Communications

Fast Lithium Ion Conduction in Garnet-Type Li$_7$La$_3$Zr$_2$O$_{12}$**

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Rechargeable (secondary) all-solid-state lithium batteries are considered to be the next-generation high-performance power sources and are believed to have remarkable advantages over already commercialized lithium ion batteries utilizing aprotic-solution, gel, or polymeric electrolytes with regard to battery miniaturization, high-temperature stability, energy density, and battery safety. Solid electrolytes with high Li ion conductivity but negligible electronic conductivity, with stability against chemical reactions with elemental Li (or Li–metal alloys) as the negative electrode (anode) and Co-, Ni-, or Mn-containing oxides as the positive electrode (cathode), and with decomposition voltages higher than 5.5 V against elemental Li are especially useful to achieve high energy and power densities as well as long-term stability.

Lithium ion conduction has been reported for a wide range of crystalline metal oxides and halides with different types of structures.[1,2] In general, oxide materials are believed to be superior to non-oxide materials for reasons of handling and mechanical, chemical, and electrochemical stability.[1] So far, most of the discovered inorganic lithium ion conductors have had either high ionic conductivity or high electrochemical stability, but not both. Some oxides are excellent lithium ion conductors; for example, Li$_{3x}$La$_{(2/3)-x}\square_{(1/3)-2x}TiO_3$ ($0 < x < 0.16$; "LLT"; $\square$ represents a vacancy) exhibits a bulk conductivity of 10^{-3} S cm^{-1} and a total (bulk + grain-boundary) conductivity of 7×10^{-5} S cm^{-1} at 27 °C and $x \approx 0.1$. However, this compound becomes predominantly electronically conducting within the lithium activity range given by the two electrodes.[3] It has been attempted to replace the transition metal Ti in LLT with Zr, which is fixed-valent and more stable (against chemical reaction with elemental lithium); however, this attempt was unsuccessful owing to the ready formation of the pyrochlore phase La$_2$Zr$_2$O$_7$.[4] Although a large number of possible lithium electrolytes have been reported for the Li$_2$O–ZrO$_2$ system, none of them

is suitable for battery applications because of their low conductivity and sensitivity to air.[5]

A novel class of fast lithium ion conducting metal oxides with the nominal chemical composition Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta), possessing a garnet-related structure, has been reported from our laboratory.[6] The bond-valence analysis of Li$^+$ ion distribution confirms transport pathways which relate to the experimentally observed high Li$^+$ ion conductivity, and the Li$^+$ ions are predicted to move in a 3D network of energetically equivalent, partially occupied sites.[7] Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) were the first examples of fast lithium ion conductors possessing garnet-like structures and gave rise to further investigations of conductivity optimization by chemical substitutions and structural modifications.[8,9] Among the investigated compounds with garnet-related structures, Li$_6$BaLa$_2$Ta$_2$O$_{12}$ exhibited the highest Li$^+$ ion conductivity of 4×10^{-5} S cm^{-1} at 22 °C with an activation energy of 0.40 eV.[9] Although Li$_6$BaLa$_2$Ta$_2$O$_{12}$ is stable against reaction with metallic lithium, moisture, air, and common electrode materials, the bulk and total conductivity observed at room temperature is not sufficiently high to develop an ideal all-solid-state lithium ion rechargeable battery.

Herein, we report the synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$, a new chemical composition with garnet-like structure and predominantly ionic conduction. The high lithium ion conductivity, good thermal and chemical stability against reactions with prospective electrode materials, environmental benignity, availability of the starting materials, low cost, and ease of preparation and densification of Li$_7$La$_3$Zr$_2$O$_{12}$ suggest that this zirconium-containing lithium garnet is a promising solid electrolyte for all-solid-state lithium ion rechargeable batteries.

