Synthesis and Characterizations of Lithium Aluminum Titanium Phosphate (Li1+xAlxTi2-x(PO4)3) Solid Electrolytes for All-Solid-State Li-ion Batteries

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Synthesis and Characterizations of Lithium Aluminum Titanium Phosphate $(\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3)$ Solid Electrolytes for All-Solid-State Li-ion Batteries

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

By

JIANPING YANG

B.E., Dalian Jiaotong University, 2010

2017
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jianping Yang ENTITLED Synthesis and Characterizations of Lithium Aluminum Titanium Phosphate (Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$) Solid Electrolytes for All-Solid-State Li-ion Batteries BE ACCEPTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENT FOR DEGREE OF Master of Science in Materials Science and Engineering.

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Abstract

Yang, Jianping. M.S.M.S.E., Department of Mechanical and Materials Engineering, Wright State University, 2017. Synthesis and Characterizations of Lithium Aluminum Titanium Phosphate (Li_{1+x}Al_xTi_{2-x}(PO_4)_3) Solid Electrolytes for All-Solid-State Li-ion Batteries.

New-generation low-emission transportation systems demand high-performance lithium-ion (Li-ion) batteries with high safety insurance at broad operable temperatures. Highly conductive solid electrolyte is one of the key components for such applications. The objective of this thesis is to synthesize and characterize aluminum doped lithium titanium phosphate, i.e. Li_{1+x}Al_xTi_{2-x}(PO_4)_3 (LATP), one of the solid-state electrolytes for potential applications to all solid-state lithium-ion batteries. In this research, sol-gel method and one-step solid-state reaction approaches were explored and critical processes were optimized towards maximizing lithium ion conductivities at room temperature. The impacts of the processing conditions on the structures, morphologies, compositions of the LATP products, and lithium ion conduction were presented. Particle growth kinetics and lithium ion conduction mechanism were briefly discussed. The highest conductivities of LATPs achieved via the sol-gel and solid-state synthesis are 1.24E-04 S/cm and 1.86E-04 S/cm, respectively, exhibiting the feasibilities of applying them to all-solid-state Li-ion batteries.
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1 Introduction

Lithium ion batteries are attractive for their high-energy density, good Coulombic efficiency and long charge/discharge cycle life. A single cell typically operates in the range of 2.5V to 4.2V, which is three times higher than traditional alkaline batteries. These merits render lithium ion batteries the choice of power supply for portable electronics with the order of billions of units every year (see Figure.1-1), since lithium-ion batteries were developed and commercialized in 1990s [1]. Lithium ion batteries have triggered the growth of market of portable devices or mobile tools. Lithium-ion batteries also have great potential for packaging into large modules serving in hybrid and electric vehicles, although there are still many technical challenges to be resolved, such as safety, costs, operational temperature, restricted by electrode and electrolyte materials.

![Figure 1-1. Evolution of lithium-ion batteries sale in consumer electronics and HEV](image)

**Figure 1-1. Evolution of lithium-ion batteries sale in consumer electronics and HEV**
The major advantages and disadvantages of lithium-ion batteries, compared with the other types of batteries, are summarized in Table 1-1 [2, 3]. The high specific energy (150 Wh/kg) and energy density (400 Wh/L) of commercial products makes them attractive for weight or volume sensitive applications. Li-ion batteries offer a low self-discharge rate (2% to 8% per month), long cycle life (greater than 1000 cycles) and a broad temperature range of operation. A wide array of Li-ion batteries in sizes and shapes is now available from a variety of manufacturers. Li-ion batteries can offer high rate capability. Discharge at 5°C in the continuous mode or 25°C in the pulse mode has been demonstrated.

*Table 1-1. Advantages and Disadvantages of Lithium ion batteries*

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealed cells; no maintenance required</td>
<td>Moderate initial cost</td>
</tr>
<tr>
<td>Long cycle life</td>
<td>Degrades at high temperatures</td>
</tr>
<tr>
<td>Broad temperature ranges of operation</td>
<td>Need for protective circuitry</td>
</tr>
<tr>
<td>Long shelf life</td>
<td>Capacity loss or thermal runaway when overcharged</td>
</tr>
<tr>
<td>Low self-discharge rate</td>
<td>Venting and possible thermal runaway when crushed</td>
</tr>
<tr>
<td>Rapid charge capability</td>
<td>Cylindrical designs typically offer lower power</td>
</tr>
<tr>
<td>High rate and high-power discharge capability</td>
<td>density</td>
</tr>
<tr>
<td>High columbic and energy efficiency</td>
<td></td>
</tr>
<tr>
<td>High specific energy and energy density</td>
<td></td>
</tr>
<tr>
<td>No memory effect</td>
<td></td>
</tr>
</tbody>
</table>

This chapter briefly reviews the basic principle of lithium-ion batteries, electrode materials, and also all kinds of electrolytes used in lithium-ion batteries with emphasis on the solid-state electrolytes which are believed to be crucially important in the replacement of liquid electrolytes for flexible and or miniature electronics.

1.1  **Principle of lithium-ion battery**

Li-ion batteries operate, during discharge/charge processes, via reversibly incorporation or intercalation into and removal of lithium ions from electrode host without causing a
significant structural change. The positive electrode, i.e. cathode, materials in a Li- ion cell are usually lithium transition metal oxides (Li$_x$M$_y$O$_z$, M=Co, Ni, Mn etc)) with either a layered structure like LiCoO$_2$ or tunneled structure like LiMn$_2$O$_4$. Recently, olivine-structured LiFePO$_4$ is the dominant cathode in many Li-ion batteries. The negative electrode, i.e. anode, materials varies from amorphous or crystalline structured carbon, metals, or metal oxides [4].

Figure 1-2. Schematic of lithium ion battery electrochemistry during discharge

Figure 1-2 illustrates a lithium -ion cell made up of graphitic carbon anode, layer-structured LiMO$_2$ separated by a separator soaked with electrolyte. When the lithium-ion cell is discharged, the anode material is oxidized and the cathode material is reduced. In general, the oxidation is the loss of electrons, and the reduction is the gain of electrons. In the process, the lithium ions are de- intercalated from the anode material and intercalated into cathode materials. The reactions at each electrode and in the cell, are shown below [5]:
Cathode/Positive electrode: \( \text{LiMO}_2 \rightleftharpoons \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \)

Anode/Negative electrode: \( \text{C} + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_x\text{C} \)

Overall: \( \text{LiMO}_2 + \text{C} \rightleftharpoons \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2 \)

1.2 Positive/Cathode electrode materials

Cathode materials must have a high capacity for handling Li-ions, i.e., the structure should be able to deliver and uptake a large number of lithium ions. During the charge and discharge processes, the materials must reversibly exchange the lithium-ion with less structural change to permit high Columbic efficiency and long cycle life. The lithium exchange reaction must occur at high potential relative to lithium to achieve high voltage and high energy density. The materials must have high electronic conductivity and lithium ion mobility to make sure the high charge/discharge rate. Also, the electrode must neither be soluble in nor react with electrolyte. Ideally, the low-cost process and materials are necessary. These factors guide the selection and development of cathode materials.

Up to date, several materials have been investigated intensively, which are \( \text{LiCoO}_2, \text{LiNiO}_2, \text{LiMn}_2\text{O}_4, \) and \( \text{LiFePO}_4 \) [6]. Various derivatives based these through doping with various elements at different levels have been reported. Each type of the four materials has its own distinctive merits and drawbacks, which are summarized in Table 1-2.
### Table 1-2. Advantages & disadvantages of a few representative cathode materials

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Merits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>Flat discharge curve profile; High charge/discharge efficiency at the first cycle; Passable discharge capacity on the weight basis; Stability at significantly high temperature</td>
<td>High cost; Lack of cobalt resources; degradation or failure when overcharged</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>Slightly sloping discharge curve profile and rather lower operating voltage than LiCoO$_2$; Lower charge/discharge efficiency at the first cycle than LiCoO$_2$; Higher discharge capacity than LiCoO$_2$; Lower cost and higher energy density</td>
<td>Instability at higher temperatures; Poor cyclability; less ordered</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>Flat discharge curve profile; Lower charge/discharge efficiency; Highest stability; Low cost; Abundance of manganese resources</td>
<td>Poor cyclability; A little higher operating voltage than LiCoO$_2$; low capacity</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>Can be used at high current density; Much better cyclability; lower operating voltage; flat discharge curve profile; discharge efficiency is a little bit higher than the other cathode materials; poor conductivity of pure LiFePO$_4$</td>
<td>Narrow voltage range; low capacity at low current density; relative low discharge capacity.</td>
</tr>
</tbody>
</table>

### 1.3 Negative/anode electrode materials

In the 1970s and early 1980s, lithium was used as the anode for its high specific capacity [7]. Although some impressive lithium batteries were developed and commercialized, lithium anode has a vital safety issue due to the morphological change of lithium upon cycling. Carbon electrode emerged in the replacement of lithium metal because of its stable morphology over its discharge/charge cycling. There are many types of carbon available for the commercial purposes. The structures of carbon have significant influence on their electrochemical properties, such as lithium intercalation capacity and potential.

The basic type of carbon material is a planar sheet of carbon atoms arranged in a hexagonal array. In graphite, these sheets are stacked in ABABAB type resulting in hexagonal or 2H graphite, or in ABCABC style resulting in rhombohedral or 3R graphite. Various types of
carbon can be obtained and modified through pyrolysis of different precursor materials in liquid, vapor, or solid phase. For the implements, the carbon anode materials should supply high specific capacity without high irreversible capacity. In general, the BET surface area should be relatively small, but the particle size should be less than about 30 \( \mu \)m to facilitate lithium rapid diffusion. Table 1-3 lists the performances and properties of several carbon anode materials reported in lithium-ion batteries [8-10].

Table 1-3. Properties and performances for a few carbon anodes

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Type</th>
<th>Specific capacity (mAh/g)</th>
<th>Irreversible capacity (mAh/g)</th>
<th>Particle size (( \mu )m)</th>
<th>Surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS44</td>
<td>Synthetic graphite</td>
<td>345</td>
<td>45</td>
<td>44</td>
<td>10</td>
</tr>
<tr>
<td>MCMB 52-28</td>
<td>Graphite sphere</td>
<td>305</td>
<td>19</td>
<td>26</td>
<td>0.86</td>
</tr>
<tr>
<td>Sterling 2700</td>
<td>Carbon black</td>
<td>200</td>
<td>152</td>
<td>0.075</td>
<td>30</td>
</tr>
<tr>
<td>XP30</td>
<td>Petroleum coke</td>
<td>220</td>
<td>55</td>
<td>45</td>
<td>N/A</td>
</tr>
<tr>
<td>Repsol LQNC</td>
<td>Needle coke</td>
<td>234</td>
<td>104</td>
<td>45</td>
<td>6.7</td>
</tr>
<tr>
<td>Grasker</td>
<td>Carbon fiber</td>
<td>363</td>
<td>35</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>Sugar carbon</td>
<td>Hard carbon</td>
<td>575</td>
<td>215</td>
<td>N/A</td>
<td>40</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-wall nanotubes</td>
<td>980</td>
<td>750</td>
<td>0.4</td>
<td>500</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-wall nanotubes</td>
<td>1500</td>
<td>1300</td>
<td>0.4</td>
<td>915</td>
</tr>
<tr>
<td>Graphene</td>
<td>Nanosheet</td>
<td>744</td>
<td>540</td>
<td>N/A</td>
<td>2630</td>
</tr>
</tbody>
</table>

1.4 Electrolytes in lithium-ion batteries

There are three types of electrolyte which have been used in lithium ion batteries: liquid electrolytes, polymer electrolytes, and ceramic electrolytes. Each of them has their unique properties and characteristics.

1.4.1 Liquid electrolytes

Liquid electrolytes are solutions of a lithium salt in organic solvents. There are plenty of lithium salts used in different types of lithium-ion batteries (see Table. 1-4).
**Table 1-4. Lithium salts commonly used in electrolytes for lithium ion batteries**

<table>
<thead>
<tr>
<th>Common name</th>
<th>Formula</th>
<th>g/mol</th>
<th>Impurities</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium hexafluorophosphate</td>
<td>LiPF$_6$</td>
<td>151.9</td>
<td>H$_2$O (15ppm)</td>
<td>Most commonly used</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HF (100ppm)</td>
<td></td>
</tr>
<tr>
<td>Lithium tetrafluoroborate</td>
<td>LiBF$_4$</td>
<td>93.74</td>
<td>H$_2$O (15ppm)</td>
<td>Less hygroscopic than LiPF$_6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HF (75ppm)</td>
<td></td>
</tr>
<tr>
<td>Lithium perchlorate</td>
<td>LiClO$_4$</td>
<td>106.39</td>
<td>H$_2$O (15ppm)</td>
<td>When dry, less stable than alternatives</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HF (75ppm)</td>
<td></td>
</tr>
<tr>
<td>Lithium hexafluoroarsenate</td>
<td>LiAsF$_6$</td>
<td>195.85</td>
<td>H$_2$O (75ppm)</td>
<td>Contains arsenic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HF (15ppm)</td>
<td></td>
</tr>
<tr>
<td>Lithium triflate</td>
<td>LiSO$_3$CF$_3$ (LiTF)</td>
<td>156.01</td>
<td>H$_2$O (100ppm)</td>
<td>Al corrosion above 2.8 V, stable to water</td>
</tr>
<tr>
<td>Lithium bisperfluoroethane-sulfonamide</td>
<td>LiN(SO$_2$C$_2$F$_3$)$_2$ (LiBETI)</td>
<td>387</td>
<td>N/A</td>
<td>No Al corrosion below 4.4 V, stable to water [11]</td>
</tr>
<tr>
<td>Lithium bis-trifluoromethane-sulfonimide</td>
<td>Li(CF$_3$SO$_2$)$_2$N (LiTFSI)</td>
<td>287.09</td>
<td>N/A</td>
<td>Less toxic and more stable, high dissociation and conductivity [12]</td>
</tr>
<tr>
<td>Lithium bis-oxalate borate</td>
<td>LiB(C$_2$O$_4$)$_2$ (LiBOB)</td>
<td>193.79</td>
<td>HBO$_2$, HCO$_3$Li, H$_2$O</td>
<td>Charge-discharge capacity [13]</td>
</tr>
</tbody>
</table>

The most commonly used lithium salt in liquid electrolytes is LiPF$_6$ whose solution offers high ionic conductivities (> $10^{-3}$ S/cm), high lithium ion transference number (~0.35), and acceptable safety properties. However, LiPF$_6$ is costly and hygroscopic. It generates hydrofluoric acid (HF) upon reaction with water, thus must be handled in a dry environment. Organic lithium salts like LiTFSI and LiBETI have recently been received significant attention because of several unique characteristics, including high conductivities, stability to trace of water, easily dried, and less corrosive to aluminum current collector.
Table 1-5. Characteristics of organic solvents commonly used in electrolytes

