Comparison of a high lithium-ion conductivity solid electrolyte prepared by two methods

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Abstract. A NASICON-type structured solid electrolyte of precursor for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ with high lithium-ion conductivity was prepared with solid-state reaction. Two samples have same structures without impurity phases. The highest total electrical conductivities of sintered pellets made with two methods of press method and tape casting calculated at 25°C were 4.65×10^{-4} S/cm and 7.1×10^{-4} S/cm, respectively. The conductivity of sample synthesized with tape casting is significantly increased, but relative density is 90% which is lower than relative density of 96% for sintered pellets synthesized with press method.

1. Introduction

In recent years, the rechargeable lithium-ion battery is widely studied as power equipment of mobile electronic product and electrically driven vehicle [1]. Currently, the commercial lithium-ion battery exists safety issue due to leakage and combustibility. That the solid state electrolyte possesses higher stability excellent mechanical properties and non-flammable can optimize safety issue. Hence many solid electrolyte have been studied such as monocrystal Li_3N, sulfide-base glasses, LISICON, NASICON [2].

1976, Goodenough designed a new solid electrolyte formed with the three-dimensional network structure and named Na super ionic conductor (NASICON) [3]. The NASICON-type structure consist of MO_6 octahedra and PO_4 tetrahedra and is linked with corner to form a $[Ti_2(PO_4)_3]^-$ rigid three-dimensional skeleton. The two different sites for mobile lithium ions are A_1 and A_2, respectively. The A_1 sites are fully occupied by lithium ions and lie an elongated octahedral oxygen environment, but the A_2 sites are completely vacant [4]. Anon [2][5] has reported $LiTi_2(PO_4)_3$ with poor ionic conductivity and high porosity, if the Ti^{4+} sites are partially substituted by some trivalent M^{3+} (M=Al or Sc) in the $LiTi_2(PO_4)_3$ systems, the conductivity has effective enhancement and the maximum can reach 7.0×10^{-4} s/cm at 298 k for $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$. The Ti^{4+} partially replaced by $Al^{3+}+Li^+$ and the Li^+ insertion onto the A_2 sites are not effect for the Li^+ mobility. The conductivity enhancement is mainly attributed to the grain boundary but no correlation with bulk. So the grain boundary is main factors to improve the conductivity in $LiM_2(PO_4)_3$ systems [6].

In general, the LATP precursor is synthesized by conventional melting-quenching [7][8], sol-gel [9] or solid-state method. 1996, Fu reported LATP specimens obtained by using melting-quenching method, the maximum conductivity of 1.3×10^{-3} s/cm was measured at room temperature [7]. The LATP nano-powder reported by Y. Yoon et al sintered at 900°C for 3 hours by using a sol-gel method has a room temperature conductivity of 7.8×10^{-5} s/cm [9]. However, the melting-quenching inevitably cause a lose of Lithium due to sintered pelleted need heating 1450°C [7] and the sol-gel method need higher cost coprecipitator [10]. But the solid-state is a method of simple, low cost and suitable for mass

production. E. Kazakevicius et al reported a new material $Li_{1.3}Ge_{1.4}Ti_{0.3}Al_{0.3}(PO_4)_3$ by Ge^{4+} partial substitution Ti^{4+} in the LATP NASICON structure, which exhibit good electrolytic property [11]. Then, Zhang et al reported the highest total electrical conductivity of 1.29×10^{-3}s/cm at 25°C from $Li_{1.4}Al_{0.4}Ti_{1.4}Ge_{0.2}(PO_4)_3$ [14], but the study about $Li_{1.4}Fe_xAl_{0.4-x}Ti_{1.6}(PO_4)_3$ was not significant break contrasted with $Li_{1.4}Al_{0.4}Ti_{1.4}Ge_{0.2}(PO_4)_3$ [15]. The water-stable lithium ion conducting solid electrolyte can be used as an interlayer to insulate air and water [12] and the LATP-Epoxy hybrid sheets obtained by pouring 2,2-bis(4-glycidyloxyphneyl)propane and 1,3-phenylenediamine in tetrahydrofuran into the LATP sheets have the conductivity of 4×10^{-4}s/cm and watertightness [13]. In this study, we attempted to research LANTP by pentavalent Nb partial substitution Ti sites, and prepared $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}$ $(PO_4)_3$ sheets by tape casting and press method, and discussed the performance.

