All-solid-state lithium ion batteries containing solid electrolytes are considered to be safer than lithium ion batteries that use liquid organic electrolytes. Therefore, new solid electrolytes are strongly required to improve the performance of all-solid-state lithium ion batteries. The lithium garnet-type oxide Li$_7$La$_3$Zr$_2$O$_{12}$ is expected to be a promising candidate as a solid electrolyte because it has advantages such as high chemical stability and a wide potential window. However, the lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ is ~0.2 mS cm$^{-1}$ at 25 $^\circ$C, which is approximately two orders of magnitude lower than that of conventional liquid organic electrolytes. In this study, the lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ was successfully improved by Nb-doping and optimization of the composition. The lithium ion conductivity of Li$_{7-X}$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ increased with the Nb content and reached a maximum of ~0.8 mS cm$^{-1}$ (25 $^\circ$C) at around X = 0.25, which is comparable to that of other fast lithium ion conducting oxides such as NASICON type oxides. An all-solid-state lithium ion battery was constructed using Li$_{6.75}$La$_3$(Zr$_{1.75}$, Nb$_{0.25}$)O$_{12}$ (solid electrolyte), lithium (anode) and LiCoO$_2$ (cathode), and good charge and discharge characteristics were obtained. Therefore, it is concluded that Li$_{6.75}$La$_3$(Zr$_{1.75}$, Nb$_{0.25}$)O$_{12}$ is a promising candidate as a solid electrolyte for all-solid-state lithium ion batteries.
cation and anion)). The lithium ion conductivity of Li$_3$La$_3$Nb$_2$O$_{12}$ and its derivatives,\(^{(7-11)}\) which were examined within the last decade, was still low (~1 \(\mu\)S cm\(^{-1}\) at R.T.), but Li$_7$La$_3$Zr$_2$O$_{12}$ reported by Thangadurai and Weppner in 2007\(^{(12)}\) shows high lithium ion conductivity (~0.1 mS cm\(^{-1}\) at R.T.) that is approximately two orders of magnitude higher than that of conventional lithium garnet-type oxides. Moreover, Li$_7$La$_3$Zr$_2$O$_{12}$ has high chemical stability and a wide potential window, and is thus, considered to be a promising candidate solid electrolyte. However, it is necessary to improve the lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ to develop an all-solid-state lithium ion battery with good electrochemical performance. To improve the lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$, the composition was optimized by Nb-doping. As a result, the lithium ion conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ was successfully improved to a maximum conductivity of ~0.8 mS cm\(^{-1}\) at 25 °C.

3. Nb Substituted Li$_7$La$_3$Zr$_2$O$_{12}$

Nb substituted Li$_7$La$_3$Zr$_2$O$_{12}$ (Li$_7$-$X$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ ($X = 0-2$) was prepared by conventional solid-state reaction.\(^{(13)}\) Figure 1(a) shows XRD patterns of the Li$_7$-$X$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ samples. All of the observed diffraction peaks were indexed as a cubic lithium garnet-like structure (space group: Ia-3d). Lattice parameters of the Li$_7$-$X$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ samples calculated from their XRD patterns are shown in Fig. 1(b). The Lattice parameter of Li$_7$-$X$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ decreased linearly with increasing Nb-content ($X$) according to Vegard’s law, indicating that Nb$^{5+}$ (86.0 pm) was substituted at Zr$^{4+}$ (70.9 pm) sites.

The electrical conductivity of the samples was measured in air using a two-probe AC impedance method with an Agilent 4294A in the frequency range of 40 Hz to 110 MHz at temperatures from 25 to 150 °C. The density of all measurement samples was between 89 and 92% of the theoretical density calculated from the lattice parameters. Figure 2 shows a Nyquist plot of Li$_6.75$La$_3$(Zr$_{1.75}$, Nb$_{0.25}$)O$_{12}$ at 25 °C in air. The plot can be well-resolved into bulk, grain-boundary, and electrode resistances. The semicircle in the high-frequency region represents the bulk resistance, and the other one represents the grain-boundary resistance. The appearance of a tail at the low-frequency region suggests that the electrode blocked mobile lithium ions. The solid line in Fig. 2 represents fitted data based on an equivalent circuit model consisting of two parallel resistance (R) and capacitance (C) contributions (R$_b$C$_b$)(R$_{gb}$C$_{gb}$)(R$_{el}$), where b, gb, and el denote the bulk, grain-boundary, and electrode, respectively. The values of R$_b$ and R$_{gb}$ at 25°C were 211 \(\Omega\)cm$^2$ and 49 \(\Omega\)cm$^2$, respectively (sample size: 13 mm$\phi$, 2 mm$\phi$). The grain boundary contribution to the total resistance (R$_{gb}$/(R$_b$ + R$_{gb}$)) was ~20%, which is comparable to that of any other family of lithium garnet-type oxides.\(^{(7-12)}\) The Nyquist plots of Li$_7$-$X$La$_3$(Zr$_{2-X}$, Nb$_X$)O$_{12}$ remained constant for
a week, independent of exposure time in air at room temperature, demonstrating the stability of Li_{7-X}La_3(Zr_{2-X}, Nb_X)O_{12} at room temperature in air.

