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# Lithium storage capability of lithium ion conductor $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$

J.K. Feng, L. Lu*, M.O. Lai

*Department of Mechanical Engineering, National University of Singapore, 9, Engineering Drive 1, Singapore*

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ABSTRACT

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) with a NASICON ($LiM_2(PO_4)_3$) structure has been successfully prepared using solid-state reaction. Structural characterization shows $LiM_2(PO_4)_3$ to be the main phase. The total conductivity of the as-prepared LAGP is about $3.5 \times 10^{-6}$ S/cm with an electrical conductivity of $10^{-9}$ S/cm. Electrochemical study reveals that the LAGP is stable up to 7 V with a slight reduction at about 0.85 V (vs. $Li/Li^+$). For the first time, the electrochemical performance of the LAGP as an anode for lithium battery is tested, showing that the LAGP could be used as an anode material with good cycleability.

## 1. Introduction

All-solid-state lithium ion batteries are promising power sources for large scale applications because of their high safety, excellent cycleability and low packing cost compared to common batteries using liquid electrolyte. Among all components in the all-solid-state lithium ion batteries, the solid electrolyte is one of the most important key components that controls the properties of the batteries. The solid electrolytes must meet a number of requirements before they can be practically used, including high conductivity, large cationic transport number, wide potential window and low electronic conductivity [1–4].

In the past decades, extensive investigations have been carried out on NASICON-type structured lithium ion conductor with the general formula of $LiM_2(PO_4)_3$ where M is the tetravalent cation that possesses high ionic conductivity. $LiTi_2(PO_4)_3$ based materials with NASICON-type structure have the most suitable tunnel size for Li ion migration among the series of $Li_{1+x}A_xM_{2-x}(PO_4)_3$ (M = Ti, Ge, Hf, Sr, Zr, Sn, etc. and A = Al, La, In, Cr, etc.) [5–20]. However, since they consist of $Ti^{4+}$ ions, they are easy to be reduced when they are in contact with lithium metal, hence limiting their applications [5–12].

Recently, the glass-ceramic $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) has gained special interest because it is particularly stable against Li metal and has a high ionic conductivity (as high as $4.62 \times 10^{-3}$ S/cm at 27 °C) [16,21–27]. Partial substitution of $Ge^{4+}$ with $Al^{3+}$ has shown improved porous density of $LiGe_2(PO_4)_3$ as well as enhanced $Li^+$ ion conductivity. It has also been found that Ge and Ge oxide are capable of interaction with lithium to form $Li_xGe$ alloy compounds [28–30], which means that Ge compounds are capable of electrochemical reactive at low voltage. Therefore it would be interested to know whether LAGP is electrochemically stable with lithium.

In the present work, Ge instead of $GeO_2$ has been used to synthesize $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ through solid-state process at a low temperature. The electrochemical properties of the LAGP have been systematically investigated by means of cyclic voltammetry, AC impedance, DC conductivity measurement and battery test.

## 2. Experimental

Stoichiometric amounts of lithium carbonate (Aldrich), aluminum oxide (Aldrich), germanium (Aldrich), and ammonium dihydrogen phosphate (Aldrich) were used as the starting materials to prepare LAGP by a conventional solid solution method. 10% excess lithium carbonate was employed to compensate loss of lithium during the processing. The powder mixture was first thoroughly mixed by ball milling and then heated in a platinum crucible at 700 °C for 2 h to release any volatile compounds. The synthesized powders were then reground followed by calcination at 950 °C under a heating rate of 1 °C/min for 2 h. The as-prepared product was cold-compacted into pellets at 10 MPa for 20 min and then sintered at 950 °C for 10 h.

Structure of the synthesized powders was investigated using a Shimadzu XRD-6000 X-ray diffractometer with Cu Ka radiation. The data were collected at a scan rate of 2°/min. Surface morphology of the sintered pellets was characterized using a Hitachi S-4100 field emission scanning electron microscopy.

