



RESEARCH ARTICLE

EFFECT OF PHASE ABUNDANCE AND GRAIN SIZE ON IONIC CONDUCTIVITY OF
SOLID STATE LATPELECTROLYTE

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ABSTRACT

$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) electrolyte was prepared within the temperature range of 700-1050 °C. The structure characteristics (phase abundance and grain size) were investigated by X-ray diffraction analysis using MAUD program. The electrical properties (electronic and ionic conductivity) were measured by impedance spectroscopy using equivalent circuit based on brick-layer model to fit the data (Nyquist plot). The maximum LATP content of 95% was obtained at a preparation temperature of 1000°C. However, the ionic conductivity of the electrolyte showed a maximum value of $6.6 \times 10^{-4} \text{ S cm}^{-1}$ at a temperature of 950°C where the LATP phase has high concentration of 85% as well as the largest grain size of 750 nm. Thus, structure/properties correlation proves that the ionic conductivity of the electrolyte is affected by both the abundance of LATP phase as well as its grain size.

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INTRODUCTION

With the development of the micro-electronic industry, the micro-power sources are more and more strongly demanded (Roundy *et al.*, 2004; Albano *et al.*, 2007). All solid state lithium batteries are the most powerful candidate in many applications (Eftekhari, 2004; Nagasubramanian and Doughty, 2004) due to its excellent advantages, such as high specific energy, long cycle life, good safe performance and environmental friendliness (Bates *et al.*, 1995; Dudney and Neudecker, 1999). In fact, battery performance strongly depends on that of the electrolyte. One of the key materials for this device is the ion conductor materials, which act as a solid electrolyte (Thangadurai and Weppner, 2006) with high ionic conductivity on one hand and on the other with negligible electronic conductivity. Lithium-ion conducting electrolytes used for all-solid-state rechargeable lithium batteries should provide some required properties such as high ionic conductivity, electrochemical and thermal stability, good performance at low and high temperatures, environmentally benign, non-hygroscopic, and low cost and ease of preparation. Lithium Titanium Phosphate, $\text{LiTi}_2(\text{PO}_4)_3$, which is based upon

the NASICON framework with the space group of R-3c, has been studied as a lithium ion-conductive solid electrolyte. This is because of its high stability structure of open framework with holes that make ions to migrate, its high chemical and thermal stability, good mechanical strength, low and anisotropic thermal expansion and easy chemical substitutions (Padma Kumar and Yashonath, 2006).

However, its conductivity is not high enough for practical applications. Aono *et al.* (1989) has studied the conductivity of the doped Lithium Titanium Phosphate, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (M = Al, Sc, Y and La) and reported that Al-doping is effective for the enhancement of its Li-ion conduction. Since then, much attention has been paid for its possible use in solid-state lithium-ion batteries (Kunshina *et al.*, 2013; Andreev *et al.*, 2013; Duluard *et al.*, 2013; Ming Wu *et al.*, 2011). This work aims at the preparation and investigation of Lithium Aluminium Titanium Phosphate, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), as ionic conductor electrolyte for all-solid-state rechargeable Li-batteries. X-ray diffraction and impedance spectroscopy will be used for the study of the structural (phase abundant and grain size) and electrical (ionic conductivity) properties. Structure /properties correlation will be considered.

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MATERIALS AND METHODS

Experimental work

LATP Preparation

The flow chart of the LATP sintered pellets preparation is depicted in Fig. 1. Stoichiometric amounts of $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O} + \text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O} + \text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$. The $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was successively dripped into the mixture under constant stirring to form LATP precursor solution of 0.8 mol/L. Then several drops of deionized water was added into the solution followed by a drying at 140°C for 4 h to form LATP gel. The gel was calcined at different temperatures in the range of $700\text{--}1050^\circ\text{C}$ for 2 h and then grounded by mortar. The powders were mixed with a suitable amount of 3% polyvinyl alcohol solution as binder. The temperature of binder preparation was in the range of $80\text{--}90^\circ\text{C}$, under stirring and covered in order to dissolve but not change to another compound. The ingot was pressed at a pressure of 100 MPa into pellets of ~ 1.3 cm diameter and ~ 0.3 cm thickness. Each pressed pellet was sintering at the same temperature of calcination for 2 h to obtain LATP sintered pellets.

