Annealing Effect on the Ionic Conductivity of $\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$ Made by Double Mechanical Alloying Method

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Abstract: Perovskite $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ with $x = 0.11$ (called LLTO11) powders were prepared by double mechanical alloying method from TiO_2 (99.99%), Li_2CO_3 (99.99%) and La_2O_3 (99.9%) powders, in ideal cation stoichiometry for $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$. The obtained single phase of LLTO11 powder was isostatically pressed under a pressure of 450 MPa and annealed at a temperature ranging from 1,100 °C to 1,250 °C. Optimal morphology and grain structure for the ionic conductivity of the samples were achieved at annealing temperature of 1,200 °C. For this ceramic, the lithium ionic grains and grain-boundaries conductivities at room temperature possess a value of 1.5×10^{-3} S/cm and 4.8×10^{-5} S/cm, respectively. The improvement in the grain-boundaries conductivity was explained due to the decrease of the number of grains, included grain boundaries and the diminution of the pores in LLTO samples annealed at 1,200 °C. The obtained results suggest useful applications of $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ ($x = 0.11$) ceramics for the production of the solid state electrolytes, for high-temperature Li-ionic batteries, in particular.

Key words: $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$, double mechanical alloying method, impedance spectra, lithium ionic conductivity, activation energy.

1. Introduction

Recently, multi-compound superionic conductors with a perovskite structure such as $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ have increasingly been studied due to their potential applications in all-solid-state ionic batteries, energy storage and conversion, and in environmental monitoring electrochemical sensors, etc. [1-3]. These materials have a high Li-ion conductivity at not very high temperature and can be served as a non-toxic solid electrolyte that exhibits easy preservation and comfortable use. Many works have shown that a new

family of the perovskite structure of $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ materials (hereafter called as LLTO) give the best lithium ionic conductors. At room temperature, their grain conductivity possesses a value up to 10^{-3} S/cm [2, 4-7]. Using the extended synchrotron X-ray absorption fine structure (EXAFS) analysis, the author in [8] demonstrated that the lithium ion conductivity is governed by main two factors: (1) the Coulombic repulsion force between the lithium ion and the titanium ion and (2) the bottle neck distortion in the lithium ion channels consisted of four oxygen ions. For all the Li-content ranging from $x = 0.06$ to 0.15, the activation energy of the disordered (high temperature phase, HT) structure is much lower than that of ordered

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(low temperature phase, LT).

This results in the increase of the ionic conductivity of the HT phase of LLTO. Ibarra et al [6] showed that the crystalline structure of $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ almost maintains tetragonal (P4/mmm) structure with a range of x from 0.06 to 0.15, and the ionic grain conductivity (σ_g) attains a best value of 1.1×10^{-3} S/cm, corresponding to $x = 0.11$. This was also confirmed later in our work [9]. Since in practical applications, polycrystalline LLTO with numerous grains are used much more than the single-crystalline materials, grain-boundary resistances are commonly observed in addition to the grain resistances. When the grain-boundary resistances are much larger than the grain resistances in the bulk sample, the neglected effect of the grain-boundary must be taken into account to determine the ionic conduction. According to the reported analyses, the ionic conductivity of grain-boundaries (ca. 10^{-5} S/cm) is about two orders of magnitude lower than that of the grain ($\sim 1 \times 10^{-3}$ S/cm) [10]. Harada et al also indicated that the grain-boundary resistances are ~ 50 times the grain resistances for all $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ samples [3]. As a result, the ionic conduction of the grain boundary exhibits a rate-limited step over the ionic transport of the bulk samples, so that the total ionic conductivity for the polycrystalline LLTO samples is reduced to ca. 10^{-5} S/cm.

In recent years, to enhance the Li^+ ion conductivity, great efforts have been devoted to analyzing structural and other intrinsic attributes of the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ oxides, such as Li coordination [4], structural distortions [11], vacant site distribution [7, 12], charge carrier mobility [13], and the concentrations of charge carriers and vacancies [3, 10]. Previous reports also showed that the electrical performance of LLTO ceramics strongly depended on their chemical homogeneity, particle size and morphology of LLTO powders. The importance of this factor depends very much on fabrication methods, thus synthesis of LLTO powders always played a significant role in obtaining LLTO ceramics with desired properties.

