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ARTICLE

Effects of Li_3PO_4 Particles on Electrical Property in $Li_{0.5}La_{0.5}TiO_3$ /Li_3PO_4 Composite Solid Electrolyte

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Abstract: The ionic conductivity of Li_3PO_4 dispersed $Li_{0.5}La_{0.5}TiO_3$ (LLTO) composite solid electrolyte was examined by complex impedance analysis. The X-ray powder diffraction (XRD), scanning electron microscope (SEM) observation and relative density measurement were also performed to study the dispersion of the second phase into the LLTO electrolyte. Results indicate that the addition of Li_3PO_4 into LLTO matrix decreases the ionic conductivity, though the composites added by the Li_3PO_4 particles show a high compactness. The reasons for the conductivity deterioration were clarified based on the lattice structure of LLTO, microstructures at the grain boundary regions, and the lithium content. The variation of the lithium content and microstructures in the LLTO matrix dispersed by Li_3PO_4 particles are mostly responsible for the behaviors in the ionic conduction.

Key words: $Li_{0.5}La_{0.5}TiO_3$; Li_3PO_4; ionic conductivity; composite solid electrolyte

A wide variety of inorganic solid state electrolytes are promising for the secondary solid state lithium batteries owing to their high-energy and high safety [1-7]. Among them, $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) ceramics with perovskite structure ABO_3 have been extensively studied, well-known as the highest bulk conductivity of 10^{-3} S/cm at room temperature[8]. LLTO crystal is constructed by TiO_6 octahedra, Li^+ and La^{3+} occupying in the A-sites. The vacancies created are responsible for the lithium ion motion throughout the LLTO lattice structure; hereafter the crystal possesses the ionic conductivity over a wide range of compositions[9]. However, its grain boundaries impede the enhancement of the total conductivity of the LLTO ceramics. As known, the total conductivity of the LLTO ceramics is mainly dominated by the grain boundary contribution[8,10]. Thereafter, the enhancement of the ionic conductivity of LLTO ceramics urges great interests since the discovery of LLTO. On the one hand, the substitution of A and B ions by other atoms was extensively attempted; however the doping plays little improved effect on the ionic conductivity of LLTO electrolyte[11-16]. On the other hand, the mixing of second phases with solid inorganic electrolytes could greatly increase the total conductivity due to increased lithium concentration, good sinterability and high densification, or/and the formation of the space charge layer at the grain boundaries and so on[17-24]. And the dispersion of a second inactive phase into the LLTO matrix could affect the lithium ion conduction behavior in the LLTO composites [25-27]. So far, the ionic conductivity of LLTO was improved with the dispersion of SiO_2 additive by our group[25]. It was reported that the ionic conductivity could be increased by one order of magnitude by the mixing of SiO_2 ionic conductor with LLTO matrix. This work aims to present the influence of the dispersion of Li_3PO_4 on the ionic conductivity of LLTO ceramics. The addition of Li_3PO_4 causes a decrease in the ionic conductivity of LLTO ceramics. We discussed the correlation between ionic conductivity and the lithium ion composition and microstructures at the grain boundaries in the LLTO- Li_3PO_4 composite electrolytes by means of XRD, SEM and relative density measurements.

1 Experiment

LLTO powder examined in the present work was

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synthesized by a sol-gel method using $LiNO_3$, $La(NO_3)_3$ $6H_2O$, tetrabutyl titanate and acetylacetone (acac) as starting materials. The ingredients of $LiNO_3$ and $La(NO_3)_3\cdot 6H_2O$ were weighed and dissolved in ethylene glycol monomethyl ether (EGME), and then mixed with the mixture solution of tetrabutyl titanate and acac to prepare LLTO sol. The LLTO sol was gelated at 90 °C for 2 h and dried at 70 °C for 5 d. The gel was then subjected to calcination at 900 °C for 6 h in air to produce the white LLTO powder. Mass fractions (wt%) of 3, 7, 10 and 15 Li_3PO_4 particles were mixed with the LLTO powder using a simple mechanical ball-milling for 12 h. The mixed powders were dried at 75 °C and pressed into green pellets (2 mm in thickness and 12 mm in diameter), and then sintered at 1350 °C for 6 h.

