Water-stable lithium ion conducting solid electrolyte of iron and aluminum doped NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$

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Abstract

High lithium ion conductivity solid electrolytes of $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ and $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) with the NASICON-type structure were synthesized using a precursor prepared by the sol-gel method. The highest electrical conductivity was obtained for the $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LFATP) composition sintered at 1040 °C for 7 h in air. The total, grain boundary, and bulk conductivities of the pellet were stable after storage for one month and were 1.01×10^{-3} , 2.17×10^{-3} and $1.81 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, respectively. The contribution of electron (or hole) conductivity to the total conductivity was negligibly small. LFATP was unstable in water, but stable in saturated LiOH and LiCl aqueous solution.

1. Introduction

The lithium-air battery is a very promising power source because it has a far higher theoretical energy density than lithium-ion batteries. Two types of lithium-air batteries, non-aqueous [1] and aqueous [2], have been investigated. The non-aqueous system (3460 Wh kg^{-1}) has higher energy density than the aqueous system (1910 Wh kg^{-1}); however, the non-aqueous system has some serious problems that must still be addressed, such as the corrosion of lithium by water and CO_2 ingress when operated in air, precipitation of high resistance reaction products (lithium oxide) on the air electrode, and high polarization during the charge and discharge processes. These problems with the non-aqueous system could be overcome for the aqueous

system, which was proposed by Visco *et al.* in 2004 [3]. The key material of the aqueous system is a water-stable lithium ion conducting solid electrolyte, without which the aqueous system could not be realized.

Lithium ion conducting solid electrolytes with various crystalline structures, such as Li_3N [4], Li_2S -based glass [5], NASICON-type $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) [6], garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) [7], and perovskite-type $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ (LLTO) [8] have been investigated extensively. Recently, Kamaya *et al.* [9] reported a lithium superionic conductor of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, which has an extremely high lithium ion conductivity of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. However, at present, only three types of high lithium ion conductivity solid electrolytes, LATP, LLZ and LLTO, are known to be stable in an aqueous solution with a high concentration of lithium ions. The electrical conductivity of LLZ, which is stable in contact with lithium metal, is comparable to those of LATP and LLTO, but the $\text{Li}/\text{LLZ}/\text{Li}$ cell is short-circuited after a very short period of polarization at 0.5 mA cm^{-2} and 25°C [10,11]. The LATP and LLTO electrolytes are unstable in contact with lithium metal [8,12]; therefore, an interlayer is required between lithium metal and LATP (and LLTO) for the water-stable lithium electrode. Zhang *et al.* [13] and Visco *et al.* [3] have successfully used a lithium conducting polymer electrolyte and Li_3N as interlayer materials.

To obtain acceptable cell performance for aqueous lithium-air batteries at a high current density requires a water-stable solid lithium ion conductor with a total conductivity of above $10^{-3} \text{ S cm}^{-1}$ at the operation temperature. The ionic conductivity of the NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$ has been considerably increased by substitution of Sc^{3+} , Al^{3+} , Y^{3+} , Fe^{3+} , In^{3+} and Cr^{3+} for Ti^{4+} , where the highest total conductivity of $7 \times 10^{-4} \text{ S cm}^{-1}$ was obtained for $\text{Li}_{1.3}\text{M}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ ($\text{M}=\text{Al}$ and Sc) [14]. High total conductivities of 1.3×10^{-3} and $5.08 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C were reported for the glass ceramic $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ [15] and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ [16], respectively. However, the preparation of glass ceramics is somewhat complex and the effect of aging on the conductivity is questionable. The electrical conductivity of the commercialized $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{P}_{3-y}\text{Si}_y\text{O}_{12}$ (Ohara plate) glass ceramic is $10^{-4} \text{ S cm}^{-1}$ at room temperature, while the highest conductivity of LLTO was reported to be $5.7 \times 10^{-4} \text{ S cm}^{-1}$ at 300 K [8]. We have previously reported the electrical conductivity of sintered pellets of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6-x}\text{Ge}_x(\text{PO}_4)_3$ [17]. The electrical conductivity of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ was enhanced by the substitution of Ge^{4+} for Ti^{4+} , where the ionic radius of Ge^{4+} (0.067 nm) is lower than that of Ti^{4+} (0.0745 nm). The highest

electrical conductivity of $1.29 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C was obtained for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.4}\text{Ge}_{0.2}(\text{PO}_4)_3$. The average ionic radius of Ti^{4+} and Ge^{4+} in $x=0.2$ was decreased to 0.0735 nm . In this study, the electrical conductivity behavior of the co-substitution of Fe^{3+} with a larger ionic radius (0.0785 nm) and Al^{3+} with a lower ionic radius (0.0675 nm) than Ti^{4+} (0.0745 nm) [18] for Ti in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ was investigated, where the average ionic radius of Al^{3+} and Fe^{3+} brings close to the ionic radius of Ti^{4+} . The contribution of electronic conductivity to the total conductivity and the stability of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ in water were also examined.

