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Stability of Solid-State Sintered $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ Solid Electrolytes in Various Mediums for All Solid-State Li-ion Batteries

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Abstract

Solid electrolytes are strong candidates for next-generation Li-ion batteries for Electrical Vehicle (EV) applications. However, their usage is not widely spread because of their relatively poor ionic conductivity and high electrode/electrolyte interfacial resistance compared to their commercial counterparts, organic based liquid electrolytes. Sodium Superionic Conductor (NASICON) type solid electrolytes could be an option to overcome these problems. $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) stands forward among other NASICON type solid electrolytes with their easy synthesis and processing. Yet, their stability against various mediums remain unknown and needs to be enlightened. In this study, the stability of LAGP against water, air at 85°C and 1M LiOH solution was discussed. LAGP results after sintering at 900°C for 3 hours showed impurity-free, highly dense structure with a restricted grain growth. Water and air aged samples showed a dramatical reduction on grain boundary contribution of total ionic conductivity whereas the sample aged at 1M LiOH solution exhibited both reduction in ionic conductivity and increase on grain boundary conductivity. The highest reduction on total ionic conductivity was observed on the sample aged in water. On the contrary, the sample aged in 1M LiOH solution resulted in a net increase on total ionic conductivity. The highest total conductivity of 4.3×10^{-4} S/cm was obtained from the sample aged in 1M LiOH. On the other hand, the sample aged the lowest conductivity – 1.8×10^{-4} S/cm – showed the lowest total conductivity of all samples.

Keywords: Air stability, Li-ion batteries, NASICON, Solid electrolytes, Water stability.

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1. Introduction

Li-ion batteries are attracted much interest with their outstanding gravimetric energy and power density. Moreover, they are relatively long life among other batteries. They consist of positive electrode, negative electrode and electrolyte which provides ion conduction and electrical insulation between two electrodes. Electrolytes found in commercially available Li-ion batteries are generally liquid electrolytes containing one type of Lithium salt such as $LiPF_6$ and LiTFSI dissolved in organic solvents. They exhibit outstanding ionic conductivity as well as the lowest electrode/electrolyte interface resistance. However, liquid electrolytes have several weak points. They are easily flammable and explosive at elevated temperatures which causes safety issues. Besides, they are also environmentally toxic [1–3].

Solid electrolytes are considered as a future candidate that replaces organic based liquid electrolytes with their outstanding safety, high electrochemical stability window up to 7V vs. Li/Li^+ which allows the usage of various kinds of electrode materials including Lithium and high voltage cathodes [4]. However, their most important drawbacks are their poor ionic conductivity and large electrode/electrolyte interfacial resistance.

Various kinds of solid electrolytes are investigated until now. Li_3N, LiPON, perovskite, anti-perovskite, sulfide, argyrodite, garnet, Lithium Superionic Conductor (LISICON) and Sodium Superionic Conductor (NASICON) structures are the most widely studied Li-ion conductive crystal structures. Among them, NASICON-type Li-ion conductors with a formula of $LiM_2(PO_4)_3$ differ from other structures with their enhanced sinterability and ease of production as well as excellent stability in ambient atmosphere [5].

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) is, nowadays, one of the popular compounds among NASICON type Li-ion conductors. It shows promising stability against Lithium metal enabling the extensive use of Lithium metal batteries. Relatively lower sintering temperatures of LAGP could also resulted in lithium loss prevention from the stoichiometry and secondary phase formation [6]. Although LAGP's advantages are inarguable, researches in the field of LAGP are not comprehensive and well-documented. Most of the studies are based on material development, process optimization and performance manipulations by incorporating dopants [6–9]. However, the stability and handleability at various conditions is important as it will guide researchers for developing and proper use of them in order to exploit LAGP's performance. Hence, more work related to in-use conditions should have been done. In this regard, the stability of LAGP in different mediums such as water, air and LiOH aqueous solution was investigated in the present paper. The effect of aging in such mediums on electrochemical performance was discussed.

2. Experimental

Nano sized $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) powders were purchased from MTI Corp. 1 g of powders were uniaxially pressed by applying 150 MPa into 15mm diameter pellets. Then pellets were sintered in a muffle type furnace under air atmosphere at 900 °C for 3 hours with a heating rate of 10 °C/min. Alumina crucible was used for heat treatment. Sintered pellets were polished by SiC grinding papers down to 1200 grit. The ionic conductivity of the polished samples was then measured. After that, pellets were placed in the water, 1M LiOH aqueous solution and an oven at 85 °C in order to assess the conductivity changes in different mediums.

