LiF Assisted Synthesis Perovskite-type $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ Solid Electrolyte for Rechargeable Lithium-metal Batteries

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Research Article

Keywords: Solid-state electrolytes, LiF addition, Total conductivity, V2O5, Electrochemical performances

Posted Date: December 18th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-128544/v1>

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LiF assisted synthesis perovskite-type $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ solid electrolyte for rechargeable lithium-metal batteries

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Abstract: Perovskite-type solid-state electrolytes, $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_{3-x}\text{wt}\% \text{LiF}$ (LLTO-Fx, $x = 0, 2, 4$ and 6), were successfully synthesized through solid-state reaction method. The effects of LiF addition amount on LLTO crystal structure, morphologies and ionic conductivity have been investigated. All samples formed perovskite structure and the grain sizes were gradually increased with the increase of LiF content. Moreover, owing to the highest relative density (95.4%), LLTO-F2 electrolyte exhibited a highest total conductivity of $1.02 \times 10^{-4} \text{ S/cm}$ with a relative low activation energy of 0.26 eV, which is suitable for use in solid-state batteries. The cell $\text{Li/LLTO-F2/V}_2\text{O}_5$ exhibited a specific capacity about 270 mAh/g in the first few cycles and maintained 156 mAh/g after 100 cycles, demonstrating good cycling properties. Moreover, cells assembled with different cathodes, such as LiFePO_4 and LiCoO_2 , also displayed excellent electrochemical performances. The results suggest that sintering additive (LiF) is very effective step towards ultimately achieve a safe solid-state lithium battery system.

Keywords: Solid-state electrolytes; LiF addition; Total conductivity; V_2O_5 ; Electrochemical performances

1. Introduction

All-solid-state lithium batteries have attracted extensive attention due to their high safety and theoretical energy density, and become the focus of the next generation of battery system in comparison with conventional lithium-ion batteries [1-3]. Solid-state electrolytes (SSEs), as a key material for solid-state batteries (SSBs), exhibit wide electrochemical windows and stable ion transport, generating uniform electrodeposition, thus promoting stable circulation of the battery

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system^[4-6]. Therefore, benefiting from the excellent solid characteristic, the dendrite growth of the metal negative electrode and the generation of side reactions could be inhibited, which eliminates the potential leakage, vaporization, flammability and explosion of lithium ion batteries with organic liquid electrolyte^[1, 7-9]. With the development and optimization of SSEs, two types of SSEs can complement each other to meet the application requirements: organic polymers and inorganic glass or ceramics electrolytes^[2, 4]. Generally, organic polymers SSEs could exhibit excellent manufacturability and lightweight, but still suffer from low ionic conductivity and flammability, which is a potential safety hazard. On the contrary, inorganic SSEs, such as sulfide-based and oxide-based ceramics, have displayed wide electrochemical windows (0 - 9V vs Li/Li⁺), high ionic conductivity ($>10^{-4}$ S/cm) and low raw material cost, easier to realize large-scale preparation^[10, 11].

Among all of the inorganic SSEs, perovskite-type lanthanum lithium titanate (LLTO) displays excellent electrochemical window (8 V vs Li/Li⁺), and the bulk conductivity is as high as 10^{-3} S/cm at room temperature, demonstrating the best lithium ion conductivity for SSBs^[4, 12]. Unfortunately, the boundary resistance of LLTO is extremely large, which is related to its structure and chemical instability, such as particle reduction from Ti⁴⁺ to Ti³⁺, lithium depletion and deformation of Ti-O polyhedron^[13, 14]. Generally, doping silicate additives (Al, Cr, etc.) could be the simple and effective strategies to improve ionic conductivity of LLTO electrolyte. Susana Garcí'a-Martí'n^[15] prepared the $\text{La}_{0.56}\text{Li}_{0.3}\text{Ti}_{0.97}\text{Al}_{0.03}\text{O}_3$ electrolyte, and the ionic conductivity could be improved by 2.95×10^{-3} S/cm at 295K. Nan^[16] et al. added $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) composite electrolyte sol to LLTO precursor powder, where Zr ions doped mainly in grain boundary, improving the total ionic conductivity to 1.2×10^{-4} S/cm. However, in order to prepare dense ceramics, it is necessary to provide a higher temperature and a longer time, which leads to the loss of lithium element, and ultimately weakens the performance of electrolyte.