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>BP (°C)</th>
<th>MP (°C)</th>
<th>Density (g/ml)</th>
<th>Viscosity (cP)</th>
<th>Dielectric Cons.</th>
<th>Donor #</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>248</td>
<td>39</td>
<td>1.41</td>
<td>1.86</td>
<td>89.6</td>
<td>16.4</td>
<td>88.1</td>
</tr>
<tr>
<td>PC</td>
<td>242</td>
<td>-48</td>
<td>1.21</td>
<td>2.5</td>
<td>64.4</td>
<td>15.0</td>
<td>102.1</td>
</tr>
<tr>
<td>DMC</td>
<td>90</td>
<td>4</td>
<td>1.07</td>
<td>0.59</td>
<td>3.12</td>
<td>8.7¹⁰</td>
<td>90.1</td>
</tr>
<tr>
<td>EMC</td>
<td>109</td>
<td>-55</td>
<td>1.0</td>
<td>0.65</td>
<td>2.9</td>
<td>6.5¹⁰</td>
<td>104.1</td>
</tr>
<tr>
<td>DEC</td>
<td>126</td>
<td>-43</td>
<td>0.97</td>
<td>0.75</td>
<td>2.82</td>
<td>8.7¹⁰</td>
<td>118.1</td>
</tr>
<tr>
<td>1,2-DME</td>
<td>84</td>
<td>-58</td>
<td>0.87</td>
<td>0.455</td>
<td>7.2</td>
<td>-</td>
<td>90.1</td>
</tr>
<tr>
<td>AN</td>
<td>81</td>
<td>-46</td>
<td>0.78</td>
<td>0.34</td>
<td>38.8</td>
<td>14.0</td>
<td>41.0</td>
</tr>
<tr>
<td>THF</td>
<td>66</td>
<td>-108</td>
<td>0.89</td>
<td>0.48</td>
<td>7.75</td>
<td>-</td>
<td>72.1</td>
</tr>
<tr>
<td>γ-BL</td>
<td>206</td>
<td>-43</td>
<td>1.13</td>
<td>1.75</td>
<td>39</td>
<td>-</td>
<td>86.1</td>
</tr>
</tbody>
</table>

(EC = ethylene carbonate, PC = propylene carbonate, DMC = dimethyl carbonate, EMC = ethyl methyl carbonate, DEC = diethyl carbonate, DME = dimethylether, AN = acetonitrile, THF = tetrahydrofuran, γ-BL = γ- butyrolactone).

Electrolytes are formulated with a wide variety of solvents, from carbonates and ethers, to acetates. Industries have their focal interest on the carbonates because they offer excellent stability, good safety properties and compatibility with electrode materials. The neat carbonate solvents typically have dielectric constant > 3 and ability of dissolving lithium salts to high concentration [14]. Table. 1-5 lists properties of several common solvents.

In most cases, these organic solvents are not used individually in the lithium ion electrolytes. Mixed solvents provide higher conductivity, a broader temperature range, and better performances in lithium-ion batteries. For instance, EC has desirable properties when it is used with graphitic negative electrodes, such as low irreversible capacity and low capacity fade. But it is highly viscous and becomes solid at room temperature due to its high freezing point. Other solvents are usually added to EC to lower the freezing point and viscosity in the mixture. Table. 1-6 presents several electrolytes which are available for all lithium-ion applications from consumer electrics to the EV cells [15].
Table 1-6. Conductivity of different amount of LiPF₆ in various solvent mixtures

<table>
<thead>
<tr>
<th>Composition</th>
<th>Electrolyte salt</th>
<th>Density (g/cm³)</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC: EMC 1:1</td>
<td>LiPF₆ 1 M</td>
<td>1.20</td>
<td>9.5</td>
</tr>
<tr>
<td>EC: DMC: EMC 2:2:1</td>
<td>LiPF₆ 1 M</td>
<td>1.21</td>
<td>10.5</td>
</tr>
<tr>
<td>EC: DEC: EMC 1:1:1</td>
<td>LiPF₆ 1 M</td>
<td>1.21</td>
<td>11.0</td>
</tr>
<tr>
<td>EC: PC: DEC 3:3:4</td>
<td>LiPF₆ 1.5 M</td>
<td>1.20</td>
<td>8.5</td>
</tr>
<tr>
<td>EC: DEC 1:1</td>
<td>LiPF₆ 1.5 M</td>
<td>1.21</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Although the conductivities of such mixed liquid electrolyte are satisfactory (~ 10 mS/cm at room temperature), the main limitation is the flammable solvents which may cause safety hazards. For lithium-ion batteries used for hybrid electric vehicle, the size of the batteries is relatively large and hence difficult for rapid heat dissipation. With the developments of lithium ion batteries, the organic liquid electrolyte becomes one of the big obstacles towards the advancement in electric vehicles. Therefore, extensive efforts are directed towards non-flammable electrolytes.

1.4.2 Polymer electrolytes

Advantages of polymer electrolytes include improved safety properties, dimensional stability, and the ability to prevent lithium dendrite formation resulting from their low volatility and high viscosity. Moreover, polymer electrolytes are attractive for flexible battery designs. Polymer electrolytes can be classified into two types, dry polymer electrolytes and gel-polymer electrolytes.

A dry polymer electrolyte is a liquid- and solvent-free material. It is formed by dissolving a lithium salt directly into a relevant high molecular weight polymer. The most commonly used polymer material for lithium battery is poly-ethylene oxide (PEO). PEO is effective with solvating lithium salts such as LiTF, LiTFSI, LiBETI, LiClO₄, and LiBOB [16]. The
conductivities of PEO with the different salts are in a similar range, with the highest conductivities occurring for LiTFSI and the lowest for LiBETI. PEO is stable with lithium metal. PEO electrolytes have been used in batteries with various electrodes including LiMn$_2$O$_4$ and LiFePO$_4$ cathodes, as well as carbon and MoO$_x$ anodes. However, higher conductivities are needed for room temperature applications.

The ionic conduction is believed to occur in the amorphous area of PEO. Accordingly, some of the plasticizers have been added into PEO to increase the conductivities. Plasticizers, such as succinonitrile (SN), polysquarate (PPS) or ethylene carbonate (EC)/propylene carbonate (PC), reduce crystallization of PEO and increase ionic conductivities in it [17].

Another way to improve the PEO conductivities is to add a room temperature ionic liquid (RTIL), such as 1-ethyl-3-methylimidazolium (EMI) or N-methyl-N-butylpyrrolidinium bis (trifluoromethansulfonyl) imide (PYTRA$_{14}$TFSI). These kinds of ionic liquids are used to weaken the interaction between the lithium ions and polymer chains to increase lithium-ion mobility.

The third way to increase the conductivities is to dope with the ceramic nanoparticles, such as alumina and silica. The increase of conductivity is because the ceramic particles will decrease the crystallization of polymer and simultaneously the conduction can occur at polymer- ceramic interfaces. The ceramic particles can also improve the strength of polymer. This is advantageous in designing polymer electrolytes in comparison with the approach of adding of plasticizers or RTILs which is harmful to mechanical performance.

Gel-polymer electrolyte is to form a polymer gel by compounding an organic liquid electrolyte and lithium salt with polymer matrix. Basically, the gel electrolytes have several
advantages over liquid electrolytes, such as, high gravimetric energy density, no electrolyte leakage, excellent safety characteristics and flexibility for cell fabrication.

The most commonly used gel-polymer electrolyte is poly-vinylidene fluoride (PVDF)-based materials [18]. Hexafluoropropylene (HFP) is always added into PVDF to reduce the crystallinity of PVDF. Lithium salt is usually LiPF₆, and carbonate solvents can be EC, PC, DMC, and EMC. In general, the conductivity of PVDF-HFP with EC-PC as solvents is the highest compared with the other solvents, which is around 10⁻² Scm⁻¹. The conductive mechanism of gel polymer electrolyte is similar with liquid electrolyte.

Ceramic particles can be added to improve the pore structure to facilitate transport of lithium in the solvents, such as BaTiO₃ or TiO₂. The conductivities at room temperature with the two additives are 10⁻² Scm⁻¹ and 10⁻³ Scm⁻¹, respectively [19]. The addition of ceramic particles can improve the conductivities; however, the large number of particles would degrade the mechanical properties of batteries.

RTIL was used to replace organic solvents such as EC-PC. There are several ionic liquids, such as Py₂₄TFSI, PP₂₄TFSI, or PYRA₁₂₀₁TFSI added to PVDF-HFP. The conductivities with these ionic liquids are in the similar range of organic solvents.

Additives can also improve the battery operating performance. For example, the organic (biphenyl) or inorganic additives (AlF₃) improved the stability during battery cycling, and the silica fibers increased the electrode capacity. The PVDF-HFP gel-polymer electrolyte can be used with the most of known cathode materials, such as LiCoO₂, LiMn₂O₄, LiFePO₄, and LiNi₀.₈Co₀.₂O₂ [20].
1.4.3 Ceramic electrolytes

For the purposes of improving the lithium ion batteries’ design as well as the safety and durability, ceramic electrolytes have been extensively studied in the past decades. It has many advantages, such as absence of electrolyte leakage, elimination of liquid vaporization problems, improvements of phase transitions at low temperature, ease of the miniaturization, and as well as very suitable for high temperature and aggressive environments. All solid-state lithium-ion batteries have showed excellent storage stability and very long cycle life.

The major technical challenge is that solid electrolytes are not as conductive as liquid electrolytes at room temperature. Ionic conductivities of lithium ion conducting liquid electrolytes are mostly greater than $10^{-2}$ S/cm. But for lithium-based solid electrolytes, the level of ionic conductivities is normally around $10^{-4}$ S/cm [21]. Major efforts have been emphasized on developing solid electrolytes with high ionic conductivity at ambient temperature. The Li$_3$N electrolytes were discovered almost half century ago, its lithium ionic conductivity as high as $10^{-3}$ S/cm at room temperature. However, its low decomposition potential at approximate 0.5V prevents its applications in LIBs. Afterwards, lithium sulfide-based glasses, oxides, and phosphate have gradually emerged.

1.4.3.1 Sulfides

The sulfides compounds were mostly studied at the beginning of ceramic electrolyte developments because of its relative high ionic conductivities, comparable with organic electrolytes used in lithium ion batteries. The sulfides compounds can be crystalline, amorphous, and partially crystalline. The compounds mostly used are Li$_2$S-P$_2$S$_5$ or glass-ceramic. Table. 1-7 lists some representative sulfide electrolytes with their ion conductivity
values at room temperature, reported recently.

**Table 1-7. Typical sulfide electrolytes and their conductivities at room temperature**

<table>
<thead>
<tr>
<th>Sulfide electrolyte</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66Li_2S - 0.33P_2S_5</td>
<td>10(^{-4})</td>
<td>Water quenching [22]</td>
</tr>
<tr>
<td>0.40LiI - 0.36Li_2S - 0.24SiS_2</td>
<td>1.8(\times)10(^{-3})</td>
<td>Liquid N(_2) quenching [23]</td>
</tr>
<tr>
<td>0.01Li_3PO_4-0.63Li_2S-0.36SiS_2</td>
<td>1.5(\times)10(^{-3})</td>
<td>Twin- roller quenching [23]</td>
</tr>
<tr>
<td>0.6Li_2S- 0.4SiS_2</td>
<td>1.5(\times)10(^{-4})</td>
<td>Mechanical milling [24]</td>
</tr>
<tr>
<td>Li(<em>{3.25})Ge(</em>{0.25})P(_{0.75})S(_4)</td>
<td>2.2(\times)10(^{-3})</td>
<td>Solid- state reaction [25]</td>
</tr>
<tr>
<td>70Li_2S- 30P_2S_5</td>
<td>3.2(\times)10(^{-3})</td>
<td>Glass- ceramic [26]</td>
</tr>
</tbody>
</table>

**Table 1-8. Buffer layers added to Li-ion cells between LiCoO_2 cathode and sulfide electrolytes to improve battery performances**

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>Sulfide electrolyte</th>
<th>Current density (mAcm(^{-2}))</th>
<th>Resistance ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_4Ti_5O_12</td>
<td>Li(<em>{3.25})Ge(</em>{0.25})P(_{0.75})S(_4)</td>
<td>10</td>
<td>44</td>
</tr>
<tr>
<td>LiNbO_3</td>
<td>Li(<em>{3.25})Ge(</em>{0.25})P(_{0.75})S(_4)</td>
<td>10</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Li_2O- SiO_2</td>
<td>80Li_2S- 20P_2S_5</td>
<td>6.4</td>
<td>160</td>
</tr>
<tr>
<td>LiTaO_3</td>
<td>Li(<em>{3.25})Ge(</em>{0.25})P(_{0.75})S(_4)</td>
<td>N/ A</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Li_2Ti_2O_5</td>
<td>80Li_2S- 20P_2S_5</td>
<td>6.4</td>
<td>100</td>
</tr>
<tr>
<td>Li_4SiO_4- Li_3PO_4</td>
<td>80Li_2S- 20P_2S_5</td>
<td>6.4</td>
<td>48</td>
</tr>
</tbody>
</table>

Although having the highest ion conductivities, sulfide electrolytes have not been widely utilized in practical products for several reasons. The first problem is environmental and health concern. This kind of electrolyte is quite hygroscopic and unstable in the open air. The sulfides can react with water at a certain temperature generating hydrogen sulfide which is harmful to humans. Humidity control is still challenging in consideration of using them in lithium batteries. Meanwhile, lithium depleted layer can form between positive electrode and sulfide electrolyte leading to the increase of the resistance of the battery. To solve this problem, some oxides have been used as the buffer layer between electrodes and
electrolyte. Table 1-8 shows several oxides used as buffer layer to improve the current density of lithium ion batteries using LiCoO$_2$ as cathode materials [27].

1.4.3.2 Oxides

In the development of the buffer layer to solve the problem occurred in lithium-ion batteries using sulfide-based electrolyte, oxide solid electrolytes emerged. One example of lithium ion conducting oxides is the perovskite structured lithium lanthanum titanate, i.e. (La, Li) TiO$_3$ (Li$_{3x}$La$_{2/3-x}$TiO$_3$, or LLTO) [28]. In LLTO, Ti atoms octahedrally coordinated with oxygen atoms occupy the corner of cube (B-site), and the center of cube (A-site) is occupied by La$^{3+}$, Li$^+$ ion or vacant. LLTOs have the ion conductivities of $10^{-3}$ - $10^{-4}$ S/cm. There are two factors impact the ionic conductivities, which are bottleneck size and site percolation. The bottleneck size is determined by the lattice parameters. The large lattice parameter, and hence the enlarged bottleneck size, will increase the conductivities. The site percolation is determined by the number of lanthanum. In another word, the number of La$^{3+}$ should be low enough to make a group of lithium ions and vacancies percolate through the whole system.