The crystal structure of the sintered pellet was determined by using Rigaku MiniFlex 600 X-ray diffractometer (XRD) with a scan speed of 2°/min and step size of 0.02° by using Cu Kα X-Ray source.

Fractured surfaces of each pellet were analyzed by using scanning electron microscope (SEM-Zeiss SUPRA 50VP). To prevent charging, fractured surfaces of the pellets were sputter-coated by Au–Pd prior to SEM.

In order to measure ionic conductivity Au, as a Li-ion blocking electrode, was sputtered on both sides of the pellets. AC Impedance method was used to evaluate the ionic conductivity of the sintered pellets. Potentiostatic EIS mode was selected to obtain Nyquist curves in the frequency range from 1Hz to 1MHz, with AC perturbation voltage of 30 mV.rms in Gamry Reference 600 Potentiostat/Galvanostat.

3. Results & Discussion

Fig. 1 represented the XRD pattern of the pellet sintered at 900 °C for 3 hours.

All the peaks in Fig. 1 can be indexed as LAGP (ICDD No: 80-1924) pointing out a successful densification without a degradation and/or thermal decomposition of the compound. The Nyquist plots of the three different pellets were depicted in Fig. 2.

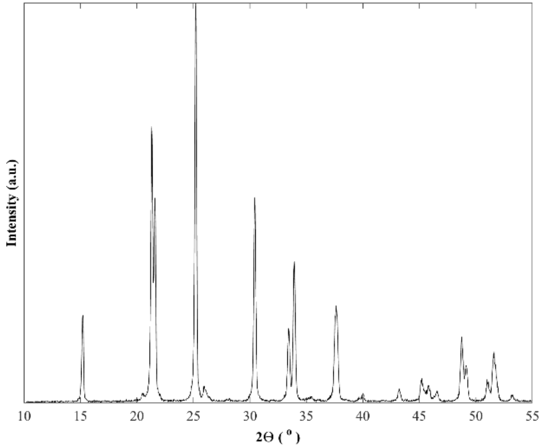

Fig. 1. XRD pattern of sintered LAGP pellet

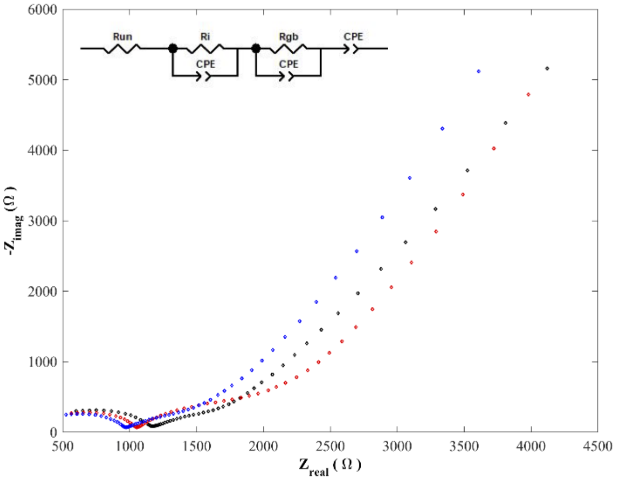

Fig. 2. Nyquist plots of freshly prepared three different samples (Sample #1 – Black; Sample #2 – Red; Sample #3 – Blue)

The Nyquist plots for three different samples consisted of one semicircle at high-frequency region, one semicircle at mid-frequency and a linear tail at low-frequency region. At higher frequencies, the response observed in Nyquist curves was ionic resistance of the solid electrolyte whereas the response observed in mid and low-frequency regions were grain boundary resistance and the resistance in Li-ion blocking electrodes, respectively. Grain boundary resistance was observed because of the presence of the grain-grain interfaces in the polycrystalline structure of the sintered pellets and can be altered by porosity, grain size and shape, possible impurity phases and wettability of the grains [10]. The linear-like tail could be attributed to the capacitive ion conduction behavior within Au electrodes [11]. Slight shifts were also observed for the samples sintered at the same conditions. The reason of such shifts is considered as the lithium losses due to temperature instability of the furnace as a result of low sintering temperature and short sintering time. The data obtained was fitted by using the equivalent circuit which was given inlet of Fig. 2. The calculated ionic and grain boundary conductivities were given according to the fit results in Table 1 denoted as fresh samples (Fresh@Water, Fresh@Air and Fresh@LiOH)

Table 1. Fitted data of LAGP pellets.

