



# Visualization of conduction pathways in a lanthanum lithium titanate superionic conductor synthesized by rapid cooling



Kazuhiro Mori<sup>a,\*</sup>, Shogo Tomihira<sup>a</sup>, Kenji Iwase<sup>b</sup>, Toshiharu Fukunaga<sup>a</sup>

<sup>a</sup> Research Reactor Institute, Kyoto University, 2-1010 Asashiro-Nishi, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

<sup>b</sup> Department of Materials Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

## ARTICLE INFO

### Article history:

Received 10 June 2014

Received in revised form 18 September 2014

Accepted 27 September 2014

Available online 20 October 2014

### Keywords:

Lithium-ion conductor

Lanthanum lithium titanate

Local structure

Neutron diffraction

Reverse Monte Carlo modeling

Bond valence sum

## ABSTRACT

Three-dimensional structure and conduction pathways of the lithium ions in  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  quenched with liquid nitrogen were studied using reverse Monte Carlo modeling and the bond valence sum approach using neutron diffraction data. The lithium ions were primarily located in the region between the off-center positions of the A-sites and bottlenecks defined by four coordinating oxygen ions. The bottlenecks in the predicted conduction pathways of the lithium ions were classified into three types (I, II, and III) by their size. The type II bottlenecks were the most accessible to lithium-ion migration and more than 70% of the bottlenecks were type II.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Solid lithium-ion conductors are critical for improving the energy density, power capacity, operation lifetime, and reliability of all-solid-state lithium-ion batteries (LIBs) [1,2], and improved electrochemical and structural understanding of the most well-known solid Li-ion conductors would be beneficial to the further development of LIBs. From the structural point of view, the perovskite crystal structure ( $\text{ABX}_3$ ) is one of the most important aspects of excellent solid lithium-ion conductors. In particular, a perovskite lanthanum lithium titanate, or  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  ( $A = \text{La}$ ,  $B = \text{Ti}$ , and  $X = \text{O}$ ), exhibits the highest ionic conductivity at room temperature (RT) of the lithium-ion conducting oxides [3–6]. The behavior of the ionic conductivity is quite complicated; the optimum Li content for obtaining maximum ionic conductivity ( $\approx 10^{-3}$  S/cm) at RT is  $3x = 0.3$ – $0.4$ , and the ionic conductivity drastically decreases at lower Li content ( $3x < 0.3$ ) and higher Li content ( $3x > 0.4$ ). At the optimum Li content, the ionic conductivity is enhanced by rapid cooling; the ionic conductivity of  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  quenched from high temperature (“quenched  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ ”) is several times as large as that of  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  cooled slowly from high temperature in a furnace (“furnace-cooled  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ ”) [7,8].

Numerous structural investigations of  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  using X-ray powder diffraction (XRD) and neutron powder diffraction (NPD) have been conducted [8–14]. At lower Li content, the crystal structure can be represented by a unit cell with dimensions  $a_0$  ( $\approx 2a_p$ )  $\times$   $b_0$  ( $\approx 2a_p$ )  $\times$   $c_0$  ( $\approx 2a_p$ ) in the orthorhombic system (space group:  $Cmmm$ ), where  $a_0$ ,  $b_0$ , and  $c_0$  are the lattice parameters and  $a_p$  is the lattice parameter of a pseudo-cubic perovskite. The superlattice ( $a_0 \times b_0 \times c_0$ ) is produced by tilting of the  $\text{TiO}_6$  octahedra and alternating stacks of La-rich layers (“La(1),” Wyckoff notation:  $4i$  site) and La-poor layers (“La(2),”  $4j$  site) along the  $c$ -axis. This stacking will be referred to as the “La-ordering,” hereafter. Additionally, it has been proposed that Li ions are located at the off-center positions of the A-sites (particularly, the  $4j$  site) [13]. The conduction pathways of the Li ions in furnace-cooled  $\text{Li}_{0.16}\text{La}_{0.62}\text{TiO}_3$  were revealed by a combination of the Rietveld analysis and the maximum entropy method (MEM) [14]. The MEM nuclear-density distribution map indicates that the Li ions are located at the  $2c$  site surrounded by four O ions in a square (“the bottleneck”) and migrate along the “ $2c$ – $4f$ – $2c$ ” and “ $2c$ – $2d$ – $2c$ ” conduction pathways on the La-poor (002) layer. However, the positions of the Li ions are still controversial since the furnace-cooled  $\text{Li}_{0.16}\text{La}_{0.62}\text{TiO}_3$  does not provide optimal conductivity in a series of  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  samples. The optimum  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  Li-ion conductors with higher Li content exhibit several Bragg peaks that are somewhat broad in both the XPD and NPD patterns, and further broadening occurs when the samples are rapidly cooled. The crystal structure of the perovskites can be represented approximately by the tetragonal system ( $a_0$  ( $\approx a_p$ )  $\times$   $a_0$   $\times$   $c_0$  ( $\approx 2a_p$ )) [10], although the