AC impedance and steady-state DC electronic current measurements were carried out using a Solartron impedance analyzer (model 1260) in the frequency range between $10^{-1}$ Hz and $10^6$ Hz [2]. To study the electrical and ionic behaviors of the specimens, Ag was coated onto one or two sides of the specimens according to whether lithium reference and counter electrode were needed. The Ag-coated specimen was assembled into a cell using stainless steel (SS) as current collector to test the AC impedance [22]. To study the cyclic voltammetric (CV) performance of the specimens, one side of the specimen was coated with a Ag layer as a working electrode while the other side was attached with a lithium foil as a counter electrode.

Steady-state DC electronic current measurements and CV were undertaken to obtain the electronic conductivity and electrochemical window of the electrolyte

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* Corresponding author. Fax: +65 67791459.
*E-mail addresses:* luli@nus.edu.sg, mpeluli@nus.edu.sg (L. Lu).

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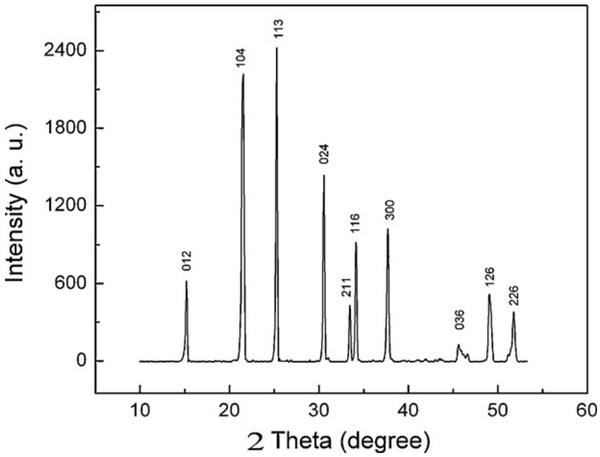

**Fig. 1.** X-ray diffraction spectrum of the LAGP sintered at 950 °C for 10 h.

using an electrochemical work station (Solartron 1287) with a scanning rate of 0.1 mV/s between −0.6 V and 7 V [2].

Battery test was carried out using a Solartron 1287 two terminal cell test system with a laboratory-made cell. The working electrode consisted of 80% LAGP, 10% acetylene black and 10% PTFE binder as working electrode. A lithium foil was used as both counter and reference electrodes. 1 M $LiPF_6$ in ethyl carbonate/dimethyl carbonate solution (EC/DEC, 1/1 vol% Ozark Fluorine Specialties, Inc.) was used as the electrolyte. Galvanostatic charge/discharge cycling experiment was performed in the potential range from 0.01 V to 2.5 V at a current density of 0.1 mA/cm$^2$.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ calcined at 950 °C for 24 h. All the diffraction peaks of the specimen are well matched with NASICON $LiGe_2(PO_4)_3$ (JCPDS 41-0034) structure [16,21–27], indicating that LAGP has been formed. Although 25% of Ge has been substituted by Al, the diffraction peaks are not dramatically shifted, attributing to the similarity in ionic radius between $Ge^{4+}$ (0.053 nm) and $Al^{3+}$ (0.050 nm).

The scanning electron microcopy (SEM) image of the specimen is shown in Fig. 2. It can be seen that the LAGP sample consists of large crystallized grains (particles) of about 2 μm together with featureless image which may be amorphous phase. It is known that electrical conductivity consists of two contributions from grain and grains boundaries. The reduction in grain boundaries by increasing the grain size and incorporating with low boundary glass electrolyte may greatly reduce the grain boundary resistance [24,25].