Despite the large number of X-ray diffraction (XRD) studies on Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) garnets, there has been controversy in the description of the structure regarding the space group and position of lithium cations.[10] Recently, a neutron diffraction investigation revealed that Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) crystallize in the space group $Ia\bar{3}d$, that Li$^+$ is located on both the tetrahedral and octahedral sites, and that vacancies exist on both of these sites.[11] The measured powder XRD pattern of Li$_7$La$_3$Zr$_2$O$_{12}$ matches well with the standard pattern of the known garnet phase Li$_5$La$_3$Nb$_2$O$_{12}$ and indicates the ability of the garnet structure to accommodate cations of different valence states and different sizes without any major change in the symmetry. We could index the diffraction pattern for a cubic cell with a lattice constant of $a = 12.9682(6)$ Å. We plan to perform neutron diffraction studies to understand the nature of Li$^+$ environments in Li$_7$La$_3$Zr$_2$O$_{12}$.

A typical impedance plot obtained at 18 °C for a thick pellet of Li$_7$La$_3$Zr$_2$O$_{12}$ is shown in Figure 1. The appearance of the tail at low frequencies in the case of ionically blocking

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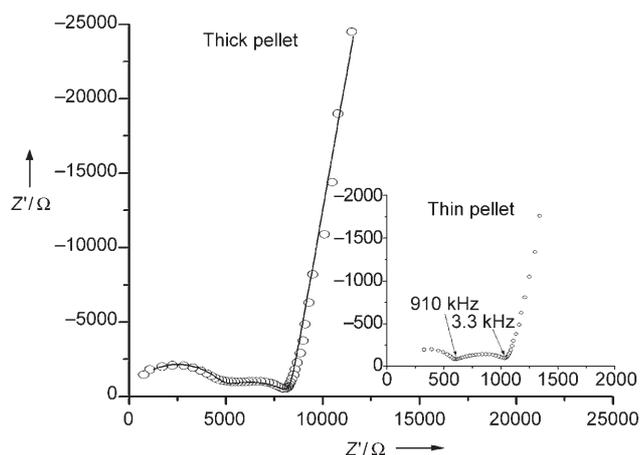
Figure 1. Impedance plot (5 Hz–13 MHz) of $Li_7La_3Zr_2O_{12}$ measured in air at 18°C for the thick pellet (1.02 cm in thickness and 0.92 cm in diameter). ○: Experimental values. The solid line represents simulated data with an equivalent circuit consisting of $(R_bQ_b)(R_{gb}Q_{gb})(Q_{el})$ (where R is the resistance, Q is the constant phase element, and the subscripts g, gb, and el refer to the grain, grain boundary, and electrode) using the Equivalent program.[13] The impedance plot measured in air at 18°C for the thin pellet (0.18 cm in thickness and 0.98 cm in diameter) of $Li_7La_3Zr_2O_{12}$ is shown in the inset.

electrodes is an indication that the investigated material is ionically conducting in nature.[12] A similar behavior has been observed for the earlier-investigated materials with garnet-related structures.[6,8,9] The impedance plot could be well-resolved into bulk, grain-boundary, and electrode resistances. The solid line in Figure 1 represents fitted data with an equivalent circuit consisting of $(R_bQ_b)(R_{gb}Q_{gb})(Q_{el})$ using the Equivalent program.[13] The impedance plot measured at 18°C for the thin pellet of $Li_7La_3Zr_2O_{12}$ is shown in the inset of Figure 1. The bulk and total conductivity of thick (1.02 cm in thickness and 0.92 cm in diameter) and thin (0.18 cm in thickness and 0.98 cm in diameter) pellets of $Li_7La_3Zr_2O_{12}$ observed at various temperatures were derived from the intercepts of the high- and low-frequency semicircles with the real axis and are tabulated in Table 1. The impedance data presented in Figure 1 and in Table 1 indicate similar electrical properties exhibited by both the thick and thin pellets of $Li_7La_3Zr_2O_{12}$. The thin pellet shows a slightly higher bulk and total conductivity than the thick pellet sample. Moreover, an interesting observation is that the grain-boundary contribu-

