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Preparation, Characterization and Stability of Li-ion Conducting $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ Glass-Ceramic with NASICON-Type Structure

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ABSTRACT

A super ionic conducting lithium aluminum germanium phosphate (LAGP) glass-ceramic with a formula of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ was synthesized by melt-quenching method and subsequent crystallization at 850 °C for 8 h. The prepared glass-ceramic was characterized using differential scanning calorimetry (DSC), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and AC impedance techniques. The XRD patterns exhibited the existence of $LiGe_2(PO_4)_3$ as the dominant phase with a little impurity phase of GeO_2. SEM images revealed the presence of large LAGP crystals. A high conductivity of 5.36×10^{-3} S/cm at 25 °C was obtained for the pristine LAGP glass-ceramic. Furthermore, the stability of the LAGP was examined in 1 M $LiNO_3$ aqueous solution by XRD and conductivity measurements. XRD pattern and ionic conductivities of the immersed LAGP show no changes compare to the pristine LAGP and indicate the high ionic conductivity and good stability in $LiNO_3$ aqueous electrolyte and these two properties are essential for lithium-protective layer in aqueous lithium-air batteries.

1. INTRODUCTION

With rapid growth of various portable applications, especially electric vehicles (EVs) and hybrid electric vehicles (HEVs), it is necessary to develop rechargeable batteries with high energy and power density, and high safety [1–3]. Rechargeable lithium ion batteries are of great interest due to their high volumetric and gravimetric energy density [4]. However, to drive an electric vehicle for long distances, the energy density of conventional Li-ion batteries is insufficient [5]. Moreover, these types of batteries usually use liquid organic electrolytes, which are flammable and volatile. Hence, these electrolytes are not appropriate for transportation industry due to the explosion probability during high-rate charge or discharge [6]. These problems have restricted the utilization of conventional lithium batteries in electric vehicles.

Lithium-air batteries have attracted a lot of attentions over the past years because of their high theoretical energy density which is higher than that of the conventional lithium ion batteries [7]. These batteries have great potentials to meet the electric vehicle needs [8-11]. All Li-air battery systems employ lithium metal as the anode and oxygen gas, supplied from outside of the battery, as the cathode material. Two types of lithium-air batteries have been developed; aqueous and non-aqueous systems. The non-aqueous system has higher energy density than the aqueous system, but it has some serious problems, including high polarization for the charge and discharge processes, electrolyte decomposition, and electrolyte contamination by moisture from the cathode side [12, 13]. The replacement of organic electrolyte with the aqueous electrolyte is an effective way to solve these problems [14]. In spite of the advantages of aqueous electrolytes, metallic lithium anode reacts severely with water and should be covered with a water-stable lithium conducting solid electrolyte as membrane [15]. This protective layer should have some critical properties, including high lithium ion conducting, aqueous electrolyte stability, stability in contact with lithium metal and impermeability for water molecules and air [14, 16].

Ceramic ionic conductors based on the NASICON-type structure such as $LiTi_2(PO_4)_3$ and $LiGe_2(PO_4)_3$ are promising groups of oxide-based solid lithium-ion conductors [17]. However, in relation to Li ions, Ti4+

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may not be as stable as Ge^{4+} [18, 19]. $LiGe_2(PO_4)_3$ NASICON-type glass-ceramic were crystallized in 3D network structure (rhombohedral crystal system, space group R3c) which has appropriate channels for Li ions migration. There are two types of polyhedrons, GeO_6 octahedra and PO_4 tetrahedra, which are attached by their corners to form $[Ge(PO_4)]^-$ frame with 3D interconnected channels and two types of interstitial cavities, A_1 and A_2. Li ions migrate in channels of this frame. Li ions can occupy in A_1 and A_2 sites. In $LiGe_2(PO_4)_3$ with no dopant, A_2 sites are vacant while A_1 sites are occupied by Li ions [20]. Partial substitution of Ge^{4+} ions by trivalent cations such as Al^{3+} ions increases the unit cell dimensions and residual negative charges are neutralized by additional Li ions. Changing in unit cell dimensions and Li ion concentration in crystal leads to increment in ionic conductivity [20, 21].

One of the major issues facing aqueous lithium-air batteries is protection of metallic lithium anode against aqueous electrolytes. In the present study, NASICON-type $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) glass-ceramic was prepared by melt-quenching method and its microstructure and ionic conductivity were investigated. In addition, the stability of the LAGP glass-ceramic immersed in $LiNO_3$ aqueous electrolyte was examined by XRD and AC impedance measurements. The obtained results show that the prepared LAGP glass-ceramic has high ionic conductivity and good stability in $LiNO_3$ aqueous electrolyte, and both properties are essential for lithium-protective layer in aqueous lithium-air batteries.

