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

Shang Xuefu¹, Cheng Si, Zhang Jinhao, Wang Yawei

Department of Physics, Faculty of Science, Jiangsu University, Zhenjiang, Jiangsu, 212013

¹ Corresponding author. E-mail address: shangxuefu@yeah.net

Abstract. A NASICON-type structured solid electrolyte of precursor for Li₁.₃Al₀.₅Ti₁.₃Nb₀.₂(PO₄)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 Li₃N, 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 MO₆ octahedra and PO₄ tetrahedra and is linked with corner to form a [Ti₂(PO₄)₃] rigid three-dimensional skeleton. The two different sites for mobile lithium ions are A₁ and A₂, respectively. The A₁ sites are fully occupied by lithium ions and lie an elongated octahedral oxygen environment, but the A₂ sites are completely vacant [4]. Anon [2][5] has reported LiTi₂(PO₄)₃ with poor ionic conductivity and high porosity, if the Ti⁴⁺ sites are partially substituted by some trivalent M³⁺ (M=Al or Sc) in the LiTi₂(PO₄)₃ systems, the conductivity has effective enhancement and the maximum can reach 7.0×10⁻⁴ s/cm at 298 k for Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃. The Ti⁴⁺ partially replaced by Al³⁺+Li⁺ and the Li⁺ insertion onto the A₂ 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 LiM₂(PO₄)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 $1.29\times10^{-3}$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$_{x}$Al$_{0.4-x}$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 $4\times10^{-4}$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$_2$CO$_3$, TiO$_2$, Nb$_2$O$_5$, Al$_2$O$_3$, and NH$_4$H$_2$PO$_4$ 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 boundary 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$_2$PO$_4$, and monoclinic NASICON-type Li$_2$AlTi(PO$_4$)$_3$. Previously, Shang reported the XRD patterns of the L$_{1+\delta}$(x+y)Al$_x$Nb$_y$Ti$_{2-x}$PO$_{4}$$_3$(x=0-0.6, y=0-0.3) systems by press method and the impurity...
phases were not detected in the XRD patterns of Li1.3Al0.5Ti1.3Nb0.2 (PO4)3, but the impurity phases of Li2AlTi(PO4)3 and Al(PO4)3 were observed in the other type Li1x-yAlxNb2-x-y(PO4)3 [18]. The lattice parameters calculated by the hexagonal unit cell of Li1.3Al0.5Ti1.3Nb0.2 (PO4)3 prepared with two methods are same and there are a=0.8513 Å and c=2.0878 Å. The relative densities of Li1.3Al0.5Ti1.3Nb0.2 (PO4)3 pellets sintered at 900 °C for 7 h were calculated from the ratio of theoretical and actual measurement densities, the relative density of 96% was obtained for Li1.3Al0.5Ti1.3Nb0.2 (PO4)3 pellet synthesized by using press method, which is larger than the relative density of 90% for Li1.3Al0.5Ti1.3Nb0.2 (PO4)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 Li1.3Al0.5Ti1.3Nb0.2 (PO4)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 Li1.3Al0.5Ti1.3Nb0.2 (PO4)3 is the maximum compared with other patterns of Li1x-yAlxNb2-x-y (PO4)3 [18]. The highest grain boundary conductivity and bulk conductivity of Li1.3Al0.5Ti1.3Nb0.2 (PO4)3 prepared with press method sintered at 900°C for 7 h were found, which are 1.35×10⁻³ S/cm and 7.1×10⁻⁴ S/cm at 25 °C, respectively. The larger grain boundary conductivity and bulk conductivity of sample prepared with tape casting method are 2.38×10⁻³ S/cm and 1.08×10⁻³ S/cm at 25 °C, the total conductivity of 7.4×10⁻⁴.
Figure 2. Impedance profiles of Au/Li1.3Al0.5Ti1.3Nb0.2(PO4)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 Li1.3Al0.5Ti1.3Nb0.2(PO4)3 are higher than Li1.3Al0.3Ti1.7(PO4)3(2.3×10^{-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 Li1.3Al0.5Ti1.3Nb0.2(PO4)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 three-point bending strengths are 50 N mm^{-2} and 90 N mm^{-2}, respectively. The NASICON-type lithium-ion conducting structured solid electrolyte of LATP by partially adding pentavalent Nb ion can increase the total conductivity. The two samples all have highlight performance for promising candidate of solid electrolyte.

Acknowledgment
The authors gratefully acknowledge the financial supports from the National Natural Science Foundation of China (11304125) and the Research Foundation for Advanced Talents, Jiangsu University (10JDG077).

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.