.* **2016**, *116*, 140-162.
7. Richards, W. D.; Miara, L. J.; Wang, Y.; Kim, J. C.; Ceder, G., Interface Stability in Solid-State batteries. *Chem. Mater.* **2015**, *28*, 266-273.
8. Luntz, A. C.; Voss, J.; Reuter, K., Interfacial Challenges in Solid-State Li Ion Batteries. *J. Phys. Chem. Lett.* **2015**, *6*, 4599-4604.
9. Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A., A Lithium Superionic Conductor. *Nat. Mater.* **2011**, *10*, 682-686.
10. Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R., High-Power All-Solid-State Batteries Using Sulfide Superionic Conductors. *Nat. Energy* **2016**, *1*, 16030.
11. Seino, Y.; Ota, T.; Takada, K.; Hayashi, A.; Tatsumisago, M., A Sulphide Lithium Super Ion Conductor Is Superior to Liquid Ion Conductors for Use in Rechargeable Batteries. *Energy Environ. Sci.* **2014**, *7*, 627-631.
12. Miara, L. J.; Suzuki, N.; Richards, W. D.; Wang, Y.; Kim, J. C.; Ceder, G., Li-Ion Conductivity in

Li₉S₃N. *J. Mater. Chem. A* **2015**, 3, 20338-20344.

13. Murugan, R.; Thangadurai, V.; Weppner, W., Fast Lithium Ion Conduction in Garnet-type Li₇La₃Zr₂O₁₂. *Angew. Chem. Int. Edit* **2007**, 46, 7778-7781.
14. Yoshiyuki, I.; Chen, L.; Mitsuru, I.; Tetsurō, N.; Takashi, U.; Hiromasa, I.; Masataka, W., High Ionic Conductivity in Lithium Lanthanum Titanate. *Solid State Commun.* **1993**, 86, 689-693.
15. Morimoto, H.; Awano, H.; Terashima, J.; Shindo, Y.; Nakanishi, S.; Ito, N.; Ishikawa, K.; Tobishima, S.-I., Preparation of Lithium Ion Conducting Solid Electrolyte of NASICON-Type Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (x = 0.3) Obtained by Using the Mechanochemical Method and Its Application as Surface Modification Materials of LiCoO₂ Cathode for Lithium Cell. *J. Power Sources* **2013**, 240, 636-643.
16. Han, F.; Gao, T.; Zhu, Y.; Gaskell, K. J.; Wang, C., A Battery Made from a Single Material. *Adv. Mater.* **2015**, 27, 3473-3483.
17. Geiger, C. A.; Alekseev, E.; Lazic, B.; Fisch, M.; Armbruster, T.; Langner, R.; Fechtelkord, M.; Kim, N.; Pettke, T.; Weppner, W., Crystal Chemistry and Stability of "Li₇La₃Zr₂O₁₂" Garnet: A Fast Lithium-Ion Conductor. *Inorg. Chem.* **2011**, 50, 1089-1097.
18. Bernstein, N.; Johannes, M. D.; Hoang, K., Origin of The Structure Phase Transition in Li₇La₃Zr₂O₁₂. *Phys. Rev. Lett.* **2012**, 109, 205702-205706.
19. Li, Y.; Han, J.-T.; Wang, C.-A.; Xie, H.; Goodenough, J. B., Optimizing Li⁺ Conductivity in a Garnet Framework. *J. Mater. Chem.* **2012**, 22, 15357-15361.
20. Huang, M.; Shoji, M.; Shen, Y.; Nan, C.-W.; Munakata, H.; Kanamura, K., Preparation and Electrochemical Properties of Zr-site Substituted Li₇La₃(Zr_{2-x}M_x)O₁₂ (M = Ta, Nb) Solid Electrolytes. *J. Power Sources* **2014**, 261, 206-211.
21. Wang, D.; Zhong, G.; Dolotko, O.; Li, Y.; McDonald, M. J.; Mi, J.-X.; Fu, R.; Yang, Y., The Synergistic Effects of Al and Te on the Structure and Li⁺-Mobility of the Garnet-Type Solid Electrolytes. *J. Mater. Chem. A* **2014**, 2, 20271-20279.
22. Li, Y.; Wang, Z.; Cao, Y.; Du, F.; Chen, C.; Cui, Z.; Guo, X., W-doped Li₇La₃Zr₂O₁₂ Ceramic Electrolytes for Solid State Li-Ion Batteries. *Electrochim. Acta* **2015**, 180, 37-42.
23. Afyon, S.; Krumeich, F.; Rupp, J. L. M., A Shortcut to Garnet-Type Fast Li-Ion Conductors for All Solid State Batteries. *J. Mater. Chem. A* **2015**, 3, 18636-18648.
24. El Shinawi, H.; Janek, J., Stabilization of Cubic Lithium-Stuffed Garnets of the Type

“Li₇La₃Zr₂O₁₂” by Addition of Gallium. *J. Power Sources* **2013**, 225, 13-19.