\* Corresponding author. Tel.: +81 72 451 2363.  
E-mail address: [kmori@rri.kyoto-u.ac.jp](mailto:kmori@rri.kyoto-u.ac.jp) (K. Mori).

Rietveld analysis and the MEM are no longer applicable to the structural refinements or the visualization of the conduction pathways of the Li ions in the quenched  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ .

In this work, we synthesized an excellent lithium-ion conductor of quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  ( $3x = 0.4$ ) and performed the time-of-flight NPD (TOF-NPD) analysis. TOF-NPD is useful for precisely determining the positions of light elements such as  ${}^7\text{Li}$  and O ions in solids, since the scattering of neutrons by  ${}^7\text{Li}$  and O nuclei is larger than that of X-rays. The three-dimensional local structure of the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  was determined using reverse Monte Carlo (RMC) modeling. Additionally, the conduction pathways of the Li ions in the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  were predicted and visualized using the bond valence sum (BVS) approach [15–18].

## 2. Materials and methods

### 2.1. Synthesis and characterization of sample

The quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  was synthesized by a solid-state reaction. Use of the lithium isotope  ${}^7\text{Li}$  allowed the precise determination of the positions of Li ions in the neutron diffraction analyses because the absorption cross section,  $\sigma_a$ , of  ${}^7\text{Li}$  nuclei (0.045 b) is considerably lower than that of Li (naturally occurring lithium) nuclei (70.5 b). Notably, the barn unit, with symbol “b,” is defined as  $10^{-28} \text{ m}^2$ . A mixture of  $\text{La}_2\text{O}_3$  (99.99% purity, Rare Metallic),  $\text{TiO}_2$  (99.99% purity, Rare Metallic), and  ${}^7\text{Li}_2\text{CO}_3$  (99.94% purity, Euriso-Top) in the appropriate molar proportion was heated at 800 °C for 4 h in air. After grinding the product, it was pressed into disks and reacted at 1300 °C for 4 h in air. This process was repeated, and then the sintered specimen was quenched by rapid cooling to the temperature of liquid nitrogen (77 K).

The sample was characterized using XRD with Cu-K $\alpha$  radiation (SmartLab, Rigaku). Simultaneously, the electrical conductivity was measured at temperatures between 284 and 374 K using four-probe ac impedance. We smeared Ag-paste on the disk-shaped sintered samples ( $\approx 3$  mm thick) to use as electrodes. The sample was loaded on a cell for measurements of electrochemical properties under controlled atmospheres at high temperatures (ProboStat<sup>TM</sup>, NorECs) equipped with a frequency response analyzer (6440B, Wayne Kerr Electronics Ltd.) with a frequency range of 20 Hz to 3 MHz.

### 2.2. TOF-NPD experiment and RMC modeling

The TOF-NPD experiment was performed using the Neutron Powder Diffractometer (NPDF) at the Lujan Center of the Los Alamos Neutron Science Center (LANSCE), Los Alamos National Laboratory (LANL). The resolution of the NPDF,  $\Delta d/d$ , for each detector bank was 0.15% at  $2\theta = 148^\circ$ , 0.28% at  $2\theta = 119^\circ$ , and 0.31% at  $2\theta = 90^\circ$ , where  $2\theta$  is the scattering angle. The polycrystalline sample of the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  was put into a cylindrical vanadium holder (9.2 mm in diameter). The TOF-NPD data were collected at RT in the  $Q$  range 1–300  $\text{nm}^{-1}$ , where  $Q = (4\pi \cdot \sin\theta) / \lambda$  is the magnitude of a scattering vector, where  $\lambda$  is the neutron wavelength.

