High lithium ion conductivity solid electrolyte of chromium and aluminum co-doped NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$

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Abstract

High lithium ion conductivity solid electrolytes of $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) and $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) with the NASICON-type structure were synthesized using a precursor prepared by the sol-gel method. The highest total electrical conductivity of $3.55 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C was obtained for $x=0.4$ in $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LACTP) sintered at 1120 °C for 6 h in air. Higher electrical conductivity was observed by the partial substitution of Cr^{3+} with Al^{3+} . The highest total electrical conductivity of $1.06 \times 10^{-3} \text{ S cm}^{-1}$ and bulk conductivity of $1.77 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C were obtained for $x=0.3$ in $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered at 1070 °C for 6 h in air. The contribution of electronic conductivity to the total conductivity was negligibly small. $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ was unstable in water, but stable in saturated LiOH with saturated LiCl aqueous solution.

1. Introduction

High lithium ion conductivity solid electrolytes are attractive for nonflammable all-solid-state batteries [1, 2] and have potential application as a separator for the water-stable lithium electrode of lithium-air rechargeable batteries [3]. Lithium-air batteries are receiving increased attention for use as power sources in electric vehicles, because of their high theoretical energy density. Two types of Li-air battery systems, non-aqueous and aqueous, have been developed to date. The calculated specific energy densities (including oxygen) of the non-aqueous and aqueous systems are 3460 and 1910 Wh kg^{-1} , respectively, which are several times higher than that of 387 Wh kg^{-1} for conventional lithium-ion batteries with a carbon anode and LiCoO_2 cathode [4]. The water-stable lithium electrode is a key component to protect the lithium electrode from water in aqueous lithium-air batteries, and also to protect the lithium electrode from water in the air for the non-aqueous system. The water-stable lithium electrode was proposed by Vicso *et al.* in 2004 [5] for a battery that consisted of lithium metal, a water-stable lithium ion conducting solid of NASICON-type doped $\text{LiTi}_2(\text{PO}_4)_3$, and a lithium stable interlayer of Li_3N . The inter layer was used to

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prevent direct contact of the solid electrolyte and lithium metal, because the solid electrolyte is unstable in contact with lithium metal.

Various types of solid lithium conducting electrolytes have been reported [6-11]. At present, there are only three types of high lithium-ion conducting solid electrolytes; NASICON-type $\text{Li}_{1+x}\text{A}_x\text{Ti}_{1-x}(\text{PO}_4)_3$ (A=Al, Fe, Sc, etc.) (LATP) [9], perovskite-type $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ (LLTO) [8], and garnet type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) [10] are known to be stable in water with a high content of lithium ions. The electrical conductivities of the LATP, LLTO and LLZ are comparable and in the range of 10^{-3} to 10^{-4} S cm^{-1} at room temperature. The garnet-type LLZ is stable in contact with lithium metal, although the Li/LLZ/Li cell showed a short-circuit after a very short period of polarization at 0.5 mA cm^{-2} and 25 °C [12]. LATP and LLTO are unstable in contact with lithium metal. Therefore, a lithium conducting polymer electrolyte and Li_3N have been proposed as the interlayer between LATP and lithium metal by Zhang *et al.* [13] and Visco *et al.* [5], respectively.

A water-stable solid lithium ion conductor used as the protective layer in lithium-air batteries should have a high lithium conductivity of more than 10^{-3} S cm^{-1} at the operation temperature to achieve acceptable cell performance at higher current densities greater than 1 mA cm^{-2} to reduce the IR drop due to the electrolyte. High total conductivities of 1.3×10^{-3} and 5.08×10^{-3} S cm^{-1} at 25 °C were reported for a glass ceramic of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [14] and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ [15], respectively. However, the preparation of glass ceramics is somewhat complex and the effect of aging on the conductivities is questionable. A sintered pellet prepared using the glass ceramic powder had a lower conductivity of 1.48×10^{-4} at 25 °C [16]. We have previously reported [17] an enhancement in conductivity by the substitution of Fe^{3+} for Al^{3+} in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$, from 5.8×10^{-4} to 1.1×10^{-3} S cm^{-1} at 25 °C in $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$. The effective ionic radius of Fe^{3+} (0.0645 nm) is higher than that of Al^{3+} (0.0535 nm) [18]; the average ionic radius of Al^{3+} and Fe^{3+} in 0.25 Fe and 0.15 Al is 0.0603 nm, which is close to the ionic radius of Ti^{4+} (0.0605 nm). In this study, the effect of Cr^{3+} substitution (0.0615 nm) for Al^{3+} in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ on the electrical conductivity behavior was examined.