Crystalline phase identification of the LLTO ceramic composites was carried out by X-ray diffraction (XRD, Rigaku D/max 2500 diffraction meter with Cu Kα radiation) in the 2θ range from 10° to 90° with the scan speed of 6°/min. The lattice parameters were determined by means of PowderX program. The microstructures in LLTO/Li_3PO_4 composites were observed using scanning electron micrographs (JSM-6460LV scanning electron microscope). The compositions of various elements in LLTO composites were analyzed by X-ray energy dispersive analysis (EDX).

The LLTO samples for electrical measurements were sputtered with blocking Au electrodes on both surfaces of the sintered pellets. The lithium ionic conductivity measurements of the LLTO ceramics were performed by impedance measurement in a frequency range from 1 Hz to 5 MHz over the temperature range from room temperature to 110 °C in a thermostat. The Z-view impedance software was used for fitting the impedance data.

2 Results and Discussion

The XRD patterns of LLTO ceramics dispersed with various mass fractions of Li_3PO_4 are shown in Fig.1. As seen, the diffraction peaks in the patterns for all these LLTO composites in spite of Li_3PO_4 addition could be completely indexed in the light of the tetragonal symmetry P4/mmm without significant difference in crystal lattice (see the enlarged XRD patterns in the inset in Fig.1). And the superlattice diffraction peaks (denoted by the arrows in Fig.1) are present due to the ordering arrangement of cations Li^+, La^{3+} and vacancies in A-sites along the *c*-axis. Furthermore, when the addition of the second phase increases up to 15%, the reflections of Li_3PO_4 are not detected by XRD measurement, and X-ray diffraction results demonstrate that no second crystalline phase is present after Li_3PO_4 modification. It suggests that the lattice structure of LLTO matrix shows no strong relation with different mass fraction of the second phase Li_3PO_4. And Li_3PO_4 could exist in the glassy state. It is clear that the Li_3PO_4 phase does not incorporate into the LLTO crystal lattice and then form solid solution system. And LLTO phase does not react with Li_3PO_4 particles. But a little bit of lithium ions in the Li_3PO_4 phase might insert into the cavities in the framework of LLTO matrix, and a similar behavior was proposed in Ref.[25]. As known, the lithium element is light, and not able to affect the symmetry of LLTO crystal structure with the addition of Li_3PO_4 always keeping the tetragonal symmetry. However, through the calculation of lattice constants *a* and *c* using PowderX program, as shown in Table 1, it is found that the lattice distortion (defined as *c/a*) for pure LLTO ceramics is much bigger compared with that for LLTO composites with Li_3PO_4. In addition, the local lattice distortion becomes gradually smaller with the increase of the Li_3PO_4 addition. The tetragonal local lattice distortion could be owing to the ordering of Li^+, La^{3+} and vacancies on the neighboring layers, which results in the superstructure peaks. In case of LLTO composites with Li_3PO_4, the lithium ions going into LLTO bulk structure from Li_3PO_4 phase could cause higher lithium concentration and less ordered arrangement of cations and thus a smaller lattice distortion. It was also evidenced by the broadening of the superlattice peaks besides *c/a* values in Table 1. Therefore, big bottlenecks for lithium ion motion could not be achieved, which is not helpful for the enhancement of the grain bulk ionic conductivity. Conversely, too high lithium concentration in LLTO bulk structure worsens the conductivity because there are not enough sites for lithium ion migration.

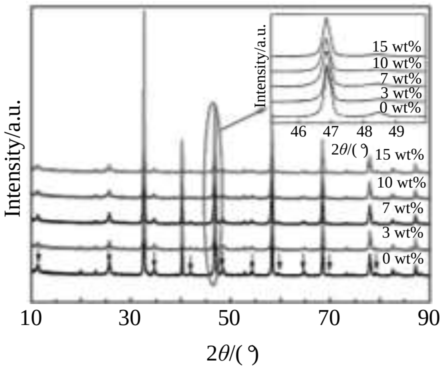

Fig.1 XRD patterns for LLTO composites with different Li_3PO_4 content adding

Fig.2 is the SEM observations of LLTO composites after sintering at 1350 °C with different Li_3PO_4 contents (wt%)

Table 1 Lattice structure of LLTO composites with different Li_3PO_4 contents

Li_3PO_4/wt%	Symmetry	*a*/nm	*c*/nm	*c/a*
0	Tetragonal	0.38667	0.7617	2.0073
3	Tetragonal	0.38693	0.7501	2.00296
7	Tetragonal	0.38679	0.7466	2.00277
10	Tetragonal	0.38680	0.7468	2.00275
15	Tetragonal	0.38697	0.7462	2.00177