2. EXPERIMENTAL

2.1. LAGP Glass-Ceramic Preparation

The melt-quenching method was used to prepare the LAGP glass-ceramic. Stoichiometric amounts of germanium dioxide (GeO_2, 99.8%, Merck, 112177), lithium carbonate (Li_2CO_3, 99.9%, Merck, 105680), aluminum oxide (Al_2O_3, 99.5%, Sigma-Aldrich, 265497) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$, 99.5%, Merck, 101126) were used as the starting materials to prepare $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramic. Powders were weighed with an accuracy of 0.0001 g and mixed for 20 min in an agate mortar and pestle. Then they were heated in electrical furnace at 700 °C for 2 h in order to decompose ammonia, carbon dioxide and water vapor out from the starting materials. Finally, the puff shape materials were crushed in agate mortar and pestle and were transformed in a platinum crucible and heated in electrical furnace at 1450 °C for 1 h. The homogeneous melted glass was pressed and quenched between two preheated (300 °C) stainless steel plates. The transparent thin glass sheets were transferred to another furnace and were annealed at 550 °C for 2 h to release the thermal stresses and then cooled down to room temperature. To obtain the glass-ceramic specimens, annealed glass sheets were crystallized at 850 °C for 8 h with a heating rate of 5 °C/min.

2.2. Characterization and Stability Examination

Thermal behavior of the glass (glass transition temperature (T_g) and crystallization temperature (T_c)) was analyzed by Differential Scanning Calorimetry (DSC, NETZSCH 404 F1 Pegasus-High Temperature DSC, Germany) on the fine powdered glass with a heating rate of 5 °C/min. The crystal structure of the specimens was identified by X-ray diffraction analysis (XRD, Xmd300 Unisantis, Germany) at room temperature using Cu Kα radiation source in 2θ range from 0 to 60°. The microstructure and energy dispersion spectroscopy (EDS) of the glass-ceramic specimen were obtained with a field emission scanning electron microscope (FESEM, Σigma-vp Zeiss, Germany) on the fractured surfaces.

In order to investigate the stability of the LAGP sample, the LAGP plate was immersed in 1 M $LiNO_3$ aqueous solution for 1 month. After this time, the sample was washed with water and dried at 200 °C for overnight to remove the residual water content. The changes of XRD patterns and the ionic conductivity after immersion were examined. The ionic conductivity of the crystallized sample before and after immersion test was determined at the temperatures of 20, 26, 30, 40, 50, 60, 70 and 80 °C using impedance spectroscopy analyzer (Metrohm Autolab PGST302, Netherlands) in the frequency range of 10^{-1}-10^5 Hz, with the voltage amplitude of ±100 mV. Samples for the AC impedance measurement were polished to obtain uniform thickness and flat surfaces. Furthermore, the opposite faces were coated with silver paint for good electrical contact. The impedance data were analyzed using the ZSim program.

3. RESULTS AND DISCUSSION

The DSC curve for the non-annealed LAGP glass is shown in Figure 1. The LAGP glass exhibited a distinct and strong exothermic crystallization peak, Tc, at around 628 °C with a glass transition temperature, Tg, at around 533 °C. The exothermic peak is attributed to the crystallization temperature, Tc. The estimated Tg and Tc values well match with previously reported values in similar systems [16, 22]. Based on this result, crystallization was performed at a temperature above Tc for ensuring perfect crystallization.

Figure 2 shows the XRD patterns of the LAGP specimen before and after thermal treatment at 850 °C for 8 h. In the case of LAGP glass-ceramic, the main diffraction peaks are related to the NASICON-type phase of $LiGe_2(PO_4)_3$ (JCPDS card 80-1924). Unlike the extensive substitution of Al^{3+} at the Ge^{4+} sites, the diffraction patterns match closely and no peaks related to

the Al_2O_3 phase are observed. The extensive substitution of $Al3^+$ for $Ge4^+$ is attributed to the similar ionic radii of Ge^{4+} (0.53 Å) and Al^{3+} (0.54 Å) [23, 24]. The LAGP phase is dominant in the glass-ceramic sample, and other peaks indicate the presence of GeO_2 phase. However, based on this thermal treatment procedure, no impurity $AlPO_4$ phase is observed in the XRD pattern of LAGP glass-ceramic. The $AlPO_4$ impurity is electrically insulating phase and is expected to decrease the conductivity of the glass–ceramic material, even in smaller concentrations [24].

