Optimizing Li⁺ conductivity in a garnet framework

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The garnet-related oxides with the general formula Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ (0 ≤ x ≤ 1) were prepared by conventional solid-state reaction. X-ray diffraction (XRD), neutron diffraction and AC impedance were used to determine phase formation and the lithium-ion conductivity. The lattice parameter of Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ decreased linearly with increasing x. Optimum Li-ion conductivity in the Li-ion garnets Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ is found in the range 0.4 ≤ x ≤ 0.6 for samples fired at 1140 °C in an alumina crucible. A room-temperature σ₁₄ ≈ 1.0 × 10⁻³ S cm⁻¹ for x = 0.6 with an activation energy of 0.35 eV in the temperature range of 298–430 K makes this Li-ion solid electrolyte attractive for a new family of Li-ion rechargeable batteries.

Introduction

Integration of alternative energy technologies into the grid depends on the availability of adequate electrical-energy storage. The most important challenge for further development of Li-ion batteries for this application is increased capacity. Limitations of the flammable organic liquid-carbonate electrolytes of the Li-ion battery have stimulated interest in Li-ion solid electrolytes. The garnet-related oxides with the general formula Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ (0 ≤ x ≤ 1) were prepared by conventional solid-state reaction. X-ray diffraction (XRD), neutron diffraction and AC impedance were used to determine phase formation and the lithium-ion conductivity. The lattice parameter of Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ decreased linearly with increasing x. Optimum Li-ion conductivity in the Li-ion garnets Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ is found in the range 0.4 ≤ x ≤ 0.6 for samples fired at 1140 °C in an alumina crucible. A room-temperature σ₁₄ ≈ 1.0 × 10⁻³ S cm⁻¹ for x = 0.6 with an activation energy of 0.35 eV in the temperature range of 298–430 K makes this Li-ion solid electrolyte attractive for a new family of Li-ion rechargeable batteries.

Garnet-related Li-rich metal oxides have been studied extensively since the observation of a Li-ion conductivity σ₁₄ > 10⁻⁴ S cm⁻¹ at 25 °C in Li₇Li₃Zr₂O₁₂, which is stable on contact with a lithium anode. A variety of compositional variations have been investigated, including Li₇Li₃M₂O₁₂ (M = Nb, Ta, Sb, Bi)⁴⁻⁶ and Li₆Al₆M₂O₁₂ (A = Ca, Sr, Ba; M = Nb, Ta)⁴⁻⁶ in order to vary the lattice constant and Li-ion population. Kotobuki et al.⁷ have shown that addition of Al₂O₃ helps sintering of Li₇Li₃Zr₂O₁₂ without hindering the Li⁺ framework. The highest σ₁₄ = 8 × 10⁻⁴ S cm⁻¹ was obtained in the Li₆.75Li₃Zr₁.75Nb₀.25O₁₂ garnet by Shingo Ohita et al.⁸

The garnet structure A₃B₆C₆O₁₂ contains a B₆C₆O₁₂ framework structure of B cations in 8-coordination sites and C cations in octahedral sites. The framework contains a 3D-connected interstitial space consisting of the tetrahedral 24d-A sites bridged by a single octahedron sharing on opposite sides a common face with each of the two neighboring A sites. The bridging tetrahedral sites share common edges. The existence of 3 tetrahedral-A and 6 bridging-octahedral sites for a total of 9 sites per formula unit can provide a low activation energy for motion of guest lithium ions if the lithium ions are disordered with a partial occupancy of both sites.

In previous work, we studied by neutron-diffraction a cubic aluminum-free Li₆La₃Zr₂O₁₂ sample prepared at 750 °C;⁹ we deduced that since coulomb repulsions prevent occupancy of an octahedral site with two near-neighbor tetrahedral sites occupied, x = 7.5 is the upper limit of x that can be tolerated in a Li₆B₃C₆O₁₂ garnet framework and that this ideal limit requires 1.5 per formula unit of long-range-ordered vacancies in the tetrahedral 24d sites. We have found that Ta-doped Li₆La₃ZrₓTa₁₋ₓO₁₂ (ref. 11) has shown high lithium conductivity σ₁₄ > 10⁻⁴ S cm⁻¹. Doping with higher-valence cations increases the Li-ion vacancy concentration and significantly reduces the degree of local ordering. A σ₁₄ = 1.0 × 10⁻³ S cm⁻¹ has been obtained by MD simulations in Li₆.75La₃Zr₁.75Ta₀.25O₁₂.¹² In order to determine the optimum concentration of Li-ions in the garnet framework, we have undertaken a study of nominal Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂; Ta(v) was chosen as the dopant as, like Zr(v), it is not reduced on contact with lithium. Here we report a solid oxide Li-ion electrolyte having a Li-ion conductivity σ₁₄ ≈ 1.0 × 10⁻³ S cm⁻¹ at room temperature.

