Co-Precipitation Synthesis and Electrochemical Properties of NASICON-Type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ Solid Electrolytes

Zhongran Yao

Nanjing University of Aeronautics and Astronautics

K.J. Zhu (✉ kjzhu@nuaa.edu.cn)

college of aerospace engineering

Kongjun Zhu

Nanjing University of Aeronautics and Astronautics

Jie Zhang

Nanjing University of Aeronautics and Astronautics

Xia Li

Nanjing University of Aeronautics and Astronautics

Jiatao Chen

Nanjing University of Aeronautics and Astronautics

Jing Wang

Nanjing University of Aeronautics and Astronautics

Kang Yan

Nanjing University of Aeronautics and Astronautics

Jinsong Liu

Nanjing University of Aeronautics and Astronautics

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Abstract

NASICON-type solid-state electrolytes have gathered wide attention to meet the requirements of high-energy-density batteries. In this study, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) were synthesized through co-precipitation method. The composition, phase transformation, microstructure and particle size of LATP powder were characterized in detail. Pure LATP without any detectable secondary phases can be obtained at 800 °C with size about 590 nm. The relatively dense surface microstructure for LATP ceramics was clearly observed. In addition, the ionic conductivities of LATP pellets increased at first and then decreased with the increased sintering temperature and time. Owing to the highest relative density (95.6%), LATP (sintered at 900 °C for 6h, LATP-900₆) exhibited a highest total conductivity of 2.19×10^{-4} S/cm with a low activation energy of 0.32 eV. The results suggest that co-precipitation synthesized LATP-900₆ ceramic electrolyte could be a promising alternative towards achieve a safe solid-state battery. Moreover, the co-precipitation method is suitable for the preparation of other oxide ceramic electrolytes.

Introduction

Lithium ion battery has become the standard power supply for mobile electronic devices such as electric vehicles, laptops and mobile phones because of its high output voltage, high energy density and small environmental pollution, etc ^[1, 2]. However, the polyolefin diaphragm with poor thermal dimensional stability and flammable and volatile organic liquid electrolytes restricted the development of lithium ion battery towards large-scale and high-energy direction. In order to overcome the safety problem of liquid organic electrolyte, a lot of researches have been carried out on solid-state batteries (SSBs), which has become the focus of the next generation of battery system in comparison with conventional lithium-ion batteries ^[3]. Solid-state electrolytes (SSEs) exhibit stable ion transport and wide electrochemical windows, thus promoting stable circulation of the battery system ^[4–6]. 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 vaporization, flammability and explosion of lithium ion batteries with organic liquid electrolyte.

As a typical inorganic SSEs with NASICON type structure (rhombohedral unit, space group R3hc), $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) has attracted significant attention because of its high Li^+ conductivity and excellent chemical stability to $\text{O}_2/\text{H}_2\text{O}$, so that material preparation and battery assembly can be carried out in an air environment, which further reduces manufacturing costs ^[7–10]. At present, there are many methods for successfully preparing LATP particles, such as melt quenching ^[11], sol-gel method ^[12] and solid-state reaction ^[13], etc. Among these methods, melt-quenching method could can effectively reduce the porosity of LATP ceramics and then obtain high ionic conductivity ($\sim 10^{-3}$ S/cm at room temperature), which is much higher than that of LATP obtained by solid-state reaction ^[13]. However, it is difficult to form smaller grain sizes for the material via melt-quenching method or solid-state reaction, which limits their scope of application ^[7]. Wet chemical synthesis method has received extensive

attention in preparing uniform fine ceramic particles because of uniform reaction at the molecular level, which can not only adjust the microstructure of the powder to improve the ion conductivity, but also effectively reduce the sintering temperature and reduce the total energy consumption of the crystallization process^[14, 15].

Co-precipitation method, as a typical wet chemical synthesis route, could effectively control the composition and morphology of the material at molecular level and prepare inorganic powders on a large scale in a short time and under low temperature conditions^[16], making it suitable for the preparation of ceramic electrolytes. Therefore, in this work, LATP solid electrolyte was prepared by co-precipitation method to confirm and expand the application of co-precipitation method in solid electrolytes. The phase transition process was conducted via thermogravimetry-differential scanning calorimetry (TG-DSC), X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR). Crystallized LATP powder is obtained at 800°C for 6h with primary particle size of ~ 590 nm. In addition, densified LATP electrolytes were successfully fabricated at 900°C for 6h with the co-precipitation-derived powder and their structure and electrochemical properties were investigated systematically via electrochemical impedance spectroscopy (EIS). Moreover, the electrolyte displayed excellent stability and battery performance at room temperature, and structure-property relationships were additionally discussed.