Another group of oxide electrolyte has the garnet structure. Typical type of garnet compound is Li$_7$La$_3$Zr$_2$O$_{12}$, which has $8 \times 10^{-4}$ S/cm of conductivity [29]. The other one is Li$_5$La$_3$M$_2$O$_{12}$ (M= Nb, Ta) which has about $10^{-6}$ S/cm of conductivity [30]. This type of structure has small boundary resistance and stability against lithium metal. Table 1-9 shows the ionic conductivities of several common oxide electrolytes at room temperature (25 $^\circ$C) based on recent researches.
Table 1-9. Ionic conductivities of some oxide electrolytes [31]

<table>
<thead>
<tr>
<th>Oxide electrolytes</th>
<th>Ionic conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₅La₃Ta₂O₁₂</td>
<td>1.3×10⁻⁴</td>
</tr>
<tr>
<td>La₀.₅₁Li₀.₃₄TiO₂.₉₄</td>
<td>1.4×10⁻³</td>
</tr>
<tr>
<td>Li₇La₃Zr₂O₁₂</td>
<td>0.8×10⁻³</td>
</tr>
<tr>
<td>Li₇La₃Zr₂O₁₂</td>
<td>3×10⁻⁴</td>
</tr>
</tbody>
</table>

1.4.3.3 Phosphates

In the past decades, extensive researches have been directed on the lithium phosphate materials which are similar to the sodium ion superconductor (NASICON) [32]. This kind of materials are identified as the promising lithium-ion electrolytes because of their particular stability and relatively high ionic conductivities. The general formula of phosphates electrolytes is LiM₂(PO₄)₃, where M is the tetravalent cation that contributes to high ionic conductivities. This structure has the most suitable tunnel size for Li ion migration among series of Li₁₊ₓAₓM₂₋ₓ(PO₄)₃ (M= Ti, Ge, Hf, Sr, Zr, Sn, etc. and A= Al, La, In, Cr, etc.) [33]. Recently, the highest conductivities (10⁻⁴~10⁻³ Scm⁻¹) are observed in Li₁₊ₓAlₓTi₂₋ₓ(PO₄)₃ (LATP) series [34]. In addition to Al³⁺ as substitution, other trivalent metals like Fe³⁺ or Cr³⁺ can be appropriate substitution for Ti⁴⁺. Experimental results showed improved the Li⁺ ionic conductivity. The basic difference is that ionic radius of each substitute dopant. Al cation has an ionic radius of 0.535 Å, which is smaller than titanium (0.605 Å). In contrast, Cr³⁺ (0.615Å) and Fe³⁺ (0.645Å) are larger than titanium [35]. As a consequence, neither chromium nor ion cation would reduce unit cell dimension. Only aluminum improves the densification during electrolyte processing, which enhances the bulk and grain boundary conductivity by more than orders of magnitude compared with other dopants.
**Table 1-10. Ionic conductivities (at 25°C) of phosphate based lithium ion conductors**

<table>
<thead>
<tr>
<th>Phosphate electrolytes</th>
<th>Ionic conductivities (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>2.₄×10⁻⁴ [38]</td>
</tr>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>4.₂×10⁻³ [39]</td>
</tr>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>1.₉×10⁻⁴ [40]</td>
</tr>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>2.₀×10⁻⁴ [41]</td>
</tr>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>1.₃₃×10⁻⁴ [42]</td>
</tr>
<tr>
<td>Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃</td>
<td>4.₆₂×10⁻³ [43]</td>
</tr>
<tr>
<td>Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃</td>
<td>7.₀×10⁻⁴ [44]</td>
</tr>
<tr>
<td>Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃</td>
<td>3.₀×10⁻³ [45]</td>
</tr>
<tr>
<td>Li₀.₇Al₀.₃Ti₁.₄₀(PO₄)₃</td>
<td>1.₃×10⁻³ [46]</td>
</tr>
<tr>
<td>Li₁.₄Al₀.₄(Ge₀.₆₇Ti₀.₃₃)(PO₄)₃</td>
<td>6.₂₁×10⁻⁴ [47]</td>
</tr>
</tbody>
</table>

Li₁₊ₓAlₓGe₂₋ₓ(PO₄)₃ (LAGP) type of electrolytes were studied as a substitution for LATP, which has the ionic conductivity around 10⁻⁴ S cm⁻¹ [36]. Zirconium based phosphates LiTi₀.₅Zr₁.₅(PO₄)₃ have been investigated as the potential phosphate electrolytes, although its conductivity is lower than the titanium and germanium-based phosphates [37]. Table 1-10 shows ionic conductivities of various phosphate electrolytes reported recently.

### 1.5 Objective and Scope of This Research

The new generation of low-emission transportation systems requires the new level of safe batteries with high performances. Highly conductive solid electrolytes are in demand for such applications. Among various reported solid lithium-ion conducting ceramics, the NASICON-type materials are very attractive for their high ionic conductivities (in the range of 10⁻³~10⁻⁴ S/cm) and good stability with air and moisture, among which LATP is a promising candidate for its low-cost materials. The objective of this thesis is to explore novel low-cost approach to synthesize LATP-based solid state electrolytes applicable to the all solid-state lithium-ion batteries. The materials will be subjected to the systematic structural and electrochemical characterizations.
In the thesis, **Chapter 2** reviews the research and development on LATP-based solid electrolytes with emphasis on synthesis optimization, structural and morphological characterizations, and understanding of lithium conduction mechanism towards improving the electrochemical performances. **Chapter 3** describes the experimental synthesis and characterization approaches used in this study. **Chapter 4** presents the results and discussion of LATPs in terms of phase, morphology, and ionic conductivities at various synthesize conditions. **Chapter 5** summarizes this thesis work, followed by an outlook and discussion of potential future works of solid-based electrolytes.
2 Research Status of NASICON-Structured LATP

2.1 Introduction

As presented in the previous chapter, the LATP (lithium aluminum titanium phosphate, Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$) has been proved to be one of the best candidates, among all kinds of NASICON-type lithium ion conductors, for all solid-state Li-ion batteries. In this chapter, specific details about LATP, such as synthesis approaches, structures, morphologies, conduction properties, and the key factors which may influence its structures and properties, will be discussed based on the reported results in literatures.

2.2 Synthesis Approaches

Since LATP was firstly reported, many synthesis approaches have been developed from solid state reaction, co-precipitation, sol-gel, melting-quenching, and so on. The co-precipitation and sol-gel are most commonly used LATP synthesis methods because these two approaches require relatively low synthesize temperature and short time to produce uniform particles. The sol-gel process is a chemical procedure using metal alkoxide solution and metal chlorides for the fabrication of small molecules solid materials, such as metal oxide, glassy and ceramic materials. The sol-gel process is a cheap and low-temperature technique that allows for the accurate control of chemical composition. Even really small quantities of dopants can be added into the sol and turn out a uniform distribution of particles in the final product. Figure. 2-1 shows the basic schematics of sol-gel method.
The unique advantage makes sol-gel very popular in the study of LATP synthesis and investment. The ‘sol’ (or solution) is normally formed by the lithium, aluminum, titanium, and phosphate precursors mixed with a selected catalyst like citric acid to promote the ionization and complexation of titanium. Then, the ethylene-glycol (EG) could be added into the solution to promote polyesterification. At certain temperatures (80–200 °C) with continuous magnetic stirring, the sol gradually transformed into gel, a continuous chain-like polymer network through hydrolysis polymerization and polycondensation. The remaining liquid phase in the gel needs to be removed through the drying process along with a significant amount of shrinkage and densification. A heat treatment is always necessary to ensure the further polycondensation. The final sintering process occurs around 800–1000 °C to enhance mechanical properties, structural stability, densification and grain growth [49]. The final microstructure of LATP will be strongly impacted by the changes of temperature, components, and structural template during this processing.

Although the solid-state reaction has its weakness in terms of energy consumption and
uniform grains generation compared with sol-gel, it is also widely used for preparation of LATP polycrystalline materials for its simple process. The first step is to select precursors that contain the desired elements and to determine correct ratio. The critical step is to ensure intimate mixture to maximize react contact surfaces if all the reactants are powders. Normally, all the reagents can be mixed with sufficient amount of some volatile organic liquid (like acetone or alcohol or methanol) to aid homogenization. The agate mortar and pestle or ball mill method can be used to mix the reactants. The last step is the high temperature treatments are to facilitate reaction and atom diffusion limited. The sintering temperature for LATP is 800~1000 °C to guarantee an appreciable reaction rate. After 2 or 3 hours, the powder will be needed to grind and to be pressed into pellet to enhance the contacts between the grains. The final calcination may last 6~10 hours.

Table. 2-1 summarizes some recently synthesis information of LATP from published literatures, which includes the chemicals, methodologies and conductivities.
Table 2-1. Summary of some representative LATP synthesis methods and results

<table>
<thead>
<tr>
<th>Product</th>
<th>Chemicals</th>
<th>Methods</th>
<th>Conductivities S/cm</th>
<th>Ref #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Al-Ti-P-O</td>
<td>Li2CO3; Al(OH)3; TiO2; NH4H2PO4</td>
<td>Cold press and sinter</td>
<td>2.46×10^{-3}</td>
<td>2011</td>
</tr>
<tr>
<td>LATP</td>
<td>LiNO3; H2O; Al(NO3)3; H9O2; Ti(OCH3)4; NH4H2PO4; citric acid; ethylene glycol</td>
<td>Sol-gel</td>
<td>-</td>
<td>2011</td>
</tr>
<tr>
<td>LATP</td>
<td>LiCO3; (NH4)2HPO4; Al2O5; TiO2</td>
<td>Solid state reaction</td>
<td>3.4×10^{-3}</td>
<td>2015</td>
</tr>
<tr>
<td>Li1.4Al0.4Ti1.6(PO4)3</td>
<td>Al(NO3)3; 9H2O; Li2C2O4; Ti(OCH3)4; NH4H2PO4 with NH4HCO3</td>
<td>Co-precipitate</td>
<td>2.19×10^{-3}</td>
<td>2011</td>
</tr>
<tr>
<td>Li1.3Al0.3Ti1.7(PO4)3</td>
<td>γ- Al2O3; Li2O; P2O5; TiO2</td>
<td>MM</td>
<td>10^{-4}</td>
<td>2013</td>
</tr>
<tr>
<td>Li1.5Al0.5Ti1.5(PO4)3</td>
<td>CH3COOLi; Al(CH2O)3; Ti(C3H8)3; H3PO4; isopropanol; CH3COOH; H2O</td>
<td>Sol-gel</td>
<td>-</td>
<td>2013</td>
</tr>
<tr>
<td>Li1.3Al0.3Ti1.7(PO4)3</td>
<td>CH3COOLi; Ti(OCH3)4; Al(tri-sec-OBu); Ti(OPr)4</td>
<td>Co-precipitate</td>
<td>1.6×10^{-4}</td>
<td>2013</td>
</tr>
<tr>
<td>Li1.5Al0.5Ti1.5(PO4)3</td>
<td>CH3COOLi; Ti(OCH3)4; Al(OCH3)4; NH4H2PO4; n-C4H9OH; H2O</td>
<td>Sol-gel &amp; colloidal crystal</td>
<td>5.3×10^{-5}</td>
<td>2011</td>
</tr>
<tr>
<td>Li1.3Al0.3Ti1.7(PO4)3</td>
<td>-</td>
<td>Microcracking</td>
<td>0.67×10^{-3}</td>
<td>2012</td>
</tr>
<tr>
<td>Li1.3Al0.3Ti1.7(PO4)3</td>
<td>-</td>
<td>-</td>
<td>3×10^{-3}</td>
<td>2014</td>
</tr>
<tr>
<td>Li1.5Al1.5Ti2-x(PO4)3</td>
<td>γ- Al2O3; Li2O; P2O5; anatase-type TiO2</td>
<td>MM</td>
<td>2.9×10^{-4}</td>
<td>2014</td>
</tr>
<tr>
<td>Li1.5Al3.5Ti2-x(PO4)3</td>
<td>LiNO3, Fe/Cr/ Al(NO3)3; 9H2O, NH4H2PO4; TiC2H4O4; citric acid; ethylene glycol</td>
<td>Pechini method (sol-gel)</td>
<td>6.2×10^{-3}</td>
<td>2014</td>
</tr>
<tr>
<td>Li1.5Al0.5Ti1.5(PO4)3</td>
<td>Li2C2O4 and Al(NO3)3; 9H2O; NH4HCO3; NH4H2PO4; Ti(C3H8)4</td>
<td>Co-precipitate</td>
<td>5.22×10^{-4}, 9.95×10^{-4}</td>
<td>2014</td>
</tr>
<tr>
<td>Li1.7Al0.3Ti1.7Si0.4P2.6O12</td>
<td>LiOH.H2O2; Si(OH)3H4; (C3H2O)3PO2.N(CH2CH2OH)3; CH3CH2 COOH; H(OCH2CH2)2OH; (C3H4O2)n; Ti(OiPr)4</td>
<td>Sol-gel</td>
<td>&gt;10^{-3}, 4.3×10^{-4}</td>
<td>2014</td>
</tr>
</tbody>
</table>

2.3 Structure and Morphology

The LATP is based on the LiTi2(PO4)3 (LTP) NASICON-type structure, in which trivalent aluminum substitutes titanium cation. The LiTi2(PO4)3 crystal structure belongs to...
rhombohedral system and is formed by infinite ribbons of \([\text{Ti}_2(\text{PO}_4)_3]^–\) units. The \([\text{TiO}_6]\) octahedral and \([\text{PO}_4]\) tetrahedral linked by their corners form three-dimensional conducting network. In this structure, there are two important interstitial sites \(M_1\) and \(M_2\). The main one (\(M_1\)) is a six-fold coordinated site, which is identical to the un-substituted LTP parent structure corresponding to distorted octahedral oxygenated environment. The coordinates for \(M_1\) is usually defined as \((0,0,0)\) for the convenience of structure study. The \(M_2\) \((x,0,1/4)\) is an irregular eight coordinated site, which is the consequence of the substitution of trivalent metals to \(\text{Ti}^{4+}\). The occupancy of these two sites in the LATP system plays an important role for lithium ion conductivity. Figure 2-2 shows the structure of \(\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3\) [64].

