



Preparation and chemical compatibility of lithium aluminum germanium phosphate solid electrolyte

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ABSTRACT

The NASICON-type $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ electrolytes were synthesized by a facile aqueous-based sol-gel process with alcohols free. Compared with the samples prepared by solid-state reaction, the modified sol-gel derived $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ electrolyte exhibited a rhombohedral crystal symmetry without impurity phase and higher ionic conduction behavior. After sintered at 850 °C for 5 h, the sol-gel specimen showed a total ionic conductivity of 3.1×10^{-4} S/cm at 30 °C and 1.0×10^{-3} S/cm at 60 °C. In addition, the chemical and phase stability of the as-prepared $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ with three types of cathode materials (i.e. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$) was investigated in the temperature range of 500 to 700 °C. This work proposes a synthesis choice for $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$, and also favors to the electrode identification for all-solid-state lithium secondary battery using NASICON-type electrolyte.

1. Introduction

Lithium-ion batteries (LIBs) are attractive power source for portable electronic devices. Their further applications in the electrical vehicles and large-scale energy storage system require high safety, large energy density and wide temperature compatibility [1]. However, the conventional organic liquid electrolytes limit the battery application due to their flammability and low electrochemical window [2]. Therefore, research interest has focused on the all-solid-state lithium secondary batteries to solve the safety issue of LIBs. As the key component in the solid-state battery, the solid electrolytes are expected to possess high ionic conductivity, wide electrochemical window and good chemical compatibility with electrodes [3].

Among all the electrolyte materials, the NASICON-type electrolytes, e.g. $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$, are promising candidates due to their high ionic conductivity. Similar to other NASICONs, the $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ lattice contains two types of polyhedra, GeO_6 octahedra and PO_4 tetrahedra, linked by corners to form the $[\text{Ge}_2(\text{PO}_4)_3]^-$ skeleton. This rigid framework provides the 3D interconnected channels for Li^+ migration [4]. Various techniques have been reported to prepare $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ electrolytes, i.e. melt-quenching method [5,6], solid-state reaction [7,8], sol-gel synthesis [9,10], flame spray technique [11], etc. The $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ glass-ceramics synthesized by melt-quenching often possess high ionic conductivity with dense microstructure [12]. However, this technique involves a high-temperature melting process (1350–1600 °C) and long

annealing time, which probably requires high energy consumption and laborious grinding work. Besides, the heat treatment over 1200 °C can easily lead to lithium losses [13]. Consequently, to develop a low-temperature synthesis method is of practical interest for $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ electrolyte. As mentioned above, sol-gel method has been applied in the preparation of NASICON-type electrolytes. However the alcohols system or organic solvents are commonly used, either to dissolve metal alkoxide or to prevent precipitation and promote polyesterification [7,9,14]. Then a facile aqueous-based sol-gel method is highly required.

In addition, to fabricate all-solid-state lithium secondary battery using ceramic electrolytes, the annealing procedure at high temperature is usually necessary for crystallization of cathode film and better components connection [15]. It has been reported that the unfavorable interaction between cathodes and solid electrolyte during annealing can lead to the interfacial resistance growth, and then capacity decay [16]. Therefore, the chemical stability (or say chemical compatibility) of solid electrolyte with electrode materials becomes quite important for the cell performance. However, the high-temperature compatibility of $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ with different cathode materials has not been widely investigated yet.

In this work, the $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) electrolyte was prepared by a facile sol-gel method in aqueous solution with simple and economical $\text{Ge}(\text{OCH}_3)_4$ as germanium source. The structure-electrochemical property relationship of the as-prepared LAGP was investigated. Besides, three kinds of promising cathode materials, i.e.

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$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, were selected to interact with LAGP for chemical compatibility analyses. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has a high charge/discharge voltage plateau of c.a. 4.7 V vs. Li/Li^+ , favorable for high energy density [17]. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ presents a superior discharge specific capacity of ca. 200 mAh/g among current commercial cathode materials [18]. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, similar to $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$, is also a polyanion-type phosphate material but with a lower crystallographic symmetry [19].

The aim of our work is to provide a preparation choice for LAGP electrolyte, and also favor to clarify the interaction mechanism of LAGP with cathode materials for better electrode identification in all-solid-state lithium secondary batteries.

2. Experimental

2.1. Material synthesis

The $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ precursor was prepared by a facile aqueous-based sol-gel process. Stoichiometric amounts of LiNO_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were first dissolved in de-ionized water by magnetic stirring. Citric acid (CA) was added into the nitrate solution as the chelating agent with the molar ratio of $[\text{CA}] / [\text{Li}^+ + \text{Ge}^{4+} + \text{Al}^{3+}] = 2$. Then stoichiometric $\text{Ge}(\text{OCH}_3)_4$ was dissolved to form a transparent homogeneous solution. The reaction system was heated at 80 °C for polyesterification. When the viscous gel was formed, it was transferred to an oven and heated up to 170 °C for 15 h to evaporate water and promote polymerization and gelation. The dried gel was ground and then pyrolyzed at 500 °C for 5 h to release the volatile compounds. The as-prepared LAGP precursor was reground, die-pressed into pellets, and sintered at 850 °C for 5 h in air on a platinum sheet to avoid reaction with alumina crucible. For comparison, $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ was also synthesized through the conventional solid-state reaction. The stoichiometric mixtures of Li_2CO_3 , GeO_2 , Al_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ were ball-milled and calcined at 700 °C. The precursor was then ground and die-pressed into pellets, followed by sintering at 850 °C for 5 h as well.