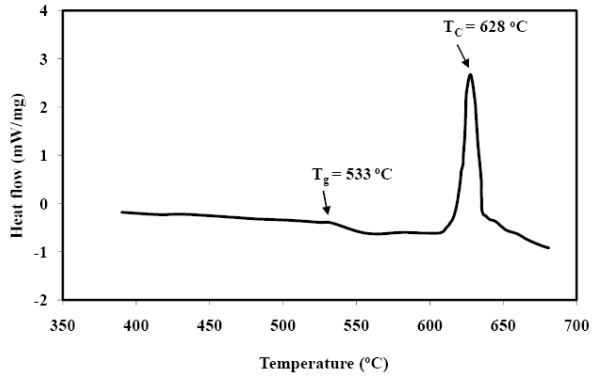

Figure 1. Differential scanning calorimetry plot of as-cast LAGP sample

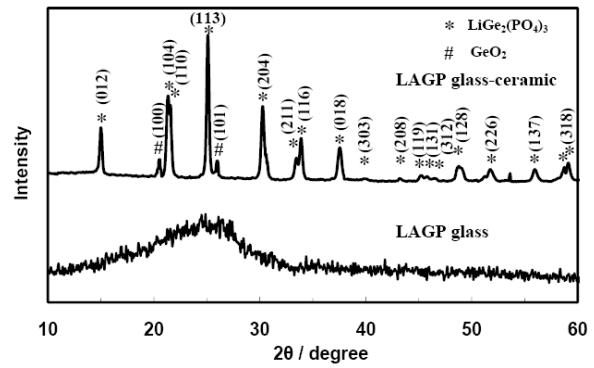

Figure 2. XRD patterns of the LAGP specimen before and after thermal treatment at 850 °C for 8 h

The field emission scanning electron microscopy (FESEM) micrographs of the fractured surfaces of the LAGP glass and glass–ceramic specimens are shown in Figure 3(a) and (b), respectively. In Fig. 3(a), there is no crystal or grain due to the fast cooling of melt. It indicates that a complete amorphous phase was obtained using this synthesis procedure (melt-quenching between two stainless steel sheets). As can be seen, the LAGP glass is very dense and uniform and no pores are observed. It is believed that the existence of the pores in the solid conductive samples decreases the ionic conductivity. The micrograph of the LAGP glass-ceramic shows grown and well-defined crystals and the grains and grain boundaries are completely distinct. The grains are mostly in cubic shape and the grain size distribution is almost uniform. On the other hand, Figure 4 shows energy-dispersive X-ray spectroscopy (EDS) of the LAGP glass-ceramic. The obtained result from the EDS analysis of the specified area is in good agreement with initial stoichiometry. In general, lithium element cannot be determined by EDS analysis. However, Li has only 2.5 wt% in overall formula of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, which does not have great effect on analysis of other elements. Table 1 shows the obtained values from the elemental analysis of the specified area on Figure 4.

To apply glass-ceramics in the aqueous lithium-air batteries, it is necessary to check the stability of glass-ceramics in the aqueous electrolytes. Hence, the stability of the prepared LAGP glass-ceramic was evaluated by immersing the LAGP sample in 1 M $LiNO_3$ aqueous solution for 1 month at 25 °C. Figure 5 shows the XRD patterns of the LAGP glass-ceramic before and after 1 month immersion test. As shown in this figure, no change in the XRD pattern of the immersed LAGP sample is observed. In fact, no notable decrease in peak intensities or no new diffraction peaks are observed after immersion test. This result indicates that the LAGP glass-ceramic is stable and durable for a long period of time in contact with $LiNO_3$ aqueous electrolyte and can be used in the lithium-air batteries with this electrolyte.