2. Experimental

The precursor of $\text{Li}_{1+x+y}\text{Al}_x\text{Fe}_y\text{Ti}_{2-x-y}(\text{PO}_4)_3$ 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 then added to a 0.2 M aqueous solution of citric acid with continuous stirring 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 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ were added to the gel solution. The molar ratio of citric acid to $\text{Li}^+ + \text{Al}^{3+} + \text{Fe}^{3+} + \text{Ti}^{4+}$ was $4:1$. After a homogeneous solution was formed, the gel was kept at 170°C for several hours to allow evaporation of the water and to promote esterification and polymerization. The gel was then 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 powder samples before sintering at 800°C for chemical reaction and to remove organic residues. The precursor was then ground by wet milling using a planetary mill (Fritsch planetary micro mill) for 15 h to produce fine powders. The fine powder was isostatically pressed at 150 MPa into a pellet (*ca.* 12 mm diameter and 15 mm thick) and then sintered at various temperatures on a gold sheet to protect the samples from reaction with the alumina refractory board. The stability of the sintered pellets in aqueous solutions was evaluated by immersion into distilled water, saturated LiCl , and saturated LiOH and LiCl aqueous solutions at 50°C for one week. After immersion in these solutions, the pellets were carefully washed with distilled water and dried in a vacuum at 220°C for 20 h before electrical conductivity and X-ray diffraction (XRD) measurements.

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. Si powder was used as an internal standard. Scanning electron microscopy (SEM; Hitachi S-486 SEM) observations were conducted and the relative elemental contents of the samples were measured using energy dispersive X-ray spectrometry. 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 in 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 [19] method for LiCoO₂/electrolyte sample/Au cells. The DC conductivities of the electrolyte samples were examined using non-blocking LiCoO₂/electrolyte sample/LiCoO₂ cells, where the LiCoO₂ and Au electrodes were sputtered onto the pellets.

3. Results and discussion

The pressed pellets of Li_{1+x}Fe_xTi_{2-x}(PO₄)₃ (LFTP) were sintered at various temperatures for 7 h. The XRD patterns of LFTP with x=0.1-0.5 sintered at 900 and 950 °C were indexed as the NASICON-type structure, although impurity phases such as FePO₄, Fe₂O₃ and Ti₄O₇ were also present. The LFTP samples with x=0.1, 0.2 and 0.3 sintered at 1000 °C for 7 h showed no impurity phases, while an impurity phase of FePO₄, Fe₂O₃ and Ti₄O₇ was observed in LFTP with x=0.4 and 0.5, as shown in Fig.1. The impurity phase disappeared for LFTP with x=0.4 when sintered at 1040 °C, but was still observed for LFTP with x=0.5 sintered at the same temperature, as shown in Fig. 1.

Figure 2 shows impedance profiles measured at 25 °C for LFTP sintered at 1000 °C for 7 h as a function of x and those for LFTP with x=0.4 and 0.5 sintered at 1040 °C for 7 h. The impedance profiles have a semicircle that is attributed to the grain boundary resistance, the diameter of which indicates the magnitude. The intercept of the semicircle on the real axis at high frequency represents the bulk resistance. The semicircle due to the bulk was not observed, because this was out of the frequency range of the frequency analyzer [20]. The grain boundary resistances for LFTP were significantly dependent on x in Li_{1+x}Fe_xTi_{2-x}(PO₄)₃, while the bulk resistances were increased slightly with increasing x.