25. Jalem, R.; Rushton, M.; Manalastas, W.; Nakayama, M.; Kasuga, T.; Kilner, J. A.; Grimes, R. W., Effects of Gallium Doping in Garnet-Type Li₇La₃Zr₂O₁₂ Solid Electrolytes. *Chem. Mater.* **2015**, 27, 2821-2831.
26. Bernuy-Lopez, C.; Manalastas, W.; Lopez del Amo, J. M.; Aguadero, A.; Aguesse, F.; Kilner, J. A., Atmosphere Controlled Processing of Ga-Substituted Garnets for High Li-Ion Conductivity Ceramics. *Chem. Mater.* **2014**, 26, 3610-3617.
27. Rettenwander, D.; Geiger, C. A.; Tribus, M.; Tropper, P.; Amthauer, G., A Synthesis and Crystal Chemical Study of the Fast Ion Conductor Li_{7-3x}Ga_xLa₃Zr₂O₁₂ with x = 0.08 to 0.84. *Inorg. Chem.* **2014**, 53, 6264-6269.
28. Rettenwander, D.; Langer, J.; Schmidt, W.; Arrer, C.; Harris, K. J.; Terskikh, V.; Goward, G. R.; Wilkening, M.; Amthauer, G., On the Site Occupation of Ga and Al in Stabilized Cubic Li_{7-3(x+y)}Ga_xAl_yLa₃Zr₂O₁₂ Garnets as Deduced from ²⁷Al and ⁷¹Ga MAS NMR at Ultrahigh Magnetic Fields. *Chem. Mater.* **2015**, 27, 2821–2831.
29. Wu, J.-F.; Chen, E.-Y.; Yao, Y.; Liu, L.; Wu, Y.; Pang, K.; Peterson, V.; Guo, X., Gallium-Doped Li₇La₃Zr₂O₁₂ Garnet-Type Electrolytes with High Lithium-Ion Conductivity. *ACS Appl. Mater. Interfaces* **2017**, 9, 1542-1552.
30. Moratia-Orrantia, A.; Garcia-Martin, S.; Morán, E.; Alario-Franco, M. Á., New La_{2/3-x}Sr_xLi_xTiO₃ Solid Solution: Structure, Microstructure, and Li⁺ Conductivity. *Chem. Mater.* **2003**, 15, 363-367.
31. Teranishi, T.; Kouchi, A.; Hayashi, H.; Kishimoto, A., Dependence of the Conductivity of Polycrystalline Li_{0.33}Ba_xLa_{0.56-2/3x}TiO₃ on Ba Loading. *Solid State Ionics* **2014**, 263, 33-38.
32. Phan, V. P.; Pecquenard, B.; Cras, F. L., High-Performance All-Solid-State Cells Fabricated with Silicon Electrodes. *Adv. Funct. Mater.* **2012**, 22, 2580-2584.
33. Zhu, J.; Lu, L.; Zeng, K., Nanoscale Mapping of Lithium-Ion Diffusion in a Cathode within an All-Solid-State Lithium-Ion Battery by Advanced Scanning Probe Microscopy Techniques. *ACS Nano* **2013**, 7, 1666-1675.
34. Haruta, M.; Shiraki, S.; Suzuki, T.; Kumatani, A.; Ohsawa, T.; Takagi, Y.; Shimizu, R.; Hitosugi, T., Negligible "Negative Space-Charge Layer Effects" at Oxide-Electrolyte/Electrode Interfaces of Thin-Film Batteries. *Nano Lett.* **2015**, 15, 1498-1502.
35. Han, X.; Gong, Y.; Fu, K.; He, X.; Hitz, G. T.; Dai, J.; Pearse, A.; Liu, B.; Wang, H.; Rubloff, G.;