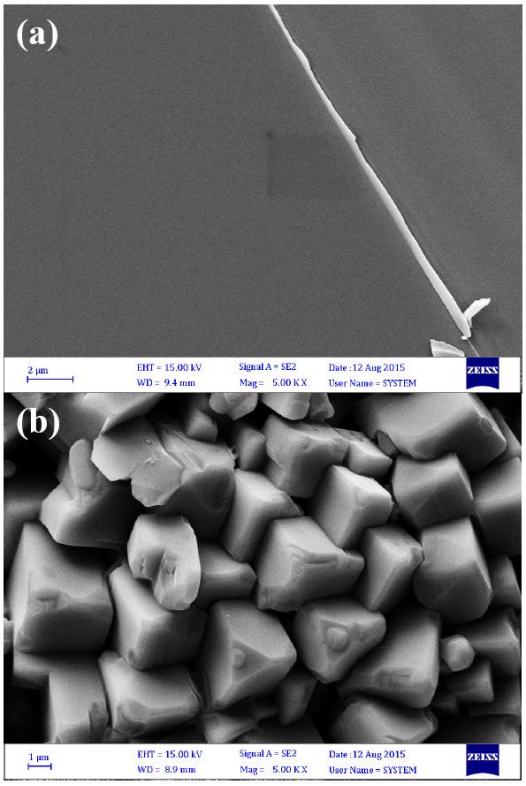

Figure 3. FESEM images of the LAGP specimen (a) before and (b) after crystallization

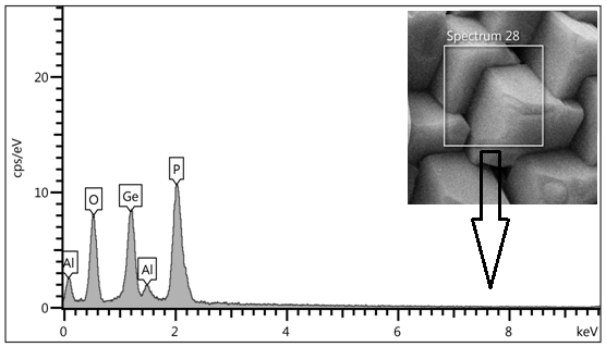

Figure 4. Energy-dispersive X-ray spectroscopy (EDS) of the specified area for the prepared LAGP glass-ceramic

TABLE 1. Elemental analysis (weight percent) of the specified area in Figure 4

	Al	Ge	P	O	Li
Theoretical values in $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$	3.23	26.08	22.24	45.96	2.49
Measured values	3.1	27.3	22.6	47.0	-

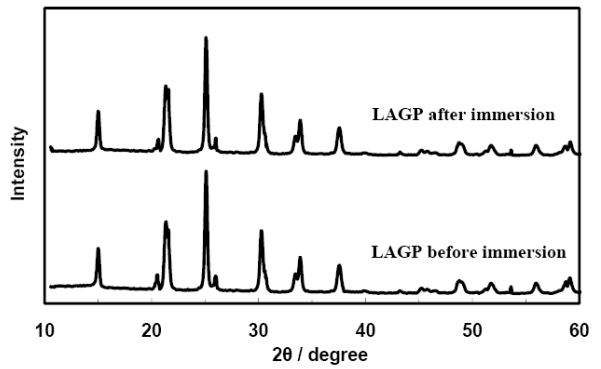

Figure 5. XRD patterns of the pristine LAGP and the LAGP immersed for 1 month in 1 M $LiNO_3$ aqueous solution

The stability of the LAGP glass-ceramic sample immersed in 1 M $LiNO_3$ aqueous solutions was also confirmed from the impedance spectroscopy observations. In fact, the stability of ionic conductivity is a key factor for glass-ceramics for commercial application in the aqueous lithium batteries. In Figure 6, the complex impedance plot of the pristine LAGP sample is compared with those of the LAGP specimen immersed in the 1 M $LiNO_3$ aqueous solution at room temperature for 3 days, 1 week and 1 month. All spectra show a semicircle, attributed to the grain boundary resistance of the LAGP glass-ceramic. Indeed, due to the high ionic conductivity of the grains at room temperature, the semicircle related to the grain conductivity cannot be observed. The intercept of the semicircle on the real axis at high-frequency region represents the bulk resistance, and the straight line in the low-frequency region corresponds to the Warburg impedance (W), which may be attributed to specimen interaction observed for a typical ion conducting solid electrolyte with a blocking electrode [25-27]. In fact, the coarse grains result in decrease in the grain boundaries, lead to enhance lithium ion mobility and hence a higher total conductivity. In order to analyze the obtained EIS spectra, equivalent circuit displayed in Figure 6 was employed. Total ionic conductivity was calculated by following equation [16]:

$$\sigma_t = \frac{d}{S.R_t} \quad (1)$$

Where R_t, S and d are total resistance (summation of grain and grain boundary resistances), painted area and thickness of specimen, respectively. The ionic conductivities of the LAGP glass-ceramic before and after immersing in various times are summarized in Table 2. As can be seen from Figure 6 and Table 2, no significant change of the impedance profiles is observed for immersion time up to 1 month and only the grain boundary resistance slightly increases. The conductivity of the glass-ceramics depends on the microstructure. Hence, the conductivity stability of the LAGP sample during immersion test shows that no significant change occurs in its microstructural characterization. This result is consistent with the XRD results and both show the stability of the LAGP glass-ceramic with $LiNO_3$ aqueous electrolyte.