LiF is a good sintering additive that can not only reduce sintering temperature, but also promote densification of the ceramics because of low melt temperature (848 °C)^[17]. The lithium loss of ceramic electrolyte in sintering process can also be added. There is no study about the LiF assisted synthesis $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ solid electrolyte for lithium-metal battery. In the work, we prepared $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ ceramic electrolyte with LiF as sintering assistant. The ionic conductivity and densification of the $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ electrolyte were significantly improved. Moreover, the electrolyte displayed excellent stability and battery performance at room temperature, and structure-

property relationships were additionally discussed.

2. Experimental Section

2.1. Materials synthesis

$\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ -xwt%LiF (LLTO-Fx, $x = 0, 2, 4$ and 6) solid electrolyte solid ceramic electrolytes were prepared by conventional solid-state method using LiCO_3 (98%), La_2O_3 (99.99%) and TiO_2 (99%) as raw materials. All of the materials were purchased from Sinopharm Chemical Reagent Co., Ltd., China. After weighing according to the stoichiometric ratio, the raw materials were mixed homogenized by planetary ball milling for 10 h at 300r and then calcined at 800 °C for 2 h. After that, LiF (98%) were mixed with above mixture and milled again 10 h at 300r. The powders were pressed into pellets with the thickness of 1mm and diameter of 15 mm under the pressure of about 10 MPa, and then sintered at 1100 °C for 10 h. To minimize volatilization of lithium, the pellets were buried in the sacrificial LLTO powders.

Due to the rapid development of solid-state electrolytes and the renaissance of lithium metal anode, it is necessary to revisit Li-free cathode with high energy density. The Li-free V_2O_5 cathode was prepared by a facile oxidation strategy using $\text{VO}_2(\text{B})@\text{C}$ as a precursor^[18]. The unique V_2O_5 micro/nano-structures possess excellent electrochemical properties (> 230 mAh/g at 100 mA/g), which could be promising cathode materials for SSBs.

2.2. Assembly of different cells

CR2032-type coin cells were used as the testing cells. All batteries are assembled in an Ar-filled glove box ($\text{O}_2 < 5$ ppm, $\text{H}_2\text{O} < 5$ ppm). As the cathode, V_2O_5 , LiFePO_4 (LFP), and LiCoO_2 (LCO) were used to verify the compatibility with different cathodes, respectively. The cathode active materials (80wt%), acetylene black (10wt%), and polyvinylidene fluoride (10wt%) were mixed and then spread onto aluminum foil with a loading of 1.2–1.6 mg/cm². The cathode/LLTO-Fx/Li battery was assembled, where LLTO-Fx pellet acts as the separator and solid electrolyte. To protect LLTO from being reduced by Li metal, Celgard 2400 soaked by liquid electrolyte was sandwiched between LLTO pellet and Li metal. Moreover, the interface between the LLTO and cathode is improved by dropping liquid electrolyte ($\sim 5\mu\text{L}$ 1M $\text{LiPF}_6/\text{EC-DMC}$) on the other side of LLTO-Fx pellet^[19, 20].

2.3. Characterizations.

The density of sintered ceramics was measured by Archimedes method. The thermal

decomposition of the raw mixed powder was conducted using a thermal gravimetric (TG) and differential scanning calorimeter (DSC) synchronous analyzer (TG-DSC, STA449F5 Jupiter, Germany). The phase structure was determined on a Bruker D8 diffractometer X-ray powder diffraction (XRD) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology was characterized with a scanning electron microscopy (SEM, HITACHI S-4800, Japan). The lithium ion conductivity was determined by electrochemical impedance spectroscopy (EIS) in a temperature ranging of 298-343 K, employing two blocking silver electrode layers coated on each side. The analysis of EIS were conducted using the CHI 660C workstation in a frequency range from 0.1Hz to 1MHz at 5 mV. The galvanostatic charge-discharge performances were evaluated using a Land CT2001A (China) battery test system.