Sample Name	Ionic Conductivity (10^4 S/cm)	Grain Boundary Conductivity (10^4 S/cm)	Total Conductivity (10^4 S/cm)
Fresh@Water	1.7	2.4	4.1
LAGP_Water	1.3	0.5	1.8
Fresh_Air	2.7	2.2	4.9
Air @ 85°C	2.3	1.8	4.1
Fresh_LiOH	2.3	1.6	3.9
1M LiOH	1.5	2.8	4.3

According to the calculated conductivity data from the fresh samples, the ionic conductivity values varied between 1.7 x 10^{-4} and 2.7 x 10^{-4} S/cm which is strongly correlated with the reported LAGP pellets [12]. The fluctuations due to the Li evaporation during sintering was not affected seriously as the variance from three different samples were around 10^{-9}.

After that, pellets were repolished down to 1200 grit and placed in the 1M LiOH aqueous solution, water and in an oven at 85 °C and aged for seven days. After aging, pellets were dried, wiped, if necessary and subjected to Au sputtering for ionic conductivity measurements. The Nyquist plots for seven-day aged samples were given in Fig. 3. Plots for fresh sample were also added for comparison.

Fig. 3 showed nearly the same type of Nyquist plots which was presented in Fig. 2. Only, the diameter of semicircles at high and mid-frequency region was changed meaning that ionic and grain boundary contribution of total conductivity were different from the fresh samples.

Curves were fitted according to the equivalent circuits mentioned in Fig. 2 and the results were added in Table 1 as Water, Air@85 °C and 1M LiOH samples.

It's apparent from the data in Table 1 that total conductivity which is the sum of both ionic and grain boundary conductivity is reduced for the samples aged in distilled water and air at 85°C; increased for the sample aged in LiOH. In general, ionic conductivity of all the aged samples were reduced. Notably, even though a small change on ionic conductivity was observed for the sample aged in water, grain boundary conductivity was reduced dramatically. A specific attention should be paid to the sample aged in 1 M LiOH aqueous solution. It was observed that although ionic conductivity was obviously decreased, total conductivity was increased thanks to the increment on grain boundary contribution of total conductivity. In all, it can be said in the conductivity point of view that the stability of LAGP in 1 M LiOH solution is the best.