**Figure 2-2. Schematics of the structure of \(\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3\) (left) 3-dimensional; (right) 2-dimensiona projection**

X-ray diffraction (XRD) spectroscopy plays a very important role in LATP crystal structure determination. Knowing the wavelength (\(\lambda\)) and diffraction angle (\(\theta\)), the crystal interplanar spacing (\(d\)) can be calculated based on Bragg’s law: \(\lambda=2dsin(\theta)\). The spacing \(d\) can correlate with the crystal systems to predict lattice parameters by using plane-spacing equations. In this way, it is very convenient to monitor structure changes under different circumstances such as composition or temperature, from which to identify how those
factors impact LATP structures and further to correlate the structure changes with LATP properties. Figure 2-3 shows the XRD spectra and lattice parameter quantification LATP with different stoichiometric values synthesized using sol- gel method and solid-state reaction [65, 66]. It shows that the single phase of rhombohedral NASICON structure was achieved with the molar ratio of aluminum is less or equals to 0.5. Above that, the impurity intensity peak is observed and identified as AlPO$_4$, which has been proved by many other authors. The data of lattice parameters show that substitution of titanium cation with aluminum cation will cause the structure shrink, since the ionic radii of Al$^{3+}$ (0.535Å) is smaller than the radii of Ti$^{4+}$ (0.605Å). XRD analysis proves that no matter what method was used to synthesize LATP, upon increasing amount of aluminum, (1) AlPO$_4$ impurities will be generated at $x \geq 0.4$; (2) lattice parameters area reduced. The XRD can also be used to estimate the average crystallite size by using Scherrer equation: $t=0.9\lambda/B\cos(\theta)$ [67]. In the equation, $t$ is the average grain size; $\lambda$ is the wavelength; $B$ is full width with half- maximum (FWHM), which is high width of diffraction peaks in intensity spectra; and $\theta$ is the diffraction angle.
Morphologies of LATP are found to be also important to their electrochemical properties, which can be determined by using Scanning Electron Microscopy (SEM). Studies have been reported on different particle sizes via different synthesis procedures, or grain growth and grain boundary changes after different sintering time or temperature heat treatments.
Figure 2-4. SEM images of LATP03 samples synthesized via different approaches. (a)&(b) solid state reaction; (c) co-precipitation; (d) sol-gel

Figure. 2-4 presents SEM images of LATP03 \((Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3)\) powders via totally different synthesis processes based on different literatures. All these powders have all been through the first calcination treatment \((850 \, ^\circ \text{C} \, \text{for} \, 2 \, \text{hours})\). The average grain size of LATP03 synthesized via solid state reaction is approximate 500 nm, if some of the abnormal agglomerates were ignored. The grain sizes of LATP03 powder are a little bit smaller \((200 \, \text{nm} - 400 \, \text{nm})\) and more uniform when LATP are synthesized via co-precipitation (Figure. 2-4 c) and sol-gel (Figure. 2-4 d) [68-70].

25
Seen in Figure 2-5, all LATP samples are composed of uniform crystal grains. Among them the LATP sample with NH₄H₂PO₄ shows well sintered grains with grain boundary was hardly seen [72]. These two examples indicate that different precursors have great impacts on the purity and microstructures which results in different ionic conduction properties of the final LATP products.

Figure 2-5. SEM images of LATP samples using a, b (NH₄)₂HPO₄, c,d, NH₄H₂PO₄ e,f H₃PO₄

2.4 Conduction Properties

Conductivities of solid electrolytes are usually determined with the help electrochemical impedance spectroscopy (EIS). EIS also allows us to distinguish bulk from grain boundary conduction mechanism. Figures 2-6 and 2-7 present the Nyquist complex impedance results of two LATP synthesized using different aluminum and phosphor
precursors. LATP synthesized using Al(C₃H₇O)₃ (fig 2.6a) has a lower resistance than the that synthesized using Al(NO₃)₃. The total conductivities of LATP electrolytes were calculated as 4.5*10⁻⁴ S/cm and 7.1*10⁻⁵ S/cm for Al(C₃H₇O)₃ and Al(NO₃)₃ precursors, respectively [71]. Similarly, in Figure 2-7, it shows that LATP using NH₄H₂PO₄ has the lowest conduction impedance and hence the highest ionic conductivity, which was attributed to pure compositions and better grain boundary conditions. LATP using (NH₄)₂HPO₄ system has a better ionic conductivity than that using H₃PO₄ precursor due to the absence of AlPO₄ impurity, which is a resistance layer hindering lithium ion conduction. But such LATP has worse grain boundary conditions compared the LTAP synthesized with NH₄H₂PO₄ system. The total conductivities of LATP pellet prepared by H₃PO₄, (NH₄)₂HPO₄, and NH₄H₂PO₄ are 9.95E-05, 2.16E-04, and 5.22E-04S/cm [72].

Figure 2-6. Nyquist plots of LATP synthesized using (a) Al(C₃H₇O)₃, and (b) Al(NO₃)₃
Figure 2-7. Nyquist plots of LATP synthesized using different phosphor precursors (a) $H_3PO_4$, (b) $NH_4H_2PO_4$, (c) $(NH_4)_2HPO_4$. The right figure is a zoom-in of (b).

Figure 2-8. Arrhenius plots of LATP samples synthesized with (a) $Al(C_3H_7O)_3$ and (b) $Al(NO_3)_3$. 
The activation energy of conduction is another factor to be considered, which can be calculated from Arrhenius plots based on the equation is:

$$\sigma^* T = \sigma_0 \exp \left( -\frac{E_a}{RT} \right)$$

where $T$ is the absolute temperature, $R$ is the gas constant, $\sigma_0$ is the pre-exponential constant, and $E_a$ is the activation energy [73]. The Arrhenius plots of two LATP synthesized from (a) Al(C$_3$H$_7$O)$_3$, and (b) Al(NO$_3$)$_3$ are shown in Figure 2-8. The linear systems were well fit with the accuracies ($R^2$) greater than 0.99. The bulk and total activation energies were 0.13 eV and 0.28 eV, 0.19 and 0.35 eV for LATP using Al(C$_3$H$_7$O)$_3$ and Al(NO$_3$)$_3$ [74], respectively.

2.5 Conducting Mechanism

To understand the migration pathway of Li$^+$ ions in LATP structure, the high-resolution neutron diffraction analyses were reported. Fourier’s maps were computed to visualize the difference between the real structure and NASICON models and to show the positions of atoms missing in the original model. Accordingly, the locations of lithium ions can be determined. Figure 2-9 shows the Fourier’s map of LATP03 in the range of 77K to 540K. Since the lithium has negative coherent scattering length compare with neutrons, it shows up as negative scattering density. It is seen that Li$^+$ ions are highly anisotropic thermal displacement in M$_1$ site. At 77K the M$_1$ site (0,0,0) is negative scattering density. With increasing temperature, the expansion of negative scattering density is identified and the M$_1$ position is totally delocalized due to the high values of thermal coefficient (B). Because of the Ti octahedral, this B coefficient would give the Li ions in M$_1$ site a preference thermal dislocation at x-y plane and negligible along the z direction. Further analysis of these maps shows additional lithium atoms scattering density with the location of M2’ (b,0.31,1/4).
which is close to the M₂ position except the y direction. So, the lithium ions are speculated from M₁ position via bottlenecks along a path of M₁-M₂'-M₁ [64, 75].

Figure 2-9. Fourier's maps of LATP 03 in xy plane with Z=0 of neutron diffraction data at selected temperature range of 77K to 540K. In these maps, blue represents negative and orange is for positive.

Figure 2-10. Crystal structure of LATP showing conducting path of lithium ions.

The M₂ sites are generated by the substitution of Al cations, and it may decrease the lattice parameters and increase the bottleneck size. Figure 2-10 shows the conducting path of
lithium ions, and also the atoms in M_1(Li1) and M_2'(Li2’). The narrowest places of bottleneck cavities are big enough for lithium ion to go through without changing the whole network [75].

2.6 Key Factors Affecting Structures and Properties of LATP

2.6.1 Various Precursors

Plenty of precursors have been explored through different synthesis methods. For example, LATP05 solid electrolytes were synthesized via sol-gel method using two different precursors, e.g. water-soluble Al(NO_3)_3 and water-insoluble Al(C_3H_7O)_3. Figure 2-11 shows the XRD patterns of the two LATP samples after the exactly same synthesis procedures [76]. The XRD spectra showed that the LATP sample prepared by Al(NO_3)_3 generated Al(PO_4)_3, while the other LATP synthesized from Al(C_3H_7O)_3 has no impurity. The reason for the difference is deduced as the water solubility difference between different precursors. For instance, the Al(NO_3)_3 is water-soluble but the Ti(C_3H_7O)_4 is not water soluble. The insufficient mixing of Al source and Ti source caused the Al(PO_4)_3 impurity. It is suggested that the water solubility should be considered when the precursors were chosen in order to avoid the unfortunate property results.
Different PO₄ sources also have significant influences on crystal structures and morphology of LATP product. Figure 2-12 shows the XRD patterns of LATP calcined at
1000°C 6 hours with various PO₄ sources, i.e. (a) (NH₄)₂HPO₄, (b) NH₄H₂PO₄, (c) H₃PO₄,
(d) LTP, (e) AlPO₄. NASICON-structured LATP were successfully formed from all five
different precursors. But AlPO₄ impurities was observed in the sample prepared with
H₃PO₄. The AlPO₄ impurities in H₃PO₄ system were attributed to the acidic pH values
which should be paid attention during the synthesis [77].

2.6.2 Temperature

To optimize the synthesis process, the other key important factor is the heat-treatment
temperature. Many researches have studied the impacts of sintering temperature on the
relative density, impurity components, and morphology of LATP products. Figure 2-13
shows the XRD spectrums of LATP pellets after different sinter temperatures. Increasing
the sinter temperature will impact the final compositions of LATP samples For instance,
Lezhi et al (2011) calcined LATP pellets which were synthesize by exactly same co-
precipitation method in a range of temperature from 900 to 1300 °C [78]. It can be seen in
Figure 2-13(a) that AlPO₄ initially formed at 900 °C and intensity kept increasing with the
temperature increment. Similar phenomena were also reported by Sandrine et al (2013),
accompanied with the appearance of other impurities like TiO₂ and Li₄P₂O₇ (see Figure 2-
13(b)) [79].
Figure 2-13 XRD spectra of LATP sintered at different temperatures a) LATP04 via coprecipitation; b) LATP03 via solution chemistry

High temperature calcination will simultaneously result in the grain growth. Figure 2-14 shows the difference of grain structures after different sinter temperatures [80]. The
increasing sinter temperature will cause larger grain size according to the principle of
diffusion. When the sinter temperature reached certain level, the cohesion between large
grains is weak, which caused the fracture between grains. This situation would lead to a
serious impact on ionic conductivity, which needs to be prevented for the optimization of
LATP solid electrolyte.

![SEM images of LATP grain surfaces sintered at (a) 950℃, (b) 1000℃](image)

Figure 2-14. SEM images of LATP grain surfaces sintered at (a) 950℃, (b) 1000℃

When the sinter temperature reached certain level, e.g. 900 ℃, the evaporation of lithium
may start. And this kind of situation will become severe upon increasing temperature and
or prolong the sintering time at high temperatures. The decomposition of lithium
component in LATP samples will result in the density loss. A sudden drop of relative
density was observed after LATP was sintered at 900 °C for 6 hours, which is coordinated with this interpretation.

### 2.6.3 Aluminum Contents

Figure 2-15 shows Fourier maps of LATP samples with different stoichiometry measured under different temperatures. It is seen that the substitution of Ti⁴⁺ by Al³⁺ provided the expansion of negative scattering density around M₁ site, and it is fully delocalized when x is greater than 0.3 as a molar ratio. These results suggested that the increment of Al cation does improve the Li⁺ ion mobility. However, the amount of aluminum dopants should be controlled under appropriate ratios to prevent the AlPO₄ impurity formation. As discussed previously (see Figure 2-3), when molar percentage of Al³⁺ dopant reached 0.4 in the LATP samples, there is a big chance to generate AlPO₄ impurity which is a resistive layer for grain boundary conductivity [75].
Figure 2-15. Different Fourier maps of neutron diffraction at selected temperature of Li$_{1-x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ ($x=0, 0.05, 0.1, 0.3, 0.4$) electrolytes.
2.7 Summary

LATP’s unique NASICON structure and M₁-M₂’-M₁ conducting mechanism ensure LATP’s high level of lithium ionic conductivity (10⁻⁴~10⁻³ S/cm). It has been demonstrated that LATP can be readily synthesized using either simple solid-state reaction or sol-gel wet chemical route. The key factors influencing LATP structures and morphologies include precursors, sintering temperature and time, in addition of composition. Those factors need to be well controlled in order to achieve the high conductivities.

Based on these previous studies, this thesis research is directed to determine the experimental optimal synthesis conditions in our reaction systems. Structure and conductivities will be characterized in order to identify the correlation between the processing, structure, morphology and conductivity property.
3 Experimental Aspects of Synthesizing and Characterizing of LATP Electrolyte

In this thesis, the sol-gel method as well as solid state reactions have been studied to synthesize LATP solid electrolytes. The XRD was used to determine the crystal structure of the LATP products. SEM was used to visualize the morphology. Electrochemical impedance spectroscopy was used to determine the ionic conductivity.

3.1 Synthesis of LATP using sol-gel method

3.1.1 Chemicals and Amounts

The experimental precursors used in this research are C₆H₅Li₃O₇·4H₂O (powder), 70% HNO₃ (liquid), Al(OH)₃ (powder), NH₄H₂PO₄ (powder); TiC₁₂H₂₈O₄ (liquid); citric acid (CA, powder); ethylene glycol (EG, liquid), and distilled water. Those precursors were purchased from different chemical vendors like Sigma Aldrich, Fluka etc. without any further treatment. The basic properties of all the precursors are listed in Table 3-1.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Molecular weight M (g/mole)</th>
<th>Density ρ (g/ml)</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅Li₃O₇·4H₂O</td>
<td>281.98</td>
<td>-</td>
<td>99%</td>
</tr>
<tr>
<td>100% HNO₃</td>
<td>63.01</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>70% HNO₃</td>
<td>-</td>
<td>1.42</td>
<td>70%</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>78</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>115.03</td>
<td>-</td>
<td>98%</td>
</tr>
<tr>
<td>TiC₁₂H₂₈O₄</td>
<td>284.26</td>
<td>0.96</td>
<td>97%</td>
</tr>
<tr>
<td>citric acid</td>
<td>192.12</td>
<td>-</td>
<td>99%</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>62</td>
<td>1.132</td>
<td>99%</td>
</tr>
<tr>
<td>Li$_{1+x}$Al$<em>x$Ti$</em>{2-x}$(PO$_4$)$_3$</td>
<td>Molar ratio Li:Al:Ti:P</td>
<td>C$_6$H$_5$Li$_3$O$_7$·4H$_2$O (g)</td>
<td>Al(OH)$_3$ (g)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------------</td>
<td>-----------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>LTP(x=0)</td>
<td>1:0:2:3</td>
<td>0.33</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.1:0.1:1.9:3</td>
<td>3.67</td>
<td>1.00</td>
</tr>
<tr>
<td>0.2</td>
<td>1.2:0.2:1.8:3</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.25</td>
<td>1.25:0.25:1.75:3</td>
<td>1.67</td>
<td>1.00</td>
</tr>
<tr>
<td>0.3</td>
<td>1.3:0.3:1.7:3</td>
<td>1.44</td>
<td>1.00</td>
</tr>
<tr>
<td>0.4</td>
<td>1.4:0.4:1.6:3</td>
<td>1.17</td>
<td>1.00</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5:0.5:1.5:3</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6:0.6:1.4:3</td>
<td>0.89</td>
<td>1.00</td>
</tr>
<tr>
<td>0.7</td>
<td>1.7:0.7:1.3:3</td>
<td>0.81</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3-3. The actual amount of weight or volume of precursors used to synthesize different LATPs at the stoichiometric ratio with sol-gel approach