3. Results and discussions

In order to determine the accurate calcination temperature, the thermal decomposition of the raw mixed powder (LLTO-F0) was conducted using TG-DSC analysis. As shown in **Fig. 1**, the significant weight loss of 8% can be observed under 500 °C, corresponding to the endothermic peaks at 364°C on the DSC curve, which could be related to the evaporation of water and the decomposition of carbonate (Li_2CO_3). In addition, there is an obvious weight loss within 600 °C and 850 °C, corresponding to the endothermic peaks at 750°C on the DSC curve, which may be attribute to the activation point for crystallization of the raw powders and corresponded to the formation of perovskite-type $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$. No significant weight change could be measured at the temperature above 850 °C, indicating that transformation of the mixture precursor powders to the crystalline oxide starts above this temperature. Therefore, 850 °C was chosen as the calcination temperature to ensure the phase formation and improve the electrochemical performance of the LLTO ceramic electrolytes.

Fig. 2 shows the XRD patterns of LLTO-Fx pellets sintered at 1100°C for 10h. The results show that all diffraction peaks match well with perovskite structure (PDF#46-0465) within the scope of instrument measurement, and no impurity peak appears, indicating the introduction of LiF has no obvious effect on the crystalline structure of LLTO. Moreover, LiF, as additive salt, is not present in the XRD patterns, which could be related to the volatilization of fluorine during the synthetic reaction at 1100 °C^[17].

The SEM images of the LLTO-Fx ceramics were showed in **Fig. 3**. The grains of the samples are in good contract with each other and well-defined with no obvious void space. In addition, LLTO-F0 exhibits the smallest grain size, suggesting that LiF can improve grain growth thus reduce the number of grain boundaries and suppress the occurrence of defects ^[21]. Similar results could also be observed in NASICON-type $\text{LiTi}_2(\text{PO}_4)_3 + m \text{ mol LiF}$ solid electrolyte ^[17]. Moreover, the relative densities (ρ_{rd}) of the LLTO-Fx ceramics are measured by the archimedes method to further confirm the effect of LiF on LLTO ceramics. As LiF content rises, the ρ_{rd} firstly increased from 94.2% for $x = 0$ to 95.4% for $x = 2$, which could be related to that LiF, as additive salt, reduced the reaction barrier at interface of the reactants thus increase the relative densities. However, with the further increase of LiF content ($x = 4$ and 6), the relative density decreases slightly to 95.1% and 94.7%, which may be caused by the increased interspace between the large grains ^[17, 21]. Despite the decrease, as shown in **Table 1**, all of the samples have a high relative density ρ_{rd} ($> 94.5\%$), suggesting the LLTO-Fx ceramics have been well sintered at 1100°C , which is beneficial to the improvement of conductivity ^[21].

The impedance spectra of the LLTO-Fx ceramics was displayed in **Fig. 4a**. All plots of samples are consisted of a low-frequency tail and a high-frequency semicircle, which are typical characteristic profiles of ionic conductive ceramics. It is hard to distinguish the resistance of grain boundary from the impedance profile, only the bulk resistance (R_b) and the total resistance (R_t) of samples are discussed in this paper^[17, 22]. Compared with pure LLTO, a steeper slope in the low frequency region and a smaller semicircle diameter in the high frequency region could be found for LLTO-Fx ($x > 0$), reflecting reduced ionic transfer resistance of the as-obtained samples. Generally, the ionic conductivity can be calculated from R_b and R_t , based on the equation: $\sigma = L/R \cdot S$. Where σ , R , L and S represent ionic conductivity, resistance, thickness and area of LLTO-Fx ceramic electrolyte, respectively. The total (σ_t) and bulk (σ_b) conductivities of the samples were shown in **Fig 4b** and **Table 1**. It is found that the total conductivities (σ_t) of the LLTO-Fx increased at first, and then decreased with the increase of LiF addition. The LLTO-F2 sample exhibit a maximum σ_t value of $1.02 \times 10^{-4} \text{ S/cm}$ with a relatively high σ_b value ($2.78 \times 10^{-4} \text{ S/cm}$), which is much higher than that of LLTO-F0 sample ($1.57 \times 10^{-5} \text{ S/cm}$ for σ_t and $2.74 \times 10^{-4} \text{ S/cm}$ for σ_b). Hence, appropriate amount of LiF has obviously positive impact on Li-ion migration in LLTO solid electrolyte. This result could be attributed to the appropriate increased grain size, as shown in **Fig. 3**, which not only