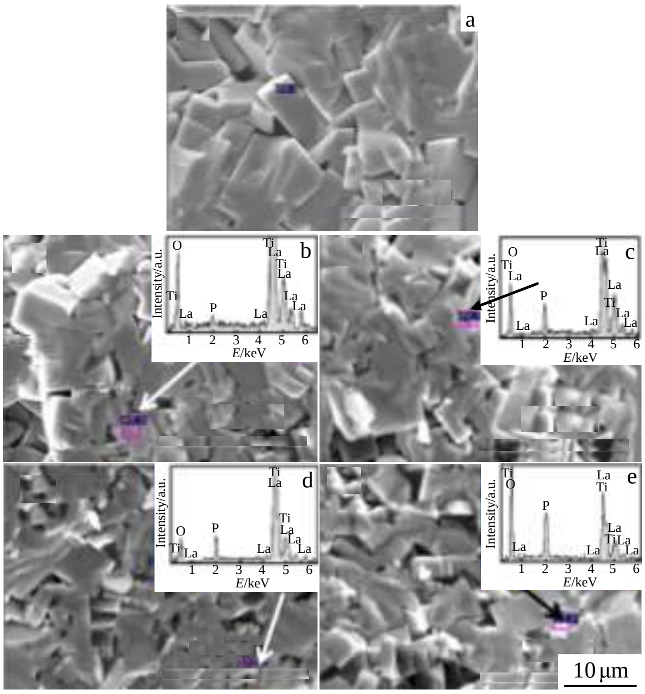

Fig.2 Fractured surface images of LLTO composites added with different Li_3PO_4 contents: (a) 0 wt%, (b) 3 wt%, (c) 7 wt%, (d) 10 wt%, (e) 15 wt% (the inset is EDX spectra of point marked by arrows)

of 0, 03, 7, 10 and 15. The addition of the second phase indeed plays a key role on the morphology of the LLTO ceramics. The tetragonal-shaped grains are LLTO phase. As known, Li_3PO_4 tends to form glass, not in existence of crystalline phase. Thus an amorphous-Li_3PO_4 containing surface layer could form at the interfaces of the LLTO grains. P element at the interfaces is detected obviously by EDX measurement, as shown in the inset of Fig.2.

The tetragonal grains of pure LLTO ceramics are much more regular than that of the other composites with Li_3PO_4. With the increase of the addition of Li_3PO_4, regular grains in the LLTO composites get gradually twisted. And the interfaces between grains present unclear. Namely, the section surface morphologies are densely twisted grains for LLTO composites. So the addition of Li_3PO_4 could significantly affect the microstructures of LLTO ceramics, leading to a very disordered situation at the grain boundaries (i.e., surfaces of the LLTO grains) and detoured tunnels for lithium ion motion. This would give rise to the lithium ion motion with difficulty, which could successfully explain the change of the lithium ionic conductivity in the next section.

Owing to the low melting point of about 837 °C. Li_3PO_4 acts as the sintering aid and leads to a good sinterability; maybe a liquid sintering taking place because of partial melting and solidification during the sintering. It is reasonable that high compactness is achieved when Li_3PO_4 is added into LLTO matrix. So the modified LLTO composites show significantly better relative density than pure LLTO, as shown in Fig.3.

A typical impedance spectrum is plotted in the Nyquist complex plane, displayed in Fig.4, for the LLTO composites with ion-blocking Au electrodes. Similar electrical behavior has been seen for all the LLTO composites with addition of Li_3PO_4. For such electrochemical cells of Au||LLTO/Li_3PO_4||Au, a simplified equivalent circuit as shown in the inset of Fig.4 can be used[28]. One response in the high frequency region arises from the relaxation process in the grain boundaries, corresponding to one semi-circular arc at high frequency. The other response at low frequency is attributed to polarization behavior of the blocking electrode, which is expressed as a blocking spike. The grain relaxation response in the impedance plots is not obviously detected due to the frequency we used in this study is not high enough. Such an equivalent circuit (see the inset in Fig.4) contains a grain resistance (denoted by R_1), a grain boundary resistance (R_2) and capacitance (CPE1) of the grain boundary, which can be applied to well fit the impedance data to refine the contributions from grain and grain boundary. CPE1 arises from the rough nature of the electrolyte [28]. CPE2 is assigned to the ionic movement behavior in the blocking electrodes. The errors of all obtained parameters are below 5%.