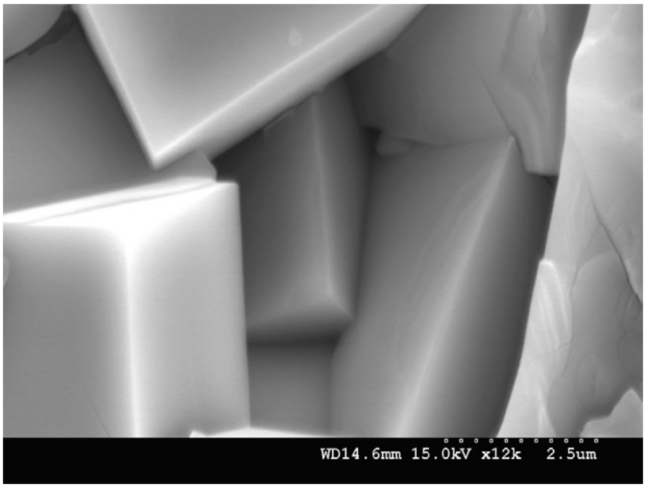

**Fig. 2.** SEM micrograph of fracture surface of sintered LAGP.

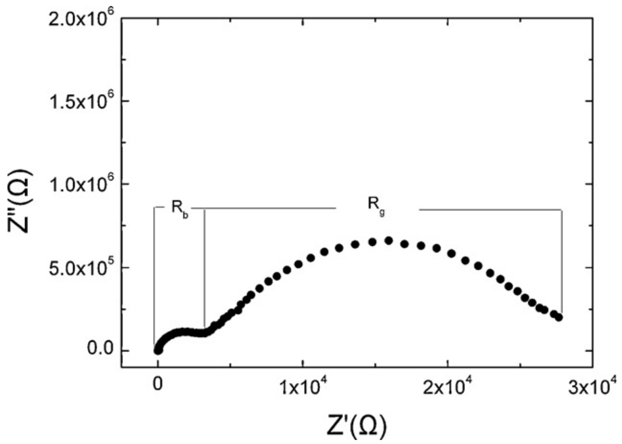

**Fig. 3.** Complex impedance plot for LAGP pellet at room temperature.

A typical AC impedance spectrum of the LAGP sample is shown in Fig. 3. Two semicircles are observed. The semicircle in the high frequency range is due to the bulk ionic resistance while the appearance of the low-frequency semicircle is an indication of the grain boundary resistance of NASICON-type material [16,24,25]. The grain boundary resistance is relatively large due to the well crystallization. The total resistance, $R_t$, of the samples can be approximately obtained from the right intercept of the second semicircle with the real axis in the plot while the bulk resistance, $R_b$, may be obtained from the left intercept of the first semicircle with the real axis. From Fig. 3, the total conductivity, $\sigma$, is evaluated to be $3.5 \times 10^{-6}$ S/cm from $\sigma = d/(R_t A)$ where $d$ (0.2 cm) is the thickness of the sample and $A$ (2 cm$^2$) is the surface area of the pellet. The conductivity of the sample, although comparable with most reported data [16,22–24], is lower than the best data reported [25].

Fig. 4 shows the electrical conductivity of LAGP measured by DC polarization using Ag/LAGP/Li electrode between 0 V and 7 V (vs. Li/Li$^+$). The steady-state current is caused only by the flow of electrons and holes. The estimated electrical conductivity is about $10^{-9}$ S/cm at room temperature. However, a sharp increase of about 10 times in electrical conductivity is observed at below 0.85 V. The increase in electrical conductivity is due mainly to the reduction of the sample. Although there is a large increase in electrical conductivity, its final value is still low ($10^{-7}$ S/cm). The LAGP sample is therefore still acceptable for application as electrolyte. The transference number of lithium is calculated to

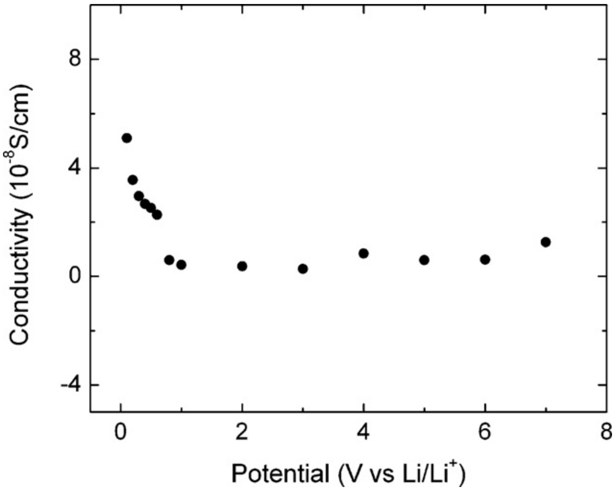

**Fig. 4.** Steady-state electronic conductivity vs. potential of SS/LAGP/Li.