2 Experimental

The precursor of $\text{Li}_{1+x+y}\text{Al}_x\text{Cr}_y\text{Ti}_{2-x-y}(\text{PO}_4)_3$ was prepared by the sol-gel method using citric acid, as reported previously [17]. A stoichiometric amount of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (Aldrich) was dissolved in ethylene glycol and added to 0.2 M aqueous solution of citric acid, and then stirred continuously with a magnetic stirrer at 120 °C for 12 h to obtain a homogeneous solution. After preparation of the gel was completed, stoichiometric amounts of LiNO_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$

were added to the gel solution. The molar ratio of citric acid to $\text{Li}^+ + \text{Al}^{3+} + \text{Cr}^{3+} + \text{Ti}^{4+}$ was 4:1. After a homogeneous solution was formed, the gel was kept at 170 °C for several hours to allow water to evaporate and to promote esterification and polymerization. The gel was heated at 500 °C for 4 h to complete the chemical decomposition of nitrates and organic compounds. The black product with residual carbon was ground to a uniformly fine powder using an agate mortar and pestle to increase the surface area of the samples before sintering at 800 °C for chemical reaction and to remove organic residues. The precursor was then wet milled using a Fritsch planetary mill for 15 h to obtain fine powders. The fine powder was isostatically pressed at 150 M Pa into a pellet and then sintered at various temperatures. The pellet was covered with the mother power to prevent lithium volatilization at the high sintering temperature.

The samples were stored in a dry box filled with air for one month to examine the aging effect. The stability of the sintered pellets was evaluated by immersion in distilled water, saturated LiCl, and saturated LiOH with saturated LiCl aqueous solution at 50 °C for one week. The pellets were then carefully washed with distilled water and dried in a vacuum at 220 °C for 20 h before electrical conductivity measurements and X-ray diffraction (XRD) analysis.

XRD data were obtained using a diffractometer (Rigaku Rint 2500) with Cu K α radiation in the 2 θ range from 10 to 90° at a scanning step rate of 0.02° s⁻¹ using Si powder as an internal standard. The chlorine and carbon contents of these samples were analyzed using energy dispersive X-ray spectroscopy (EDX; Hitachi S-486 SEM). The AC impedance of the sintered pellets with sputtered gold electrodes was measured in air using a frequency response analyzer (Solartron 1260) in the temperature range from 20 to 80 °C and the frequency range of 0.1 Hz to 1 MHz. The impedance profiles were analyzed to estimate the bulk and grain boundary conductivities using a non-linear instant fit program in the Zview software package. The electron conductivity was estimated using the Hebb-Wagner method [19] for LiCoO₂/electrolyte/Au cells, where LiCoO₂ and Au were sputtered onto the electrolytes.

3. Results and discussion

Aono *et al.* [9] reported the compositional dependence of the electrical conductivity for $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{1-x}(\text{PO}_4)_3$ and $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, where the highest conductivity was at $x=0.3$ in the former system and $x=0.5$ in the latter system. The $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ system was re-examined to determine the composition that exhibited the highest conductivity. Figure 1 shows XRD patterns of the $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ system sintered at 1150 and 1180 °C for 6 h. All diffraction peaks were indexed as the

NASICON-type structure and no impurity phases were observed. The impedance profiles of $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ sintered at 1150 °C as a function of x and $\text{Li}_{1.4}\text{Cr}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered at 1180 °C are shown in Fig. 2. The impedance profiles show a semicircle that is attributed to the grain boundary resistance, the diameter of which indicates the magnitude [20]. The intercept of the semicircle on the real axis at high frequency represents the bulk resistance. The semicircle due to the bulk resistance was not observed, because this was out of the frequency range of the frequency analyzer. The highest total and bulk conductivities of 3.55×10^{-4} and $4.94 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C were observed for $x=0.4$ in $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ sintered at 1150 °C. The samples sintered at 1180 °C showed a slightly higher grain boundary resistance. The total conductivity of $\text{Li}_{1.4}\text{Cr}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ is comparable to that of $\text{Li}_{1.3}\text{Cr}_{10.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ reported by Aono *et al.* [9].