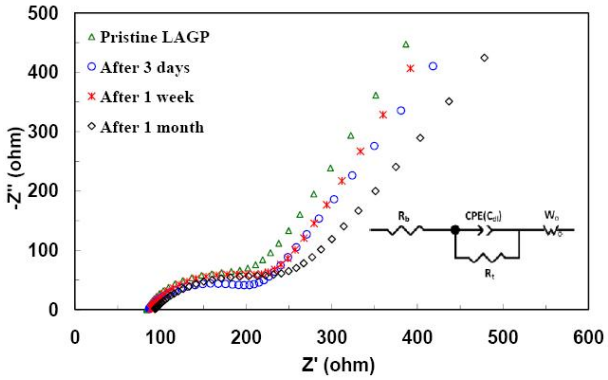

Figure 6. Complex impedance plots at room temperature of the LAGP specimen immersed in 1 M $LiNO_3$ aqueous solution for various times

TABLE 2. Ionic conductivities of the LAGP glass-ceramic before and after immersion in 1 M $LiNO_3$ aqueous solution for various times

Immersion time	Ionic conductivity (S/cm)
Before immersion	5.36×10^{-3}
3 days	5.11×10^{-3}
1 week	4.82×10^{-3}
1 month	4.57×10^{-3}

The temperature dependence of the total conductivity of the pristine LAGP glass-ceramic and the LAGP sample immersed in 1 M $LiNO_3$ aqueous solution for 1 month is shown in Figure 7. These conductivities were obtained from the impedance spectroscopy tests performed in the temperature range of 20-80 °C. As can be seen, the plots of $\log(\sigma_t)$ versus 1000/T are found to be linear and well fit the Arrhenius equation taken by following equation [28]:

$$\sigma_t = Aexp(\frac{-E_a}{kT}) \quad (2)$$

Where A, E_a, K and T are pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively. The consistent of the plots with the Arrhenius equation demonstrates that there were no structure and phase change for both samples in the testing temperature range [3]. It has been shown that if an impurity phase such as $AlPO_4$ forms at the grain boundaries by increasing the temperature, the conductivity-temperature plots will be nonlinear [5, 16, 17, 29]. The $AlPO_4$ phase is a dielectric and has a blocking effect that prevents from easy migration of lithium ions. However, linearity of the obtained plots shows the stability of the prepared LAGP glass-ceramic against elevated temperatures. As a result, the activation energy of the prepared LAGP glass-ceramic was measured to be 0.286 eV. Moreover, it can be seen from this figure that total electrical conductivity of the LAGP sample is the same both before and after immersion, and indicates the stability of the LAGP sample in contact with $LiNO_3$ aqueous electrolyte.

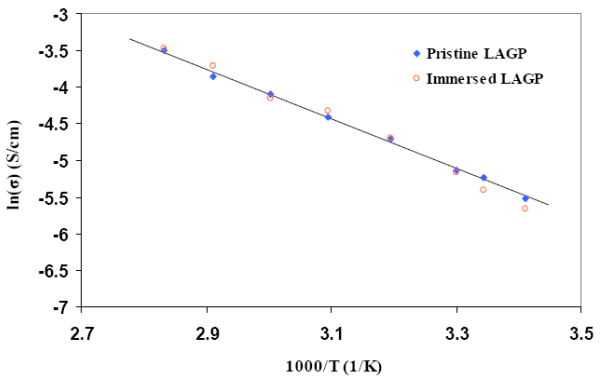

Figure 7. Temperature dependence of ionic conductivity of the LAGP specimen before and after 1 month immersion in 1 M $LiNO_3$ aqueous solution

4. CONCLUSION

A NASICON-type glass ceramic with a formula of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ as fast lithium ion conductor was synthesized by melt-quenching method and subsequent crystallization. The prepared glass-ceramic was characterized by DSC, XRD and FESEM and its ionic conductivity was examined by impedance spectroscopy. Then, the stability of the LAGP sample in 1 M $LiNO_3$ aqueous solution was examined. XRD patterns of the LAGP immersed in the solution at room temperature for 1 month show no changes. Also, no significant conductivity change was observed during immersion test. The above results show the stability of the LAGP glass-ceramic in contact with this aqueous electrolyte, which is very important for practical application in the aqueous lithium-air batteries or other lithium batteries with aqueous electrolytes.

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