

Effects of Sintering Temperatures on the Crystallinity and Electrochemical Properties of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ via Solid-State Sintering Method

Yi Fei¹, Shipai Song¹, Fang Wu¹, Zongkai Yan¹, Dingding Yuan², Chen Fu¹, Jiayuan Shi¹, Xiaokun Zhang¹, Yong Xiang^{1,*}

¹Scholl of Energy and Science Engineering, University of Electronic Science and Technology of China, Chengdu, 611731, China

²EVE Energy Corporation, Huizhou, 516000, China

*Corresponding author e-mail: xyg@uestc.edu.cn

Abstract. In this study, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) powder material was prepared via solid-state sintering method under the environment where oxygen and water is isolated. The influences of different sintering temperatures on crystallinity and electric electrochemical properties of the prepared LGPS powder were investigated. The experiment results indicate that the LGPS powder prepared with different sintering temperatures show good crystallinity, and the crystallinity of the LGPS powder is improved at a higher sintering temperature. Moreover, the ionic conductivity of the prepared LGPS powder material increased firstly and then decreased with the increasing sintering temperature, and the highest ionic conductivity of the prepared LGPS powder obtained at 570 °C reached about 1.6×10^{-3} S/cm (room temperature).

1. Introduction

Recently Li-ion battery is quickly rising, and it has attracted broad interest due to its high energy density, relatively fast charging and discharging rate, good voltage stability and cycle performance. The realization of highly safety Li-ion battery is one of the major challenges in developing advanced energy storage technologies. Electrolyte is the key issue to improve the battery the safety [1]. Electrolyte can be divided into liquid electrolyte, gel electrolyte and solid electrolyte. Much efforts has been focused on solid electrolyte for its better security and better performance than organic liquid electrolyte [2]. Moreover, solid electrolyte has higher ionic conductivity than organic liquid electrolyte with either a one-dimensional (1D) ionic tunnel or a 3D network [3-7].

Among various materials used in solid electrolyte, the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) has a high conductivity due to its three-dimensional framework structure composed of $\text{Ge}(\text{P})\text{S}_4$ tetrahedra, PS_4 octahedra and LiS_6 octahedra [8]. The LGPS has been reported to own the highest solid Li ion conductivity of 12 mS/cm at room temperature in 2011 by Kamaya et al [3]. Very recently, highly conductive Li electrolytes with conductivity of several mS/cm were also found in the similar family of compounds $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ and $\text{Li}_{11}\text{Si}_2\text{PS}_{12}$ [9, 10]. For example, Ogn et al synthesised $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ by projector augmented-wave approach with an conductivity of 6 mS/cm and an activation energy of 0.24 eV in 2012 [11]. HASSOUN et al fabricated LGPS powder via ball mill and high temperature quenching, the obtained LGPS shows a high conductivity of 1.0 mS/cm, a fast lithium ion transfer rate of 0.99, and a



wide electrochemical window over 6 V [12]. The electrical property of LGPS has a strong interaction with the structure framework of LGPS, especially its crystallinity. However, little attention has been paid to investigate the interaction between the crystallinity and the electrical property.

In this paper, we fabricate the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) powder via solid-state sintering method under an inert environment of isolated oxygen and water, and the effect of sintering temperature on the electrochemical properties and crystallinity of LGPS were studied. X-ray powder diffraction (XRD) and electrochemical impedance spectroscopy (EIS) were used to investigate the crystallinity and the ionic conductivity of LGPS that fabricated under different sintering temperature. By comparing the crystallinity and the ionic conductivity of different LGPS samples under different sintering temperature, the effect of the crystallization on the electrochemical properties of the sample was obtained.

2. Experiment

2.1. The preparation of LGPS

LGPS solid electrolyte was prepared by the mechanical ball grinding and pressing sintering of the planetary ball mill under an inert environment of isolated oxygen and water. First, the initial mixture solution employed in this study were Li_2S (99.9%, Alfa Aesar.), P_2S_5 (99.9%; BT reagents), GeS_2 (99.9%, BT reagents) at a mole ratio of 5:1:1, and mixed in glove box, and followed by grinding in a planetary ball mill (QM-3SP2) for 6 hours to obtain the powder. Second, the powder was transformed into pellet with a pressed wafer under a pressure of 300 MPa for 10 minutes, where the pressed wafer is placed into the sealed quartz sintering tube. Third, the obtained pellet was sintered in the tube furnace at 550 °C, 560 °C, 570 °C, 580 °C, 590 °C for 8 hours. And finally, to obtain the LGPS electrolyte, the sintered pellet was cool slowly to room temperature, grinded into powder and then repressed under the pressure of 300 MPa.

2.2. X-ray diffraction patterns

X-ray diffraction patterns of the powdered LGPS were obtained using an X-ray diffractometer (Rigaku Ultima IV., Japan) with CuK α radiation. The X-ray diffraction data was collected in a 0.02° step width over the 2 θ range of 20° to 60°. The solid electrolyte LGPS is placed in a grooved quartz grinder and sealed with a polyester film in a glove box to prevent the material from reacting to the oxygen and water in the air.

2.3. X-ray diffraction patterns

The EIS tests (VersaSTAT 3F, Princeton Applied Research, America) of the LGPS sample fabricated under different temperature of 550 °C, 560 °C, 570 °C, 580 °C, 590 °C was characterization by applying 10 mV with a scanning frequency of 0.1 Hz - 10000 Hz at room temperature. The LGPS sample was assembled in a glove box in three steps: pasted with two silver layers, dried and assembled into a sealed three electrode. Furthermore, the ionic conductivity under different temperature of 20 °C, 50 °C, 75 °C, 100 °C, 125 °C of the sample with the highest ionic conductivity was also tested via the EIS measurement. The ionic conductivity was calculated through the formula:

$$\sigma = \frac{d}{R \times A} \quad (1)$$

D is the thickness of the LGPS pellet, and A is the area of the conductive surface (the area covered by the single silver pulp), and R is the resistance of the sample. Activation would change with the temperature.