Experimental

Materials synthesis. LATP are synthesized by a modified co-precipitation method. **Figure. 1a** shows the graphical illustration of the co-precipitation process. Initially, CH_3COOLi and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved into a 100 mL deionized water with stirring at 80 °C. $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to keep the pH ~ 9.5 and the value was checked and kept steadily during precipitating. Afterward, 20 mL ethanol solution containing $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and 20 mL $\text{NH}_4\text{H}_2\text{PO}_4$ solution were introduced into the above solution to obtain white precipitate. The dispersion was stirred for another 2h at 80 °C. After vaporizing the solvent at 150 °C for 1 day, the remained powder was transferred to a ceramic crucible and kept at different temperatures (500–1000 °C, 6h) to further determine the optimal calcination temperature. The resulting powder was then uniformly ground and pressed into disc-shaped pellets at 200 MPa and then sintered at different temperatures (800°C-1000°C) to investigate their sinter ability. To minimize volatilization of lithium, the pellets were buried in the sacrificial LATP powders. Finally, the samples were polished to a thickness of 1 mm and two blocking silver electrode layers coated on each side for electrochemical performance analysis.

Characterizations. The density of sintered ceramics was measured by Archimedes method. TG-DSC (STA449F5 Jupiter, Netzsch, Germany) and FTIR (Nicollet NEXUS670, USA) were performed to analyze the phase transition process. A Bruker D8 diffractometer XRD and Bettersize2600 laser particle size analyzer (Bettersize Instruments LTD. China) were carried out to investigate the phase structure and particle size distribution. The morphology and microstructure were recorded by scanning electron microscopy (SEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL-

2100F). EIS was conducted to evaluate the ionic conductivities of the LATP samples, employing two blocking silver electrode layers coated on each side (10^{-1} – 10^6 Hz, 5mV, CHI660E, Shanghai Chenhua Instrument Co., Ltd.).

Results And Discussion

The scheme (**Figure 1a**) presents the detailed steps for LATP particles obtained by co-precipitation method. During the whole co-precipitation process, $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added continuously to keep the pH ~ 9.5 . At the same time, the temperature was kept at 80 °C to ensure the rapid precipitation of metal cations (Al^{3+} , Ti^{4+}). Finally, white LATP powder was obtained by drying and sintering. In order to determine the optimal calcination temperature, the precursor LATP powder was decomposed by TG-DSC. As shown in **Figure 1b**, significant weight loss can be observed at 200 °C, corresponding to the larger endothermic peak of DSC curve, which may be related to the volatilization of small molecule additives such as water and alcohol in precursor powder^[17]. In addition, in the temperature range of 200-400 °C, there is a weight loss platform corresponding to two exothermic peaks in DSC curve, which is mainly related to the decomposition of organic carbon in the precursor powder^[18]. In the temperature range of 400-1000 °C, only an obvious exothermic peak near 700 °C was obtained, indicating that the precursor powder has undergone phase transformation at this temperature until stable LATP phase is formed, which further confirmed by the following XRD data.

Figure 1c shows the XRD patterns of LATP powders obtained at different calcination temperatures (500-1000 °C) to further determine the optimal calcination temperature. No diffraction peak could be found for the sample at 500 °C, indicating that the powder is still in an amorphous state. When the calcination temperature rises to 600 °C and 700 °C, the sample shows a more obvious characteristic peak, and has a good matching degree with the pure $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) standard XRD pattern (PDF#35-0754)^[19], indicating that LATP phase formed at this temperature range, which is consistent with the exothermic peak near 700 °C in **Figure 1b**. Meanwhile, the characteristic peak of LATP shifts to a large angle compared with LTP because of the ionic radius of Al^{3+} (0.54 Å) is smaller than that of Ti^{4+} (0.60 Å). Moreover, when the calcining temperature increased to 800 °C, pure LATP was formed without impurity peaks, indicating that 800 °C was the lowest temperature for obtaining pure LATP powder. AlPO_4 impurity peaks is observed at 900 °C and 1000 °C, which may be related to the volatile loss of lithium at high temperature^[20, 21]. **Figure 1d-e** showed the particle size analysis and SEM of LATP samples obtained at 800°C 6h to further analyze the particle state. The particle size of LATP powder is relatively uniform, and the particle size is mostly around 590nm ($D_{50} \sim 0.59 \mu\text{m}$). The uniform and fine powders can effectively reduce the sintering temperature and increase the density to some extent, which is beneficial to obtain LATP ceramic electrolyte with excellent performance.