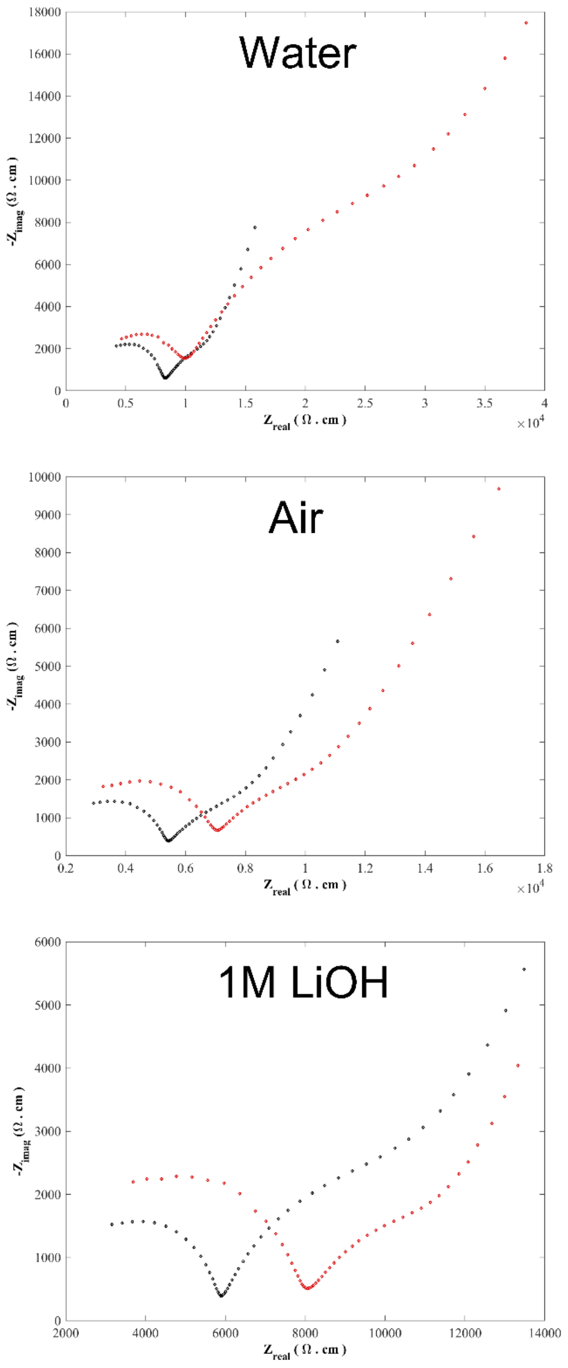

Fig. 3. Nyquist Plots for aged samples

But, the water stability of LAGP is the worst. The main reason for this difference can be attributed to the lithium changes in the nominal composition of LAGP. Fig. 4 showed the fractured surface SEM pictures of the aged LAGP samples. A nearly porosity-free microstructure with submicron sized grains was observed from all aged samples pointing out a well-densified LAGP structure. The governing fracture mechanism was intergranular fracture for the air and LiOH aged LAGP samples whereas trans granular fracture can also be found more for the water aged LAGP sample. The reason underlying the different fracture mechanisms can be attributed to the enhanced chemical degradation of LAGP by Li^+/H^+ ion-exchange when contacting water.

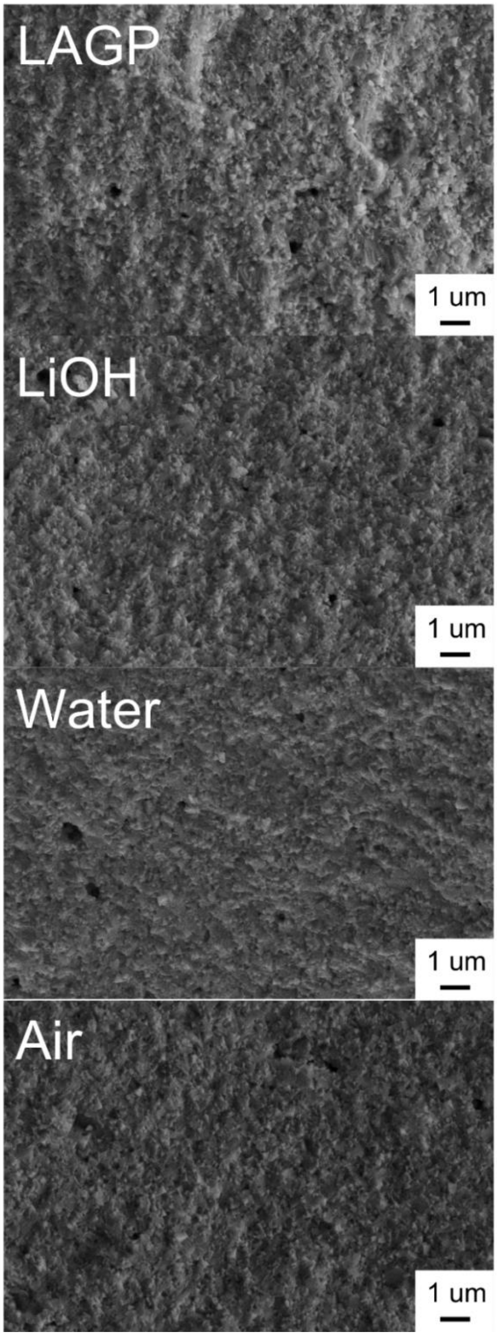

Fig. 4. Fractured surface SEM images of fresh LAGP and LiOH, water and air aged samples

The dramatical reduction on grain boundary conductivity as discussed in Table 1 could also support the outcome. In all, water was found as the most aggressive solution by creating the most significant reduction on total ionic conductivity.

The current technological threshold for total ionic conductivity is reaching above 0.5 mS/cm values. LAGP type solid electrolytes having a total conductivity as high as 0.4 mS/cm exhibit quite similar values when compared to LLZO – one of the widely studied solid electrolyte – with outstanding advantages like ease of material synthesis and handleability. LAGP sintering is much easier than LLZO sintering and doesn't require powder bed sintering techniques which improves the production feasibility and makes it a good candidate for enabling bulk-type battery assembly techniques. However, there is still a way to go for improving the electrolytic performances of LAGP including overcoming interfacial resistance.

4. Conclusions

Solid state sintered LAGP pellets were synthesized in order to discuss their stability against various medium conditions such as water, air at 85°C and 1M LiOH solution. According to the results obtained, mediums consisting of Li^+ ions have a positive effect on total ionic conductivity by enhancing the grain boundary conductivity. On the other hands, the results proved that air and water have a negative effect on ionic conductivity by a dramatic reduction on gran boundary conductivity. In all cases, ionic contribution on total ionic conductivity was reduced. Water was determined as the most aggressive mediums effecting the total ionic conductivity not only reducing ionic contribution, but it also significantly reduced the grain boundary conductivity.

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