The temperature dependence of the total (bulk plus grain-boundary) lithium ion conductivity of Li_{7-X}La_3(Zr_{2-X}, Nb_X)O_{12} is shown in Fig. 3(a). The lithium ion conductivity was linear and obeyed the Arrhenius law ($\sigma = A \exp(-E_a/kT)$, where $A$ is the frequency factor, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $E_a$ is the activation energy, indicating that no structure or phase changes occurred in the observed temperature range. The lithium ion conductivity at 25 °C and the activation energy are plotted in Fig. 3(b). The lithium ion conductivity increased with X, reaching a maximum of 0.8 mS cm$^{-1}$ at X = 0.25. In contrast, the activation energy reached a minimum value of $\sim$30 kJmol$^{-1}$ at the same value of X = 0.25. The crystal structure of lithium garnet-type oxide is shown in Fig. 4. Lithium ions occupy the 24 d and 96 h sites, so it is considered that the lithium ion conduction pathway exists between these sites. However, not all of the lithium ions in the crystal structure contribute to conduction. The lithium ions that occupy certain sites can only act as charge carriers when the adjacent site is vacant. Therefore, the number of the lithium ions that contribute to conduction is dependent on the occupancy and vacancy of each lithium ion site. The composition dependence of each lithium ion site in Li_{7-X}La_3(Zr_{2-X}, Ta_X)O_{12} is already known. The occupancy of the two lithium ion sites (24 d and 96 h) then become the same at X = 0.25. Therefore, improvement in the lithium ion conduction of Li_{7}La_3Zr_2O_{12} by Nb substitution is expected to improve the number of conduction carriers by optimization of each of the lithium sites in lithium garnet-type oxide.

The potential window of Li_{6.75}La_3(Zr_{1.75}, Nb_{0.25})O_{12} was measured using cyclic voltammetry (Fig. 5). Lithium deposition and dissolution peaks were observed near
0 V. However, no other reactions were indicated up to 9 V, which indicates that Li_{6.75}La_3(Zr_{1.75}, Nb_{0.25})O_{12} has a wide electrochemical window. Therefore, Li_{6.75}La_3(Zr_{1.75}, Nb_{0.25})O_{12} is a promising solid electrolyte material for all-solid-state lithium ion batteries. An all-solid-state lithium ion battery was constructed to assess the feasibility of using Li_{6.75}La_3(Zr_{1.75},Nb_{0.25})O_{12} as a solid electrolyte material.

4. All-solid-state Lithium Ion Battery Using Li_{6.75}La_3(Zr_{1.75},Nb_{0.25})O_{12} as a Solid Electrolyte

We investigated the electrochemical performance and charge transfer resistance of an all-solid-state lithium ion battery consisting of Li_{6.75}La_3(Zr_{1.75}, Nb_{0.25})O_{12} (LLZONb). The most critical parameter is the interface resistance between the electrodes and LLZONb. This is because the dominant contributor to the internal resistance of all-solid-state lithium ion batteries is not the bulk resistance of the solid electrolyte, but the interfacial resistance between the electrodes and the solid electrolyte.\(^{(15-18)}\) In order to clarify the electrochemical performance and interfacial resistance of between cathode and Nb-doped LLZO, an all-solid-state lithium ion battery was fabricated using LLZONb (solid electrolyte), lithium (anode), and LiCoO\(_2\) (LCO; cathode), which was deposited by pulsed-laser deposition (PLD). LCO was deposited by PLD (408-Nd:yttrium-aluminum-garnet (YAG) laser, \(\lambda = 266\) nm, \(~1\) J cm\(^{-2}\) pulse\(^{-1}\), \(~20\) ns, 10 Hz) on the top side of the sintered LLZONb pellet and annealing at 600 °C. The deposited thickness of the LCO film was ca. 500 nm, which was estimated from cross-sectional field emission scanning electron microscopy (FE-SEM/Hitachi S-5500) image. On the bottom of the pellet, a lithium metal foil was attached as the anode.

**Figure 6** shows charge-discharge curves of the all-solid-state lithium ion battery. The plateau of the charge curve starts at approximately 3.7 V, which is slightly lower than the conventional extraction/insertion reaction of LCO (3.9 V), due to the lower crystallinity of LCO\(^{(19,20)}\) prepared by PLD. The theoretical electrochemical capacity of LCO is 137 mAh g\(^{-1}\), which corresponds to 0.5 Li per CoO\(_2\). The charge and discharge capacity at the 1st cycle were 130 and 129 mAh g\(^{-1}\), respectively, which are approximately 90% of the theoretical capacity.

