Short communication

Improvement of Li-ion conductivity in A-site disordering lithium-lanthanum-titanate perovskite oxides by adding LiF in synthesis

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ABSTRACT

$La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ ($y = 0.017$, 0.05) were prepared by a conventional solid-state reaction from a mixture of La_2O_3, $LiCO_3$, TiO_2, and 10% excess LiF. The variation of the lattice parameter with increase of y value in $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ was different from that in conventional lithium-lanthanum-titanate series perovskite oxides, $La_{0.56-y}Li_{0.33+3y}TiO_3$. Bulk Li-ion conductivities of the $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ are higher than those of $La_{0.56-y}Li_{0.33+3y}TiO_3$. Li-ion conductivity of $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ ($y = 0.017$) was 2.30×10^{-3} S cm^{-1} at 30 °C, which is, to our knowledge, one of the highest Li-ion conductivities in the oxide compounds.

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1. Introduction

Inorganic solid-state materials with high Li-ion conductivities are essential for the development of all-solid-state lithium secondary batteries. Among them, A-site deficient perovskite oxides (ABO_3) containing lithium ion, such as $La_{0.67-x}Li_{3x}TiO_3$ (LLT) series, are much more interest because of their high Li-ion conductivities, ca 10^{-3} to 10^{-5} S cm^{-1} at room temperature, in spite of their relatively high reduction potential [1–3]. To clarify the reason for their high Li-ion conductivities, many researchers have studied the characteristic crystallographic properties in A-site deficient perovskite oxides containing lithium ion [4–8], as well as the change of the properties caused by various degree of alternative ordered arrangements of A-site cations [9,10]. Particularly, Harada et al. reported that the α-LLT (space group: $Pm3m$, $x = 0.12$) with the disordered arrangement of the A-site cations showed the highest Li-ion conductivity ($\sigma = 1.53 \times 10^{-3}$ S cm^{-1} at 25 °C) among all the lithium perovskite oxides, and the β-LLT (space group: $P4/mmm$) with the ordered arrangement of the A-site cations along the c-axis showed lower Li-ion conductivity ($\sigma = 6.88 \times 10^{-4}$ S cm^{-1} at 25 °C) than α-LLT [10].

In the A-site deficient perovskite LLT, A-site and/or B-site ions may influence the Li-ion conductivity, and the A-site and/or B-

site ions can be easily substituted by other elements. In order to enhance the Li-ion conductivity on LLT, many researchers have reported the effect of cation doping into A-site and/or B-site. However, most of the relative materials indicated lower conductivities than the original LLT except in a few reports [11]. For example, by substituting La (A-site cation) by other lanthanide ions (Ln = Pr, Nd, or Sm), the ionic conductivity of LnLT was decreased because the bottleneck consisted of four O atoms through which the lithium ions hop was close to due to the shortening of the Ln-O distances [12]. On the other hand, it was also important to control the location of oxide ions constructing the bottleneck for lithium ion hopping. Li et al. have reported that the substitution of F$^-$ for O^{2-} by adding LiF in synthesis process might be one of the major factors influencing the Li-ion conductivity in β-$La_{2/3-x}Li_{3x-y}TiO_{3-y}F_y$ [13].

In this paper, we enhanced the Li-ion conductivity of α-LLT by adding LiF as reagent during the synthesis process to obtain $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$, and measured the Li-ion conduction of these materials. Here, the concentration of lithium ion kept the constant value because the unfavorable factor for lithium-ion conduction with the decrease of the concentration of lithium ion was dissolved.

2. Experimental

$La_{0.56-y}Li_{0.33+3y}TiO_3$ ($y = 0$, 0.01, 0.02, and 0.04) and $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ ($y = 0.017$ and 0.05) were prepared by a conventional solid-state reaction. The mixture of La_2O_3, $LiCO_3$,

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TiO$_2$, and 10% excess LiF was heated initially at 650 °C for 2 h to expel CO$_2$ gas and calcined at 800 °C for 12 h on a Au boat. The reground products were cold-pressed into a pellet, followed by sintering at 1350 °C for 1.5 h on a Pt plate. The sintered pellet was quenched from the sintering temperature to liquid N$_2$ temperature to obtain α-form.

The identification of the perovskite phase and the refinement of the lattice parameter were carried out by powder X-ray diffraction with CuKα radiation. Si powders were used for optimizing of the peak shift. The X-ray absorption spectroscopy (XAS) measurements for Ti K-edge spectra were carried out in transmission mode using synchrotron radiation at the beam line BL-7C, Photon Factory, Tsukuba, Japan.

Li-ion conductivities were measured by using a two-electrode cell with gold electrodes in steinless chambers filled with Ar gas. AC impedance spectroscopy was performed by using an AC impedance analyzer (HP4192 A LF) in the frequency range from 10 Hz to 10 MHz. Li-ion conductivities at 30 °C were estimated from their Nyquist plots.