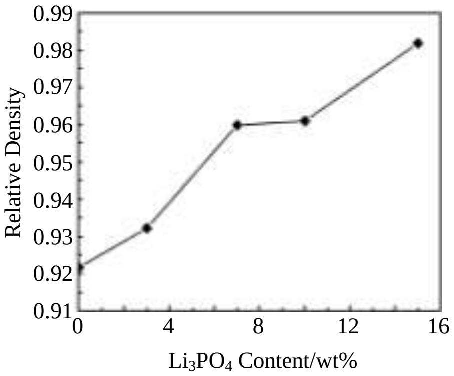

Fig.3 Relative density variation with the increase of Li_3PO_4 content in the LLTO composites

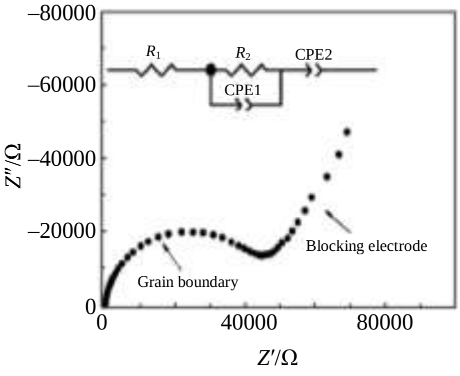

Fig.4 Equivalent circuit and a typical complex impedance of LLTO composite

The ionic conductivity dependence on the temperature for LLTO/Li_3PO_4 composites is shown in Fig.5. We can see that the conductivity of the composites with Li_3PO_4 addition decreases with the increase of the Li_3PO_4 addition content, no matter in grains, grain boundaries or the overall conductivity trend. Fig.6 is the variations of the room temperature ionic conductivity with the increase of the Li_3PO_4 content. It can be found that the grain conductivities present almost no change with the addition of Li_3PO_4, only with a little bit decrease in values (see Fig.6a). It is thought that Li_3PO_4 leads to a smaller lattice distortion of the LLTO structure, unfavorable for the lithium ion movement in the bulk grains, suggesting a slight decrease in the grain bulk conductivity in LLTO/Li_3PO_4 composites. Meanwhile, the decrease of the bulk ionic conductivity in the LLTO crystal structure is assigned to lithium ion insertion into the vacancies in the LLTO lattice, which leads to increased number of lithium ions involved in the ion migration, however, also decreased number of vacancies for lithium ion motion. As known, the ratio of lithium ion to vacancy should be in a moderate range[29]. It can be said that a decreased number of mobile lithium ions take part in the lithium ion conduction and decrease the ionic conductivity for LLTO composites with introduction of Li_3PO_4.

LLTO-Li_3PO_4 composites reveal low grain boundary (GB)ionic conductivities in comparison with pure LLTO ceramics. Glassy Li_3PO_4 forms at the grain boundaries of LLTO ceramics, resulting in highly disordered grain boundaries and serious mismatching between the passageways for lithium ion migration. Meanwhile, the pathways become more detoured and longer, and then the number of the mobile lithium ions at the same time decreases. That is, at the grain boundary regions, mobile lithium ions are confined and blocked, leading to the lithium ion transport with more difficulty when the Li_3PO_4 was added. So Li_3PO_4 considerably affects the microstructures of the LLTO ceramics, which is dominantly responsible for the decrease of the grain boundary ionic conductivity with the increase of the addition of Li_3PO_4 (see Fig.6b).

Because the grain boundaries govern the total ionic conductivity, the overall conductivities have an identical change tendency as the grain boundary conductivity with the increase of Li_3PO_4 addition. A gradual decrease of the total ionic conductivity is observed with the increase in the amount of Li_3PO_4 for the LLTO composites (see Fig.6c).

Generally, the high densification of these obtained pellets is desirable for the improvement of ionic conductivity. But the lithium content is a key factor determining the ionic conductivity, and the microstructures at the grain boundaries show an intense relationship with the ionic conduction. The enhancement effect of the high relative density on the ionic conductivity is not able to overwhelm the adverse effect produced by the above two factors. It was believed that the ionic conductivity for LLTO ceramics was controlled by the lithium ion content and the microstructures. Consequently, more efforts should be devoted to improve the microstructures at the grain boundaries in order to enhance the ionic conductivity of the LLTO ceramics.