In order to further determine the structure of the powders, the FTIR results of samples at different temperatures (120-1000°C) are given in **Figure 2**. The structure of the powder changes obviously before and after heat treatment. The samples prepared by co-precipitation (120°C, 6h) showed clear

transmission peaks at 1389 and 3143 cm^{-1} , corresponding to the N-H bands in NH_4^+ [22]. The powders preheated at different temperatures (500-1000 °C) showed peak values at 734, 577, 645, 1625 and 1038 cm^{-1} . The peak at 1625 cm^{-1} is related to the absorption of H-O-H bond of water on the sample surface [23]. The peak at 1038 cm^{-1} is attributed to the asymmetric and symmetric stretching vibration of P-O band in PO_4 tetrahedron [24]. Due to the Ti-O stretching vibration of TiO_6 octahedron, there are several intensity peaks near 577-734 cm^{-1} [25, 26]. In addition, NH_4^+ characteristic peaks gradually disappeared at 800 °C, and other characteristic peaks were sharp and visible in the range of 577-734 cm^{-1} ; meanwhile, there is no obvious change in the structure peaks with calcining temperature increasing, indicating the crystal orientation of LATP is gradually formed after calcination at 800 °C [26, 27], which is consistent with the results of XRD diffraction pattern in **Figure. 1c**. On this account, FTIR spectra can also screen the crystallinity of the samples to determine the phase structure changes of the powders.

The TEM and HRTEM images were carried out to further identify the phase composition and morphology of the LATP particles obtained by co-precipitation. As shown in **Figure 3a**, the LATP particles have an irregular morphology, being in good agreement with the SEM results (**Figure 1e**). **Figure. 3b** and **c** shows the enlarged (b) and (c) regions drawn in the white frame in **Figure. 3a**, respectively. The HRTEM images clearly showed that the LATP grains were surrounded by amorphous regions. A similar phenomenon exists in $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ electrolyte [18]. The interplanar spacings of nanocrystalline grains of 0.42, 0.36 and 0.60 nm correspond to (104), (113) and (012) lattice planes of LATP, respectively. The selected area electron diffraction pattern (inset of **Figure. 3b**) indicates a well-defined crystal structure for these regions of the particles. The above results indicate that the LATP obtained at 800 °C is partially crystalline, while crystalline nanoparticles and amorphous regions coexist. The EDX spectrum (**Figure. 3d**) further confirm the elements of Al, Ti, O and P; meanwhile, as shown in the EDS of the LATP particle (**Figure. 3e1-e4**), the Al, Ti, O and P elements dispersed in the nanosheets homogeneously, which further confirmed that Al^{3+} replaced Ti^{4+} to synthesize LATP electrolyte powder successfully.

Figure. 4a shows the XRD patterns of LATP pellets sintered at 800, 850, 900, 950 and 1000 °C for 6h, respectively. The characteristic peaks of all samples are well corresponding to those of pure LTP (PDF#35-0754), indicating that all samples have NASICON-type structure. The increased sintering temperature is helpful to improve the crystallinity of LATP ceramics. However, the AlPO_4 peaks began to appear at 900 °C, and the intensity of the diffraction peak became more obvious with the increase of sintering temperature. When the temperature rises to 1000 °C, the characteristic peak intensity of LATP is weakened, which indicates that too high sintering temperature seems to be harmful to the crystallinity of LATP. **Figure. 4c-f** shows the surface SEM images of LATP ceramic obtained at different sintering temperatures. It can be seen that with the increase of sintering temperature, the grain size first increases and then tends to be constant. It is reported that AlPO_4 phases are mostly aggregated at the grain boundaries of LATP, which could limit the growth of grains obtained at 900-1000 °C [28]. Additionally, the increased grain size reduced the number of grain boundaries and suppress the occurrence of defects, thus increase the density and electrochemical performance of LATP ceramics [18, 29]. **Figure 4** and **Table 1**

showed the relative densities (ρ_{rd}) of LATP electrolytes at different sintering temperatures. The LATP sample sintered at 900 °C for 6h (LATP-900₆) exhibited the highest relative density (95.6%). A small amount of grain boundary AlPO₄ phase at 900 °C fills the grain boundary gap and improves the density of the ceramics [18, 30]. However, with the sintering temperature further increasing, the ρ_{rd} value decreased to 95.4% and 92.3% for LATP sample sintered at 950 °C and 1000°C, respectively. This performance degradation could be related to the excessive formation of secondary AlPO₄ phases across the grain boundaries, thereby inducing severe microcracks through the lattice shrinkage of AlPO₄, and then leading to a decrease of the relative density [29].