Structure investigation

Structural characterization of the LATP powder was performed by Panalytical Empyrean X-Ray diffractometer with Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.540 \text{ \AA}$) at 45 kV and 30 mA. Step scanning with step size 2θ of 0.1° and counting time of 3 sec were used in the 2θ -range of $10\text{--}60^\circ$. Rietveld refinement using MAUD program was applied for quantitative phase analysis and the crystallite size determination.

Electrical measurement

Ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) in the frequency range from 0.1 Hz to 1 MHz. The EIS measurements were done using the potentiostat at SP-150 that is controlled by EC-Lab software (Biological Science Instruments). An equivalent circuit (Fig. 2) based on the brick layer (Fleig, 2000) was used to fit the data (Nyquist plot) and estimate both the electronic as well as the ionic conductivity.

RESULTS AND DISCUSSION

Structural investigation

The diffractograms of LATP samples prepared at different temperature are shown in Fig. 3. Two phases are identified: LATP and TiP_2O_7 . At 700°C the sample is mainly TiP_2O_7 and as the preparation temperature ascended, diffraction peak intensity of this phase decreases while that of LATP increases. At 1000°C mainly single phase of LATP is present. As the temperature ascends higher than 1000°C , the LATP phase composes and its peak intensity decreases while that of TiP_2O_7 increases. The quantitative phase data are estimated from the refinement of X-ray diffraction patterns and is depicted in Fig. 4 and given in Table 1. It can be clearly shown that the maximum concentration of LATP (95%) is obtained at 1000°C .

Table 1. Phase contents at different preparation temperatures

Temperature ($^\circ\text{C}$)	Phase (wt. %)	
	LATP	TiP_2O_7
700	3	97
800	22	78
900	60	40
950	85	15
1000	95	5
1050	85	15

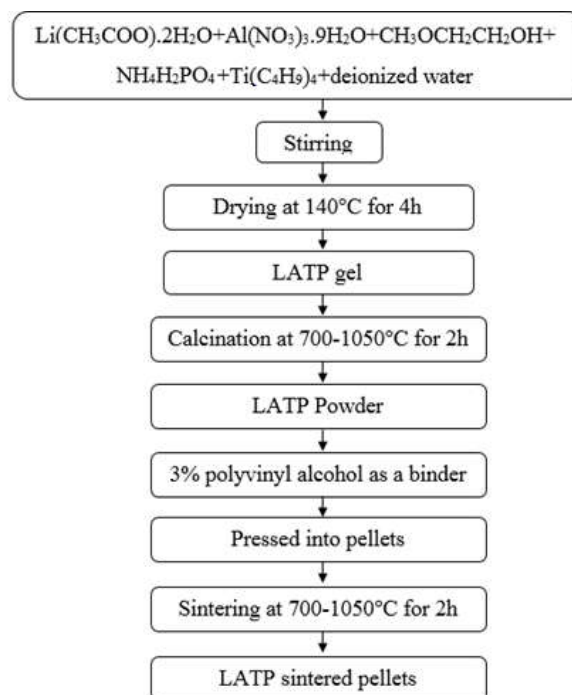


Fig. 1. Flow chart of LATP preparation

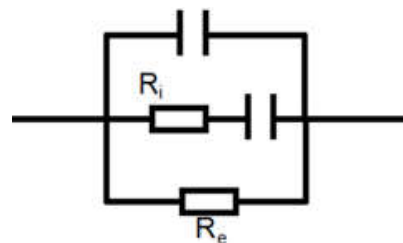


Fig. 2. Equivalent circuit for Nyquist curve including the contribution of ionic and electronic conduction