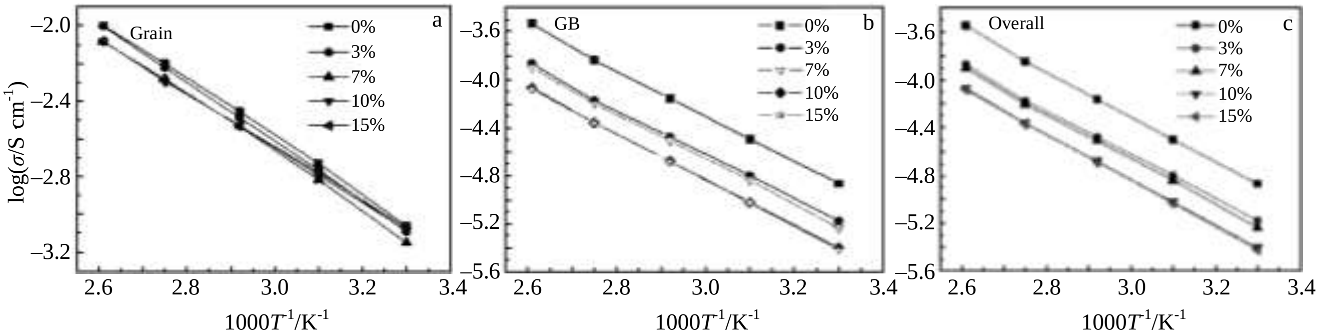

Fig.5 Ionic conductivity dependence on the temperature for the LLTO composites with different Li_3PO_4 contents

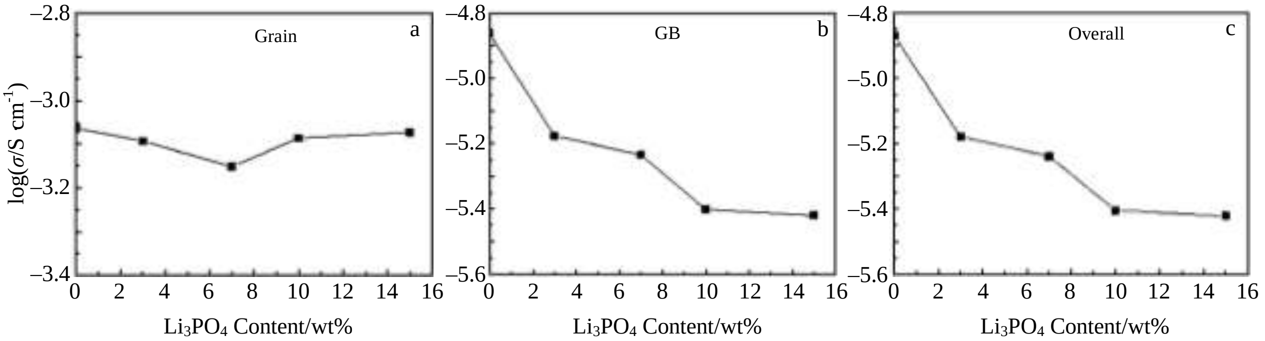

Fig.6 Ionic conductivity as a function of Li_3PO_4 content for the LLTO composites

3 Conclusions

1) The ionic conductivity of compact ceramics with Li_3PO_4 addition into the LLTO matrix decreases with the increase of the Li_3PO_4 addition.

2) LLTO phase in all composites still belongs to tetragonal symmetry. The local lattice distortion becomes smaller with the increase of the second phase and partial lithium ions insert into the LLTO lattice, both resulting in a slight decrease in the grain bulk conductivity.

3) The morphologies of LLTO grains are very twisted and the tunnels for lithium ion migration are much detoured when the Li_3PO_4 is introduced, which decrease the grain boundary conductivity noticeably. It can be concluded that the change of the ionic conductivity is mainly ascribed to the variation of the lithium content and microstructures of the LLTO matrix dispersed by Li_3PO_4 particles.