Methods

Compounds with the nominal chemical formula Li₇₋ₓLa₃ₓZr₂₋ₓTaₓO₁₂ were prepared by solid-state reaction of stoichiometric amounts of Li₂CO₃, La₂O₃ (heated at 900 °C for 12 h), ZrO₂ and Ta₂O₅. 10 wt% excess Li₂CO₃ was added to compensate for the loss of lithium during annealing. The
powders were ground and heated to 900 °C to decompose the metal salts. Finally, the powders were ground again, pressed into a pellet, and annealed at 1120 °C for 8 h ($x = 1$ and 0.8), 1140 °C for 16 h ($x = 0.6, 0.4,$ and 0.2), at 1230 °C for 36 h ($x = 0$) in air while the pellet was covered with the same mother powder. The annealing was done in an alumina crucible.

Powder X-ray diffraction (Philips PW1830, Cu Kα) was employed to monitor the phase formation in the 2θ range from 10 to 70° with a step size of 0.02°. The lattice parameters were calculated from the diffraction peaks in the range 20–60° with Jade software. A field-emission scanning electron microscope (Quanta FEG650) was used to obtain the fracture surface microstructure of the pellet. The composition distribution of the elements was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and energy dispersive spectroscopy.

Neutron diffraction experiments were conducted with the high-pressure preferred-orientation neutron diffractometer (HIPPO) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory. Bulk samples were placed in a vanadium holder and time-of-flight data were collected under vacuum at room temperature. Neutrons were detected with 27 detector panels of 3He detector tubes arranged on three rings with nominal diffraction angles of 40°, 90°, and 144°. The GSAS program was used to perform Rietveld refinement with background functions type 1 and 20 for background coefficients.

Ionic conductivity was measured from 298 to 430 K with a Solartron Impedance Analyzer (Model 1260); the applied frequency range was from 10° to 1 Hz with an AC amplitude of 10 mV. Both parallel surfaces of the pellet were sputtered with Li-ion-blocking Au electrodes. The electronic resistivity measurement at room temperature was performed with a four-probe technique on specimens with a rectangular geometry (2 mm × 2 mm × 1 mm).

The electrochemical windows of the samples were evaluated by cyclic voltammetry (CV) with a Solartron Impedance Analyzer (Model 1260) at a scanning rate of 1 mV s⁻¹ between −0.5 and 5 V (vs. Li⁺/Li). A gold electrode and lithium metal were attached to opposite faces of the pellet as working electrodes and counter electrodes; the cell was fabricated in a glove box under Ar atmosphere.

**Results and discussion**

Fig. 1(a) shows the powder XRD patterns for different compositions sintered in an alumina crucible; the diffraction peaks observed after heat treatment were assigned to a well-crystallized garnet-related structure. All the garnet frameworks crystallize in the space group $Ia\overline{3}d$. The lattice parameter of $Li_{7-x}La_xZr_{2-x}Ta_xO_{12}$ decreased nearly linearly with increasing $x$ according to Végard’s law as shown in Fig. 1(b). The lattice parameters are influenced somewhat by different Li⁺ and Al³⁺ distributions in the interstitial space.

For $x = 0.6$, ICP confirmed the presence of 2.5 wt% Al³⁺ originating from the alumina crucible. The molar ratio of the elements Li⁺:Al³⁺:La³⁺ was 6.32:0.08:2.91. In addition, we have shown with electron-energy dispersive spectroscopy that most (Fig. 2(b)), if not all, of the Al³⁺ entering a polycrystalline sample from the alumina crucible is located in the grain boundaries for $x = 0.6$. The Li₂O-doped Al₂O₃ in the grain boundaries acts as a sintering aid, provides Li-ion conductivity across the grain boundaries, and suppresses excess Li loss from the sample at sintering temperatures above 850 °C. Good connection between the powders after sintering (as seen in Fig. 2(a)) can reduce the intergrain ionic resistance as well.

In order to identify the Li-ion distribution inside the garnet grains, neutron diffraction was introduced to confirm the structures of $Li_{6.5}La_{1.5}Zr_{2}Ta_{0.5}O_{12}$ and $Li_{11}La_{3}Zr_{2}O_{12}$ powders. O’Callaghan and Cussen have used neutron diffraction to follow the site occupancies with increasing $x$; they report that the occupancy of the tetrahedral A sites $24d$ decreases monotonically with $x$ in the range $5 \leq x < 6.6$ with an associated increase with $x$ in the $96h$ sites. These data indicate that the Li-ions have a site preference for the $24d$ site, and the octahedral $48f$ lithium ions are displaced to the $96h$ site by Li⁺ occupancy of one neighboring $24d$ site. Their data also indicate the possible onset of short-range ordering of $24d$-site vacancies for $x > 6.4$. Since regions of short-range order would inhibit Li-ion mobility, we had particular interest in the evolution of $\sigma_{Li}$ with $x$ of nominal $Li_{7-x}La_xZr_{2-x}Ta_xO_{12}$ in the interval $0.4 < x < 0.8$.