2. Experimental

The NASICON-type $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ precursor obtained by using solid-state reaction[16]. Stoichiometric amounts of Li_2CO_3, TiO_2, Nb_2O_5, Al_2O_3, and $NH_4H_2PO_4$ were ball-milled with Zirconia balls in a zirconia vessel for 2h at 400 rpm using high-energy mechanical milling (HEMM) with a planetary micro mill, and the mixed powder calcined at 600°C for 4 h. The obtained powders again was ball-milled using HEMM before pressed into pellets at 150 MPa, then calcined at 850°C for 5 h. The sintered pellets were reground and thirdly ball-milled for 10h. The fine precursor powder was made into $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellets by isostatically pressing at 150 MPa and tape casting reported by P. Zhang [17]. Briefly, the fine $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ powder dispersed in a mixed solution of ethanol and toluene (1:1) using menhaden fish oil (2 wt% to LANTP) as a dispersant. Then the mixed slurry was ball-milled at 400 rpm using a ZrO_2 vessel and ZrO_2 ball for 12h with HEMM. Then, the Polyvinyl butyl alcohol (8 wt% to LANTP) as a binder and butyl benzyl phthalate (7 wt% to LANTP) as a plasticizer was poured into the mixed slurry and ball-milled using the HEMM at 150 rpm for another 12 h. Then the slurry was be removed air bubbles by using a planetary vacuum mixer (Thinky, Japan) for 9 min. After tape casting, the green sheets were kept in a sealed box with a small amount of ethanol in a refrigerator to slowly dry at 5°C for 24 h. Several green sheets were hot pressed at 90°C for 10 min and then sintered at 900°C for 7 h. The diameter of obtained pellets with thickness of approximately 0.3 mm is 7 mm.

The phases analysis was operated by a Rigaku Rint 2500 diffractometer with Cu Kα radiation in the 2θ range from 10° to 90° at a scanning step rate of 0.02°/s as X-ray diffraction (XRD) analysis. The samples both side were sputtered a thin gold layer as electrodes, then the electrical conductivity was measured by using an impedance phase analyzer in the frequency range of 0.1 Hz- 1 MHz with the bias voltage at 10mV. The bulk and grain boundray conductivity of samples were calculated from complex plots using Zview 2. Three-point bending strength of LANTP samples was measured at room temperature using a materials tester (Shimadzu EX-SX 500 N). Then the dates of the samples were obtained by using two method of tape casting and press method were compared and discussed.

3. Results and Discussion

Figure.1 shows the XRD patterns of the $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellets made with two methods of press method and tape casting and sintered in the temperature 900°C for 7h. The two samples prepared by using two methods were compared about the impurities phases and the lattice constants, and the analysis indicates the two samples of the NASICON-type structure $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ without impurity phases such as $AlPO_4$, Li_3PO_4, and monoclinic NASICON-type $Li_2AlTi(PO_4)_3$. Previously, Shang reported the XRD patterns of the $Li_{i1+x-y}Al_xNb_yTi_{2-x-y}(PO_4)_3$(x=0-0.6, y=0-0.3) systems by press method and the impurity
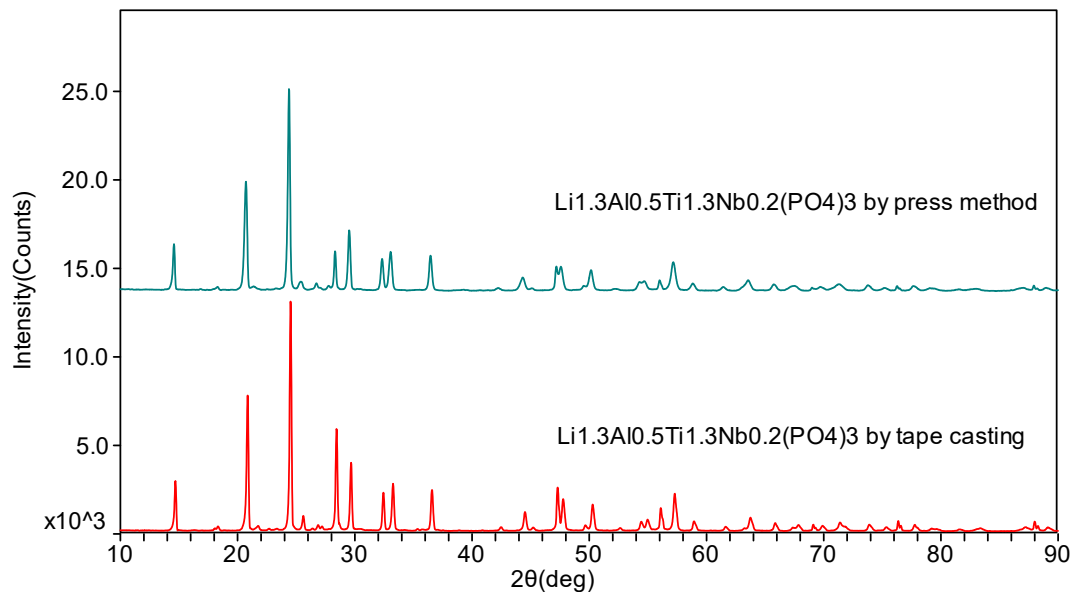
Figure 1. XRD patterns for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ by two methods sintered at 900 °C for 7 h.