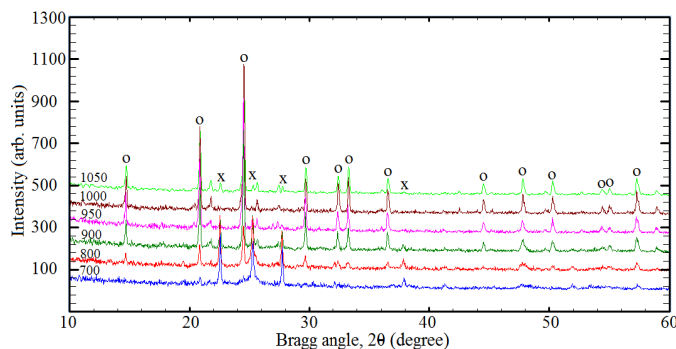


Fig. 3. X-ray diffraction diffractograms of samples prepared at different temperatures (o: LATP, x: TiP_2O_7)

Using profile analysis (MAUD program), the crystallite size is calculated and depicted in Fig.5. The crystallite size of LATP increases to a maximum value at temperature of 950°C, then decreases as the temperature ascends to 1050°C. First, LATP phase is continually formed and its grain grows up to 950°C. However, at higher temperatures, LATP phase starts to decompose and the formed secondary phase precipitates on the grain boundaries. This hinders the normal grain growth and results in the observed decrease of the formed grains.

Electrical measurement

The relation between the real and imaginary impedance (Nyquist plot) of the LATP electrolyte prepared at different temperatures is illustrated in Fig. 6. Fitting of these curves using the equivalent circuit in Fig. 3, both the electronic and the ionic conductivities are estimated. The data shows that the electronic conductivities is very low $\sim 10^{-18} \text{ S cm}^{-1}$.

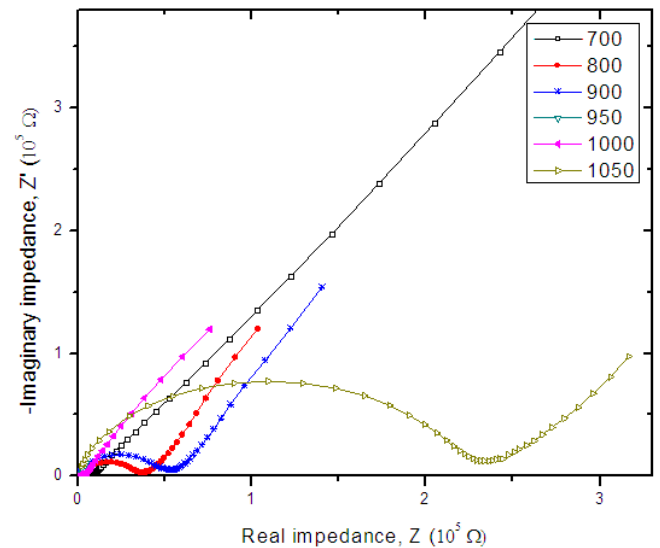


Fig. 6. Nyquist plot of LATP samples prepared at different temperatures

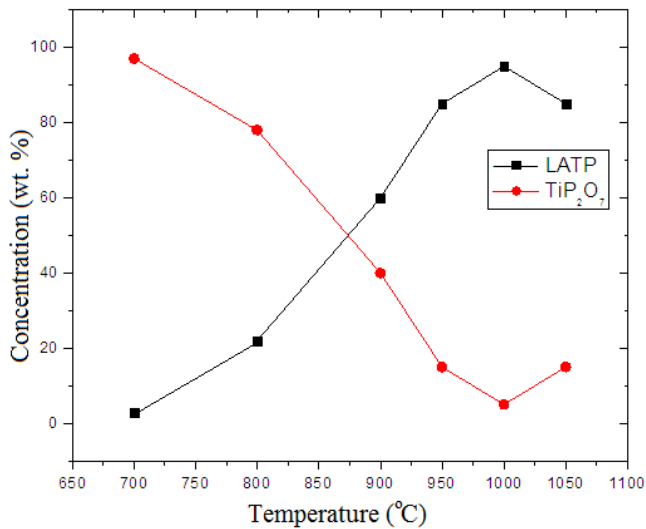


Fig. 4. Content of LATP and TiP_2O_7 phases at different preparation temperatures