The structure of cubic Li₆BaLa₂Ta₂O₁₂, in which the lithium was disordered with occupancies of 22% octahedral sites (48g), 21.8% displaced in octahedral sites (96h), and 67.4% tetrahedral sites (24d), was adopted as the initial structure model for all garnet materials here. The lattice parameters, atomic positions and occupancies, isotropic displacement parameters, and peak widths in the profile function were all refined. With these refinement conditions, the reliability factors converged to satisfactory values. The details of the data collection and a fitted diffraction pattern “$Li_{6.5}La_{1.5}Zr_{1.5}Ta_{0.5}O_{12}$” and “$Li_{11}La_{3}Zr_{2}O_{12}$” are shown in Tables 1 and 2 and in Fig. 3.
In space group $Ia\overline{3}d$, the Zr(Ta) and La ions of the La$_2$ZrTaO$_{12}$ garnet framework occupy, respectively, octahedral 16$a$ and 8-coordinated 24$c$ sites. Our cubic garnet $``7Li_6.5La_3Zr_1.5Ta_0.5O_{12}''$ and $``7Li_7La_3Zr_2O_{12}''$ had space group $Ia\overline{3}d$ with lattice parameter $a = 12.9450$ and $12.9720$ Å at room temperature; $5.85$ and $6.79$ lithium ions per formula unit, respectively, were located at three different positions ($48g$, $96h$, and $24d$). The Li-ions occupying the three different positions form a continuous 3D network of moving Li$^+$ ions in the interstitial space of the 3D garnet framework. The four-coordinated 24$d$ Li sites and displaced 96$h$ sites show a significantly larger displacement parameter than that of the octahedral 48$g$ Li sites.

In Li$_2$B$_2$C$_2$O$_{12}$, the cubic garnet phase is difficult to obtain for $x > 7.0$, and $x = 7.5$ is the upper limit of $x$ that can be tolerated in a Li$_2$B$_2$C$_2$O$_{12}$ garnet framework; more Li$^+$ can lead to short Li$^+$–Li$^+$ distances that destabilize the garnet framework. For $x = 3$, Li$_3$Ln$_3$Te$_2$O$_{12}$ (Ln = rare earth) with Li$^+$ ions only in the tetrahedral sites shows lower Li$^+$ conductivity by 2–3 orders of magnitude compared to Li$_2$La$_3$ZrTaO$_{12}$, while the Li$^+$ conductivity in Li$_2$La$_3$ZrTaO$_{12}$ is comparable to that in Li$_2$La$_3$Zr$_2$O$_{12}$, which indicates that the Li$^+$ conductivity may be optimized in the interval $6 < x < 7$. In both as synthesized $x = 0.5$ and $x = 0$ samples, the lithium ions occupy about 36% tetrahedral sites. With the Li population increase to $x = 0$, the octahedral lithium ions force more Li off the tetrahedral sites; 38.8% Li occupancy of the tetrahedral site in $``7Li_6.5La_3Zr_1.5Ta_0.5O_{12}''$ is reduced to 36.3% in the $``7Li_7La_3Zr_2O_{12}''$ and 24.7% Li occupancy of the octahedral sites is increased to 35.0% in the $``7Li_7La_3Zr_2O_{12}''$, which is consistent with extrapolation of O’Callaghan and Cussen’s data. The tetrahedral sites (24$d$) were 67.4%, 38.8% and 36.3% occupied, while the octahedral sites (48$g$ and 96$h$) were 65.6%, 78.2% and 95% occupied and the Li$^+$ conductivity was $4 \times 10^{-3}$, $9.2 \times 10^{-4}$ and $1.4 \times 10^{-5}$ S cm$^{-1}$, respectively, for $x = 6$ (ref. 8 and 13), 6.5 and 7 in Li$_2$B$_2$C$_2$O$_{12}$. The Li$^+$ conductivity in Li$_7La_3Zr_2$Ta$_2$O$_{12}$ increased with $x$ and reached a maximum around $x = 0.4$. The high Li$^+$ conductivity in Li$_7La_3Zr_2$Ta$_2$O$_{12}$ indicates that the appropriate Li$^+$ concentration for Li$^+$ transport is in the range $6.4 \leq x \leq 6.6$ in Li$_2$B$_2$C$_2$O$_{12}$. Some Li$^+$ vacancies in the octahedral sites improve the Li$^+$ conductivity significantly, and the best ratio of Li$^+$ occupancy/vacancy of the octahedral sites appears to be around 3 : 1.
The lithium ions occupy the 24$d$ tetrahedral and distorted octahedral sites. The short Li$^+$–Li$^+$ contact (1.987 Å for $x = 0$ and 1.986 Å for $x = 0.5$) between Li$^+$ in neighboring 24$d$ and 48$g$ sites introduces a Coulomb repulsion that displaces the lithium ions in the octahedral site to a 96$h$ site neighboring an empty 24$d$ site to give a Li$^+$–Li$^+$ separation (2.433 Å for $x = 0$ and 2.438 Å for $x = 0.5$); a lithium ion is not stable in a 48$g$ site that bridges two occupied 24$d$ sites.