For obtaining LATP ceramic electrolytes with excellent performance, control of sintering time is another crucial parameter. **Figure. 5a** shows the XRD patterns of LATP ceramic sintered at 900 °C for different holding times (3-12h, denoted as LATP-900₃, LATP-900₆, LATP-900₉ and LATP-900₁₂, respectively). It can be seen that with the increase of sintering time, the intensity of LATP diffraction peak first increases and then decreases, accompanied by the enhanced AlPO₄ impurity peaks, indicating that long-term sintering will also cause the appearance of impurities, which is similar to the situation observed with the increase of sintering temperature. **Figure. 5b-e** shows the surface SEM images of LATP ceramic obtained at different sintering times. No obvious grain changes could be found with the increase of sintering time, but the LATP-900₆ sample has the highest relative density (95.6 %, as shown in **Figure 5f** and **Table 1**). It is also proved that reasonable sintering temperature and holding time are important parameters for increasing the density of LATP ceramics.

The impedance spectra of the LATP ceramics obtained at different sintering temperature was displayed in **Figure. 6a**. All plots of samples are consisted two semicircles at the high and moderate frequencies, corresponding respectively to the grain boundary conduction and interfacial conduction [31]. The straight line in the low frequency range corresponds to the blocking electrodes, i.e., Ag, on both sides of LATP pellets, which are typical features of ionic conductive ceramics [32, 33]. A steeper slope in the low frequency region and a smallest semicircle diameter in the high and moderate frequencies region could be found for LATP-900₆, reflecting reduced ionic transfer resistance of the as-obtained samples. Generally, the ionic conductivity can be calculated from bulk resistance (R_b) and total resistance (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 LATP ceramic electrolyte, respectively. Through data fitting and calculation, the total ionic conductivity (σ_t) and bulk ionic conductivity (σ_b) of the LATP samples increased at first, and then decreased with the increase of sintering temperature (**Figure 6b** and **Table 1**). Meanwhile, compared with the impedance spectra of the samples at different sintering time (**Figure 6c**), LATP-900₆ sample exhibit a maximum σ_t value of 2.19×10^{-4} S/cm with a relatively high σ_b value (1.54×10^{-3} S/cm), which is much higher than that of other samples. This result could be attributed to the increased relative density shown in **Figure. 4** and **5**. The decreased σ_t value of the samples at high sintering temperature or long sintering time could be associated with the decreased relative density. In addition, as an impurity with extremely low ionic conductivity, AlPO₄ will hinder the grain boundary lithium ion transmission process and thus

reduce the grain boundary ionic conductivity ^[18, 30]. For a clear illustration, **Figure 6d** displays a typical Nyquist diagram of the LATP-900₆ impedance spectrum, and derives the corresponding circuit elements by fitting the experimental data points to the circuit shown in the inset. Among them, R_b represents the bulk resistance; the semicircle in the high-frequency range represents grain boundary resistance (R_{gb}); the semicircle at low frequency represents interfacial resistance (R_{int}) of LATP; and W_o is the Warburg diffusion contribution. CPE_{gb} and CEP_{int} are their associated capacitances ^[19, 31, 34].

The temperature dependence of impedance was measured to get the activation energy (E_a) of LATP-900₆ (**Figure. 7a**) in the test temperature range from 25 °C to 80 °C. Furthermore, the relationship between the E_a and σ_t of the LATP-900₆ pellets was calculated from the Equation (1) ^[18]:

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

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 LATP-900₆ is 0.32 eV. This result is slightly lower than that of other reports (**Table 2**), indicating the higher Li-ion mobility of LATP-900₆ sample, which is beneficial to the high performance of solid electrolyte in a wide temperature range ^[35]. **Table 2** summarizes the ion conductivities and activation energy of LATP electrolyte prepared via different methods ^[8, 9, 11-14, 36-39]. It is clear that co-precipitation synthesis of LATP-900₆ could deliver an ion conductivity of 2.19×10^{-4} S/cm at 25°C, which is comparable to that reported by many other groups, indicating the LATP-900₆ could prove a most advantageous in terms of electrochemical performance.