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charge-discharge curves at the 100th cycle are shown by the dotted line in Fig. 6. The charge and discharge capacity at the 100th cycle were 130 and 127 mAh g⁻¹, respectively. The retention of discharge capacity was approximately 98%, which confirms stable cycle performance for this battery.

**Figure 7** shows a cross-sectional FE-SEM image of the interface between LCO and LLZONb after 100 charge-discharge cycles. No other reaction phase or exfoliation are evident at the interface. Therefore, this battery will be chemically and structurally stable during lithium intercalation–deintercalation that occurs during charging and discharging.

One of the most important parameters to improve the performance of all-solid-state lithium ion batteries is to reduce the resistivity of the interface between the cathode and the solid electrolyte. The interfacial resistance of the battery was evaluated using a two-probe AC impedance method. Measurements were conducted after charging at 3.95 V vs. Li⁺/Li. A Nyquist plot for the all-solid-state lithium ion battery is shown by the open circles in **Fig. 8(a)**. Three resistance components are evident, with frequencies at approximately 0.5 MHz, 100 Hz, and 1 Hz, which can be well-resolved into resistance of the LLZONb bulk (R_{LLZONb}), the interface between LCO and LLZONb (R_{LCO/LLZONb}), and the interface between Li and LLZONb (R_{Li/LLZONb}), respectively. To identify the frequency dependence of the interfacial resistance between Li and LLZONb, we constructed a Li/LLZONb/Li cell with lithium metal foils attached to both LLZONb faces. A Nyquist plot for this cell is presented in **Fig. 8(b)**, which indicates that R_{Li/LLZONb} is approximately 100 Hz. Therefore, the resistance component at approximately 1 Hz is assigned to R_{LCO/LLZONb}. The resistivities for R_{LLZONb}, R_{LCO/LLZONb}, and R_{Li/LLZONb} were 120, 170, and 530 Ω cm², respectively. The interface resistivity between LCO and LLZONb was the same as the resistivity of the interface between LCO and LiPON prepared by physical vapor deposition. A Nyquist plot for the all-solid-state lithium ion battery after 100 charge-discharge cycles is shown by the solid circles in **Fig. 8(a)**. The interfacial resistance has not almost changed during 100 charge-discharge cycles.
Therefore it is considered that interface between LCO and LLZONb has a good stable cycle performance. Figure 9 shows an Arrhenius plot for each resistance at 3.95 V. Eₐ for both R_LCO/LLZONb and R_Li/LLZONb were ca. 30 kJ mol⁻¹, which are much lower than that for the interface between LCO and liquid organic electrolytes (ca. 60 kJ mol⁻¹) (22). The reason for this phenomenon can be understood as follows. It is considered that desolvation reaction occurs with lithium ion transfer at the interface between the electrodes and a liquid organic electrolyte. Therefore, Eₐ of the interfacial resistance between electrodes and liquid organic electrolytes are quite large (ca. 60 kJ mol⁻¹). However, in an all-solid-state lithium ion battery, the desolvation reaction does not occur; therefore, Eₐ of both R_LCO/LLZONb and R_Li/LLZONb would be expected to be the same as that for the LLZONb bulk electrolyte.

5 Conclusions

The lithium ion conductivity of lithium garnet-type oxide: Li₇La₃Zr₂O₁₂ was successfully improved by substitutional Nb-doping. The lithium ion conductivity was optimized, and reached a maximum of ~0.8 mS cm⁻¹ at 12.5% niobium doping. The potential window of LLZONb showed no evidence of other reactions from 0 to 9 V. An all-solid-state lithium ion battery of LCO/LLZONb/Li was constructed. The charge and discharge capacities of this battery at the 1st cycle were 130 and 129 mAh g⁻¹, respectively, which is approximately 90% of the theoretical capacity. This battery exhibited stable cycle performance, with no other reaction phase or exfoliation at the interface after 100 charge–discharge cycles. The interfacial resistance between LCO and LLZONb at 25 °C was 170 Ω cm², which is comparable to that for a lithium ion battery with a liquid organic electrolyte. The activation energy of the interfacial resistance between LCO and LLZONb was lower than that for a lithium ion battery with a liquid organic electrolyte. These results indicate that LLZONb is a promising candidate as a solid electrolyte for high-power and high-capacity all-solid-state lithium ion batteries.

References

(17) Ohta, N., Takada, K., Sakaguchi, I., Zhang, L.,
Ma, R., Fukuda, K., Osada M. and Sasaki, T., 
pp. 1486-1490.


pp. 745-748.

(22) Yamada, I., Abe, T., Iriyama, Y. and Ogumi, Z., 

Figs. 1, 2, 3 and 5

Figs. 6, 7, 8 and 9

Text

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