- Mo, Y.; Thangadurai, V.; Wachsman, E. D.; Hu, L., Negating Interfacial Impedance in Garnet-Based Solid-State Li Metal Batteries. *Nat. Mater.* **2016**, DOI: 10.1038/nmat4821.
36. Du, F.; Zhao, N.; Li, Y.; Chen, C.; Liu, Z.; Guo, X., All Solid State Lithium Batteries Based on Lamellar Garnet-Type Ceramic Electrolytes. *J. Power Sources* **2015**, *300*, 24-28.
37. Hassoun, J.; Scrosati, B., Moving to a Solid-State Configuration: A Valid Approach to Making Lithium-Sulfur Batteries Viable for Practical Applications. *Adv. Mater.* **2010**, *22*, 5198-5201.
38. Liss, K. D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S., The New High-Resolution Powder Diffractometer Being Built at OPAL. *Physica B* **2006**, *385–386*, 1010-1012.
39. Toby, B. H.; Von Dreele, R. B., GSAS-II: the Genesis of a Modern Open-Source All Purpose Crystallography Software Package. *J. Appl. Cryst.* **2013**, *46*, 544-549.
40. Wang, D.; Zhong, G.; Pang, W. K.; Guo, Z.; Li, Y.; McDonald, M. J.; Fu, R.; Mi, J.-X.; Yang, Y., Towards Understanding the Lithium Transport Mechanism in Garnet-Type Solid Electrolytes: Li⁺ Ions Exchanges and Their Mobility at Octahedral/Tetrahedral Sites. *Chem. Mater.* **2015**, *27*, 6650–6659.
41. Chen, Y.; Rangasamy, E.; Liang, C.; An, K., Origin of High Li⁺ Conduction in Doped Li₇La₃Zr₂O₁₂ Garnets. *Chem. Mater.* **2015**, *27*, 5491–5494.
42. Miara, L. J.; Ong, S. P.; Mo, Y.; Richards, W. D.; Park, Y.; Lee, J.-M.; Lee, H. S.; Ceder, G., Effect of Rb and Ta Doping on the Ionic Conductivity and Stability of the Garnet Li_{7+2x-y}(La_{3-x}Rb_x)(Zr_{2-y}Ta_y)O₁₂ (0 ≤ x ≤ 0.375, 0 ≤ y ≤ 1) Superionic Conductor: A First Principles Investigation. *Chem. Mater.* **2013**, *25*, 3048-3055.
43. Baek, S.-W.; Lee, J.-M.; Kim, T. Y.; Song, M.-S.; Park, Y., Garnet Related Lithium Ion Conductor Processed by Spark Plasma Sintering for All Solid State Batteries. *J. Power Sources* **2014**, *249*, 197-206.
44. Rettenwander, D.; Redhammer, G.; Preishuber-Pflügl, F.; Cheng, L.; Miara, L.; Wagner, R.; Welzl, A.; Suard, E.; Doeff, M. M.; Wilkening, M.; Fleig, J.; Amthauer, G., Structural and Electrochemical Consequences of Al and Ga Co-substitution in Li₇La₃Zr₂O₁₂ Solid Electrolytes. *Chem. Mater.* **2016**, *28*, 2384–2392.
45. Baral, A. K.; Narayanan, S.; Ramezanipour, F.; Thangadurai, V., Evaluation of Fundamental Transport Properties of Li-Excess Garnet-Type Li_{5+2x}La₃Ta_{2-x}Y_xO₁₂ (x = 0.25, 0.5 and 0.75) Electrolytes Using AC Impedance and Dielectric Spectroscopy. *Phys. Chem. Chem. Phys.* **2014**, *16*, 11356-11365.