<table>
<thead>
<tr>
<th>Li$_{1+x}$Al$<em>x$Ti$</em>{2-x}$(PO$_4$)$_3$</th>
<th>C$_6$H$_5$Li$_3$O$_7$·4H$_2$O (g)</th>
<th>Al(OH)$_3$ (g)</th>
<th>NH$_4$H$_2$PO$_4$ (g)</th>
<th>TiC$<em>{12}$H$</em>{28}$O$_4$ (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTP(x=0)</td>
<td>0.949</td>
<td>0.00</td>
<td>3.521</td>
<td>6.105</td>
</tr>
<tr>
<td>0.1</td>
<td>10.444</td>
<td>0.780</td>
<td>35.213</td>
<td>58.000</td>
</tr>
<tr>
<td>0.2</td>
<td>5.697</td>
<td>0.780</td>
<td>17.607</td>
<td>27.474</td>
</tr>
<tr>
<td>0.25</td>
<td>4.747</td>
<td>0.780</td>
<td>14.085</td>
<td>21.368</td>
</tr>
<tr>
<td>0.3</td>
<td>4.114</td>
<td>0.780</td>
<td>11.738</td>
<td>17.298</td>
</tr>
<tr>
<td>0.4</td>
<td>3.323</td>
<td>0.780</td>
<td>8.803</td>
<td>12.210</td>
</tr>
<tr>
<td>0.5</td>
<td>2.848</td>
<td>0.780</td>
<td>7.043</td>
<td>9.158</td>
</tr>
<tr>
<td>0.6</td>
<td>2.532</td>
<td>0.780</td>
<td>5.869</td>
<td>7.123</td>
</tr>
<tr>
<td>0.7</td>
<td>2.306</td>
<td>0.780</td>
<td>5.030</td>
<td>5.669</td>
</tr>
</tbody>
</table>

For the Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (0 ≤ x ≤ 1), aluminum component is considered as the dopant which is added into LiTi$_2$(PO$_4$)$_3$ NASICON structure to improve the lithium conducting mechanism. The theoretical molar ratio and the computed molar amount of the precursors required are listed in Table. 3-2. Table. 3-3 shows the practical experimental values of precursors used with the changing stoichiometric molar ratios. Experimentally, the molar ratio for aluminum, citric acid and ethylene glycol is fixed to Al:CA:EG = 1:2:8. The highly
concentrated nitric acid 70 wt% was diluted to 5 wt% so it can be mixed with Al(OH)$_3$ to achieve Al(NO$_3$)$_3$ solution. The molar ratio between aluminum component and nitric acid is 1:3. When the molar amount of aluminum is fixed as 0.01 mole, the molar amount of those precursors can also be determined (such as HNO$_3$=0.03, CA=0.02, EG=0.08 mole). Hence, the amounts of 70% HNO$_3$ and distilled water are 1.902 and 35.106 ml, respectively. Additionally, the amounts of citric acid and ethylene glycol are 3.881g and 4.426 ml.

3.1.2 Sol-gel experimental procedures

The water- insoluble TiC$_{12}$H$_{28}$O$_4$ was initially added to the saturated solution of CA to promote ionization and complexation of titanium component. After total dissolution, the TiC$_{12}$H$_{28}$O$_4$ became small white particles well-distributed in the solution. Then, the rest of reactants were added to solution without any particular sequence. Subsequently, the appropriate amount of EG was mixed with the precursor solution. The total volume of precursor solution is around (150 ml~200 ml) depending on the different molar ratio used in the experiments. The solution was continuously stirred with the help of magnetic stirrer at a constant speed. The temperature was increased to 140 °C to promote polyesterification. This process will not be stopped until the solution became more viscous, and finally formed a polymeric gel. The total duration for this step is approximately 20 ~ 24 hours. The obtained dry gel was manually grinded with mortar and pestle to ensure the full uniform heat transfer for the following procedures.

The gel was placed into a beaker and heat-treated at 400 °C for 3 hours. The obtained small dark granules were grinded again until homogeneous particles were obtained. Theses powders were placed into furnace to calcine at the preset temperature 800 °C for the selected time (5-10 hours). In most cases, the calcination time was set to 7 hours. This
procedure is to eliminate the extra carbon, hydrogen, nitrogen, oxygen components inside of mixture system and also to promote the initial crystallize in LATP powder.

3.2 Synthesis of LATP using solid-state reaction method

Solid state reaction is relatively simple process and it has become a common method for preparation of LATP solid electrolytes. It has also been reported that conductivities of LATP synthesized with solid state reaction are higher than those synthesized with sol-gel approach. In this study, the precursors used for the solid-state synthesis are all solid state. TiO$_2$ is the substitution for liquid TiC$_{12}$H$_{28}$O$_4$. The weight of each precursor used for synthesis of LATP with different aluminum composition were calculated and listed in Table 3-8. All the solid precursors were mixed together and manually grinded for at least half an hour in an agate mortar. A small amount of ethanol is added into the mixture as buffer solution to promote sufficient homogenization. The slurry was air-dried for 2 hours before placed into furnace. For the solid-state reaction, high temperature calcination is necessary considering diffusion limitation. In this case, the calcination process is 1000°C for 2 hours so that an appreciable reaction rate will be guaranteed.

Table 3-4. The weight amounts of precursors used to synthesize different LATP using solid state reaction approach

<table>
<thead>
<tr>
<th>$\text{Li}_{1+x}\text{Al}<em>x\text{Ti}</em>{2-x}$$\text{(PO}_4)_3$</th>
<th>Molar ratio Li:Al:Ti:P</th>
<th>C$_6$H$_5$Li$_3$O$_7$$\cdot$4H$_2$O (g)</th>
<th>Al(OH)$_3$ (g)</th>
<th>NH$_4$H$_2$PO$_4$ (g)</th>
<th>TiO$_2$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0≤x≤1</td>
<td>1:0:2:3</td>
<td>0.949</td>
<td>0.000</td>
<td>3.521</td>
<td>1.61</td>
</tr>
<tr>
<td>LTP(x=0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.1:0.1:1.9:3</td>
<td>10.444</td>
<td>0.780</td>
<td>35.213</td>
<td>15.33</td>
</tr>
<tr>
<td>0.2</td>
<td>1.2:0.2:1.8:3</td>
<td>5.697</td>
<td>0.780</td>
<td>17.607</td>
<td>7.26</td>
</tr>
<tr>
<td>0.25</td>
<td>1.25:0.25:1.75:3</td>
<td>4.747</td>
<td>0.780</td>
<td>14.085</td>
<td>5.65</td>
</tr>
<tr>
<td>0.3</td>
<td>1.3:0.3:1.7:3</td>
<td>4.114</td>
<td>0.780</td>
<td>11.738</td>
<td>4.57</td>
</tr>
<tr>
<td>0.4</td>
<td>1.4:0.4:1.6:3</td>
<td>3.323</td>
<td>0.780</td>
<td>8.803</td>
<td>3.23</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5:0.5:1.5:3</td>
<td>2.848</td>
<td>0.780</td>
<td>7.043</td>
<td>2.42</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6:0.6:1.4:3</td>
<td>2.532</td>
<td>0.780</td>
<td>5.869</td>
<td>1.88</td>
</tr>
<tr>
<td>0.7</td>
<td>1.7:0.7:1.3:3</td>
<td>2.306</td>
<td>0.780</td>
<td>5.030</td>
<td>1.50</td>
</tr>
</tbody>
</table>
For all solid-state procedures, fine contact areas are essential for grain growth during calcination and sintering. In this case, the ball mill method is very necessary for this procedure. So, the mixture of slurry was poured into zirconia jars and was grounded for 12 hours in a high-energy planetary ball mill with zirconia balls as grinding material. And also, after the calcination process, the ceramic product will be ball milled again for another 5 hours.

3.3 Pellet Preparation before LATP Final Sintering

For the convenience of conductivity measurement and the improvement of ionic conduction in LATP, the synthesized LATP white powders were pressed into pellets followed by high temperature sintering. Firstly, the calcined LATP powders were grinded and pressed into pellets of 13 mm diameter and 3 mm of thickness using a uniaxial press. Two different pressures were selected, i.e. 4000 lbs and 5000 lbs (equivalent to 150 MPa and 200 MPa, respectively) [81]. The 4000 lbs pressure was the lowest to obtain a relatively dense pellet which can be readily handled. The 5000 lbs was the highest that could be reached. Figure 3-1 displays the bench press and the obtained LATP white pellets.

![Figure 3-1. Experimental tools and samples (a) tabletop press; (b) LATP pellets](image)
In this study, the impacts of sintering conditions such as ramping rate, temperature, and duration on the morphologies and conductivities of the LTAP products have been systematically studied. Two ramping rates were studied, i.e. 15 °C/min and 5 °C/min. The sintering time change from 5 hours to 10 hours. The sintering temperatures varies from 800 °C to 1000 °C.

3.4 X-Ray Diffraction Spectroscopy

The crystalline structure analysis for LATP solid electrolyte would help to understand the structure changes under different experimental situations. The XRD machine used in this thesis study is the MD-10 Mini X-ray diffractometer manufactured by Radicon company. This facility consists of a powder base which operates a small “Cu-Kα” X-ray tube, and this tube operates at 25KV high voltage and 400 μA current. The facility is connected with computer using “MD-10” software to control every move of experiment. The range of exposure time for the LATP is 40~60 minutes to make sure the reduction of noise, and the 2-theta range is from 10~76°. During the experiment, the background intensity would be automatically eliminated by the system in order to show the clear intensity spectrum [82].

3.5 Scanning Electron Microscopy

The scanning electron microscopy machine was made by PEMTRON corporation. The model is SWMART PS-230 with 0.5~30 kV acceleration voltage and W Hairpin filament. The operation power is 187 V~253 V (50/60 Hz). The experimental samples for SEM are powders or pellets without generating any gas. After attached LATP samples on the sample stage with double-sided tapes, fixed the sample stage into holder and tighten it with screw. The vacuum level can be checked by monitoring the indicators on machine or the vacuum status on the computer. In order to find the best image, the filament voltage must be at a
saturation point (The point that the emission current doesn’t increase any more after a big jump, is a saturation point and it is proportional to brightness of the image). The HT value cannot be over 5V for the safety of filament. For different HV, the best emission current can be found by adjusting Bias after fixed the HT. The reduce mode was used to pick the specific areas inside of the whole images, which can adjust the image faster than the normal mode. When the area was fixed, the Focus, wobble and Stigmator functions will easily help to obtain the clear image at high magnification level [83].

To analyze the morphology changes under different circumstances, “ImageJ” software was used to estimate particle sizes as well as porosity. Basically, there are two different ways to collect grain sizes by using “ImageJ”. The first method is automatic measure by shaping the clear edges of particles to evaluate the LATP grain sizes using software. The “ImageJ” uses pixel as the measurement units, so, unifying the system scale with the units one would use is the necessary step. For different SEM images, the scale bar information can be easily found in image information. By using the ‘measure’ function in ‘Analyze’ section, the system length and width can easily evaluate and compare with the real length and width. In this way, the units can be unified. Then, convert the SEM images to monochrome so that the grain edges can be seen clearly. The image contrast and brightness were adjusted by using ‘threshold’ to make sure the system can identify the grains correctly. The last step is to use ‘Analyze particle’ function to collecting all the grain information inside of the whole image including the grain number and the grain areas. The data can be imported into Excel to perform further analysis. The automatic measure function is very convenient, but sometime is hard to use when the edges of grains are indistinct like amorphous morphology.

So, sometimes the conventional scraping line method needs to be used. After the
unification was done with the help of “ImageJ”, every streak length can be evaluated. Every line will cross at least 7 grains to evaluate the length of every grain. For every image at least 3 lines were chosen to collect the grain size information of LATP solid electrolyte, and the total data will be put into Excel to finish the further analysis [84].

3.6 Conductivity Determination using Electrochemical Impedance Spectroscopy

For testing the conductivity of pellet samples, high performance silver paint has been used to make good contact and electrical connection. The paint is ‘Leitsilber’ 200 Silver Paint from TED PELLA, INC. This ‘Leitsilber’ conductive silver cement is fast drying and has a flat surface texture. The drying time for this paint is around 10 minutes at 25 °C, and the application can be by brush, dipping or spraying. It has small grain size, and the maximum size is about 16 µm. The service temperature is relevantly high, which is around 120 °C. And also, the consumption rate of this product is only 0.6-2 gram per 100 cm². Those properties make sure this product could provide a good performance of conductivity test [85]. After the silver paint is completely dry, copper tapes were attached on each side of pellet to wire out electricity for the convenience of EIS measurement. For each side, the length of tapes is around 3 cm. Afterwards, silver paint was applied again to seal the edges of the copper tapes with the surface of pellets to make sure that they will have good connection for the conductivity tests.

Based on the principles of ionic transport, typical EIS spectrums show three regions. In the impedance as a function of frequency (Bode plot), the first dispersive region in the low frequency range corresponding to electrode reaction processes; with the increment of frequencies, a plateau appears related with the ionic transport along grain boundaries in the electrolyte; the ionic conduction in bulk will appear another plateau at high frequencies.
Nyquist plot represents the relation with impedance and frequency using real and imaginary part as x and y axis. In Nyquist plot each point is the impedance Z at one frequency. Low frequency data are on the right side and higher frequency are on the left. The three different conductive systems can be also distinguished inside of Nyquist plot. The diffusion or accumulation of ionic carriers in the electrodes shows as a straight line and capacitive curve. Two semicircles from intermediate to high frequencies correspond to ionic conduction along grain boundary and bulk, respectively. Sometimes, the bulk and grain boundary semicircles may overlap, rendering the difficulty to accurately distinguish the two items.

The ionic conductivity can then be evaluated according to resistance value determined from the Nyquist plot with the following equation: $\sigma = L/(R*A)$, where $L$ is the LATP electrolyte thickness, $R$ is the resistance, and $A$ is the valid electrolyte area. In reality, bulk and grain boundary conductivities in LATP are hardly distinguishable because of the overlap of the two semicircles.

The equipment used for EIS measurement is ‘Reference 600’, which is made by Camry Instruments, Inc. This ‘Reference 600’ can operate as a potentiostat, a galvanostat, and also a ZRA (zero resistance ammeter). Its features include 11-decade current auto-ranging, electrical isolation from earth ground, current interrupt iR compensation, and both analog and digital filtering. A sine wave generator on the Reference 600 allows its use for impedance measurements at frequencies up to 1 MHz. Data can be acquired at frequencies up to 300000 points per second. A unique DSP (Digital Signal Processing) data acquisition mode allows the Reference 600 to reject noise, from the instrument itself, from the
electrochemical cell, and from the lab environment. The Reference 600 offers an unprecedented combination of high speed, high sensitivity, and low noise [86].