Figure 3 shows the relative densities of the $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) pellets sintered at 1000 °C for 7 h as a function of x . The relative densities were calculated from the ratios of the observed densities calculated using the sintered pellet dimensions and weights to those determined from the lattice parameters. The relative densities of the pellets sintered at 1000 °C were increased by the substitution of Ti with Fe. The decrease in the grain boundary resistance of the sintered pellets with $x<0.4$ could be explained by the increase of the relative density. The total electrical conductivities of the as-sintered $\text{Li}_{1.4}\text{Fe}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ were $7.7\times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, which is higher than that for $\text{Li}_{1.4}\text{Fe}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ at $2.6\times 10^{-4} \text{ S cm}^{-1}$ (at 25 °C) reported by Aono *et al.* [14], which was prepared by conventional solid state reaction and sintered at 1050 °C for 2 h. The relative density of the $\text{Li}_{1.4}\text{Fe}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ pellet sintered at 1040 °C for 7 h was slightly higher (86.0%) than that sintered at 1000 °C for 7 h (83.9%) and the total conductivity was increased to $8.5\times 10^{-4} \text{ S cm}^{-1}$ at 25 °C. This sample exhibited an aging effect on the conductivity, which decreased to $7.31\times 10^{-4} \text{ S cm}^{-1}$ at 25 °C after one month.

Pressed pellets of the sol-gel precursor for co-doped $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LFATP) were sintered at 1040 °C for 7 h. The total content of Al and Ti was fixed at 0.4 because the highest conductivity was observed at $x=0.4$ in $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. Figure 4 shows XRD patterns for the LFATP samples as a function of x . An impurity phase of AlPO_4 was observed for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ sintered at 1040 °C, while all the diffraction lines were indexed according to the NASICON-type structure for LFATP with $x = 0.1-0.4$. Figure 5 shows the change in the lattice parameter with x in LFATP, where the lattice parameters were calculated using a hexagonal unit cell. The lattice parameters for the a - and c -axis increased with x because the ionic radius of Fe^{3+} (0.0785 nm) is larger than that of Al^{3+} (0.0675 nm). Figure 6 shows the relative densities of the LFATP pellets sintered at 1040 °C for 7 h as a function of x . The relative densities of the sintered pellets were increased by the substitution of Al for Fe up to $x=0.25$ and then decreased with further substitution. A maximum relative density of 93.6% was obtained for $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$. The relative density is comparable with that for the high lithium ion conducting solid electrolyte of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.4}\text{Ge}_{0.2}(\text{PO}_4)_4$ reported in our previous paper [17].

The effects of the sintering temperature and period on the electrical conductivity were examined. The impedance profiles for $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.4}(\text{PO}_4)_3$ sintered at various temperatures and for various periods are shown in Fig. 7. The grain boundary

conductivity of the as-sintered samples was dependent on the sintering temperature and period, while the effect on the bulk conductivity was not significant. The highest total conductivity of $1.19 \times 10^{-3} \text{ S cm}^{-1}$ was obtained for the sample sintered at 1040°C for 7 h. The high temperature sintering as 1040°C and long period sintering as 12 h may produce a high resistance impurity phase at the grain boundary. The $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6-x}\text{Ge}_x(\text{PO}_4)_3$ system exhibited a significant aging effect with respect to the conductivity, where the total electrical conductivity of $2.25 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C decreased to the a stable conductivity of $1.29 \times 10^{-3} \text{ S cm}^{-1}$ after one month storage [17], Therefore, the impedance of the LFATP samples sintered at 1040°C for 7 h was measured after storage for one month at room temperature in a dry box. Figure 8 and 9 show the impedance profiles and the compositional dependence of the total, bulk, and grain boundary conductivities at 25°C , respectively. The highest total conductivity of $1.01 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C was observed for $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$. The compositional dependence suggests that the grain boundary conductivity is changed significantly with x, which corresponds to the relative density of the sintered sample. Maximum bulk and grain boundary conductivities of 1.80×10^{-3} and $2.17 \times 10^{-3} \text{ S cm}^{-1}$ were obtained for $x=0.25$. The average ionic radius of Al^{3+} and Fe^{3+} in $x=0.25$ is 0.0742 nm , which is close to the ionic radius of Ti^{4+} (0.0745 nm). A similar result was reported for the conductivity enhancement of ZrO_2 by the substitution of Zr^{4+} for M^{3+} ions ($\text{M}=\text{lanthanide}$), where the closest ionic radius to Zr^{4+} was that of Sc^{3+} , which showed the highest oxide ion conductivity [21]. This behavior could be explained by the interaction between ionic vacancies produced by the substitution of Zr^{4+} for M^{3+} and by the structural effect [22]. The bulk (σ_b) and grain boundary (σ_{gb}) conductivities of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ are slightly lower than those of the as-sintered $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.4}\text{Ge}_{0.2}(\text{PO}_4)_3$ ($\sigma_b = 2.01 \times 10^{-3}$ and $\sigma_{gb} = 2.88 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C). The effect of aging on the electrical conductivity of LFATP was not as severe as that observed for the $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6-x}\text{Ge}_x(\text{PO}_4)_3$ system. The activation energies for the bulk (E_b) and grain boundary (E_{gb}) conductivities of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ were calculated to be 17.0 and 43.9 kJ mol^{-1} , respectively, from their temperature dependence in the range from 25 to 80°C . These activation energies are lower than those for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($E_b = 21.1 \text{ kJ mol}^{-1}$ and $E_{gb}=60.4$) and $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.4}\text{Ge}_{0.2}(\text{PO}_4)_3$ ($E_b=20.2 \text{ kJ mol}^{-1}$ and $E_{gb}=55 \text{ kJ mol}^{-1}$) [17].