For further studies, the total amount of Cr^{3+} and Al^{3+} was fixed as 0.4, and Cr^{3+} in $\text{Li}_{1.4}\text{Cr}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ was partly substituted by Al^{3+} . The sintering temperature was selected to obtain the highest conductivity, which is dependent on the Al^{3+} content. Figure 3(a) shows a typical impedance spectra that show the effect of the $\text{Li}_{1.4}\text{Al}_{1.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintering temperature, where the sintering period was fixed for 6 h. The highest total conductivity was observed for the sample sintered at 1070 °C for 6 h. The pellet sintered at 1090 °C for 6 h had a slightly higher grain boundary resistance than that sintered at 1070 °C. The higher grain boundary resistance could be explained by the diffusion of Al^{3+} from the alumina crucible, where the pellet was in direct contact with the alumina crucible. At the lower sintering temperature of 1040 °C, both the bulk and grain boundary resistances were higher than those of the pellet sintered at 1070 °C. The high bulk resistance suggests that the reaction was not completed. The sintering period also has an effect on the impedance profiles of the sintered pellets. Figure 3(b) shows impedance profiles for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered at 1070 °C as a function of the sintering period. The lowest bulk and grain boundary resistance were observed for 6 h sintering. Both the bulk and grain boundary resistances were increased for longer sintering periods at 1070 °C. These increases in resistance could be explained by the diffusion of Al^{3+} from the alumina crucible, as observed for the pellets sintered at 1090 °C.

Figure 4 shows XRD patterns for $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) sintered at the optimum temperatures for 6 h to obtain the highest conductivity. The sintering temperature was decreased with increasing x . All of the main diffraction peaks of the samples could be assigned to the NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$ structure. The sintering temperature of $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ to obtain a single phase was higher than that of $\text{Li}_{1.4}\text{Al}_x\text{Fe}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ (1040 °C). Figure 5 shows the change in the lattice parameters (a -axis and c -axis) with x in $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$, where the lattice parameters were calculated using a hexagonal unit cell. The lattice parameters for the

a-axis and *c*-axis decreased linearly with increasing *x* due to the smaller ionic radii of Al^{3+} (0.0535 nm) than that of Cr^{3+} (0.0615 nm). Figure 6 shows the change in the relative densities of the sintered pellets with *x* in $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$. The relative density of $\text{Li}_{1.4}\text{Cr}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ was as low as 60%. A low relative density for $\text{Li}_{1.3}\text{Cr}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ was also reported by Aono *et al.* [9]. The relative density was increased by the substitution of Cr with Al up to *x*=0.3 and then decreased by further substitution. The highest relative density of 92% was observed for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}(\text{PO}_4)_3$, which is comparable with $\text{Li}_{1.4}\text{Al}_{1.5}\text{Fe}_{2.5}(\text{PO}_4)_3$ [17] and slightly lower than that for $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [9]

Figure 7 shows impedance profiles for the as-sintered samples $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ (*x*=0-0.4) measured at 25 °C, where the sintering temperatures were determined to give the highest conductivity. The bulk and grain boundary conductivities were increased with *x* up to 0.3 and then decreased with *x*. The grain boundary resistance change with *x* corresponded with the change in the relative density. The total electrical conductivities measured at 25 °C for as-sintered and stored in dry box at room temperature for one month $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ (*x*=0-0.4) are shown as a function of *x* in Fig. 8. For sintered pellets of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6-x}\text{Ge}_x(\text{PO}_4)_3$, the electrical conductivity showed a significant aging effect, where the samples was stored in open air [21]. However, $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ (*x*=0-0.4) showed only a slight aging effect on the electrical conductivity. The compositional dependence of the electrical conductivity indicated a maximum at *x*=0.3. The highest total, bulk and grain boundary conductivities for the as-sintered $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ pellets were 1.27×10^{-3} , 1.77×10^{-3} and $3.34 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, respectively. The total and grain boundary conductivity were decreased to 1.06×10^{-3} and $2.65 \times 10^{-3} \text{ S cm}^{-1}$, respectively, after storage for one month, but the bulk conductivity showed no change. The total conductivity decrease by aging is mainly due to a decrease in the grain boundary conductivity. The bulk conductivity for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ was the same as that for $\text{Li}_{1.4}\text{Al}_{0.15}\text{Fe}_{0.25}\text{Ti}_{1.6}(\text{PO}_4)_3$ [17]. The total conductivity of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_3)_3$ was enhanced 1.8 times by the substitution of Cr^{3+} for Al^{3+} , although the bulk conductivity was increased by only 10%. The conductivity enhancement is mainly due to the decrease of the grain boundary resistance.