3. Result and discussion

Fig. 1 shows the powder X-ray diffraction patterns of La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$. In this figure, all the samples showed the single phase of the perovskite structure with the space group Pm3m and no other peaks assigned to impurities appeared in the 2θ region from 10° to 80°. The peaks of (101/2) reflections at 25.8°, which indicated the alternate arrangement of La ions along c-axis, were not observed among any samples, either. These indicate that the La ions, Li ions, and the vacancies are randomly distributed over the A-sites [10]. Fig. 2 shows the lattice parameters of La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$ with different y values. Unlike LLT, the lattice parameters of La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$ increased with the increase of y value. This tendency indicated that the relaxation of lattice structure caused by either the low Coulombs force caused by the substitution or the existence of amorphous compound resulted from the contact between LiF (lithium salt) and LLT grain-boundary
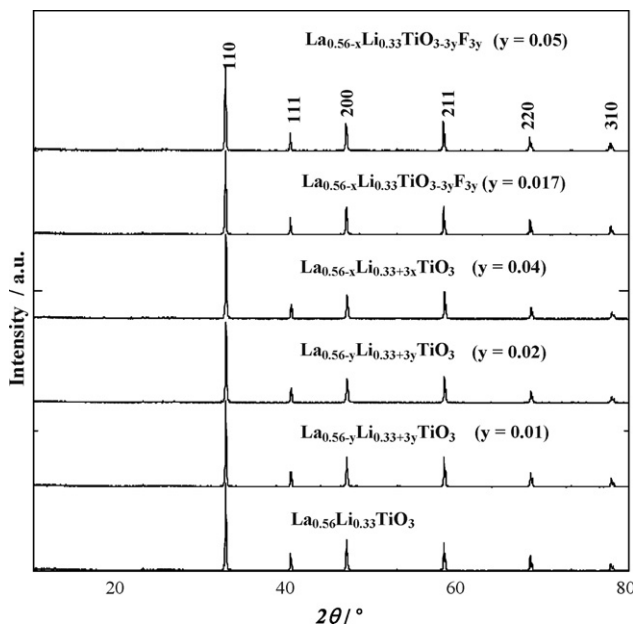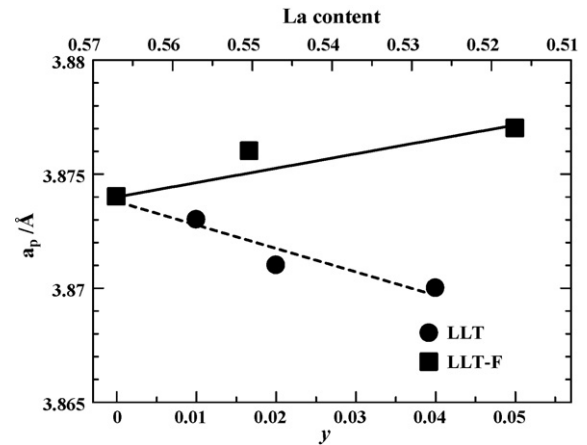

Fig. 2. Variation of the lattice parameters (space group: Pm3m) obtained by XRD measurement to y values in La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$.

[14]. These factors may expand the lattice of the perovskite structure.

Fig. 3 shows the X-ray adsorption near edge structure (XANES) spectra of La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$. In this figure, the absorption edges of Ti K-edge were not shifted with composition y. This result indicates that the charge of Ti^{4+} ion on perovskite titanium oxide was not reduced by the insertion of fluoride ion. Thus, the electronic conductivities of all the samples caused by the formation of Ti^{3+}–O^{2-} framework must be negligible.

Li-ion conductivities obtained from the Nyquist plot at 30 °C with y from 0 to 0.05 are shown in Fig. 4. Li-ion conductivities of La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ were decreased with the increase of y value. It was already reported by many researchers that La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ in the vicinity of the composition of y = 0 has the highest conductivity (σ = 1.28 × 10^{-3} S cm^{-1} at 30 °C) because the favorable condition for the Li-ion conduction in LLT is optimized by the balance between the concentration of lithium ion and the ratio of vacancy to lithium ion. The approach based on the site percolation is one of the methods to represent these relations, which have
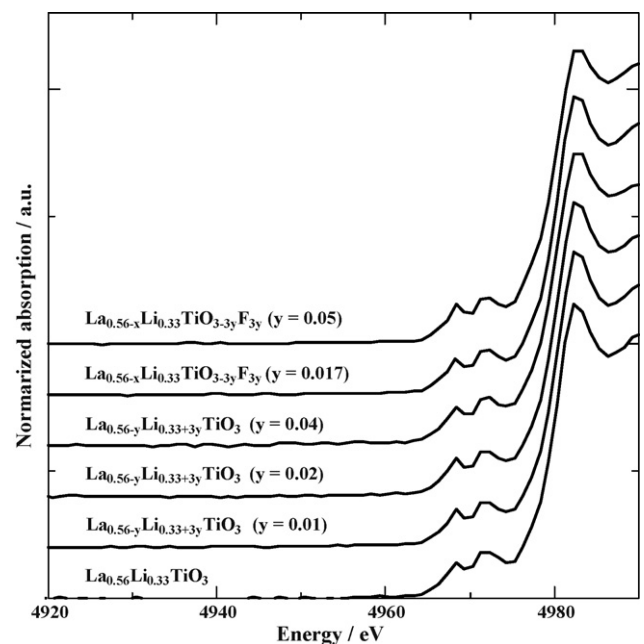

Fig. 1. X-ray diffraction patterns of La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$. All the samples were synthesized by sintering at 1350 °C and quenched into liquid N$_2$.