Conclusion

In summary, NASICON-type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) ceramic electrolytes were successfully fabricated using co-precipitation method toward high safety hybrid solid-state Li-batteries. The phase transition and microstructure of LATP precursor were analyzed by TG-DSC, XRD, SEM and HRTEM. The results showed that the pure LATP phase could be obtained at 800 °C, and the crystal structure was surrounded by amorphous regions. The LATP-900₆ electrolyte shows the highest relative density the relative density (95.6%), thereby enabling the electrolytes exhibited a high ionic conductivity of 2.19×10^{-4} S/cm at 25°C with a low activation energy of 0.32 eV. It is anticipated that the co-precipitation synthesis is an effective way to improve the electrochemical properties of ceramic electrolyte, such as ionic conductivity and compatibility with electrode, which will promote the application of solid-state electrolytes in solid-state batteries.

Declarations

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Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Tables

Table 1

The value of bulk conductivity (σ_b), total conductivity (σ_t) measured at 25°C, and relative density (ρ_{rd}) for $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) ceramic electrolyte.

Samples	800 °C	850 °C	900 °C				950 °C	1000 °C
			3 h	6 h	9 h	12 h		
Bulk conductivity (σ_b), mS/cm	1.25	1.33	1.13	1.54	1.33	1.22	1.31	1.18
Total conductivity (σ_t), mS/cm	0.119	0.159	0.133	0.219	0.156	0.067	0.183	0.08
Relative density (ρ_{rd}), % *	91.3	92.8	91.8	95.6	94.4	92.3	95.4	92.3

* Theoretical density: 2.93 g·cm⁻³

Table 2

Ionic conductivities of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) reported in literatures at 25 °C.

Methods	Sintering temperature	Relative density (%)	σ (S/cm)	Activation Energy E_a (eV)	Reference
Melt-quenching method	/	/	1.67×10^{-6} (30 °C)	0.24	[11]
Molten-flux method	800	97.3	7.02×10^{-4}	0.29	[36]
Rapid thermal annealing	750	/	2.7×10^{-6}	0.431	[8]
Mechanical Activation	900	/	6.2×10^{-5}	/	[37]
Microwave-assisted reactive sintering	850	88	3.15×10^{-4}	0.53	[38]
Modified pechini process	900	96	6.0×10^{-4}	0.31	[9]
Spray drying method	900	/	6.22×10^{-4}	/	[39]
Solid state method	/	91.8	5.06×10^{-7} (30 °C)	0.32	[13]
Solution method	800	92.5	1.21×10^{-3}	0.26	[14]
Sol-gel route	1000	86~90	$(3-4) \times 10^{-4}$	0.21	[12]
Co-precipitation method	900	95.6	2.19×10^{-4}	0.32	Present work

Figures

Figure 1

(a) Schematic preparation of LATP using a co-precipitation. (b) TG-DSC curves of the LATP precursors in the temperature range between 30°C and 1000°C with a heating rate of $10^\circ\text{C}/\text{min}$. (c) XRD patterns of particles calcined at 500 - 1000°C for 6 h. (d) Size distribution and (e) SEM image of LATP particles calcined at 800°C .

Figure 2

FTIR spectra of powders obtained at different preheating temperatures.

Figure 3

Morphologies, microstructures and element ratio of the LATP particles synthesized by a co-precipitation: (a) TEM, (b, c) HRTEM images, Inset of (b): Electronic diffraction pattern of a selected area, (d) EDX spectrum and (e) Elemental mappings for Al, Ti, P and O elements.

Figure 4

(a) XRD patterns and SEM micrographs of LATP samples sintered at (b) 800°C, (c) 850°C, (d) 900°C, (e) 950°C and (f) 1000°C for 6h.

Figure 5

(a) XRD patterns and SEM micrographs of LATP samples sintered at 900°C for (b) 3h, (c) 6h, (d) 9h and (e) 12h. (f) Detailed information on the response of the relative density (prd) as a function of sintering

time.

Figure 6

EIS measurements of the LATP samples. (a) Room-temperature impedance spectra and (b) Total and bulk conductivity of LATP sample as a function of different sintering temperature. (c) Room-temperature impedance spectra of LATP sample sintered at 900 $^{\circ}\text{C}$ with different sintering time. (d) A typical comparison between measured data and fitting line (inset: equivalent circuit) for the LATP-9006 ceramic.

Figure 7

(a) Temperature dependent impedance plots and (b) Arrhenius plot for LATP-9006 electrolyte ceramic sample.