The lithium ion conducting solid electrolyte for the protective layer in the water-stable lithium electrode for 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 Li-air cell is LiOH. The stability of the $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_y\text{P}_3\text{O}_{12}$ glass ceramic (Ohara plate) in aqueous solutions has been extensively studied by Imanishi and co-workers [10,12]. The glass ceramic decomposes in a strong acid solution and dissolves in strong alkaline solution. However, Shimonishi *et al.* reported that the glass ceramic is stable in saturated LiCl and LiOH aqueous solution, the pH value of which was around 9, due to the low dissociation of LiOH to ions in the presence of a high Li^+ ion content [23]. The stability of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ in saturated LiOH and LiCl aqueous solution was examined. The XRD patterns of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in distilled water, saturated LiCl aqueous solution, and saturated LiCl and LiOH aqueous solution at 50 °C for one week 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 $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in distilled water increased significantly from 93 to 480 $\Omega \text{ cm}^2$, and the bulk resistance also increased from 133.5 to 221.7 $\Omega \text{ cm}^2$. These increases in bulk and 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 week. However, the grain boundary and bulk resistances of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in saturated LiCl aqueous solution and saturated LiCl and LiOH aqueous solution were significantly decreased. The total conductivities of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in saturated LiCl aqueous solution and saturated LiCl and LiOH aqueous solution and then measured in the ambient atmosphere were increased from $1.19 \times 10^{-3} \text{ S cm}^{-1}$ to 3.44×10^{-3} and $4.35 \times 10^{-3} \text{ S cm}^{-1}$, respectively. The conductivities of the sample stored in a dry glove box (dew point of ca. -80 °C) for several hours was decreased to the almost same value as that observed for the pristine sample. A similar enhancement of conductivity by immersion in saturated LiCl aqueous solution was reported for LATP by Takahashi *et al.* [26]. The conductivity enhancement was explained by the formation of $\text{LiCl} \cdot \text{H}_2\text{O}$ at the grain boundary. Approximately 0.16 wt% Cl was detected by EDX analysis in $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ that was immersed in saturated LiOH and LiCl. Therefore, the conductivity enhancement in the present study could also be explained by the formation of $\text{LiCl} \cdot \text{H}_2\text{O}$ at the grain boundary, and it was concluded that

$\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ is stable in saturated LiOH and LiCl aqueous solution.

The low electron (and/or hole) transport number in the solid electrolyte is an important requirement for use of the electrolyte in batteries. The electronic conductivity of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ was estimated using the Hebb-Wagner method [25] for the $\text{LiCoO}_2/\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cell, where LiCoO_2 was used as the cathode to fixed the lithium potential, because $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ 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 11 shows voltage vs. polarization period curves for the $\text{LiCoO}_2/\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cell as a function of the applied voltage. After application of a voltage through the cell, the current will get to steady state as the ionic current is stopped with an ion blocking electrode. The electronic conductivity of sample can then be obtained from the Wagner relation:

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

where σ_h and σ_e are 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, L is the thickness of the sample, and E is the applied voltage. However, the current-voltage curves do not obey the Wagner equation. The deviation from the Wagner equation may be due to the potential change of the LiCoO_2 electrode, because we could not use lithium metal with a constant lithium activity. The electronic conductivity at 25 °C was estimated from the current and steady state cell voltage as $2.5 \times 10^{-7} \text{ S cm}^{-1}$ at 0.4 V and $8.8 \times 10^{-7} \text{ S cm}^{-1}$ at 1.14 V. Therefore, it was concluded that the contribution of electronic conductivity to the total conductivity is very low.