**Table 1:** Impedance data of $Li_7La_3Zr_2O_{12}$ measured in air.[a]

Pellet type	T [°C]	σ_{bulk} [S cm^{-1}]	σ_{total} [S cm^{-1}]	$R_{gb}/R_b + R_{gb}$ [b]
thick pellet	18	3.37×10^{-4}	1.90×10^{-4}	0.44
	25	4.67×10^{-4}	2.44×10^{-4}	0.48
	50	1.19×10^{-3}	6.15×10^{-4}	0.49
thin pellet	18	3.97×10^{-4}	2.32×10^{-4}	0.42
	25	5.11×10^{-4}	7.74×10^{-4}	0.41
	50	1.45×10^{-3}	3.01×10^{-4}	0.47

[a] Thick pellet 1.02 cm in thickness and 0.92 cm in diameter; thin pellet 0.18 cm in thickness and 0.98 cm in diameter). [b] R_{gb} = grain-boundary resistance, R_b = bulk resistance.

tion to the total resistance is less than 50% at all measured temperatures (Table 1) for both the thick and thin pellet. At higher temperatures (above 75°C for the thick pellet and above 50°C for the thin pellet), it is difficult to separate the bulk and grain-boundary contributions accurately; accordingly, we have considered the sum of the bulk and grain-boundary contributions for the determination of the electrical conductivity over the temperature range investigated. The total conductivity (3×10^{-4} S cm^{-1} at 25°C) of the new crystalline fast lithium ion conductor $Li_7La_3Zr_2O_{12}$, possessing a garnet-like structure, is better than that of any other family of solid lithium ion conductors and all previously described lithium garnets.[6,8,9,11b] This finding of the total and bulk conductivities of the same order of magnitude is a most attractive feature of the $Li_7La_3Zr_2O_{12}$ garnet-type oxide compared to other ceramic lithium ion conductors. For many applications of solid electrolytes in electrochemical devices, such as batteries, sensors, and electrochromic displays, the total conductivity should be as high as possible. We expect that the bulk and total conductivity can be further improved by low-temperature synthesis of fine-grain $Li_7La_3Zr_2O_{12}$ with easily available reactants and also by further densification by a suitable sintering process.

The Arrhenius plots for the bulk and total electrical conductivity of $Li_7La_3Zr_2O_{12}$ obtained in two heating and cooling cycles for the thick pellet are shown in Figure 2a. There is no appreciable shift in the conductivity for both cycles. This observation implies that the investigated garnet-like structure is thermally stable without any phase transition in the investigated temperature range between room temperature and 350°C. Similar Arrhenius behavior has also been observed for the thin pellet of $Li_7La_3Zr_2O_{12}$. In Figure 2b, the data for the thick and thin pellets of $Li_7La_3Zr_2O_{12}$ obtained during the first heating process are compared. The activation energies obtained for both bulk and total conductivity of the thin pellet (0.32 eV at 18–50°C and 0.30 eV at 18–300°C, respectively) are slightly lower than for the bulk and total conductivity of the thick pellet (0.34 eV at 18–70°C and 0.31 eV at 18–300°C, respectively). The conductivity obtained for the thin pellet is slightly higher than that of the thick pellet. The charge transfer across the individual grain boundaries occurs with the same activation energy as the transfer with the bulk of the grains. This phenomenon may be related to the ease in sintering the polycrystalline samples. Since oxygen, zirconium, and lanthanum in $Li_7La_3Zr_2O_{12}$ are rigidly bound in the framework of the garnet-like structure,[7,11] we believe that their mobility will be negligible at operating temperatures and, hence, the ionic motion is due to the transport of Li$^+$ ions.
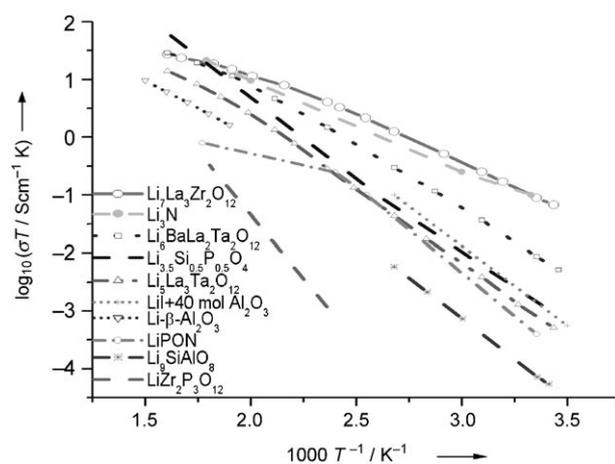
Besides impedance analysis, the ionic nature of the electrical conductivity was confirmed by preliminary electromotive force (emf) measurements employing $Li_7La_3Zr_2O_{12}$ as a solid electrolyte between elemental lithium and Al or LiAl, Al electrodes. The sample was covered with an aluminum sheet on the upper side and placed onto lithium, which became molten on a hot plate inside a drybox. The aluminum was alloyed both by chemical reaction with lithium and by coulometric titration of lithium into aluminum from the opposite lithium electrode. The resulting voltage was in the