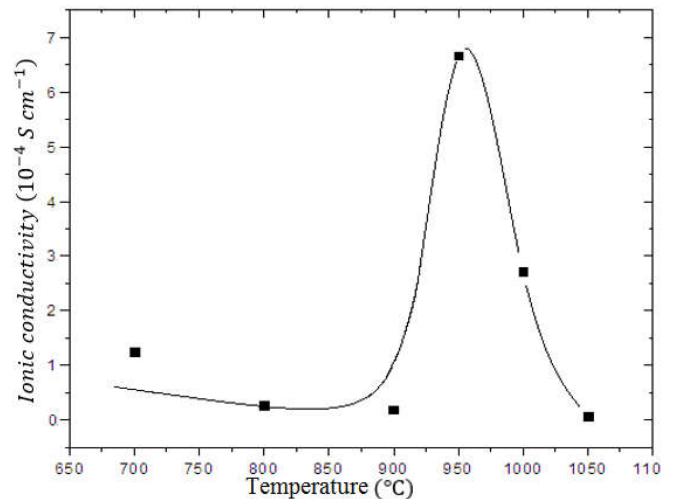


Fig. 7. Variation of ionic conductivities of LATP vs preparation temperatures

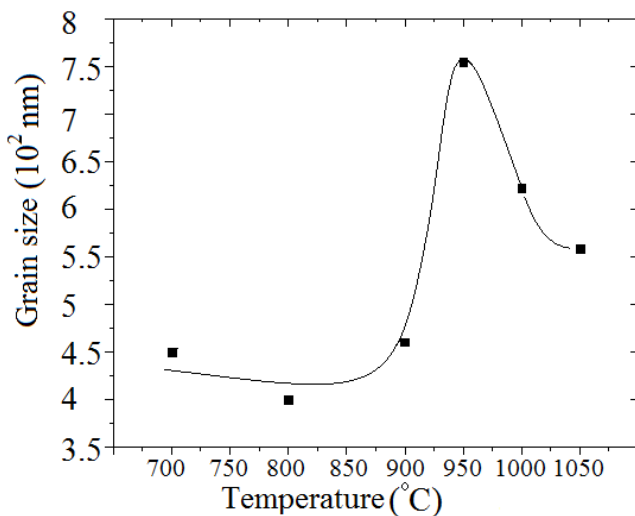


Fig. 5. Variation of grain size vs preparation temperatures

Variation of the ionic conductivity with the sintering temperature is depicted in Fig. 7. Concerning the ionic conductivities, low values were observed up to 900°C with almost no change. As the sintering temperature ascends above 900°C a pronounced increase of ionic conductivity is observed with a maximum at 950°C followed by a marked decrease as the temperature increases. The behavior of the results can be explained and discussed if the combined effect of both the phase abundance as well as the grain size is considered. LATP is a super-ionic conductor, so, as its content in a mixture increases, the ionic conductivity is increased. On the other hand, the presence of a second phase and/or impurity segregation at the grain boundary results in restricting ion migration (blocking effect) (Guo *et al.*, 2003), i.e., a decrease of the conductivity. So that, the ionic conductivity of LATP itself increases as its grain size increases. Thus, sample prepared at 950°C of high LATP concentration (85%) and, at the same time, its grain size (750 nm) is the largest one, shows the maximum ionic conductivity.

Conclusion

As the calcination temperature ascends, the concentration of LATP increases up to a maximum value at certain temperature, then further increase of temperature decomposed the formed phase and traces of a second one (TiP_2O_7) is formed. The maximum concentration of the LATP (95 %) is obtained at preparation temperature of 1000°C . Preparation temperature has also a considerable effect on the size of the formed grains. Grains grow up to maximum value at certain temperature then the precipitation of the formed second phase on the grain boundary hinders the growth resulting in a decrease of the grain size. The maximum value of the ionic conductivities is achieved at a temperature where the electrolyte has high LATP concentration and at the same time the largest grain size. Thus, convolution of both the concentration of the super ionic-conductive LATP phase with its grain size control the ionic conductivity of the electrolyte.

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