decreased the number of grain boundaries but also increased the relative density, thereby improving the ionic conductivity. However, when the LiF addition amount was far beyond the dopant concentrations limit, the σ_t value of the samples decreased to 2.46×10^{-5} S/cm for LLTO-F4 and 2.25×10^{-5} S/cm for LLTO-F6, respectively, which could be associated with the decreased relative density^[17, 21].

The temperature dependence of the impedance was measured to get the activation energy (E_a) of ion migration for LLTO-F2 sample (**Fig. 4c**) in the test temperature range from 30 °C to 70 °C. Furthermore, the relationship between the E_a and σ_t of the LLTO-F2 pellets was calculated from the Equation (1)^[21]:

$$\sigma_{\text{total}} = A \exp(-E_a/k_B T) \quad (1)$$

where k_B is Boltzmann constant, T and A are the ambient temperature and given parameter, respectively. The E_a of Li-ion conduction in LLTO-F2 is 0.26 eV. This result is slightly lower than that of other reports (**Table 2**), indicating the higher Li-ion mobility of LLTO-F2 sample, which is beneficial to the high performance of solid electrolyte in a wide temperature range^[23]. **Table 2** summarizes the reported ion conductivities and activation energy of LLTO electrolyte prepared by different methods^[4, 16, 24-27]. It is clear that LiF assisted synthesis of LLTO sintered at 1100°C could deliver an ion conductivity of 1.02×10^{-4} S/cm at 25°C, which is comparable to that reported by many other groups, indicating the LLTO-F2 could prove a most advantageous in terms of electrochemical performance.

To demonstrate the feasibility of LLTO-F2 electrolyte, the Li/LLTO-F2/V₂O₅ solid-state batteries were assembled. **Fig. 5a** shows the schematic view of the solid-state batteries, where V₂O₅ was prepared through a facile oxidation strategy^[18] and the LLTO-F2 acted as the electrolyte and separator. As shown in inset of **Fig. 5b**, the porous sponge-like V₂O₅ structure deliver a capacity of 110 mAh/g at 1C rate after 100 cycles when used in liquid lithium battery without the LLTO-Fx solid electrolytes. Moreover, a high capacity of 150 mAh/g could be conducted at 25°C and 0.05C after 120 cycles for Li/LLTO-F2/V₂O₅ solid-state battery, achieving a better electrochemical performance, as shown in **Fig. 5b**. **Fig. 5c** described the charge-discharge properties of Li/LLTO-F2/V₂O₅ cell at 2nd, 3rd, 4th, and 100th cycle at current density of 0.05C (12 μ A/cm²). It is clear that the specific capacity of the battery in the second cycle is about 270 mAh/g, which reaches 96% of the theoretical capacity of V₂O₅. After 100 cycles, the discharge capacity of the battery still

maintains 156 mAh/g with coulombic efficiency (99%). The decrease of capacity may be attributed to the instability of contact between electrode and electrolyte after multiple cycles. The rate capability of the battery was demonstrated as shown in **Fig. 5d**. The Li/LLTO-F2/V₂O₅ battery delivers specific capacities of 208, 181, 77, 35 and 5 mAh/g at current densities of 0.05, 0.1, 0.3, 0.5 and 1C, respectively. The cell got a capacity loss and the battery has almost stopped working under high current density. Interestingly, when the current density is reduced to 0.1C, the average reversible capacity can be restored to about 128mAh/g with a capacity retention rate of about 70%. The results verify that the V₂O₅ cathode and lithium metal have good compatibility with the LLTO-F2 ceramic electrolyte. In other words, LLTO-F2 electrolyte can be applied to V₂O₅/Li solid-state batteries and demonstrate excellent electrochemical stability.