46. Deviannapoorani, C.; Dhivya, L.; Ramakumar, S.; Murugan, R., Lithium Ion Transport Properties of High Conductive Tellurium Substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Cubic Lithium Garnets. *J. Power Sources* **2013**, *240*, 18-25.
47. Ren, Y.; Shen, Y.; Lin, Y.; Nan, C.-W., Direct Observation of Lithium Dendrites inside Garnet-Type Lithium-Ion Solid Electrolyte. *Electrochem. Commun.* **2015**, *57*, 27-30.
48. van den Broek, J.; Afyon, S.; Rupp, J. L. M., Interface-Engineered All-Solid-State Li-Ion Batteries Based on Garnet-Type Fast Li^+ Conductors. *Adv. Energy Mater.* **2016**, *6*, 1600736.
49. Liu, T.; Ren, Y.; Shen, Y.; Zhao, S.-X.; Lin, Y.; Nan, C.-W., Achieving High Capacity in Bulk-Type Solid-State Lithium Ion Battery Based on $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ Electrolyte: Interfacial Resistance. *J. Power Sources* **2016**, *324*, 349-357.
50. Ohta, S.; Seki, J.; Yagi, Y.; Kihira, Y.; Tani, T.; Asaoka, T., Co-Sinterable Lithium Garnet-Type Oxide Electrolyte with Cathode for All-Solid-State Lithium Ion Battery. *J. Power Sources* **2014**, *265*, 40-44.
51. Kato, T.; Hamanaka, T.; Yamamoto, K.; Hirayama, T.; Sagane, F.; Motoyama, M.; Iriyama, Y., In-Situ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}/\text{LiCoO}_2$ Interface Modification for Advanced All-Solid-State Battery. *J. Power Sources* **2014**, *260*, 292-298.
52. Jin, Y.; McGinn, P. J., Bulk Solid State Rechargeable Lithium Ion Battery Fabrication with Al-Doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Electrolyte and $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ Cathode. *Electrochim. Acta* **2013**, *89*, 407-412.
53. Ohta, S.; Komagata, S.; Seki, J.; Saeki, T.; Morishita, S.; Asaoka, T., All-Solid-State Lithium Ion Battery Using Garnet-Type Oxide and Li_3BO_3 Solid Electrolytes Fabricated by Screen-Printing. *J. Power Sources* **2013**, *238*, 53-56.
54. Matsuyama, T.; Takano, R.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M., Fabrication of All-Solid-State Lithium Secondary Batteries with Amorphous TiS_4 Positive Electrodes and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes. *Solid State Ionics* **2016**, *285*, 122-125.

Table 1 Structural parameters of $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$ obtained using NPD (space group $Ia\bar{3}d$)

Sample	Lattice parameter [nm]	R_{wp} [%]	GOF	Site	Occupancy	x	y	z	U_{iso} ($\text{\AA}^2$)
$\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$	1.29746(9)	3.36	1.46	Li1(24 <i>d</i>)	0.34(2)	3/8	0	1/4	0.009(1)
				Li2(96 <i>h</i>)	0.33(1)	0.100(1)	0.191(1)	0.421(1)	0.009(1)
				Ga(24 <i>d</i>)	0.1	3/8	0	1/4	0.009(1)
				La(24 <i>c</i>)	1	1/8	0	1/4	0.009(1)
				Zr(16 <i>a</i>)	1	0	0	0	0.009(1)
				O(96 <i>h</i>)	1	0.1004(1)	0.1954(1)	0.2816(1)	0.009(1)
$\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$	1.29653(5)	3.48	1.38	Li1(24 <i>d</i>)	0.52(3)	3/8	0	1/4	0.076(35)
				Li2(96 <i>h</i>)	0.35(1)	0.099(1)	0.190(1)	0.424(1)	0.005(2)
				Ga(24 <i>d</i>)	0.1	3/8	0	1/4	0.076(35)
				La(24 <i>c</i>)	0.967	1/8	0	1/4	0.006(1)
				Rb(24 <i>c</i>)	0.033	1/8	0	1/4	0.006(1)
				Zr(16 <i>a</i>)	1	0	0	0	0.006(1)
				O(96 <i>h</i>)	1	0.1000(1)	0.1955(1)	0.2818(1)	0.009(1)

Table 2 Relative density, total conductivity, activation energy and electronic conductivity of $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ at 25 °C

y	Relative density [%]	σ_{total} [mS cm ⁻¹]	E_a [eV]	$\sigma_{\text{Electronic}}$ [10 ⁻⁷ S cm ⁻¹]
0.00	96.3	1.12	0.25	4.6
0.05	94.6	1.62	0.26	3.9
0.10	95.1	1.53	0.26	2.6
0.15	95.7	1.04	0.28	4.4
0.20	94.3	1.16	0.27	5.1

Table 3 Literature review of the garnet-type electrolytes with Li-ion conductivities higher than 1 mS cm⁻¹, and the properties of all-solid-state