The operation of conductivity test is sample, use the potentiostatic EIS function in G EIS 300 (electrochemical impedance spectroscopy) section to test the LATP samples. The parameters of conductivity tests were set up as following constants shows in Table 3-5.

<table>
<thead>
<tr>
<th>Table 3-5. Conductivity test parameters used for EIS measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>Initial frequency (Hz)</td>
</tr>
<tr>
<td>Final frequency (Hz)</td>
</tr>
<tr>
<td>Point/ decade</td>
</tr>
<tr>
<td>AC Voltage (mV)</td>
</tr>
<tr>
<td>Initial delay</td>
</tr>
<tr>
<td>DC voltage (V)</td>
</tr>
</tbody>
</table>

Since the blocking electrode, i.e. silver and copper, a straight line at low frequency was observed. Theoretically, a big semicircle at mediate frequencies corresponding the grain boundary conductivity and the small semicircle at high frequencies corresponding to the bulk conductivity can be determined.

Figure 3-2 shows electrochemical impedance spectra (Nyquist plots) of two commercial LATP samples obtained using the experimental conditions described above. However, as seen in figure 3.2, the bulk and grain boundary impedance are overlapped resulting in only one recognizable semicircle in the two plots. In this circumstance, the total conduction impedance were estimated by taking the real impedance value at the transition point between semicircle and straight line. Equivalent circuit was used to fit the semicircle impedance. The obtained conductance impedance values obtained using the two methods and the difference is within 10%. To simplify the data analysis, the total conduction
impedance values reported in this thesis were obtained from the transition point. The
cconductivities of LATP-NEI and LATP-nGimat are 8.23E-05 S/cm and 1.32E-04 S/cm,
respectively, which are sufficiently close to values in the reference papers.

![Nyquist plots of the two commercial LATP samples at experimental conditions used in this study, from which ionic conductivities were determined.](image)

**Figure 3-2.** Nyquist plots of the two commercial LATP samples at experimental conditions used in this study, from which ionic conductivities were determined.

The activation energy is one of the most important factors in relation to ionic conduction
which obeys Arrhenius equation

\[ \sigma = \sigma_0 \exp(-E_a/RT) \]
where $T$ is the absolute temperature, $R$ is the gas constant, $\sigma_o$ is the pre-exponential constant, and $E_a$ is the activation energy of ionic conduction. Accordingly, action energy value can be determined from Arrhenius plot, i.e. $\ln \sigma$ vs $1/T$.

For this series experiments, the pellets were placed on a hotplate with preset temperatures and thermally insulated from the environment with the help of a thermal heat cap. The impedance was collected in the temperature range of 25 $^\circ$C to 75 $^\circ$C at the interval of 10 $^\circ$C. At each temperature, the pellets were allowed to reach thermal equilibrium for over 1hrs. EIS spectrum was obtained at each temperature, from which conductivities were obtained. The conductivity value as a function of temperature was plotted and the activation energies were obtained from the slope in the Arrhenius plots.
4 Structure, Morphology, Grain Growth, and Conduction Characteristics of LATPs – Results and Discussion

Based on current researches and usable experimental methods, procedures of synthesizing Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ solid electrolytes via sol-gel and one-step solid-state reaction methods are studied. The close to optimal synthesis conditions were identified and ionic comparable with published results were obtained. Detailed results and discussion in terms of structure, morphology, and conducting properties and their correlation with calcination and sinter conditions will be presented in this chapter.

4.1 Crystal Structure Characterizations

Figure 4-1 (a) and (b) presents the XRD spectra of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (x = 0 – 0.3) synthesized using sol-gel and all-solid-state methods, respectively. These spectra are obtained from the pellet specimens with the highest conductivities at each composition. It is seen that all the samples can be indexed to the R-3C space group. The plane index corresponding to each diffraction peak, based on the JCPDS database, are labeled in the figure. By comparing the intensity peaks between experimental data and references, it can be confirmed that the LATP structures are successfully achieved in all the four compositions.
Figure 4.1. XRD spectra of Li_{1+x}Al_xTi_{2-x}(PO_4)_3 (0 ≤ x ≤ 0.3) specimens synthesized using (a) sol-gel method (b) one-step all solid-state reaction method

It appears there may have been some impurities at around diffraction angles of 21° and 28° in samples synthesized both solid and sol-gel methods. These peaks are related with impurity AlPO_4. Also, there are a few tiny impurity peaks shown between diffraction angle
25° and 29°. Since those peaks are quite small and the XRD instrument used in this study has lower power contributing to its lack of accuracy, it is difficult to identify the phase of these impurities. After reviewing several references, these impurity peaks may have originated from TiO$_2$, Li$_4$P$_2$O$_7$, TiP$_2$O$_7$ or LiTiPO$_5$, etc. [87]. The existence of these traces of impurities is one of the key factors contributing to the relatively low conductivities of the LATP compared with the reported data.

The lattice parameters were calculated based on the Bragg’s Law and the hexagonal planar equation.

$$2d \sin(\theta) = \lambda$$

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Figure 4-2 presents the computed lattice parameters of LATPs (x = 0 to 0.3) synthesized by sol-gel and all-solid-state methods. The a and c values are around 8.56 and 21.9 angstroms, which are larger than the reference data, i.e. 8.5 and 21. Angstroms, respectively. On the other hand, theoretically, the lattice parameters a and c decrease continuously with increasing x because the larger Ti$^{4+}$ ion (r = 0.605 Å) is substituted by smaller Al$^{3+}$ cation (r = 0.535 Å) [88]. But those differences cannot be recognized based on the data achieved (see figure 4-2).
Figure 4-2. Lattice parameters as a function of $x$ in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 0.3$) specimens synthesized by sol-gel as well as one-step all solid-state reaction methods.

The discrepancy of the obtained XRD results from the theoretical and others’ results is believed to be originated from the instrumental error. The XRD instrument used in this study is only suitable for qualitative analyses. During the experiment, it is constantly observed the peak shift. Although the automatically calibration with the help of the software leads to better spectra but the accuracy is limited.

4.2 Morphological Analyses

In order to identify optimized synthesis condition and understand LTAP grain growth kinetics, morphologies of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ solid electrolyte samples under different experimental circumstances have been examined using SEM and analyzed using “ImageJ” software. Based on the experimental conditions and chemistries, this thesis is focused on
the influences of various heat treatment conditions procedures on the morphologies of 
Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ specimens. Different calcination and sinter conditions include 
temperatures, ramp rates, and durations.

4.2.1 Influences of processing parameters during sol-gel and all-solid-state synthesis

4.2.1.1 Calcination Discussion

LATP sample needs to go through calcination procedure to promote initial 
polycondensation and crystallization. The calcine temperature was set at 800 °C in 
consideration of complete elimination of carbon content originating from the precursors 
and initial crystallization of LATP phase. This series morphological studies were 
performed on Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (x=0.3, LATP03) powders. After the powders were dried 
out at 200°C, the sol-gel powders were divided into three parts with each calcined at 800 °C 
for 2 hours, 4 hours, and 10 hours respectively.
Figure 4-3 SEM images of LATP03 powders calcined at 800°C via sol-gel method for different times (a) 2hours; (b) 4hours; (c) 10 hours

Figure 4-3 shows the morphological difference after different calcination duration. After 2 hours, image (a) shows the LATP03 powders start crystalizing, and some small crystalline
structures with average particle size of ~ 0.5μm can be seen in the image. But still, there are many amorphous regions in the product. With the duration extend to 4 hours, seen from the image (b), most of the structures are crystallized and grains grew to the size of 1.1 μm, twice of those calcined for 2 hours. Compared the morphology of 10 hours with 4 hours, there is no significant difference between each other. The specimen calcined for 10 hours showed a little bit growth for LATP grains (~1.3μm), which is undesired. Considering the time efficiency, the duration time for calcination process around 4 hours was chosen for the following process optimization.

Figure 4-4 shows the morphology of LATP03 after calcination at 1000 °C for 2hrs during solid state reaction. It looks a little bit different compared with samples via sol-gel process. Thanks to the high temperature, most of the grains have already finished crystallization, and only few abnormal agglomerates can be seen in the images. The grain size is relatively big (~1.4μm), and the whole morphology is not symmetric.

![Figure 4-4. Morphology of LATP03 obtained at calcination 1000°C for 2 hours](image)

The energy dispersive spectroscopy (EDS) was used to determine the elemental components in the LATP03 synthesized at the optimal conditions. It is noted that lithium
element cannot be seen because of its low characteristic radiation. All other elements are easily identified (see Figure 4-5).

![Figure 4-5. EDS result of LATP03 obtained via solid state reaction]

4.2.1.2 Ramp rate during sintering

In consideration of the kinetic of grain transformation and growth, different ramping rates might cause different morphologies. In this study, the two ramping rates, i.e. 15 °C/min and 5 °C/min, were selected for LATP03 during the sintering process, while other synthesis process conditions were kept the same, i.e. calcined at 800°C for 4 hours and sintered at 1000°C for 5 hours.

Figure 4-6 presents the SEM images showing the surface morphologies of LATP03 pellets sintered at the two different ramping rates, i.e. 15 °C/min and 5 °C/min. LATP03 pellet sintered at the ramping rate of 15 °C/min contains highly asymmetric particles with large distribution and pores. In contrast, LATP03 sintered at the ramping rate of 5 °C/min contains the cubic crystalline structured particles although the particle sizes are not perfectly uniformed. Further, there is only a few small pores observed on the surface.

To quantify the impacts of different ramp rates, porosity and grain sizes were analyzed with the help of software “ImageJ”. Since the magnifications of SEMs are different, the
total sizes for 15°C/min and 5°C/min are 2526.3 and 7138.5 μm², respectively. And the sizes of pores are about 438.98 and 145.17 μm², respectively. In this case, the LATP03 pellet sintered at 15°C/min has a porosity of 17.4% and an average particle size of 3.7 μm. The LATP03 pellet sintered at 5°C/min has a porosity of 2.0% and an average particle size of 4.4 μm. This porosity measurement is estimated quantity value, which is not extremely accurate. The area evaluate should be used on flat surface, which mean the samples should be fulfilled before experiments. The normal porosity evaluate method for uneven surface is volume estimation. Since the purpose of experiment is estimating the influences of different ramp rates on sample morphologies, the accuracy was good enough to distinguish the differences.
Figure 4-6 SEM images of LATP03 pellet sintered at 1000°C for 5 hours at different ramp rate (a) 15°C/min; (b) 5°C/min

The relation between pores and ramp rate has been reported in many articles [89-91]. Although there is no specific theory to determine the final effects of ramp rate in final samples, it has been repeatedly shown that higher ramp rate will introduce more pores in the materials. During the synthesis of LATP, the specimens usually contain some elements which can vaporize at high temperatures. With rapid temperature changes, the reduction
cannot be fully completed in time. In that case, pores will be generated inside of the system. Another reason is related with grain growth kinetic, which will present in the session 4.2.2. Bottom of the line, theories and results indicate that the lower ramp rate supports better scheme for heat transfer providing a better grain growth environment, which leads to bigger and more symmetrical grains with less porosity. The conductivities for 5°C/min and 15°C/min are 2.09e-05 S/cm and 1.42e-05 S/cm, respectively. This results further proved that ramp rate does impact the final property of LATP solid electrolytes, and the lower ramp rate will lead to better results by making fine structure.

4.2.1.3 Sintering Temperature

Figure 4-7 shows SEM images of LATP03 samples sintered using different sinter temperatures with relatively long duration (10 hours) via sol-gel method. The morphology of SEM image with 900°C is more symmetrical, but with few extraordinary big grains. With the increments of sintering temperature, more and more large grains are visualized. Compared with the SEM pictures have dramatic grain growth compared with the grains after 1000°C 5 hours (figure 4-6b) or the ones just after calcination processes (figure 4-3b).
Figure 4-7. SEM images for LATP03 via sol-gel method sintered at different temperatures for 10 hrs (a) 900 °C; (b) 950 °C; (c) 1000 °C

Figure 4-8 shows the grain size distributions in the three specimens sintered at the different temperatures with the help of “ImageJ” software. All distributions approximately follow the Gaussian distribution. Based on SEM images and grain size distribution, it can clearly
be seen that high sintering temperature will simultaneously result in the grain growth. The average grain size obtained at 900 °C, 950 °C, and 1000 °C are 4.3 μm, 5.2 μm, and 7.2 μm, respectively.

![Grain size distribution of LATP03 sintered at different temperatures.](image)

**Figure 4-8. Grain size distribution of LATP03 sintered at different temperatures.**

In consideration of the benefits for ionic transport, two different aspects need to be considered. On one hand, high temperatures are beneficial to the grain growth as seen in figure 4-8. The increased grain size means the simultaneous reduction of the amount of grain boundaries which were constantly reported to have lower conductivity and higher activation energies. On the other hand, high temperature sintering will accelerate the loss of lithium component and also generate impurities (AlPO₄) to block the conductive path. In this study, the sintering temperature is selected around 900°C in order to support enough energy and to ensure grain growth but to limit the loss of lithium as well as impurity generation for facile conduction.
4.2.1.4 Sintering Time

Figure 4-9 shows morphologies of LATP03 pellets via sol-gel method sintered at 900 °C for different durations, i.e. 4 hrs, 7 hrs, and 10 hrs. From SEM image of 4 hours, the surface of LATP03 samples are highly unsymmetrical. Comparing the SEM images of LATP03 sintered for 4 hours and 7 hours, it can be clearly seen that with the extension of sinter duration, the grain size grows from 2.5 μm to 3.3 μm, and the whole morphology looks more symmetric than before. After 7 hours, the growth of grains slowed down, and the morphology does not change much after that. When the duration reached 10 hours, the average grain size is around 4 μm. Combining this SEM results with conductivity results, we can see that when the duration is only 4 hours. The sinter process had not completely ended yet, abnormal agglomerates and highly unsymmetrical morphology impacted the conductivity performance. And also, when the sinter duration exceeds the needs of polycondensation and crystallization, the loss of lithium components and oversized grains are going to be the major bad effects for the performance of Li\textsubscript{1+x}Al\textsubscript{x}Ti\textsubscript{2-x} (PO\textsubscript{4})\textsubscript{3} solid electrolytes.
Figure 4-9. SEM images of LATP03 via sol-gel method for sintered at 900 °C for different times (a) 4 hours; (b) 7 hours; (c) 10 hours
Figure 4-10 SEM images of LATP03 via solid-state sintered at 900°C but different duration (a) 4 hours (b) 7 hours (c) 10 hours

To compare the morphological difference of LATP03 pellets after different synthesis method, different sinter duration was applied via all-solid-state method. Figure 4-10 shows SEM images of LATP03 with 900 °C sintering process under different durations via all-
solid-state method. Same as the results as sol-gel images, the grain growth can be seen clearly with the duration time increments, but the systems are less systematic compared to the sol-gel system. Since the calcination temperature of all-solid-state method is relatively high compare with sol-gel system (1000 °C vs 800 °C), the grain sizes after 900 °C are bigger than sol-gel ones, which is around 2.85 μm. Also, the short calcination and sintering duration cause seriously unsymmetrical morphology for LATP pellet samples. Some of the grains are really big compare with the other un-grew grains. But, with the duration increasing, the grains received enough energy and became more systematical. Eventually, the grain sizes of 900 °C are around 4 μm, which is the same size as the ones via sol-gel methods.