To investigate the chemical stability of LAGP electrolyte towards cathode materials at high temperature, three active materials were selected, i.e. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Al}_{0.05}\text{O}_2$, and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The as-prepared LAGP and each cathode powder were first weighed in 1:1 weight ratio, mixed thoroughly and reacted at 500 °C, 600 °C and 700 °C for 1 h, respectively. Then, to further evaluate their stability in a more compact condition, the mixture of LAGP and each cathode (with 1/1wt ratio) were die-pressed into pellets, and reacted at 700 °C for 1 h. For $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Al}_{0.05}\text{O}_2$ cases, they were co-heated with LAGP in air. Since $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can be oxidized in air at high temperature, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and LAGP were co-heated in Ar_2 atmosphere.

2.2. Characterization and measurements

The crystal structures of synthesized LAGP and its composites after co-sintered with different electrode materials were investigated using a powder x-ray diffractometer (PANalytical X'pert Pro). Samples were scanned over the 2θ range of 5–90° with $\text{CuK}\alpha$ radiation at room temperature. The Rietveld refinement of as-prepared LAGP was conducted with the FullProf software [20]. The morphology and composition of the LAGP and its co-sintered pellets were characterized by a scanning electron microscope (SEM, JEOL JSM-7800F) equipped with an energy-dispersive X-ray spectroscopy (EDS). The ionic conductivity of the sintered pellets were measured by the electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (Princeton Applied Research VersaSTAT 4). A gold coating was sputtered on both sides of the pellets as Li blocking electrodes. EIS data were collected in the frequency range between 1 MHz and 1 Hz with AC amplitude of 5 mV in the temperature range of 30 to 100 °C. The activation energy (E_a) for lithium-ion conduction was calculated from the Arrhenius plot

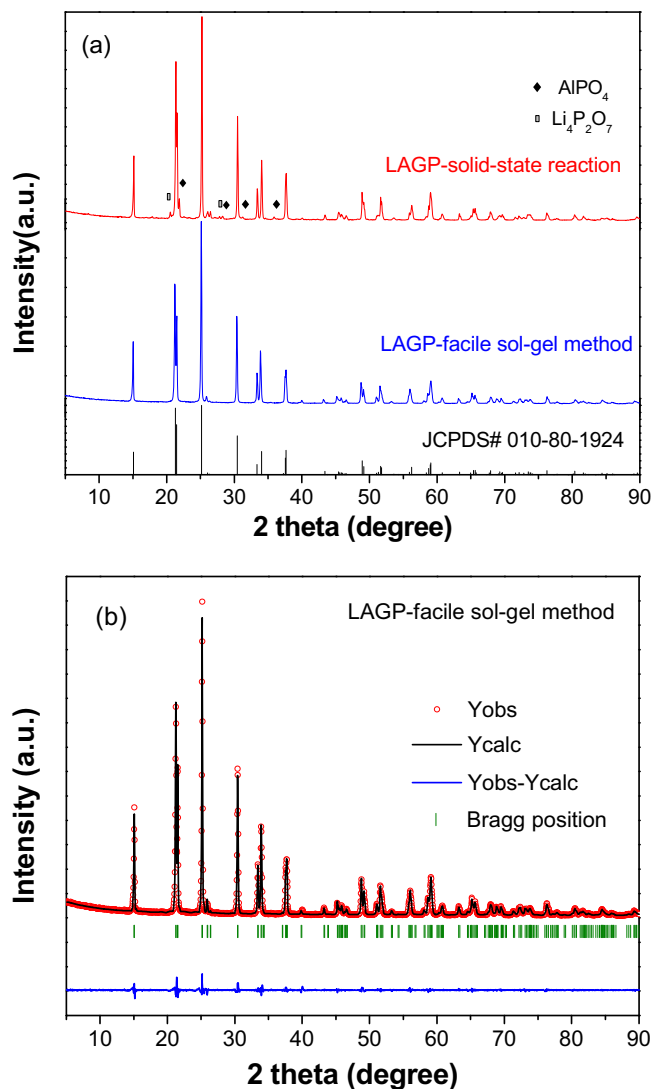


Fig. 1. (a) XRD patterns of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ sintered at 850 °C for 5 h by facile sol-gel method and solid-state reaction, (b) Observed, calculated, Bragg reflections and difference profiles of XRD patterns of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ synthesized by the facile sol-gel method.

of the total ionic conductivity to temperature. The electrochemical window of synthesized LAGP was determined by the cyclic voltammetry (CV) at a scan rate of 0.1 mV/s between –0.5 and 6.0 V. An Au layer was sputtered on one side of the specimen as a working electrode, while a lithium foil was attached on the other side as a counter and reference electrode.

3. Results and discussions

Fig. 1(a) shows XRD patterns of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ sintered at 850 °C for 5 h by facile sol-gel method and solid-state reaction, respectively. The diffraction peaks of the sol-gel derived sample can be indexed to the $\text{LiGe}_2(\text{PO}_4)_3$ with the NASICON structure (JCPDS# 01-080-1924). The Rietveld analyses of its XRD pattern in Fig. 1(b) indicated the sol-gel LAGP had a rhombohedral structure with the space group $R\bar{3}c$. The lattice parameters were calculated to be $a = 8.2604(3)$ (Å) and $c = 20.6224(8)$ (Å), which slightly varied from the size of $\text{LiGe}_2(\text{PO}_4)_3$ due to the Al^{3+} doping. The small weighted factor R_{wp} (~6.63%) suggested that single-phase LAGP can be prepared by this facile sol-gel method. As for the LAGP prepared by solid-state reaction, besides the major rhombohedral phase, its XRD spectra also exhibited

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