To verify the compatibility with different cathodes, the Li/LLTO-F2/LiFePO₄ and Li/LLTO-F2/LiCoO₂ cells were also assembled with the LLTO-F2 solid electrolyte (**Fig. 5e**). As shown in the preliminary results, all the cells exhibited good cycling stability: specific capacity of 109 mAh/g at 0.1C for LiCoO₂ and specific capacity of 83 mAh/g at 0.2C for LiFePO₄ after 50 cycles, respectively. The results confirm the good feasibility of the perovskite-type LLTO-F2 solid electrolytes for solid-state lithium-metal batteries.

4. Conclusion

In summary, LiF modified LLTO based ceramic electrolytes were successfully fabricated using conventional solid-state method toward high safety solid-state Li-batteries. The appropriate LiF not only decreased the number of grain boundaries but also increased the relative density (95.4%), thereby enabling the LLTO-F2 electrolytes exhibited a high ionic conductivity of 1.02×10^{-4} S/cm at 25°C with a low activation energy of 0.26 eV. In addition, Li/LLTO-F2/V₂O₅ solid-state battery deliver better cycling (156 mAh/g after 100 cycles at 0.05C) and rate capability (128 mAh/g capacity retention at 0.1C). Moreover, the compatibility of the LLTO-F2 electrolyte was verified with different cathodes, such as LiFePO₄ and LiCoO₂. All of the solid-state cells delivered excellent cycling performance, validating the perovskite-type LLTO-F2 solid electrolytes is suitable for lithium-metal batteries. Furthermore, it is anticipated that the sintering additive (LiF) assisted synthesis is an effective way to improve the electrochemical properties, such as ionic conductivity and compatibility with electrode, which will promote the application of solid-state ceramic electrolytes in solid-state Li-metal batteries.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (NSFC No. U1904213 and 51672130), the Key Research and Development Program of Jiangsu Province (Grant No. BE2018008-2), the special fund of 333 high-level talents training project in Jiangsu province (BRA2017424), the Research Fund of State Key Laboratory of Mechanics and Control of Mechanical Structures (Nanjing University of Aeronautics and astronautics) (Grant No. MCMS-0518K01).

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Figures

Figure 1

Electrochemical characterization of hybrid solid-state full cells. (a) Schematic of the hybrid Li/LLTO-F2/V₂O₅ full cell configuration. Electrochemical performance of the Li/LLTO-F2/V₂O₅ cell: (b) cycle performance and coulombic efficiency at 0.05C and 25 °C, (c) Galvanostatic charge/discharge

performance at 0.05C and (d) rate capability. (e) The cycle performance of Li/LLTO-F2/LiFePO₄ and Li/LLTO-F2/LiCoO₂ cells.

Figure 1

X-ray diffraction patterns of the LLTO-Fx samples calcined at 1100 $\times$ for 10 h.

Figure 1

EIS measurements of the LLTO-Fx samples. (a) Impedance spectra measured at 25 °C for LLTO-Fx ceramic samples. Inset: the enlarged view of the impedance spectra; (b) Total ionic conductivity (σ_t) and bulk conductivity (σ_b) comparison as a function of x; (c) Temperature dependent impedance plots for LLTO-F2 electrolyte ceramic sample; (d) Arrhenius plot for LLTO-F2 electrolyte ceramic sample.

Figure 1

TG-DSC curves of the LLTO-F0 precursors in the temperature range between 25 °C and 1300 °C with a heating rate of 10 K/min.

Figure 1

SEM images of the LLTO-Fx samples: (a) LLTO-F0, (b) LLTO-F2, (c) LLTO-F4 and (d) LLTO-F6.

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