a)

b)
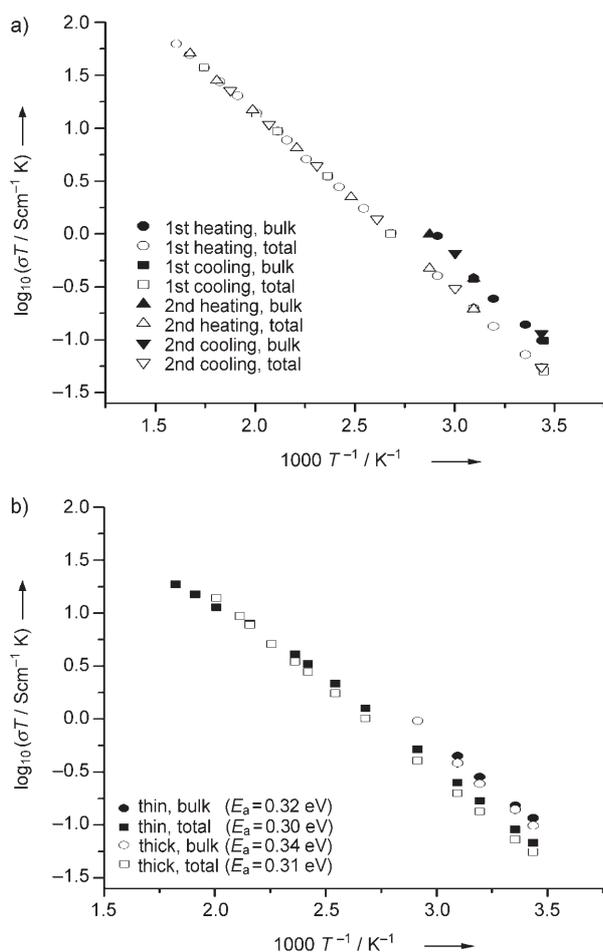
Figure 2. a) Arrhenius plots for the bulk and total (bulk + grain-boundary) electrical conductivity of the thick pellet of $Li_7La_3Zr_2O_{12}$ obtained in two consecutive heating and cooling cycles. b) Comparison of the Arrhenius plots for the thick and thin pellets of $Li_7La_3Zr_2O_{12}$ obtained during the first heating process (18–300 °C).

Figure 3. Comparison of the total (bulk + grain-boundary) conductivity of $Li_7La_3Zr_2O_{12}$ and other reported lithium ion conductors considered for battery applications.

same range as the theoretical value. The difference was due to the non-homogeneous temperature distribution and accordingly phenomena owing to irreversible processes.