Li-ion batteries based on the garnet-type electrolytes

Electrolyte			Electrode		Battery performance				
Composition	Preparation method	Conductivity (RT) [mS cm ⁻¹]	Material	Deposition of cathode	Capacity [μAh cm ⁻²]	Multiple cycles	Current density [μA cm ⁻²]	Working Temp. [°C]	Ref.
Li _{6.20} Ga _{0.30} La _{2.95} Rb _{0.05} Zr ₂ O ₁₂	Normal sintering	1.62	LiFePO ₄	Slurry coating	110 mAh g ⁻¹	20	8.5 mA g ⁻¹	60	This work
Li _{6.25} Ga _{0.25} La ₃ Zr ₂ O ₁₂	Normal sintering	1.46							29
Li _{6.4} Ga _{0.2} La ₃ Zr ₂ O ₁₂	Normal sintering	1.32	--	--	--	--	--	--	44
Li _{6.55} Ga _{0.15} La ₃ Zr ₂ O ₁₂	O ₂ Sintering	1.3	--	--	--	--	--	--	26
Li _{6.4} La ₃ Zr _{1.4} Ta _{0.6} O ₁₂	Normal sintering	~1	--	--	--	--	--	--	19
Li _{7-x} La ₃ Zr _{1.5} Ta _{0.5} O ₁₂	SPS ^{b)}	1.35	--	--	-	--	--	--	43
Li _{6.25} Al _{0.25} La ₃ Zr ₂ O ₁₂	Normal sintering	0.5	Li ₄ Ti ₅ O ₁₂	Slurry coating	15 mAh g ⁻¹	3	2 mA g ⁻¹	95	48
Li _{6.75} La ₃ Zr _{1.75} Ta _{0.25} O ₁₂	Normal sintering	~1	LiCoO ₂	Slurry coating and sintering	100	1	5	RT	49
Li _{6.4} La ₃ Zr _{1.4} Ta _{0.6} O ₁₂	Hot Pressing	1.6	LiFePO ₄	Slurry coating	140 mAh g ⁻¹	100	8.5 mA g ⁻¹	60	36
Li _{6.8} La _{2.95} Ca _{0.05} Zr _{1.75} Nb _{0.25} O ₁₂	Normal sintering	0.36	LiCoO ₂	Cosintering	78 mAh g ⁻¹	1	10 ⁻³ mA g ⁻¹		50
Li ₇ La ₃ Zr ₂ O ₁₂	Normal sintering	--	LiCoO ₂	PLD ^{a)}	80 mAh g ⁻¹	25	10	RT	51
1.2 wt% Al-doped LLZO	Normal sintering	0.2	LiMn ₂ O ₄	PLD ^{a)}	1.2-1.8	3	1	--	52
Nb-doped LLZO	Normal sintering	--	LiCoO ₂	Slurry coating and sintering	85 mAh g ⁻¹	5	10	RT	53
Al-doped LLZO	Normal sintering	0.2-0.4	TiS ₄	PLD ^{a)}	500 mAh g ⁻¹	15	10	RT	54

^{a)} PLD: pulse laser deposition; ^{b)} SPS: spark plasma sintering

Figure 1. (a) Preparation process for cubic $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ garnet-type solid electrolytes, (b) optical image of a $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ pellet, (c) crystal structure of cubic $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ displayed along the [100] direction, (d) schematic of the bottleneck in Li-ion migration pathway, where a larger Li-ion diffusion pathway would be expected with Rb at La sites, and (e) schematic of the two migration pathways for Li ions.²⁹

Figure 2. (a) XRD patterns of $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples, (b) and (c) Rietveld refinement profiles using NPD data for $\text{Li}_{6.10}\text{Ga}_{0.30}\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$, respectively.

Figure 3. SEM images of $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples (top), and EDS element mapping of the region highlighted by the red square in the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ sample (below).

Figure 4. AC impedance spectra of (a) $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples at 25 °C, (b) $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ sample at different temperatures. Insets in (a) and (b) are the high frequency region of the impedance spectra and the equivalent circuits used to fit data. (c) Arrhenius plots for $\text{Li}_{6.10+2y}\text{Ga}_{0.30}\text{La}_{3-y}\text{Rb}_y\text{Zr}_2\text{O}_{12}$ samples.

Figure 5. (a, b) Frequency dependence of M'' and (c) Arrhenius plots of f_{max} for $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{6.30}\text{Ga}_{0.30}\text{La}_{2.90}\text{Rb}_{0.10}\text{Zr}_2\text{O}_{12}$.

Figure 6. (a) DC cycling performance of the $\text{Li}/\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}/\text{Li}$ battery at a current density of $5 \mu\text{A cm}^{-2}$ at 60°C . The inset shows a schematic of the battery. (b) Schematic view of the all-solid-state battery constructed from the $\text{Li}_{6.20}\text{Ga}_{0.30}\text{La}_{2.95}\text{Rb}_{0.05}\text{Zr}_2\text{O}_{12}$ electrolyte, Li anode and LiFePO_4 cathode, with the addition of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI) electrolytic salt in the cathode. (c) Cell potential versus time and discharge capacity of the all-solid-state battery during galvanostatic charge/discharge cycling at 0.05 C at 60°C , and (d) AC impedance spectra of the all-solid-state battery with and without LiTFSI electrolytic salt in the electrode. The inset shows an LED lit by the coin-type all-solid-state Li-ion battery at room temperature.

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