Influence of the pressure applied to make LATP pellets

Xiaojuan Lu
Department of Environmental Science and Engineering, North China Electric Power University, Mailbox 253, No.689 Huadian Road, Baoding, Hebei, PR China
xiaojuanlv@hotmail.com

Abstract. NASICON structured Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (0.1≤x≤0.7) powders were prepared by hydrothermal synthesis method and the pressure applied to press the powders into pellets was investigated in this study. The conductivity was measured by an impedance analyzer and the microstructures were examined by SEM. The variation trend with Al amount was almost identical for LATP pressed at high pressure and low pressure. Both the total conductivities of LATP prepared at high pressures and low pressures peaked at x=0.6. The conductivities of LATP pressed at high pressures were all higher than those at low pressures. The reason was mainly attributed to the denser microstructures achieved at higher pressure.

1. Introduction
Lithium ion batteries have attracted significant interests due to the concerns of limited supply of fossil fuels and the air pollution resulted in burning of fossil fuels. Organic liquid electrolytes which are flammable and inclined to leak, used in commercially available Li ion batteries, hinder the large scale application of Li ion batteries due to the severe safety concerns. Inorganic solid lithium ion conductors, which are chemically stable, safe and easy to miniaturization, have increasingly become popular to replace organic liquid electrolytes in lithium ion batteries. Na-superionic conductor (NASICON) structured lithium ion conductors with a general formula Li$_{1+x}$M$^{+}$M$^{''+}$x(PO$_4$)$_3$, of which Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (LATP) exhibit conductivities in the range of 10$^{-3}$-10$^{-4}$ S/cm [1–4], show a great prospect. Various methods including solid state reactions, sol-gel [5, 6], co-precipitation [7, 8] and hydrothermal synthesis [4] have been attempted to synthesize LATP. For various synthesis methods, the preparation conditions have played a vital role in affecting the performance of lithium ion conductors made. Synthesis parameters like hydrothermal reaction temperature/time, calcinations temperature and dwelling time during the subsequent sintering stage have been studied. However, the effect of pressure applied to press the powders into pellets during the preparation of green pellets, which is potentially important, has not been reported yet.

The highest ionic conductivity achieved so far was based on a high preparation temperature over 1400°C, which is detrimental to other components in the batteries. Thus, it is beneficial to lower the synthesis temperatures of LATP. Kim et al. [4] found that hydrothermal method is effective on lowering the sintering temperatures and a decent conductivity has been achieved at 900°C. Therefore, the hydrothermal synthesis was adopted to prepare LATP powers and the effect of the pressure applied to pressing the powders have been investigated in this paper.
2. Experimental

NASICON structured Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (0.1≤x≤0.7) powders were prepared by hydrothermal synthesis here. Start materials used were LiOH•H$_2$O (>99%), Al(NO$_3$)$_3$•9H$_2$O (>98%) and Ti(OCH(CH$_3$)$_2$)$_4$ (>97%) and H$_3$PO$_4$ (>98%). Firstly, 5mM of Ti(OCH(CH$_3$)$_2$)$_4$ in 100mL of deionized water was obtained by stirring at 300rpm for 2h. With the stirring maintained at 300rpm, LiOH•H$_2$O, Al(NO$_3$)$_3$•9H$_2$O and H$_3$PO$_4$ was added in an interval of 1h. The resultant solution was transferred into a Teflon vessel inside a hermetically sealed stainless steel container and placed in a furnace at 180°C for 6h. And then a powdery product was obtained after drying at 90°C for 24h. The powders were calcined at 700°C for 2h and subsequently ground in a pestle mortar to gain fine powders. Green LATP pellets in 15mm diameter were prepared by pressing the powers with varied pressures and subsequently sintered at 950°C for 4h. The pressure applied was 50kgf/cm$^2$ and 100kgf/cm$^2$ for 10min. The pellet pressed using a pressure of 100kgf/cm$^2$ was designated as LATP-H and the pellet pressed using a pressure of 50kgf/cm$^2$ was indexed as LATP-L.

Both the densities of green pellets and sintering pellets were determined by measuring their weights and apparent volumes. The microstructures were examined by using a field emission scanning electron microscope (JSM-7800F). The conductivity measurement was carried out by using a electrochemical impedance spectroscopy [9].

3. Results and Discussions

3.1. Densities evaluations of LATP-H and LATP-L

The densities of sintered LATP-H and LATP-L were determined by weighting the samples and measuring apparent volumes, shown in Fig.1. The densities did not exhibit a clear trend with the doping amount of Al, but the densities of the LATP pressed at high pressures were all higher than those pressed at low pressures.