The dc conductivity of $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ was measured using the lithium ion non-blocking $\text{Au}/\text{LiCoO}_2/\text{LFATP}/\text{LiCoO}_2/\text{Au}$ cell in open air, because in some cases the impedance profile cannot cover the behavior in the low frequency range. $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ was determined to be unstable in contact with lithium metal; therefore, LiCoO_2 was used as the non-blocking electrode. LiCoO_2 is known as a mixed electron and lithium ion conductor. The lithium ion conductivity of LiCoO_2 is approximately $10^{-7} \text{ S cm}^{-1}$ [27]. LiCoO_2 films (*ca.* 10 μm thick) were sputtered on both sides of the $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ pellet. The change in the cell voltage with time was measured as a function of the applied current at 25 °C, and typical results are shown in Fig. 12. Stable cell voltages were observed at 0.4 mA cm^{-2} . The dc conductivity calculated from the cell voltage vs. current density curves was

approximately 500 Ω , which is higher than the total cell resistance of 109 Ω cm² and the interface resistance of 55 Ω cm² estimated from the impedance profile. The high dc resistance may be due to the low lithium ion conductivity of LiCoO₂ and to electrode polarization. Consequently, Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ could be considered to be lithium ion conducting solid electrolyte. The low interface resistance between Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ and LiCoO₂ is attractive for its use as an electrolyte in an all-solid-state battery, because some lithium conducting solid electrolytes have a high interface resistance between the solid electrolyte and the electrode [28].

Conclusion

NASICON-type lithium ion conducting solid electrolytes, Li_{1.4}Fe_xAl_{0.4-x}Ti_{1.6}(PO₄)₃ (x=0-0.4), were prepared from a sol-gel precursor with sintering up to 1040 °C for 7 h. The highest total conductivity of 1.01×10⁻³ S cm⁻¹ at 25 °C was observed for Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ after storage for one month at room temperature in a dry box. The grain boundary conductivity of as-sintered Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ did not show a significant aging effect. The contribution of electron (or hole) conductivity was negligible with respect to the total conductivity. Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ showed a significant increase in resistance by immersion in distilled water; however, that immersed in saturated LiOH and LiCl aqueous solution showed a significant decrease of the bulk resistance. The decrease in resistance could be explained by the formation of a conductive phase of LiOH·H₂O at the grain boundary under a wet atmosphere. It has been concluded that Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ is a promising candidate for the protective layer of the lithium electrode in aqueous lithium-air batteries, because it has high lithium ion conductivity and stability in saturated LiOH and LiCl aqueous solution. In addition, Li_{1.4}Fe_{0.25}Al_{0.15}Ti_{1.6}(PO₄)₃ may be used as the electrolyte for all solid state lithium batteries because of its excellent compatibility with the typical cathode material of LiCoO₂ for lithium-ion batteries.

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Figure captions

Fig. 1. XRD patterns of $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) sintered at 1000 and 1040 °C for 7 h.

Fig. 2. Impedance profiles measured at 25 °C for $\text{Au}/\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$)/Au sintered at 1000 and 1040 °C for 7 h.

Fig. 3. Relative density of the $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0-0.5$) pellets sintered at 1000 °C for 7 h.

Fig. 4. XRD patterns for $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) sintered at 1040 °C for 7 h.

Fig. 5. Room temperature lattice parameters as a function of x for $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) sintered at 1040 °C for 7 h.

Fig. 6. Relative density of the $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) pellets sintered at 1040 °C for 7 h.

Fig. 7. Impedance profiles measured at 25 °C for $\text{Au}/\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.4}(\text{PO}_4)_3/\text{Au}$: (a) sintered at various temperatures for 6 h and (b) sintered at 1040 °C for various periods.

Fig. 8. Impedance profiles at 25 °C for the $\text{Au}/\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$)/Au cell stored at room temperature for one month.

Fig. 9. Bulk, grain boundary and total conductivities measured at 25 °C of the $\text{Li}_{1.4}\text{Fe}_x\text{Al}_{0.4-x}\text{Ti}_{1.6}(\text{PO}_4)_3$ ($x=0-0.4$) sintered at 1040 °C for 7 h stored at room temperature for one month.

Fig. 10. Impedance profiles at 25 °C for $\text{Au}/\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$: (a) pristine

$\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$, and $\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3$ immersed in (b) water, (c) saturated LiCl aqueous solution, and (d) saturated LiCl and LiOH aqueous solution at 50 °C for one week.

Fig. 11. Current vs. voltage characteristics for the $\text{LiCoO}_2/\text{Li}_{1.4}\text{Fe}_{0.25}\text{Al}_{0.15}\text{Ti}_{1.6}(\text{PO}_4)_3/\text{Au}$ cell at 25 °C.

Fig. 12. Cell voltage vs. polarization period curves at 25 °C as a function of current density.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12