To obtain the structure factor,  $S(Q)$ , for the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$ , appropriate corrections related to absorption, multiple scattering, and incoherent scattering were applied to the TOF-NPD data using the computer program PDFgetN [19]. According to the Faber-Ziman definition,  $S(Q)$  can be described by partial structure factors,  $S_{i-j}(Q)$ , according to

$$S(Q) = \sum_{i,j} w_{i-j} S_{i-j}(Q), \quad (1)$$

where the  $w_{i-j}$  values are the weighting factors, defined by

$$w_{i-j} = \frac{c_i c_j b_i b_j}{\langle b \rangle^2}, \quad (2)$$

and

$$\langle b \rangle = \sum_i c_i b_i. \quad (3)$$

In Eqs. (1), (2), and (3),  $c_i$  ( $c_j$ ) is the concentration of the component  $i$  ( $j$ ),  $b_i$  ( $b_j$ ) is the coherent scattering length for species  $i$  ( $j$ ), and  $\langle b \rangle$  is the average scattering length. The  $b$  values for  ${}^7\text{Li}$ , La, Ti, and O nuclei were  $-2.22$ ,  $8.24$ ,  $-3.37$ , and  $5.805$  fm, respectively. Note that the  $w_{i-j}$  values for  ${}^7\text{Li}$ –La,  ${}^7\text{Li}$ –O, La–Ti, and Ti–O correlations are negative contributions to  $S(Q)$  owing to the negative  $b$  values for  ${}^7\text{Li}$  and Ti. The pair distribution function,  $g(r)$ , for the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  was calculated by means of the Fourier transformation of  $S(Q)$ ; that is

$$g(r) = 1 + \frac{1}{2\pi^2 \rho} \int_{Q_{\min}}^{Q_{\max}} Q \{S(Q) - 1\} \sin(Qr) dQ, \quad (4)$$

where  $\rho$  is the number density of atoms and  $r$  is the interatomic distance.

RMC modeling was performed using the computer program RMC++ [20–22]. Since the structure of the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  could be regarded as a pseudo-cubic perovskite, we prepared a cubic RMC cell with  $L \approx 6.2$  nm-long edge ( $\approx 8a_p$ ) including 20,192 atoms ( ${}^7\text{Li}$ : 1638, La: 2170, Ti: 4096, and O: 12,288). The atomic composition ( ${}^7\text{Li}$ :La:Ti:O) was consistent with the molar ratio and the  $\rho$  of the RMC cell was the same as the number density of atoms obtained from the solid density measurement by a dry pycnometer (AccuPyc1330, Shimadzu Co.). La, Ti, and O ions were initially placed on the RMC-cell, taking into account the preliminary structural refinement of the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.53}\text{TiO}_3$  on the basis of the orthorhombic system (space group:  $Cmmm$ ) using the Rietveld analysis program GSAS [23–25]. La ions were randomly placed on the A-sites and  ${}^7\text{Li}$  ions were randomly located on the RMC-cell. In RMC modeling, three constraint conditions were employed: (1) the coordination number of O atoms around a Ti atom was six, with interatomic distances for Ti–O in the range 0.16–0.22 nm (i.e.,  $\text{TiO}_6$  octahedral unit); (2) the coordination number of Ti atoms around an O atom was two, with interatomic distances for O–Ti in the range 0.16–0.22 nm (i.e., corner-sharing  $\text{TiO}_6$  octahedra); and (3) the coordination number of O atoms around a La atom was twelve, with interatomic distances for La–O in the range 0.24–0.31 nm.

### 2.3. BVS approach

The BVS approach using the “softness-sensitive” BV (softBV) parameters was employed to predict the conduction pathways of the Li ions in the RMC cells. The valence of a bond between a cation  $A$  and its coordinating anion  $X$  was given by

$$s_{A-X} = \exp \left\{ (R_0 - R_{A-X}) / l \right\}, \quad (5)$$

where  $R_{A-X}$  is the bond length between  $A$  and  $X$ , and  $R_0 = 0.117$  nm and  $l = 0.051$  nm are empirical parameters describing the bonds between  $\text{Li}^+$  and  $\text{O}^{2-}$  [17,26–29]. The BVS value,  $V(A)$ , for all bonds between  $A$  and  $X$  within a cut-off radius  $R_{\text{cut-off}}$  ( $\leq 0.55$  nm) was estimated as

$$V(A) = \sum_X s_{A-X}. \quad (6)$$

The three-dimensional local structure and the predicted conduction pathways of the Li ions for the quenched  ${}^7\text{Li}_{0.4}\text{La}_{0.56}\text{TiO}_3$  were illustrated using the computer program VESTA [30].

Download English Version:

<https://daneshyari.com/en/article/1295365>

Download Persian Version:

<https://daneshyari.com/article/1295365>

[Daneshyari.com](https://daneshyari.com)