References

1 Kobayashi Y, Miyashiro H, Takeuchi T *et al*. *Solid State Ionics* [J], 2002, 152-153: 137

2 Wang Q Y, Xu L Y, Zhang Y L *et al*. *Rare Metal Materials and Engineering*[J], 2014, 43(3): 530

3 Abe T, Ohtsuka M, Sagane F *et al*. *J Electrochem Soc*[J], 2004, 151: A1950

4 Qi P, Chen Y G, Zhu D *et al*. *Rare Metal Materials and Engineering*[J], 2014, 43(5): 1073

5 Robert G, Malugani J P, Saida A. *Solid State Ionics*[J], 1981, 3-4: 311

6 Guo R S, Wu L J, An J *et al*. *Rare Metal Materials and Engineering*[J], 2013, 42(12): 2486 (in Chinese)

7 Rodger A R, Kuwano J, West A R. *Solid State lonics*[J], 1985, 15: 185

8 Inaguma Y, Chen L, Itoh M *et al*. *Solid State Commun*[J], 1993, 86: 689

9 Fourquet J L, Duroy H, Crosnier-Lopez M P. *J Solid State Chem*[J], 1996, 127: 283

10 Kawai H, Kuwano J. *J Electrochem Soc*[J], 1994, 141: L78

11 Mitsuru I, Inaguma Y. *Solid State Ionics*[J], 1996, 86-88: 203

12 Katsuma T, Matsui Y, Inaguma Y *et al*. *Solid State Ionics*[J], 1996, 86-88: 165

13 Wang G, Yao P, Bradhurst D. *J Mater Sci*[J], 2000, 35: 4289

14 Belous A G. *Solid State Ionics*[J], 1996, 90: 193

15 Garcia-Martin S, Rojo J M, Tsukamoto H *et al*. *Solid State Ionics*[J], 1999, 116: 11

16 Mizumoto K, Hayashi S. *J Ceram Soc Japan*[J], 1997, 105: 713

17 Chen R F, Song X Q. *Journal of the Chinese Chemical Society* [J], 2002, 49: 7

18 Leo C J, Subba Rao G V, Chowdari B V R. *Solid Stat Ionics*[J], 2003, 159: 357

19 Przyluski J, Siekierski M, Wieczorek W. *Electrochimica. Acta*[J], 1995, 40: 2101

20 Kobayashi Y, Tabuchi M, Nakamura O. *Journal of Powder Sources*[J], 1997, 68: 407

21 Albert S, Frolet N, Yot P *et al*. *Solid State Ionics*[J], 2006, 177: 3009

22 Maekawa H, Fujimaki Y, Shen H *et al*. *Solid State Ionics*[J], 2006, 177: 2711

23 Maekawa H, Tanaka R, Satio T. *Solid State Ionics*[J], 2004, 175: 281

24 Yamada H, Moriguchi I, Kudo T. *Solid State Ionics*[J], 2005, 176: 945

25 Mei A, Wang X L, Feng Y C *et al*. *Solid State Ionics*[J], 2008, 179: 2255

26 Kitaoka S, Inoue N. *Solid State Ionics*[J], 2009, 180: 598

27 Deng Y, Shang S J, Mei A *et al*. *Journal of Alloys and Compounds*[J], 2009, 472: 456

28 Yang K Y, Wang J W, Fung K Z. *Journal of Alloys and Compounds*[J], 2008, 458: 415

29 Geng H X, Mei A, Lin Y H *et al*. *Electrochemical Acta*[J], 2011, 56: 3406

Li_3PO_4对$Li_{0.5}La_{0.5}TiO_3/Li_3PO_4$复合固体电解质的电性能影响

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摘 要：利用复阻抗谱分析技术考察了复合Li_3PO_4的$Li_{0.5}La_{0.5}TiO_3$ (LLTO) 固体电解质的离子电导率，同时还利用X射线衍射图谱、扫描电镜观测和相对致密度测量等实验手段研究了LLTO电解质中第二相的分散情况。结果发现，加入Li_3PO_4第二相后，尽管复合固体电解质LLTO拥有比较高的致密度，但是Li_3PO_4会导致离子电导率的降低。通过分析LLTO的晶体结构，晶界的微观结构和锂含量，阐明了LLTO离子电导率恶化的原因，往LLTO基质中分散的Li_3PO_4导致的锂含量和微观结构的变化是引起锂离子传导行为改变的主要原因。

关键词：$Li_{0.5}La_{0.5}TiO_3$；Li_3PO_4；离子电导率；复合固体电解质

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