So far, polycrystalline LLTO has been mainly synthesized by two methods: solid-state reaction and sol-gel synthesis [14] or the polymerized complex method [15]. In which, the method of solid-state reactions are often used, allowing the production of a relatively large amount of materials. However, this process requires a fairly high temperature, which would cause serious loss of lithium even up to 20 mol% [10, 16]. In addition, the conventional process has other disadvantages, such as compositional heterogeneity, broad particle size distribution, and in turn leads to LLTO ceramics with poor performances. Sol-gel method allow getting LLTO powders having a particle size evenly thus improving electrical performance of LLTO ceramics but the general synthetic procedure is complex.

With the aim to improve the ionic conductivity of LLTO ceramics, we used a double mechanically alloying method (DMA) for synthesizing LLTO powder, followed by thermal annealing at a temperature range from 1,100 to 1,250 °C. The annealing effect to the morphology and grain structures, consequently to the ionic conductivity of the samples was presented.

2. Experiments

2.1 Samples Preparation

The $\text{La}_{(2/3-x)}\text{Li}_{3x}\text{TiO}_3$ crystalline powders with $x = 0.11$ (called LLTO11) was prepared from stoichiometric mixtures of dehydrated La_2O_3 (99.99%), Li_2CO_3 (99.99%) and TiO_2 (99.95%) powders which were purchased from Aldrich Ltd. The solid state reaction of the LLTO formation is as follows, replacing x by 0.11:

In the DMA method, the LLTO11 powder was synthesized according to the following procedure. The initial materials, including La_2O_3 , Li_2CO_3 and TiO_2 were mixed and grinded with absolute alcohol for 5 h, by a grinder of “Fritsch model Pulverisette 6”. In this work, the cation molar ratio in the samples is La:Li:Ti

= 0.56:0.33:1. The grinded mixture was dried at 200 °C, then preliminarily annealed at 800 °C in air for 4 h, for eliminating CO_2 . Afterwards, the mixtures were react-grinded by a grinder at speed of 600 rev/min for 6 h. The obtained powder was referred to the "precursor" hereafter. To prepare ceramic specimens, this precursor powder was isostatically pressed under ~ 450 MPa into pellets with 12.5 mm in diameter and 1.5 mm in thickness. Finally, the pellets were annealed at temperatures of 1,100, 1,150, 1,200 and 1,250 °C for 4 h with a heating rate of 5 °C/min and the cooling is natural. Hereafter, the samples annealed at $T_a = 1,100, 1,150, 1,200$ and $1,250$ °C are abbreviated to LLTO11-1, LLTO11-2, LLTO11-3 and LLTO11-4, respectively.

2.2 Characterization

Phase purity and crystalline structure of the obtained materials were determined by using X-ray diffraction (XRD) analysis (Siemen D-5000 diffractometer) at room temperature, using $\text{CuK}\alpha$ radiation in the 2θ range from 10° to 70° with a step of 0.03° . The microstructure and morphology of powders and pellets were studied with a field emission scanning electron microscope (FE-SEM, Model S4800, Hitachi).

The ionic conduction properties of all samples were characterized by impedance analysis on AutoLab. Potentiostat-PGS30 using FRA-2 impedance software. To characterize impedance spectroscopy (IS), the samples were mechanically polished and chemically treated in order to have clean and parallel surfaces, then on these surfaces a metallic silver coating with 8 mm-diameter circle was vacuum evaporated. Thus, two silver parallel electrodes of an area of $A = \pi \times (0.4)^2 \approx 0.5 \text{ cm}^2$ were used for electrical measurements. IS measurements were recorded under normal atmosphere between room temperature (RT) and 200 °C, in the frequency range of 0.1 to 10^6 Hz with an amplitude of 20 mV. The resistances of grains and grain boundaries for the samples annealed at different temperatures were obtained by fitting experimental data with the theoretical

curves using appropriate equivalent schema.