Figure 3 shows a comparison of the lithium ion conductivity of $Li_7La_3Zr_2O_{12}$ with other reported lithium ion conductors considered for battery applications. The conductivity is higher than in the case of Li-β-aluminum oxide,[14] thin-film lipon $(Li_{2.9}PO_{3.3}N_{0.46})$,[15] Li_9SiAlO_8,[16] LiI + 40 mol% Al_2O_3,[17] $LiZr_2(PO_4)_3$,[18] $Li_{3.5}Si_{0.5}P_{0.5}O_4$,[19] $Li_5La_3Ta_2O_{12}$,[6] and $Li_6BaLa_2Ta_2O_{12}$.[9] The high lithium ion conductivity and low activation energy observed in $Li_7La_3Zr_2O_{12}$ compared to other lithium-containing garnets may be the result of an increase in the cubic lattice constant, an increase in lithium ion concentration, less chemical interaction between the Li^+ ions and other ions in the lattice, and partially a result of its improved densification (92% of the theoretical density). At lower temperatures, the conductivity exhibited by the rather unstable polycrystalline Li_3N[20] $(6.6 \times 10^{-4}\ S\,cm^{-1}$ at 27 °C) is comparable to that of $Li_7La_3Zr_2O_{12}$. However, at higher temperature, $Li_7La_3Zr_2O_{12}$ exhibits a higher total conductivity.

The thermal stability of $Li_7La_3Zr_2O_{12}$, the principal advantage of the crystalline lithium ion conductor, was confirmed by thermogravimetric (TG) measurements and differential thermal analysis (DTA). The TG–DTA data collected in air revealed no significant change in mass and no detectable phase transition in both the heating and cooling processes over the temperature range 20–900 °C. The zirconium-containing $Li_7La_3Zr_2O_{12}$ was found to be stable against molten lithium and was also found to be chemically stable when exposed to moisture and air for several weeks.

The high lithium ion conductivity, good thermal and chemical stability, and ease of preparation of dense $Li_7La_3Zr_2O_{12}$ suggest that this zirconium-containing lithium garnet is a promising solid ceramic electrolyte for all-solid-state lithium ion rechargeable batteries, as well as other ionic devices such as, for example, gas sensors and electrochromic devices.

Experimental Section

$Li_7La_3Zr_2O_{12}$ was prepared by a conventional solid-state reaction procedure at high temperatures, whereby stoichiometric amounts of the following high-purity chemicals were employed: LiOH (Alfa Aesar, > 99.9%; dried at 200 °C for 6 h; 10 wt% excess was added to compensate for the loss of lithium during annealing), La_2O_3 (Alfa Aesar, > 99.99%; dried at 900 °C for 24 h), and ZrO_2 (Aldrich, > 99%). The powders were ball-milled with zirconia balls for about 12 h in 2-propanol in air, and this process was repeated after heat treatments (at 900 and 1125 °C). Subsequently, the reaction products were pressed into pellets under isostatic pressure and annealed at 1230 °C for 36 h while the samples were covered with the same mother powder. To avoid major lithium loss, the heating rate was 1 °C min^{-1} in all treatments. The sintered dense slabs were cut into thinner pellets using a diamond saw. Powder X-ray diffraction (Seifert 3000, $Cu_{K\alpha}$) was employed to monitor the phase formation.

Electrical conductivity measurements were performed in air on two pellets of different dimensions (thick pellet 1.02 cm in thickness and 0.92 cm in diameter; thin pellet 0.18 cm in thickness and 0.98 cm in diameter) using Li ion blocking Au electrodes (Au paste cured at 700 °C for 1 h) in the temperature range 18–350 °C using an impedance and gain-phase analyzer (HP 4192A, Hewlett-Packard

Co., Palo Alto, CA; 5 Hz–13 MHz). Prior to each impedance measurement, the samples were equilibrated for 3–6 h at constant temperature. For each pellet, the impedance measurements were made for two heating and cooling cycles consecutively.

TG and DTA (NETZSCH STA 409 C/CD) data were collected in air over the temperature range 20–900–20°C with a heating/cooling rate of 2°C min^{-1} and isothermally at 900°C.

The stability of $Li_7La_3Zr_2O_{12}$ with molten lithium was investigated inside an argon-filled glovebox by reacting the pellet with a large excess of molten lithium for 48 h in a molybdenum crucible.

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