The activation energies for the grain boundary and bulk conductivities were estimated from the temperature dependence of the conductivity in a temperature range of 25 to 80 °C. The lowest activation energy for grain boundary conductivity was 47 kJ mol⁻¹ for as-sintered $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ and that for the bulk conductivity was 17 kJ mol⁻¹ for as-sintered $\text{Li}_{1.4}\text{Al}_{0.35}\text{Cr}_{0.05}\text{Ti}_{1.6}(\text{PO}_4)_3$. The bulk activation energy is comparable with that for $\text{Li}_{1.4}\text{Al}_{0.15}\text{Fe}_{0.25}\text{Ti}_{1.6}(\text{PO}_4)_3$ and lower than that for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (20.2 kJ mol⁻¹) [21]. The activation energy for the grain boundary

conduction of 47 kJ mol^{-1} for as-sintered $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ is lower than that for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ at 60.4 kJ mol^{-1} . The activation energy for the bulk and grain boundary conductivities of the samples stored for one month were slightly higher than those for the as-sintered samples.

A low electron (and/or hole) transport number is an important requirement for solid electrolytes used for batteries. The contribution of the electronic conduction should be generally considered for oxides containing transition metals. The electronic conductivity of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ was estimated by the Hebb-Wagner method [19] using the $\text{LiCoO}_2/\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cell, where LiCoO_2 was used as the cathode to fix the lithium potential, because $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ is unstable in contact with lithium metal. A small direct current was passed through the cell and the steady cell voltage was measured as a function of the current density at 25°C . Figure 9 shows voltage vs. polarization period curves for the $\text{LiCoO}_2/\text{Li}_{1.4}\text{Cr}_{0.1}\text{Al}_{0.3}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ and $\text{LiCoO}_2/\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cells as a function of the applied voltage. After application of a voltage through the cell, the current will achieve steady-state as the ionic current is stopped with an ion blocking electrode. The electronic conductivity of samples can then be obtained from the Wagner relation:

$$I = (RT/LF)[(\sigma_h(1-\exp(-EF/RT)) + \sigma_e(\exp(EF/RT)-1)], \quad (1)$$

where σ_h and σ_e are the hole and electron conductivity, respectively, I is the current density, R is the gas constant, F is the Faraday constant, T is the absolute temperature, and E is the applied voltage. The relation between E and I did not obey the Wagner equation. This deviation from the Wagner equation may be due to the potential change of LiCoO_2 . The electronic conductivities at 25°C were estimated from the steady-state cell voltages at the applied current densities; $2.5 \times 10^{-9} \text{ S cm}^{-1}$ at 0.245 V and $7.2 \times 10^{-9} \text{ S cm}^{-1}$ at 0.33 V for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$, which is comparable with $1.2 \times 10^{-8} \text{ S cm}^{-1}$ at 0.25 V and $1.6 \times 10^{-8} \text{ S cm}^{-1}$ at 0.4 V for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. The electronic conductivity contribution in $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ is approximately one order of magnitude lower than that in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$, and two orders of magnitude lower than that in $\text{Li}_{1.4}\text{Al}_{0.15}\text{Fe}_{0.25}\text{Ti}_{1.6}(\text{PO}_4)_3$. Therefore, it was concluded that the contribution of electronic conductivity in $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ to the total conductivity is negligibly low and is reduced in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ by the substitution of Cr^{3+} for Al^{3+} .

The lithium ion conducting solid electrolyte used as the protective layer for the water-stable lithium electrode of aqueous lithium-air batteries should be stable in aqueous solutions with saturated LiOH , in addition to having high lithium ion conductivity, because the reaction product of the lithium-air batteries is LiOH . The