3. Results and Discussion

3.1 Crystalline Structure and Morphology

XRD patterns of the react-grinded and sintered samples at different annealing temperatures (T_a) are presented in Fig. 1. This figure shows that although being a crystalline phase, the react-grinded sample possesses pure crystallinities. This is revealed by the low intensity of the diffraction peaks (patterns "a" in Fig. 1). A single phase structure of the LLTO11 was crystallized when T_a was raised up to higher 1,000 °C: all the diffraction peaks belong to the characteristic peaks of the LLTO crystalline structure (patterns "b", "c" and "d", Fig. 1), they are quite consisted with those reported in the structures file "JCPDS 46-0465".

For the annealed samples, the intensity of the diffraction peaks increases with the increase of T_a , indicating a steady growth of the LLTO phase, so that the crystallinity increased and the grains were grown-up to several micrometers. XRD patterns of sample LLTO11-4 ($T_a = 1,250$ °C) have the strongest intensities of the main diffraction planes (110) or (102), (111), (200), (211) and (220) in comparison with the samples annealed at lower T_a (namely LLTO11-1, LLTO11-2 and LLTO11-3). This clearly demonstrates that a single phase of the LLTO crystal can be fabricated

Fig. 1 XRD patterns of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ samples: as-grinded (pattern "a"), after sintered at 1,100 °C (pattern "b"), at 1,200 °C (pattern "c") and at 1,250 °C (pattern "d").

by using the dMA method of solid-state reactions from stoichiometric oxides of TiO_2 , Li_2CO and La_2O_3 . Since ionic conductivity (σ) of the LLTO is strongly dependent on their morphology and/or grain and grain boundary structures, a technological way to enhance σ is to control the annealing temperature. A clear picture of the morphology and grain growth is observed by FE-SEM micrographs. Fig. 2 shows the FE-SEM images of the LLTO11 precursor powder. It was seen that the powder consisted of particles with diameter around 70 nm. Besides, agglomerates with loosely bound particles appeared in the powder. Fig. 3 shows the FE-SEM images obtained for the LLTO11 sample annealed at above four mentioned annealing temperatures. Although the last was raise with a not large step (namely 50 °C), the grain size increased considerably, from 1 μm (LLTO11-1) to 5 μm (LLTO11-4). In sample LLTO11-1 ($T_a = 1,100$ °C) there were observed large pores (Fig. 3a). These pores

were diminished by annealing at higher temperatures, for samples LLTO11-2 and LLTO11-3 (Figs. 4b and 4c). The largest size of the grains was obtained for sample LLTO11-4 ($T_a = 1,250$ °C), but several bigger pores appeared.

Fig. 2 SEM image of the LLTO precursor powder.

Fig. 3 FE-SEM images of the LLTO11 sample sintered at (a) 1,100 °C, (b) 1,150 °C, (c) 1,200 °C and (d) 1,250 °C.

From FE-SEM analysis, one can see that the best morphology and grain structure were observed in sample LLTO11-3 ($T_a = 1,200^\circ\text{C}$): The grain size is about $2\ \mu\text{m}$, the fewest and smallest pores were formed (Fig. 3c).

3.2 Ionic Conductivity

For characterization of ionic conductivity it is necessary to carry-out impedance spectra measurements throughout a large range of frequencies from 0.1 Hz to 100 MHz. Due to this behavior of the grain, grain-boundaries conductance and the contact resistance of the electrodes can be revealed in the complex impedance diagrams (CID) of the samples. The semicircle of impedance spectra in the higher 0.5 MHz frequencies is related to the conducting process in crystalline grains [16, 17], whereas the semicircle in the CID at average frequencies (from 10 Hz to 1 MHz) reflects the ionic conducting in the grain-boundaries [2, 17-19]. The line starting from the end of the semicircles at the frequencies lower 10 Hz is related to the diffusion process of ions in Helmholtz layer between the electrodes and the sample.