Fig. 4 displays typical room-temperature impedance plots measured in air for $x = 0$, 0.2, 0.8 and 1. The linear low-frequency portion signals that the conductivity is primarily ionic. Only one clear semicircle was observed in the high-frequency region, and the distance from zero to the intercept of the linear tail with the real axis was assigned to the total conductivity. The bulk and grain-boundary resistance could be obtained by fitting the experimental data with the conventional equivalent circuit consisting of $(R_0)(R_{gb}CPE1)(CPE2)$. The total ionic conductivities of “Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$” for $x = 0$, 0.2, 0.8 and 1 were $1.2 \times 10^{-4}$, $2.8 \times 10^{-4}$, $3.2 \times 10^{-4}$ and $1.6 \times 10^{-4}$ S cm$^{-1}$. Fig. 5(a) displays typical room-temperature impedance plots measured in air for $0.4 \leq x \leq 0.6$. The total ionic conductivities of “Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$” with $x = 0.4$, 0.5 and $x = 0.6$ at 25 °C were $7.3 \times 10^{-4}$, $9.2 \times 10^{-4}$ and $1.0 \times 10^{-3}$ S cm$^{-1}$, respectively. Since the samples had a tan color, suggestive of color centers at oxygen vacancies, a four-point system was used to determine the electronic conductivity. For the sample with $x = 0.6$ (2 mm × 2 mm × 1 mm), the electronic resistance was not measurable, which indicates that the garnet electrolyte here is a good electronic insulator.

Fig. 5 (a) Impedance plot (1–10$^6$ Hz) of Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ measured in air at 25 °C. (b) Lithium conductivity change with $x$.

Fig. 6 (a) Arrhenius plot of ionic conductivity of Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$. (b) A cyclic voltammogram of Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ electrolyte at a scanning rate of 1 mV s$^{-1}$ at 25 °C.
Fig. 5(b) shows the variation with $x$ of the room temperature conductivity $\sigma_{11}$ for $0 \leq x \leq 1$ of Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$; a maximum $\sigma_{11} \approx 1.0 \times 10^{-3} \text{ S cm}^{-1}$ was found for $x = 0.6$. Fig. 6(a) shows the Li-ion conductivity as a function of $1000/T$ for a sintered sample of “Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$” ($x = 0, 0.6$ and $1$).

The temperature dependence of the conductivity can be expressed by the Arrhenius equation:

$$\sigma T = A \exp(-E_s/kT)$$

The activation energy of “Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$” with $x = 0.6$ was estimated to be $E_s = 0.35 \text{ eV}$ from the slope of the log $\sigma T$ versus $1000/T$ plot in the temperature range of 298–430 K. A cyclic voltammogram of Li$_{6.4}$La$_{3}$Zr$_{1.6}$Ta$_{0.6}$O$_{12}$ is shown in Fig. 6(b), which reveals lithium deposition and dissolution peaks near 0 V vs. Li$^+$/Li; there is no other reaction up to 5 V vs. Li$^+$/Li, indicating that the electrolyte here is stable with lithium metal.

### Conclusion

The garnet-related oxide with the general formula Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$ ($0 \leq x \leq 1$) prepared by conventional solid-state reaction is cubic and crystallizes in the space group $Ia\overline{3}d$. The lattice parameter of Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$ decreased linearly with increasing $x$. The optimum Li-ion conductivity in the Li-ion garnets Li$_{7-x}$La$_{3}$Zr$_{2-x}$Ta$_{x}$O$_{12}$ is found in the range 0.4 $\leq x \leq 0.6$ for samples fired at 1140 °C in an alumina crucible. A room-temperature $\sigma_{11} \approx 1.0 \times 10^{-3} \text{ S cm}^{-1}$ for $x = 0.6$ makes this Li-ion solid electrolyte attractive for a new family of Li-ion rechargeable batteries. Although the oxide is reported to be unstable in an aqueous electrolyte,16 this problem can be solved. Moreover, the electrolyte may be stable in alternative liquid cathodes. The adventitious Al of the $x = 0.6$ composition appears to reside primarily in an amorphous grain-boundary phase where it acts as a sintering aid and blocks excessive Li loss at the sintering temperature.

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