When the sintering time is too long, lithium evaporation may occur leading to impurity generation. Figure 4-11 shows the surface of LATP03 pellets after 900 °C 10 hours sinter process via all-solid-state method. In the images, there are two distinguished phases can be seen. One phase with clear cubic crystalline structure corresponding to LATP grains. However, the grain sizes of the other phase are really small compared with regular ones. This kind of phase might be composed of impurity phases or failed small grains, which has bad contact area and lower ionic transport ability compared with crystallized area. The average grain sizes are around 4 μm and 1μm, respectively.
Figure 4-11. Morphology difference in LATP03 pellets synthesized via solid state reaction at sintering 900°C for 10 hours (a) large crystal phase (b) small grain phase

4.2.2 LATP Grain Growth Kinetic Analysis

Grain growth kinetics as a function of time are normally analyzed under isothermal conditions from grain size vs. time curves, in accordance with the well-known grain growth kinetics equation for fully dense bodies.

\[ D^n - D_0^n = Kt \]  \hspace{1cm} (1)

\[ K = K_0 \exp(-Q/RT) \]  \hspace{1cm} (2)
where $D$ is the average grain size at time $t$, $D_0$ is the initial grain size, $n$ is the kinetic grain growth exponent, $K$ is a rate constant, $K_0$ is a pre-exponential constant, $Q$ is the apparent activation energy for the grain growth process, $R$ is the gas constant and $T$ is the absolute temperature [92]. When $D_0$ is significantly smaller than $D$, $D_0^n$ can be neglected against $D^n$. Then, Eq. (1) can be rearranged to the exponential or logarithmic form:

$$D^n = K_0 \exp(-Q/RT) \cdot t$$  \hspace{1cm} (3)$$

$$n \log(D) = \log(K_0) - 0.434 \frac{Q}{RT} + \log(t)$$  \hspace{1cm} (4)$$

When temperature, material compositions, kinetic activation energy and the pre-exponential constant are the same, the equation can be derived as

$$n = \frac{(\log(t_2) - \log(t_1))}{(\log(D_2) - \log(D_1))}$$  \hspace{1cm} (5)$$

From which we can obtain the value of the kinetic component $n$.

In this study, the sintering temperatures are 500 °C, 700 °C and 900 °C and sintering duration were 4, 7, and 10 hours at each temperature. After performing SEM tests for LATP samples, grain sizes under different temperatures and durations are measured (shown in Table 4-1).

### Table 4-1. Summary of average grain size of LATP03 after sintering at different temperature and times, synthesized by sol-gel and solid-state reaction approaches.

<table>
<thead>
<tr>
<th></th>
<th>4 (hrs)</th>
<th>7 (hrs)</th>
<th>10 (hrs)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sol gel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500(°C)</td>
<td>1.32</td>
<td>1.75</td>
<td>2.14</td>
<td>1.90</td>
</tr>
<tr>
<td>700(°C)</td>
<td>1.91</td>
<td>2.56</td>
<td>3.1</td>
<td>1.89</td>
</tr>
<tr>
<td>900(°C)</td>
<td>2.47</td>
<td>3.31</td>
<td>3.97</td>
<td>1.93</td>
</tr>
<tr>
<td><strong>Solid state</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500(°C)</td>
<td>1.41</td>
<td>1.84</td>
<td>2.148</td>
<td>2.17</td>
</tr>
<tr>
<td>700(°C)</td>
<td>2.185</td>
<td>2.67</td>
<td>3.04</td>
<td>2.78</td>
</tr>
<tr>
<td>900(°C)</td>
<td>2.856</td>
<td>3.5</td>
<td>3.975</td>
<td>2.77</td>
</tr>
</tbody>
</table>
Comparing sol-gel and solid-state specimens, the initial grain sizes of solid-state method are slightly bigger than those of sol-gel method. The reason may be that this difference is the calcination process difference. The sol-gel method is using 800°C for 4 hours to calcinate LATP samples. For the consideration of diffusion limits during all-solid-state reaction, the calcination temperature is set up as 1000°C for 2 hours to support polycondensation and grain growth. The calcination time for solid-state method is fixed as 2 hours to avoid further lithium contents loss during the high temperature heat treatment.

*Figure 4-12. Sintering time vs grain size in logarithmic format to determine the kinetic exponent. (a) LATP03 sol-gel specimens; (b) LATP03 solid-state specimens*
The kinetic components of LATP sample for sol-gel and all-solid-state method under different situations are calculated and shown in Figure 4-12. Both sol-gel and solid-state specimens exhibit similar linear relationship. Based on the derivation of kinetic equations, the slopes of linear systems are the kinetic exponents. However, the kinetic components under different sinter temperature have slight differences. Seen in Table 4-2, the kinetic exponent for sol-gel method is close to 2 while that for solid state method is close to 3 (excluding the data at 500 °C).

For solid state reaction, the kinetic exponent value at 500°C is relatively low compared with the other sintering temperatures. The hypothesis is that when the temperature is relatively low, there is not enough energy to support grains keep growing, even though the high pressure and milling procedures have given sample better conditions to grow. Since the calcination temperature is 1000°C in solid-state method which have produced a certain number of large particles, the 500°C sintering temperature cannot be sufficient to contribute to the grain size increase. This scenario is much worse that those occurred in the sol-gel method whose calcination condition is 800°C for 4 hours and the initial grain size is relatively smaller.

Figure 4-13 shows the basic scheme of grain growth during sinter process [93]. In the optimal situation, the grain growth is controlled by the grain boundary diffusion only, which means the driving force is the decreasing free energy of grain boundaries. When the selected grains keep growing, smaller grains will be absorbed to increase their overall sizes. But, in the real situation, many other factors will also control the grain growth, such as volume, surface, or precipitates, which will cause different grain morphologies.
Theoretically, when the whole system has no defects, no precipitates, and grain growth only controlled by diffusion, the grain growth kinetics [94] can be expressed by

$$D^2 - D_o^2 = Kt$$  \hspace{1cm} (6)

In reality, the exponent values are not always the same, which gives us the derivation equation (1) & (2). Normally, the value of kinetic exponents is within the range of 2 to 5, which have been proved experimentally. One explanation for those numbers represent
different methods of diffusion, n=2 means grain growth controlled by grain boundary diffusion, number 3 represents volume diffusion, and 4 indicates surface diffusion [94]. If the grain growth is controlled by diffusion and also the precipitate phase, n is around 3. If diffusion along the grain boundary and precipitate effects are observed, then the number should be 4. And 5 means the whole grain growth is mainly controlled by precipitation [95].

As presented in Table 4-1, the values of kinetic exponent for sol-gel and all-solid-state methods are about 1.9 and 2.7 close to 2 and 3, respectively. The results may suggest the different grain growth mechanism occurred in sol-gel and solid-state reactions. Specifically, grain growth mechanism for sol-gel method is mainly through grain boundary diffusion. In contrast, volume and precipitate will dominate in solid-state grain growth. The different grain growth mechanism may be originated from the difference in initial grain composition, grain size and density.

Figure 4-13 may also be used to understand grain growth versus densification with increasing time. The grains start packing, and at certain stage of sintering, the pores restrict the grain growth. With the duration increasing, the densification will eliminate pores and finally generate the fine grains. Seen in figure 4-9 (a) and 4-10 (a), the sintering duration is 4 hours when the pores are not pitched off by grain growth and densification. But when the sintering time is prolonged, the pores are disappearing seen in Figures 4-9 (b) &(c) and Figure 4-10 (b) and (c).

After having obtained the kinetic exponent, the kinetic activation energies can be evaluated by using Arrhenius plot. The kinetic exponents obtained at different sintering durations are slightly different, hence, the average values were used for evaluating the grain growth
activation energy. For sol-gel and all-solid-state systems, the average values of kinetic components are 1.91 and 2.78, respectively.

Figure 4-14 (a) & (b) show the logarithm of $D^a$ as a function of reciprocal of temperature. Both sol-gel and solid-state systems exhibit linear relationship. Experimentally, the values obtained at 7-hour sintering time are slightly different from those obtained at 10 hours, which are 23.0kJ/mol and 22.3kJ/mol for sol-gel, 33.6kJ/mol and 32.1kJ/mol for solid state, respectively. Theoretically, the activation energies should be the same for different duration in the same system. It is submitted that the average kinetic activation energies for grain growth via the sol-gel and all-solid-state in this study are 22.6kJ/mol and 32.8kJ/mol (0.23 and 0.34 eV), respectively.

Considering the meaning of activation energy, the higher kinetic activation energy gives a relatively higher grain growth threshold barrier. This further proved that 500°C sintering temperature for all-solid-state method is not enough for supporting grain growth in sinter process. Furthermore, the activation energy is representing the boundary mobility in grain growth, and the higher activation energy, the lower grain boundary mobility it is, which also proved that all-solid-state method will have slower grain growth rate during heat treatments. The different activation energy further confirmed the different grain growth mechanism as determined from kinetic exponent.
Figure 4-14. Grain size of LATP03 as a function of temperature to determine the grain growth activation energy at different sintering duration (a) sol-gel; (b) solid-state
4.3 Ionic Conduction Analyses

4.3.1 Preliminary Survey Results

The preliminary survey on the experimental conditions included the aluminum content, sintering temperature, and pressure used to press the pellet for conductivity measurement. These results were obtained from LATPs synthesized via-sol-gel approach.

Figure 4-15(a) shows the conductivities of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ solid electrolytes as a function of aluminum dopant composition. The conductivity increases with the increment of aluminum amount of LATP samples. When the molar fraction of aluminum x reaches 0.3 the conductivity value reaches the highest. Comparing the conductivity of the LATP with the same composition, specimens sintered at 800 °C are consistently lower than those sintered at 1000 °C. It can clearly be seen (Figure 4-15(b)) that regardless of the sinter temperature or the aluminum content, the higher pressure applied to the LATP pellets results in higher conductivity values. In general, high pressure applied to the pellets before sintering is beneficial for improving grain contact and reducing internal porosity, which in turn will facilitate grain growth and structural stability. Figure 4-15 (c) shows impedance spectrums for those two samples sintered at 900 °C for 7 hours but at different ramping rate. The spectra clearly show that LATP03 solid electrolyte using 5°C/min ramp rate for sinter process has higher lithium ion conductivity. The conductivities for 5°C /min and 15°C/min are 2.09e-05 and 1.42e-05 S/cm, respectively. This results further proved that ramp rate does impact the final property of LATP solid electrolytes, and the lower ramp rate will lead to better results by making fine structure.
Figure 4-15. Preliminary survey on process conditions on LATP conductivities (a) different sintering temperature; (b) different pellet processing pressure; (c) different sintering ramping rate
4.3.2 Processing Optimization towards Improving Conductivities of LATP

4.3.2.1 Sintering temperature

Based on the preliminary results of conductivity tests, different sinter temperatures also can impact the conductivity properties of LATP samples. In this section, different temperatures and times are used to optimized the sinter process with the other procedures remaining the same. The temperatures used in the sinter process are 900 °C, 950 °C, and 1000 °C for a duration of 10 hours each. Figure 4-16 shows the conductivity results of LATP01 and LATP03 samples after different sinter temperatures. Based on the impedance spectrum, using sinter temperature as 900 °C clearly has higher ion conductivity compared with results using 950 °C and 1000 °C. The conductivity values for LATP03 are 6.1e-05 S/cm, 5.7e-05 S/cm, and 4.8e-05 S/cm for 900 °C, 950 °C, and 1000 °C, respectively. The conductivity results also show that 900 °C sinter temperature gives better conductivity for LATP01 samples. The conductivity values for 900°C, 950°C, and 1000 °C are 2.16E-05, 1.79E-05, and 1.53E-05 S/cm, respectively. With the sinter temperature increasing, the electrochemical performance of LATP samples will getting worse. The optimal sintering temperature was determined in the vicinity of 900°C, resulting the highest conductivity.

To further analyze the impacts of sintering temperatures, values grain sizes and conductivities under different temperatures are combined and shown in Figure 4-17. Based on the plot, it shows that high temperature sintering will result in the grain growth, but also result in conductivity reducing. An interpretation of this result is the high sintering temperature will give fine and systematic grain structure, but also it will cause week grain cohesive and fractures when the grain sizes reached certain level (Figure 4-7). This
situation will lead to a serious obstacle for bulk and grain boundary conduction, which result in bad conductivity values.

Figure 4-16. Conductivities of LATPs as a function of temperatures for 10hrs.

Figure 4-17. Conductivity and grain size of LATP03 as a function of temperature

4.3.2.2 Sintering time via sol-gel

The experiment samples are LATP03, and the sinter duration are 4, 7, and 10 hours at 900°C, respectively. Figure 4-18 shows the conductivity results of LATP03 as a function
of sintering time. It clearly shows that the sample sintered at 900°C for 7 hours has better conductivity. The conductivity values for 4, 7, and 10 hours are 3.5e-05 S/cm, 4.66e-05 S/cm, and 3.75e-05 S/cm, respectively.

**Figure 4-18. Conductivities of sol-gel LATP03 as a function of sintering time at 900°C**

Combining the results of Figures 4-16 and 4-18, it can be concluded that the conductivities of LATP03 pellets increased when the sintering duration increasing at 900 °C and reached the maximum value when the duration is around 7 hours. Then, with the sintering temperature increasing, the conductivity starts dropping. Although there is an experimental error between different batches caused conductivity value difference at the same temperature and time, e.g. 900 °C and 10 hours, the trend still can be seen clearly.

### 4.3.2.3 Sintering process on Conductivities of LATP via solid-state reaction

Figure 4-19 shows the conductivity results of Li_{1+x}Al_xTi_{2-x}(PO_4)_3 (0 ≤ x ≤ 0.7) as a function of aluminum content. The trend is similar to that of sol-gel method showing the conductivity starts increasing with the stoichiometric value of aluminum dopants increases, and it reaches the maximum of 7.15e-05 S/cm when the aluminum stoichiometric value is
0.3. Then the conductivity dramatically drops to a low level because the excessive aluminum components may cause the production of AlPO$_4$ impurities.