stability of the $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ glass ceramic (Ohara LATP plate) in aqueous solutions has been extensively studied by Imanishi and co-workers [22]. The glass ceramic decomposes in strong acid solution and dissolves in strong alkaline solution. However, Shimonishi *et al.* reported that the glass ceramic is stable in an aqueous solution saturated with LiOH and LiCl, which has a pH of approximately 9, due to the low dissociation of LiOH to ions in the presence of a high Li^+ ion content [23]. The stability of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}(\text{PO}_4)_3$ in an aqueous solution saturated with LiOH and LiCl was examined. XRD patterns of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}(\text{PO}_4)_3$ immersed in distilled water, saturated LiCl aqueous solution, and saturated LiOH with saturated LiCl aqueous solution at 50 °C for one month revealed no impurity phases and there was no change in the ratio of the diffraction peaks. However, the impedance profiles showed a change after immersion in these solutions, as shown in Fig. 10. The grain boundary resistance of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}(\text{PO}_4)_3$ was increased significantly from 29.1 to 990.2 $\Omega\cdot\text{cm}^2$ by immersion in distilled water, while the bulk resistance was increased slightly from 49.3 to 58.3 $\Omega\cdot\text{cm}^2$. The increases in grain boundary resistance could be explained by the ion exchange of Li^+ and H^+ observed in $\text{Li}_{3x}\text{La}_{2/3}\text{TiO}_3$ [24] and $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ [25]. The mechanical strength of the pellet was also reduced by immersion in distilled water at 50 °C for one month. The grain boundary and bulk resistances of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in the aqueous solutions of saturated LiCl and that saturated with LiCl and LiOH were significantly decreased. The total conductivities of $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in the saturated LiCl aqueous solution and saturated LiOH with saturated LiCl aqueous solution were increased from $1.28\times 10^{-3} \text{ S cm}^{-1}$ to 4.44×10^{-3} and $4.22\times 10^{-3} \text{ S cm}^{-1}$, respectively. The conductivities of the sample stored in a dry glove box (dew point ca.-96 °C) for several hours was decreased significantly and was a slightly lower than that of the as-sintered sample, as shown in Fig. 10. A similar enhancement of conductivity by immersion in saturated LiCl aqueous solution was observed for $\text{Li}_{1.4}\text{Al}_{0.15}\text{Fe}_{0.25}\text{Ti}_{1.6}(\text{PO}_4)_3$ [21] and $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ [26]. The enhancement of conductivity is explained by the formation of $\text{LiCl}\cdot\text{H}_2\text{O}$ at the grain boundaries in open air. Approximately 0.16 wt% Cl was detected by EDX analysis for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in the saturated LiCl solution. These results suggests that $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ is stable in the aqueous solution saturated with LiOH and LiCl.

4. Conclusions

NASICON-type lithium ion conducting solid electrolytes of $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) were prepared using a sol-gel precursor by

sintering between 1000 °C and 1120 °C for 6 h. The substitution of Cr^{3+} for Al^{3+} enhanced the ionic conductivity of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. The highest total conductivity of $1.06 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C was observed for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$, which is comparable with $0.59 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. The enhancement of bulk conductivity by the substitution of Cr^{3+} for Al^{3+} was only 10% and is mainly due to a decrease of the grain boundary resistance.

The contribution of electron (or hole) conductivity was negligible with respect to the total conductivity, and electron (or hole) conductivity was reduced by one order of magnitude with the substitution of Cr^{3+} for Al^{3+} . $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ was stable in the saturated LiCl aqueous solution and the aqueous solution saturated with LiOH and LiCl, while it was unstable in distilled water. It has been concluded that $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ is a promising candidate for the protective layer of the lithium electrode in aqueous lithium-air batteries, because its high lithium ion conductivity and stability in an aqueous solution of saturated LiOH and saturated LiCl.

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Reference

- [1] S. Kondo, in *Lithium ion batteries, fundamental and performance*, M. Wakihara and O. Yamamoto (Eds), Kodansha, Tokyo and Wiley-VCH, Japan, 1998, p.199
- [2] M. Tatsumishako and A. Hayashi, in *Nanoscale technology for advanced lithium batteries*, T. Osaka and Z. Ogumi (Eds), Springer, NY, USA, 2014, p. 63
- [3] N. Imanishi and O. Yamamoto, *Material Today*, 17 (2014) 24
- [4] P.G. Bruce, S.A. Freunberger, L.J. Hardwick J.-M. Tarascon, *Nature Materials*, 11 (2012) 19
- [5] S.J. Visco, B. Katz, L.C.D. Joghe, M.Y. Chu, Abstract # 53 in 12th International Meeting on Lithium Batteries, Nara Japan, 2004
- [6] U.V. Alpen, A. Rabenau, and G.H. Talat, *Appl. Phys. Lett.*, 30 (1977) 631
- [7] H.Y.-P. Hong, *Mat. Res. Bull.*, 13 (1978) 117
- [8] Y. Inaguma, I. Chen, M. Ito, T. Nakamura, T. Uchida, and M. Wakihara, *Solid State Commun.*, 86 (1993) 689
- [9] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G. Adachi, *J. Electrochem. Soc.*, 137 (1990) 1023