Since the semicircle of the complex impedance diagram in the high frequencies range is much smaller than that in the low frequencies range, the investigation of the grain and grain-boundaries ionic conductivity of

the sample is carried-out and elaborated separately each from other (Fig. 4). Fig. 4a and 4b correspond, respectively to high ($30\ \text{MHz} \div 0.3\ \text{MHz}$) and low ($0.1 \div 100\ \text{Hz}$) frequencies ranges for the Nyquist complex impedance diagram measured at room temperature for sample LLTO11-3 ($T_a = 1,200^\circ\text{C}$). The ending of the first semicircle (Fig. 4a) at about $Z' = 200\ \Omega$ is the starting of the second semicircle (Fig. 4b) which has the ending at frequency of 27 Hz with a real part of the resistance of 33 k Ω . The first semicircle exhibits the behavior of ionic conductance in grains and the second one is of grain boundaries, as described elsewhere [6, 12, 19-21].

In almost potentiostat units like "AutoLab-PGS-30", the frequencies range is from 1.0 MHz to 0.1 Hz, so in the first semicircle obtained in the range from 30 MHz to 300 kHz there observed several points with such a small value of resistance that was not revealed together with the high resistance values of the second semicircle. Thus, the grain resistance (R_g) and the total resistance ($R_g + R_{gb}$) of the sample can be evaluated, respectively from the right ending points of the first and the second semicircles in Fig. 4a and 4b. Qualitatively, one can compare R_{gb} and R_g by the ratio of the two ending point values in Z' abscissa from this figure. Indeed, the obtained ratio was found to be of $30\ \text{k}\Omega/200\ \Omega = 1.5 \times 10^2$, this means the grain-boundaries resistance is larger

Fig. 4 Complex impedance diagrams of LLTO11 sample sintered at $1,200^\circ\text{C}$. The measurements at room temperature and in the range of frequencies (a) from 30 MHz to 300 kHz and (b) from 1.0 MHz-0.1 Hz.

than the grain resistance in more than two orders in magnitude. That is why to increase the ionic conductivity is necessary to lower the grain-boundaries resistance.

Fig. 5a shows the CID curves vs annealing temperatures towards four samples LLTO11-1, LLTO11-2, LLTO11-3 and LLTO11-4. All the measurements were carried-out at room temperature. From this figure one can see that all the CIDs consist of two parts: the first part is the semicircle relating to grain-boundaries conductivity and the second one is the line obtained at low frequencies that relates to the diffusion process in the Helmholtz layer. The fact that the increase of annealing temperature resulted in the diminishing of the semicircles proves that the grain-boundaries conductance much decreased. This is explained by (1) with higher annealing temperature the grains were larger grown, consequently the number of grain boundaries decreased and (2) the crystalline structure of the grains became more perfected. This is confirmed from the SEM micrographs: the morphology and grains, included grain boundaries were much enhanced in turn, from $T_a = 1,100^\circ\text{C}$, $1,150^\circ\text{C}$ and $1,200^\circ\text{C}$.

For the accurate determination of the ionic conductivity we used a fitting method between experimental curves and the theoretical curves

obtained from equivalent schema to the CIDs. These CIDs of the LLTO sample with a structure of $\text{Ag}|\text{LLTO}|\text{Ag}$ were well fitted by the equivalent schema of $R_g(C_{gb}R_{gb})(R_cQ_c)(C_{in}[R_{in}(C_{dl}W)])$ that is illustrated in Fig. 5b. By this schema R_g is the resistance characterizing the grain conductivity; R_{gb} and C_{gb} are the resistance and capacity of grain boundaries, respectively; R_{in} and C_{in} are the resistance and the capacity formed by the contact between the Ag thin film electrode and samples surface; W and C_{dl} are the Warburg impedance characterizing the charge shift and the capacity of the double charge layer, respectively; R_c and Q_c are the resistance and the constant phase component (CPE) related to electrodes, respectively.

To determine the ionic conductivity one can use the following formula:

$$\sigma = \frac{d}{R \times A} \quad (2)$$

where, d is the thickness of the sample, A is area and R is resistance relating to ionic conductance that is determined from equivalent schema. By this way one can determine either grain conductivity (σ_g) or grain-boundaries (σ_{gb}), consequently the total or bulk conductivity (σ_b). In Fig. 6 there are plotted $\sigma \sim T_a$ curves for these three types of the Li-ionic conductivity of the LLTO11 samples. All the measurements data were obtained at room temperature.

Fig. 5 Complex impedance diagrams of (a) LLTO11 sample sintered at at different temperatures (b) and Equivalent schema used for fitting the CID data of the $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ sampes.