phases were not detected in the XRD patterns of $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$, but the impurity phases of $Li_2AlTi(PO_4)_3$ and $Al(PO_4)_3$ were observed in the other type $Li_{1+x-y}Al_xNb_yTi_{2-x-y}(PO_4)_3$ [18]. The lattice parameters calculated by the hexagonal unit cell of $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ prepared with two methods are same and there are a=0.8513 Å and c=2.0878 Å. The relative densities of $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellets sintered at 900°C for 7h were calculated from the ratio of theoretical densities and actual measurement densities, the relative density of 96% was obtained for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellet synthesized by using press method, which is larger than the relative density of 90% for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellet synthesized by using tape casting. The two different manufacture processes have insignificant effect for the lattice parameters, but the relative density is related with two different methods.

Figure.2 shows the impedance profiles of samples for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ pellets synthesized with two methods of tape casting and press method. Only one large semicircle was observed and a straight line follow it. The complex impedance plots show similar behavior with LATP. The intercept of the semicircle on the real axis at high frequency represents the bulk resistance, and the diameter of semicircle in high frequency range was attributed to the grain boundary resistance [7]. The total conductivity of $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ is the maximum compared with other patterns of $Li_{1+x-y}Al_xNb_yTi_{2-x-y}(PO_4)_3$ [18]. The highest grain boundary conductivity and bulk conductivity of $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ prepared with press method sintered at 900°C for 7h were found, which are 1.35×10^{-3} S/cm and 7.1×10^{-4} S/cm at 25 °C, respectively. The lager grain boundary conductivity and bulk conductivity of sample prepared with tape casting method are 2.38×10^{-3} S/cm and $1.08\times10{-3}$ S/cm at 25 °C, the total conductivity of $7.4\times10{-4}$
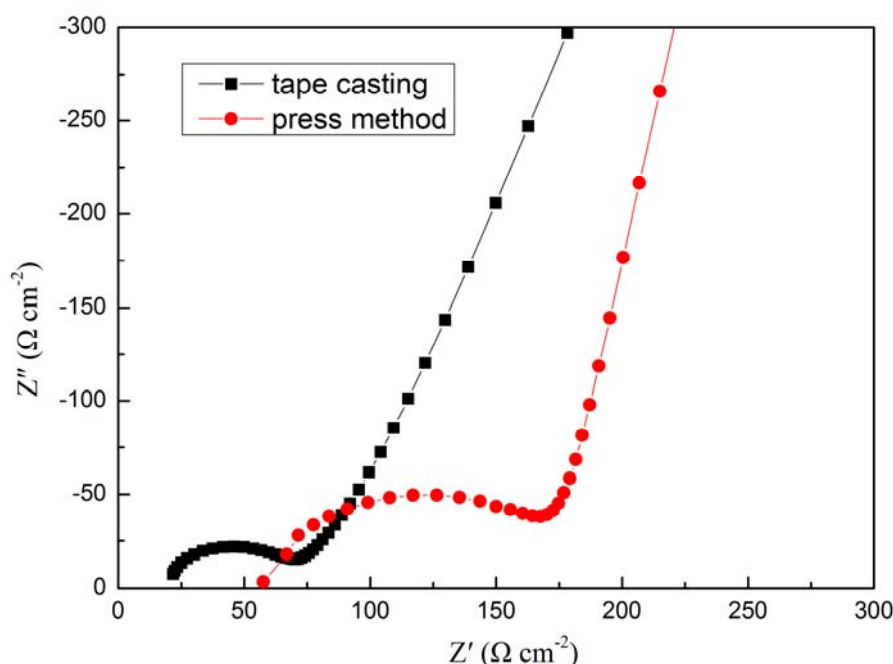
Figure 2. Impedance profiles of $Au/Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3/Au$ by two methods measured at 25 °C

S/cm is also larger than the total conductivity of 4.65×10^{-4} S/cm for sample made by using press method. The larger grain boundary conductivity of samples made by using tape casting method may be contributed to the particle distribution of sample more uniform than samples made by using press method. The total conductivities of two samples for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ are higher than $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$($2.3\times10^{-4}$ S/cm at 25 °C) [19]. The dates of three-point bending strength for two samples prepared by using press method and tape casting are 50 N mm^{-2} and 90 N mm^{-2}, respectively.