- [10] R. Murugan, V. Tangadurai, and W. Weppner, *Angew. Chem. Int. Ed.*, 48 (2007) 7778
- [11] N. Kamaya, K. Honma, Y. Yamakawa, T. Nakamura, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kado, S. Hama, K. Kawamoto, and A. Mitsui, *Nat. Mater.*, 10 (2011) 682
- [12] K. Ishiguro, Y. Nakata, M. Mastui, I. Uechi, Y. Takeda, O. Yamamoto, N. Imanishi, *J. Electrochem. Soc.*, 160 (2013) A1684
- [13] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, *J. Electrochem. Soc.*, 157 (2010) A214.
- [14] J. Fu, *J. Mater. Sci.*, 33 (1998) 154
- [15] J.S. Thokchon, N. Gupta, and B. Kumar, *J. Electrochem. Soc.*, 155, A915 (2008)
- [16] Y. Shimonishi, T. Zhang, P. Johnson, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, *J. Power Sources*, 195 (2010) 6187
- [17] P. Zhang, M. Matsui, Y. Takeda, O. Yamamoto, and N. Imanishi, *Solid State Ionics*, 263 (2014) 27
- [18] R.D. Shanonon, *Acta Cryst.*, A32 (1976) 751
- [19] J. Wagner, C. Wagner, *J. Chem. Phys.*, 26 (1957) 1597
- [20] P.G. Bruce, A.R. West, *J. Electrochem. Soc.*, 136 (1982) 662
- [21] P. Zhang, M. Matsui, A. Hirano, Y. Takeda, O. Yamamoto, N. Imanishi, *Solid State Ionics*, 253 (2014) 175
- [22] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources*, 189 (2008) 371
- [23] Y. Shimonishi, T. Zhang, N. Imanishi, D. Imm, D.-J. Lee, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, *J. Power Sources*, 196 (2011) 5128
- [24] O. Bohnke, Q.N. Pham, A. Boulant, J. Stokus, M. Barr, *Solid State Ionics*, 188 (2011) 144
- [25] C. Calven, J.L. Fourquest, M.-P. Crosmer-Lopez, L. Le Berre, *Chem. Mater.* 23 (2011) 1892
- [26] K. Takahashi, J. Ohmura, D. Im, D.-J. Lee, T. Zhang, N. Imanishi, A. Hirano, M.B. Phillipps, Y. Takeda, O. Yamamoto, *J. Electrochem. Soc.*, 159 (2012) A342

Figure captions

Fig. 1. XRD patterns for $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) sintered at 1150 and 1180 °C for 6 h.

Fig. 2. Impedance profiles measured at 25 °C for $\text{Li}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) sintered at 1150 and 1180 °C for 6 h.

Fig. 3. Impedance profiles measured at 25 °C for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered (a) at various temperatures for 6 h and (b) sintered at 1070 °C for various periods.

Fig. 4. XRD patterns for $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) sintered at optimum temperatures.

Fig. 5. Lattice parameters for $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x = 0-0.4$) measured at room temperature.

Fig. 6. Relative densities of $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$).

Fig. 7. Impedance profiles measured at 25 °C for $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered at optimum temperatures for 6 h.

Fig. 8. Total and bulk electrical conductivities measured at 25 °C for as-sintered $\text{Li}_{1.4}\text{Al}_x\text{Cr}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) and that stored for one month at room temperature.

Fig. 9. Cell voltage vs. polarization period at various current densities for (a) $\text{LiCoO}_2/\text{Li}_{1.4}\text{Cr}_{0.1}\text{Al}_{0.3}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ and (b) $\text{LiCoO}_2/\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cells measured at 25 °C.

Fig. 10. Impedance profiles measured at 25 °C for $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$: (a) pristine $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$, (b) $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in an aqueous solution saturated with LiCl and LiOH at 50 °C for 1 week measured in a glove box, and $\text{Li}_{1.4}\text{Al}_{0.3}\text{Cr}_{0.1}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in (c) saturated LiCl aqueous solution, (d) aqueous solution saturated with LiCl and LiOH, and (e) water at 50 °C for one week measured in open air.

Fig. 1

Fig. 2

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