Fig. 6 The room-temperature ionic conductivity vs. annealing temperature for LLTO samples: (a) grain conductivity, (b) grain-boundaries conductivity and (c) bulk conductivity.

From Fig. 6, it can be seen that either grain conductivity or grain-boundaries, bulk conductivities increase with increase of T_a and do not increase more for $T_a > 1,200$ °C. The sample LLTO11-3 ($T_a = 1,200$ °C) has the largest grain conductivity, namely $\sigma_g = 1.5 \times 10^{-3}$ S/cm. This value of the conductivity is fairly larger than the σ_g (1.0×10^{-3} S/cm) of the same LLTO11 ceramic which was prepared by the method of conventional solid-state reactions, as reported in Refs. [2, 3, 5, 6, 9, 10, 16-18]. This may be explained due to: (1) the negligible loss of Li ions during the low-temperature react-grinding process in the dMA method; (2) optimal structure between the size of the grains (included grain boundaries) and number of the pores.

Temperature dependence of the ionic conductivity ($\sigma \sim T$) of the LLTO11-3 sample was investigated with in-situ impedance spectroscopic measurements with a temperature range from 30 to 200 °C (Fig. 7). As shown in Fig. 7, one transition point in Arrhenius plots of the grain and grain-boundaries conductivities can be determined for different specimens, which relate to tilt or rotate the TiO_6 octahedra, leading to “open or close the bottle neck” in the perovskite structure, through which lithium ions move into nearby A-site vacancies. The increase of annealing temperature could make the tilt and/or rotate of octahedra upwards easier, this process leads to promote ion thermal support mechanism. The plots of $\ln(\sigma T)$ against $1000/T$ in Fig. 7 are found to follow the Arrhenius law expressed as:

$$\sigma = (\sigma_0/T) \cdot \exp[-(E_a/kT)] \quad (2)$$

From the Arrhenius plots (Fig. 7a) and Eq. (2) the activation energy (E_a) of LLTO11-3 sample towards the grain and grain boundaries was found to be of ~ 0.23 eV and ~ 0.32 eV (from Fig. 7b), respectively. These values are smaller than the activation energy obtained from the sample which was made by the solid phase reaction (0.36 eV [9]). From Fig. 7 one can find out that the lithium ionic conductivity of LLTO11-3 sample at 150 °C increased in one and nearly two orders in magnitude, respectively for grains and grain-

Fig. 7 Arrhenius plots of the LLTO samples sintered at 1,200 °C: (a) for grain conductivity, (b) for grain-boundary conductivity.

boundaries conductivity at room temperature (namely, $\sigma_g = 1.2 \times 10^{-3}$ S/cm and $\sigma_{gb} = 6.7 \times 10^{-5}$ S/cm). With such a large Li-ionic conductivity, $\text{La}_{(2/3)-x}\text{Li}_{3x}\text{TiO}_3$ ($x = 0.11$) ceramics can be used for solid state batteries working at temperatures around 180 °C.

4. Conclusions

Ultrafine perovskite-type LLTO powder with $x = 0.11$ was successfully synthesized at near room temperature by solid-state reactions with use of the dMA method from stoichiometric of TiO_2 , Li_2CO and La_2O_3 powders. The dMA method appeared to be more suitable due to the mixing of elements at molecular level during the synthesis. The LLTO ceramics annealed at high temperature are considered pure ionic conductive materials. Optimal morphology and grain structure for the ionic conductivity of LLTO11-3 sample were achieved at annealing temperature of 1,200 °C. At room temperature, the lithium ionic grains and grain-boundaries conductivities of the LLTO11-3 have a maximum value of 1.5×10^{-3} S/cm and 4.8×10^{-5} S/cm, respectively. The improvement in the grain-boundaries conductivity was explained due to both the decrease of the number of grains, included grain boundaries and the diminution of the pores in

LLTO11 samples annealed at 1,200 °C. This result suggests useful applications of $\text{La}_{(2/3)-x}\text{Li}_{3x}\text{TiO}_3$ ($x = 0.11$) ceramics for the production of the solid state electrolytes, for high-temperature Li-ionic batteries, in particular.

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