4. Conclusion
The precursor of NASICON-type lithium-ion conducting solid electrolyte for $Li_{1.3}Al_{0.5}Ti_{1.3}Nb_{0.2}(PO_4)_3$ was prepared by using solid-state reaction, the sintered pellets were fabricated at 900°C for 7 h by using two method of press method and tape casting. Two samples were the purity phase by XRD pattern analysis, the a lattice parameter and c lattice parameter are all 0.8513 Å and 2. 0878 Å. The relative densities of samples made with press method and tape casting are 96% and 90%, respectively. The conductivity of 7.4×10^{-4} S/cm for samples made by using tape casting is larger than the conductivity of 4.65×10^{-4} S/cm for sample made by using press method. The thr ee-point bending strengths are 50 N mm^{-2} and 90 N mm^{-2}, respectively. The NASICON-type lithi um-ion conducting structured solid electrolyte of LATP by partially adding pentavalent Nb ion c an increase the total conductivity. The two samples all have highlight performance for promising candidate of solid electrolyte.

References
[1]Armand M and Tarascon J M, 2008, *Nature* 451-652.
[2]Asachi G, Imanaka N and Aono H, 1996, *Adv Mater* 8 No.2 127-35.
[3]Goodenough J B, Hong H Y-P and Kafalas J A, 1976, *Mat. Res. Bull* 11 203-20.

[4]Martinez-Juarez A, Pecharroman C, Iglesias J E and Rojo J M, 1998, *J. Phys. Chem.* B 102 372-75.

[5]Aono H, Sugimoto E, Sadaoka Y, Imanaka N and Adachi G, 1990, *J. Electrochem. Soc* No.4 Vol.137 1023-27.

[6]Aono H, Sugimoto E, Sadaoka Y, Imanaka N and Adachi G, 1990, *Chem. Lett* 1825-28.

[7]J Fu, 1996, *Solid State Ionics* 96 195-200.

[8]Thokchom J S and Kumar B, 2006, *Solid state Ionics* 177 727-32.

[9]Yoon Y, Kim J, Park C and Shin D, 2013, *J. Ceram Process Res* Vol.14 No.4 563-66.

[10] Ma F, Zhao E, Zhu S, Yan W, Sun D, Jin Y and Nan C, 2016, *Solid State Ionics*, 29 7-12.

[11] Kazakevicius E, Urcinskas A, Keziionis A, Dindune A, Kanepe Z and Ronis J, 2006, *Electrochimica Acta* 51 6199-202.

[12] Imanishi N, Zhang T, Shimonishi Y, Hasegawa S, Hirano A, Takeda Y, Yamamoto O and Sammas N, 2010, *Chem. Commun.* 46 1661-3.

[13] Takahashi K, Johnson P, Imanishi N, Sammes N, Takeda Y and Yamamoto O, 2012, *J.Electrochem.Soc* 159(7) A1065-69.

[14] Zhang P, Matsui M, Hirano A, Takeda Y, Yamamoto O and Imanishi N, 2013, *Solid State Ionics* 253 175-80.

[15] Zhang P, Matsui M, Takeda Y, Yamamoto O and Imanishi N, 2014, *Solid State Ionics,* 263 27-32.

[16] Shang X, Nemori H, Mitsuoka S, Xu P, Matsui M, Takeda Y, Yamamoto O and Imanishi N, 2016, *Frontiers in Energy Research* Vol.4 Article.12.

[17] Zhang P, Wang H, Lee Y, Matsui M, Takeda Y, Yamamoto O and Imanishi N 2015 *J.Electrochem. Soc* 162 A1265-71.

[18] Shang X, Nemori H, Mitsuoka S, Matsui M, Takeda Y, Yamamoto O and Imanishi N, 2016, *Solid State Ionics* 297 43-8.

[19] Xu X, Wen Z, Wu J and Yang X, 2007, *Solid State Ionics* 178 29-34.