![Figure 4-19. conductivity tests of Li$_{1+x}$Al$_x$Ti$_{2-x}$ (PO$_4$)$_3$ as a function of aluminum content x, synthesized via solid state reaction](image)

Afterwards, the LATP03 composition was subjected to sintering at different durations, e.g. 4, 7, and 10 hours at the same sintering temperature of 900 °C. Figure 4-20 shows the conductivity LATP03 as a function of sintering time. In this series experiment, ball milling procedures were used instead of manually milling to ensure the fine contact areas during the chemical reaction. And also, the extra lithium was added in the precursor to compensate the loss during sintering. This will be discussed in detail in the following section. It clearly shows that the sample sintered for 7 hours has better conductivity, which is same as sol-gel sinter process. This may be related to the loss of lithium and impurity generation upon prolonging the sintering time. The conductivity values of 4, 7, 10 hours are 1.19e-04 S/cm, 1.35e-04 S/cm, and 1.25e-04 S/cm, respectively.
Figure 4-20. Conductivities of solid-state synthesized LATP03 as a function of sintering time at 900°C.

4.4 Importance of lithium compensation

For sol-gel synthesis method, the above series results suggest that 1) for the calcination process, 800 °C calcination temperature for 4 hours duration; 2) relative high pressure is necessary to produce LATP pellets with better performance; 3) slower ramp rate of 5 °C/min and suitable sintering temperature and time (900°C and 7 hours) will generate the desired grain sizes without creating impurities, resulting in highest ionic transport paths.

For all-solid-state method, after analyzed the structure, morphology and conductivity, and compared with references, the following optimal synthesis processing was selected: 1) the calcine conditions will be 1000 °C for 2 hours; 4) After the powders were grinded, pressed into pellets at 200 MPa, and pellet will be sintered at temperature from 900 °C for 7 hours at the ramping rate of 5°C /min.

At the above close to optimal conditions, whether in sol-gel or solid-state method, the highest lithium ion conductivities were found still lower than $10^{-4}$ S/cm the commonly
reported values. Reconsidering the processing conditions, it was believed that the amount of lithium in the final product, which is difficult to quantify, may be insufficient than stoichiometry in the desired LATP.

It is known that during the high temperature synthesis of lithium compound, lithium either in the precursor or in the product are readily lost because lithium oxide is volatile above 800°C. To alleviate this, additional lithium in the precursor can be beneficial to increase the lithium activity in the vapor phase during the sintering process, and hence reducing lithium loss in the product and ensuring the correct lithium composition in the electrolyte. The loss of lithium may also cause the decomposition of aluminum, which will impact the M₂’ site generation and also will generate unwanted impurities. Therefore, in this study, lithium contents in the range of 1 to 1.2 molar ratio relative to phosphor in the precursor were investigated. The extra lithium molar amount is at the internal of 0.05 increase.

Figure 4-21 presents the conductivities of LATP03 synthesized at the sample conditions but with different amount of lithium compensation in the precursors. Apparently, the conductivity of LATP03 synthesized at the stoichiometric ratio is lower than those obtained with 15 mole% more lithium added into the precursors. The conductivities increased to in the range of 1.06e-04 S/cm, which are close to the values reported in literatures. It is also observed that further compensating lithium reduced conductivities down to 1.38e-05 S/cm. These results suggested that the amount of lithium composition must be precisely controlled. Similar phenomena were observed during synthesis via one-step solid state reaction, especially the calcination temperature was raised to 1000°C, which was beneficial to increase reaction kinetics for large particle size. The highest conductivity value reached 1.86e-04 S/cm with the extra 15% lithium compensation.
So far, many factors affecting the morphologies and conductivities of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ solid electrolytes were studied, which include pellet pressure, calcination temperature, sintering temperature and duration, and lithium compensation.

The whole sol-gel synthesis method consists of many intermediate steps and each process will affect the final LATP performance from different aspects. All of these factors must be strictly controlled. Based on the series results discussed previously, the optimal processing conditions were identified. For each step during the sol-gel synthesis, 1) the molar ratio of precursor corresponding to Li: Al: Ti: P is 1.15: 0.3: 1.7:1; 2) 140 °C temperatures at the stirring rate of 800 rpm are used to mix precursor solution until the gel like system is achieved; 3) 400 °C pre-treatment for 2~3 hours is to remove most of organic components resulting in fine dark powders; 4) for the calcination process, 800 °C calcination temperature for 4 hours duration are good enough to support polycondensation, grain crystallization and initial grain growth; 5) After mixing and milling, relative high pressure
such as 200 MPa is necessary to produce LATP pellets with better performance through enhancing its densification and structural stability, which will also facilitate LATP grain growth during the following sintering step; 6) slower ramp rate of 5 °C/min will be beneficial for forming more symmetric morphology, uniform crystal structures and minimized porosity; 7) suitable sinter temperature and time (900°C and 7 hours) will generate the desired grain sizes without creating impurities, resulting in highest ionic transport paths.

For all-solid-state method, after analyzed the structure, morphology and conductivity, and compared with references, the following optimal synthesis processing was selected: 1) the precursor powders with the molar ratio of Li: Al: Ti: P is 1.15: 0.3: 1.7: 1.0; 2) the starting material mixture was heated at 120 °C in a vacuum oven for three hours to remove all the moisture; 3) the mixture of powders was mixed with pure ethanol and was grinded for 12 hours in a high-energy planetary ball mill; 4) the well-prepared slurry was then air-dried and calcined at 1000 °C for 2 hours; 5) the ceramic product was ball milled again for another 5 hours. After a dry-process in oven at 150°C, the powders were pressed to pellets at 200 MPa; 6) the pellet is sintered at temperature from 900 °C for 7 hours at the ramping rate of 5°C /min.
Accordingly, the LATP series as a function of aluminum content (x = 0.0 to 0.7) were revisited at the above optimal conditions. As seen in Figure 4-22, the aluminum content still dominates the electrochemical properties of Li_{1+x}Al_{x}Ti_{2-x}(PO_{4})_{3}. When the aluminum amount is less than 0.3, the substitution of Al^{3+} will not support enough negative scattering density around M_{1} and M_{2} positions are not sufficient for the lithium ion migration paths. In the case, the conductivity of LATP samples are still low. However, when the aluminum amount among samples is beyond 0.3, the AlPO_{4} impurities will form resistive layers inhibiting lithium ion conducting across grain boundary. Higher conductivity values for Li_{1+x}Al_{x}Ti_{2-x}(PO_{4})_{3} (0.1≤x≤0.7) are obtained with the help of lithium compensation. The
highest conductivity value of 1.24e-04 S/cm is achieved at the optimal conditions, which is close to the highest value reported in the references.

All-solid-state synthesis at the optimal processing conditions also lead to the highest conductivities at each composition. The conductivity value of LATP03 is increased to 1.86e-04 S/cm.

4.6 Conduction Activation Energies of Optimal LATP03

To gain further insight of lithium conduction mechanism, the optimal LATP03 specimens synthesized via sol-gel and solid-state reaction methods were subjected to activation energy analysis.

Figure 4-23 presents Arrhenius plots of LATP03 synthesized via the two approaches at the optimal conditions. The data fitted with a linear relationship show that the fitting coefficient of determination $R^2$ is greater than 0.993, confirming the Arrhenius conduction mechanism. The activation energies were then computed from the slope. The activation energy value ($E_a$) of sol-gel and all-solid-state methods are 32.7kJ/mole and 28.1kJ/mole (0.34 and 0.29 eV), respectively. These values corroborate well with published values.
Figure 4-23. Arrhenius plots of LATP03 synthesized at the all optimal conditions via (a) sol-gel method; (b) solid-state method

To understand the difference between these two activation energy values, the explanation of conduction systems for lithium-ion batteries is necessary. There are two components determine the lithium ion migration inside of system (the grain bulk and grain boundary),
as seen in Figure 4-24 [97]. Normally, the conductivity of grain bulk is high with low activation energy while the grain boundary conductivity is low with high activation energy. So, the total conductivity and activation energy, which is the sum of bulk and grain boundary component, may be different depending on the dominant factor. When the grain boundary is the dominant factor in LATP, the total conductivity values are expected lower and conduction activation energy are higher, in comparison with those specimen with predominant bulk conduction.

**Figure 4-24. Schematic illustrating of two different lithium ion conduction paths.**

Comparing our experimental data with references, the conductivity of 1.24e-04 S/cm with the activation energy of 0.34 eV obtained in the sol-gel LATP03 pellet are the consistent with the reported values, e.g. grain boundary activation energy (0.35 &0.33 eV) and total conductivity values as 1.2e-04 S/cm and 7.1e-05 S/cm [98-99]. In these two papers, it was reported that bulk conductivities are 1.8 e-03 S/cm and 1.2E-03 S/cm. Those results proved that when the grain boundary controls the conduction system, the total conductivity would be dramatically reduced even with high bulk conductivity.

In this study, the optimal LATP03 synthesized via solid state reaction, the conductivity of 1.86e-04 S/cm with the activation energy of 0.29 eV. These values are close to the bulk activation energy (0.29 or 0.30ev) [100-101]. It is therefore submitted that bulk conduction
plays a dominant role in the solid-state LTAP03 specimen. These results are consistent with the larger particle size.

4.7 Summary

In this study, a series of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ ($x = 0$ to $0.7$) solid electrolytes have been synthesized using sol-gel and one step solid state reaction methods. Their crystal structures, morphologies, and conductivity properties, have been characterized. Same as the reported, $x = 0.3$ in the LATP series has the highest conductivity. The optimized synthesis procedures have been identified. Calcine temperature, sintering temperature and duration will all affect the morphology and ionic conductivities in LATPs. Slow sintering ramping rate will reduce the porosity in the LATP pellet. The kinetics of grain growth in LATP are found different using the sol-gel and solid-state synthesis approach. Grain growth in sol-gel LATP is grain boundary diffusion control with kinetic exponent close to 2 and activation energy of 0.23eV. Solid state LATP has a kinetic exponent of 2.8 with higher activation energy of 0.34eV, indication the precipitate, volume or porosity will contribute to the grain growth.

The importance of lithium content compensation up to 15 mol % was desirable to achieve highest conductivities for both sol-gel and all-solid-state methods. LATP03 pellets synthesized at the optimal conditions have highest conductivities of 1.24e-04 S/cm and 1.86e-04 S/cm with activation energies of 32.7 kJ/mole and 28.1 kJ/mole (0.34 eV and 0.29 eV) for sol-gel and solid-state methods, respectively. These differences may originate with the different size of LATP. Grain boundary dominant conduction, as in sol-gel LATP03 leads lower conductivity and high conduction activation energy.
5 Conclusion

This thesis research is to explore NASICON-structured Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (LATP) solid-state electrolyte via both sol-gel and all-solid-state experimental methods. With a comprehensive review of recent studies, the synthesis approaches, basic structures, morphologies, conduction properties and mechanism and several key factors affecting LATP such as precursors, temperature and aluminum contents were summarized and used as foundation of this research. For the purpose of synthesizing and characterizing the as-synthesized LATP solid electrolytes, X-ray diffraction spectroscopy, scanning electron microscopy and electrochemical impedance microscopy have been used to determine the crystal structure and possible impurity phase, morphology including grain size and porosity, and lithium ion conductivity etc. The synthesis parameters have been varied including calcination time and temperature, ramp rate, sintering time and temperature, and lithium compensation. From the grain size as a function and sintering temperature and duration, grain growth kinetics in sol-gel and solid-state reaction synthesis are investigated. From the conductivity as a function of temperature relationship, the dominant conduction path in LATP are also studied. Theses finding are summarized in the following:

1) The optimal processing conditions for sol-gel method are identified. The molar ratio of precursor corresponding to Li: Al: Ti: P is 1.15: 0.3: 1.7:1. The gelation procedure is at 140 °C temperatures at the continuous stirring rate of 800 rpm. To remove organic components pre-treatment is at 400 °C for 2~3 hours. The initial calcination process is at
800 °C for 4 hours. After mixing and milling, relative high pressure such as 200 MPa is necessary to produce LATP pellets. The pellet will be finally sintered at 900 °C for 7 hours at the ramp rate of 5 °C/min.

2) For all-solid-state method, the following optimal synthesis processing is selected. The molar ratio of Li: Al: Ti: P in the precursor powders is 1.15: 0.3: 1.7: 1.0. All starting material mixture was heated at 120 °C in a vacuum oven for three hours to remove all the moisture. The mixture was then grinded in ethanol for 12 hours in a high-energy planetary ball mill. The well-prepared mixing powders are air-dried and calcined at 1000 °C for 2 hours. The ceramic product was ball milled again for another 5 hours. After a dry-process in oven at 150°C, the powders were pressed to pellets at 200 MPa. The pellet is sintered at temperature from 900 °C for 7 hours at the ramping rate of 5°C /min.

3) The X-ray diffraction spectra confirm the formation of NASICON-structured LATP with some AlPO₄ impurity and possible traces of TiO₂, Li₄P₂O₇, TiP₂O₇ or LiTiPO₅ which are unable to determined due to the limit power and accuracy of the instrument used.

3) The grain sizes of the calcined powders obtained via sol-gel are increased from 0.5 μm to 1.3 μm at 800 °C for different duration. The grain sizes of LATP obtained via sol-state reaction, after calcination at 1000 °C are slight larger at the same duration.

4) Sintering temperature has significant impacts on grain growth. The average grain size increased from 4.3 to 7.2μm when the temperature increased from 900°C to 1000°C. The sintering time and ramp rate also have impacts on grain growth. Lower ramping rate can further reduce the porosity, e.g. at the sintering ramping rate of 5°C/min and 15°C/min the porosities are 17.38% and 2.03%, respectively.
5) Extra lithium (up to 15%) in the precursor is indispensable to compensate the loss of lithium during the high temperature processing and to maximize the lithium ion conductivities in the LATP products.

6) The values of grain growth kinetic exponent for sol-gel and all-solid-state methods are determined to be 1.9 and 2.7, close to 2 and 3, respectively. The average kinetic activation energies for grain growth via the sol-gel and all-solid-state are 22.6kJ/mol and 32.8kJ/mol (0.23 and 0.34 eV), respectively. The results may suggest the different grain growth mechanism occurred in sol-gel and solid-state reactions. Specifically, grain growth mechanism for sol-gel method is mainly through grain boundary diffusion. In contrast, volume and precipitate will dominate in solid-state grain growth. The different grain growth mechanism may be originated from the difference in initial grain composition, grain size and density.

7) At the optimal processing conditions, the highest total conductivities of LATP03, comparable with published results, have been achieved. For sol-gel and solid-state LATP03, the conductivities are 1.24e-04 S/cm and 1.86e-04 S/cm and activation energies are 32.7kJ/mole and 28.1kJ/mole (0.34 and 0.29 eV), respectively. These differences may originate with the different size of LATP. More bulk conduction in LATP03 synthesized via solid-state reaction may contribute to the higher conductivities and lower activation energies, relative to those in sol-gel LATP03.
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