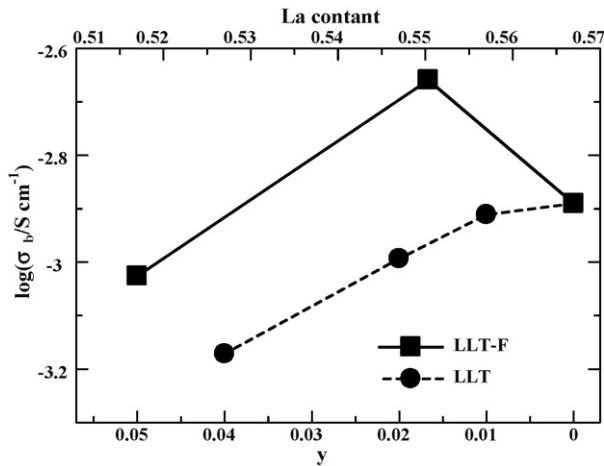**Fig. 3.** Ti K-edge XANES spectra for La$_{0.56-y}$Li$_{0.33+3y}$TiO$_3$ and La$_{0.56-y}$Li$_{0.33}$TiO$_{3-3y}$F$_{3y}$.

Fig. 4. Variation of Li-ion conductivities at 30 °C estimated from Nyquist plots to y values for $La_{0.56-y}Li_{0.33+3y}TiO_3$ and $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$.

already been reported by Inaguma et al. [15]. In this method, the conductivity of $La_{0.67-x}Li_{3x}TiO_3$ was represented by the following formula,

$$\sigma \propto sp = \frac{c(\text{lithium}) \cdot c(\text{vacancy})}{[c(\text{lithium}) + c(\text{vacancy})]^2}$$
$$\times \left\{ c(\text{lithium}) + c(\text{vacancy}) - 0.3119 \right\}^2 \qquad (1)$$

Here, $c(\text{lithium})$ and $c(\text{vacancy})$ are the concentration of lithium ion and vacancy in perovskite oxide, respectively. The sp value was decreased from 0.0031 to 0.0015 with the increase of y value (y = from 0 to 0.04) in $La_{0.56-y}Li_{0.33+3y}TiO_3$. Therefore, the bulk conductivities of $La_{0.56-y}Li_{0.33+3y}TiO_3$ were decreased with the increase of y value.

On the other hand, the conductivities of $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ increased with the increase of y value, which means adding LiF to LLT. Especially, the Li-ion conductivity in $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ (y = 0.017) is 2.30×10^{-3} S cm^{-1} at 30 °C, which is one of the highest Li-ion conductivity in the oxide compounds. Many different factors were considered to explain this phenomenon. For example, two factors may influence the Li-ion conductivities, one is the increase of sp value (from sp = 0.0031 at y = 0 to sp = 0.0042 at y = 0.017) based on the site percolation, the other is the difference of local environment around mobile Li ion with either the doping of fluoride ion or the formation of amorphous compound by adding lithium salt. Research of the effect of the concentration in $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ should clarify the balance between the con-

centration of lithium ion and the ratio of vacancy to lithium ion. On the other hand, we have already researched about the local structure around the absorbed atoms in LLT with the different ordered arrangement of A-site ions (*e.g.* α-LLT and β-LLT) by using XAS technique and the difference of Li-ion conductivities derived from the alternative arrangements of A-site ions in LLT was explained by the change of the local distortion around lithium ion [16]. Thus, focusing on the local structure around the absorbed atoms may make it possible to explain about the influence of adding LiF to the crystal structure in $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_3$

4. Conclusion

The Li-ion conductivity of $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ (y = 0.017) was 2.30×10^{-3} S cm^{-1} at 30 °C, which is, to our knowledge, one of the highest Li-ion conductivities in the oxide compounds. The change of the concentration of Li ion and vacancy or the difference of local environment around mobile Li ion by adding LiF in the synthesis process may influence the Li-ion conductivities of A-site deficient perovskite oxide containing lithium ion. The result to give a precise explanation on the influence of adding LiF to the crystal structure of $La_{0.56-y}Li_{0.33}TiO_{3-3y}F_{3y}$ by focusing on the local structure will be reported in the future.

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