![Fig.1 Densities of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ pressed at different pressures](image)

3.2. Total conductivities of LATP-H and LATP-L

Total conductivities of sintered LATP-H and LATP-L were calculated based on the impedance obtained from the impedance analyzer. It was found that the variation trend with Al amount was almost identical for LATP pressed at high pressure and low pressure. Both the total conductivities of LATP-H and LATP-L peaked at x=0.6. The value was inconsistent with the value reported previously. The reason is possibly due to the loss of lithium during the sintering stage, since no extra lithium was added to compensate which most of studies did.
Fig.2 Total conductivities of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ pressed at different pressures

The conductivities of LATP-H were all higher than LATP-L. The reason was mainly attributed to the denser microstructures achieved at higher pressure. The higher the density is, the less porosity and defects are in the samples. Therefore, when lithium ions migrated through the grain boundaries, the resistance would be smaller which facilitate the migrations of lithium ions.

3.3. Microstructures of LATP
The conductivity of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ with $x=0.6$ was much higher than the conductivity of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ with $x=0.1$. The microstructures of these two samples were observed by SEM and SEM photos are shown in Fig.3. It can be seen that the microstructure was very rough and the grains were very small when the doping amount of Al was 0.1. When the doping amount of Al increases to 0.6, the morphology became much denser and the grains grew. The change of the morphology may be attributed to the conductivity observed in Fig.2. A denser morphology will be beneficial to the improvement of conductivity which was explained by the steric effect of pores [10]. On the top of that, bigger grains indicated less grain boundaries, which would further improve the conduction of lithium ions.

Fig. 3 SEM photos of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$

4. Conclusions
NASICON structured Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ $(0.1 \leq x \leq 0.7)$ powders were prepared by hydrothermal synthesis method in this study and the pressure applied to press the powders into pellets was investigated. The variation trend with Al amount was almost identical for LATP pressed at high pressure and low pressure. Both the total conductivities of LATP-H and LATP-L peaked at $x=0.6$. The conductivities of LATP pressed at high pressures were all higher than those at low pressures. The reason was mainly attributed to the denser microstructures achieved at higher pressure.

Acknowledgements
This research was financially supported by the Fundamental Research Funds for the Central Universities (No. 2017MS138) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.
References

[1] M. Zhang, Z. Huang, J. f Cheng, O. Yamamoto, N. Imanishi, B. Chi, J. Pu, J. Li, Solid state lithium ionic conducting thin film Li$_{1.4}$Al$_{0.4}$Ge$_{1.6}$(PO$_4$)$_3$ prepared by tape casting, J. Alloy. Compd. 590 (2014) 147–152.

[2] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, Ionic conductivity of solid electrolytes based on lithium titanium phosphate, J. Electrochem. Soc. 137 (1990) 1023–1027.

[3] J. L. Narváez-Semanate, A. C. M. Rodrigues, Microstructure and ionic conductivity of Li$_{1+x}$Al$_{1-x}$Ti$_2$(PO$_4$)$_3$ NASICON glass-ceramics, Solid State Ion. 181 (2010) 1197–1204.

[4] K. M. Kim, D. O. Shin, Y. -G. Lee, Effects of preparation conditions on the ionic conductivity of hydrothermally synthesized Li$_{1+x}$Al$_x$Ti$_2$(PO$_4$)$_3$ solid electrolytes, Electrochimica Acta 176 (2015) 1364–1373.

[5] M. Kotobuki, M. Koishi, Preparation of Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ solid electrolyte via a sol-gel route using various Al sources, Ceram. Intern. 39 (2013) 4645–4649.

[6] G. B. Kunshina, O. G. Gromov, E. P. Lokshin, V. T. Kalinnikov, Sol-gel synthesis of Li$_{1.3}$Al$_{0.2}$Ti$_{1.8}$(PO$_4$)$_3$ solid electrolyte, Russ. J. Inorg. Chem. 59 (2014) 424–430.

[7] M. Kotobuki, M. Koishi, Y. Kato, Preparation of Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ solid electrolyte via a co-precipitation method, Ionics 19 (2013) 1945–1948.

[8] S. Duluard, A. Paillassa, L. Puech, P. Vinatier, V. Turq, P. Rozier, P. Lenormand, P. - L. Taberna, P. Simon, F. Ansart, Lithium conducting solid electrolyte Li$_{1.3}$Al$_{0.2}$Ti$_{1.8}$(PO$_4$)$_3$ obtained via solution chemistry, J. Eur. Ceram. Soc. 33 (2013) 1145–1153.

[9] X. Lu, D. Yang, Effect of sintering conditions on perovskite lithium-based ion conductor, Emerging Mater. Res. 6 (2017) 1-19.

[10] J. Tan, Y. Su, H. Tang, T. Hu, Q. Yu, R. Tursun and X. Zhang, Effect of calcined parameters on microstructure and electrical conductivity of 10Sc1CeSZ, J. Alloy Compd. 686 (2016) 394-398.