3. Analysis and discussion

3.1. X-ray diffraction patterns

LGPS solid electrolyte is prepared by the mechanical ball grinding and pressing sintering process under an inert environment of isolated oxygen and water. Since the sintering temperature of solid-state sintering method can influence the crystallinity of the sintered materials, and result in the change of the ionic conductivity of the solid electrolyte. Therefore, the effect of sintering temperature on the crystallinity of LGPS were firstly studied. As shown in Fig. 1, the crystallization of the samples of LGPS, which were sintered at different temperatures, were investigated via XRD. The diffraction peaks of all the samples fabricated under different temperature occur at the same positions, indicating all the samples show good crystallinity. However, there exist obvious difference in the intensity and width of the diffraction peaks. In particular, the intensity of the diffraction peaks (28.5°) of the sample fabricated under 570°C is relatively higher, and the width is relatively narrower when compared with other samples, indicating a much better crystallinity.

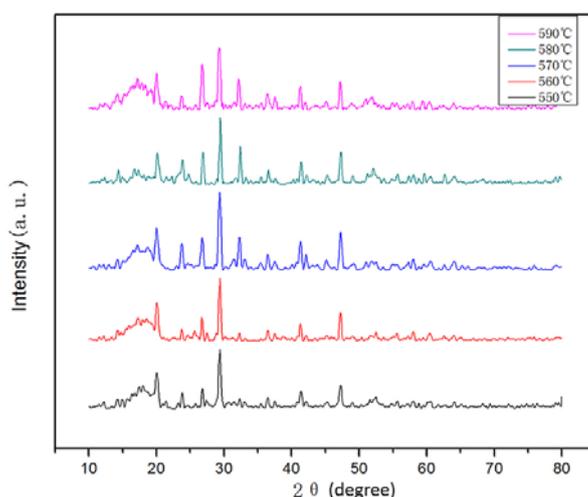


Figure 1. X-ray diffraction patterns of the LGPS in different sintering temperature.

3.2. EIS test at room temperature of the different samples

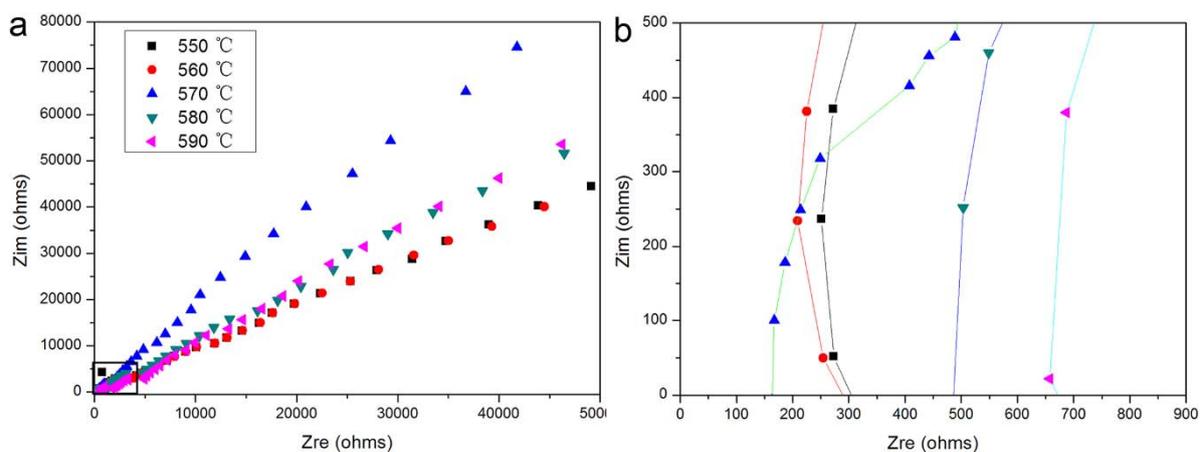


Figure 2. The EIS patterns of LGPS samples fabricated under different temperature (a) and the magnified patterns (b).

Additionally, the effect of sintering temperature on the ionic conductivity of LGPS were also studied. EIS is a common technology to investigate the electrode/electrolyte interface. The EIS test is carried out on the sample pressure plate (the sample thickness is 4 mm, the diameter is 14 mm). Fig. 2 shows the EIS patterns of the samples fabricated under different temperature at room temperature. The results show that the solid electrolyte resistance of the LGPS samples fabricated under 550 °C, 560 °C, 570 °C, 580 °C, 590 °C are 273 Ω, 254 Ω, 163 Ω, 482 Ω, 657 Ω, respectively. Based on the above results, the ionic conductivities of LGPS samples fabricated under different sintering temperature are further calculated (Fig. 3 and Table 1). As shown in Fig. 3, the ionic conductivities of the LGPS samples fabricated under 550 °C, 560 °C, 570 °C, 580 °C, 590 °C are 0.94 mS/cm, 1.1 mS/cm, 1.6 mS/cm, 0.527 mS/cm, 0.38 mS/cm, respectively. And the ionic conductivity of the prepared LGPS sample increases firstly and then decreases with the increasing sintering temperature. As we can see, the LGPS fabricated under 570 °C shows the highest the ionic conductivities. This improved ionic conductivity is caused by its better crystallinity with three-dimensional framework structure composed of Ge (P) S₄ tetrahedra, PS₄ octahedra and LiS₆ octahedra, which is favourable to the rapid transfer of Li.

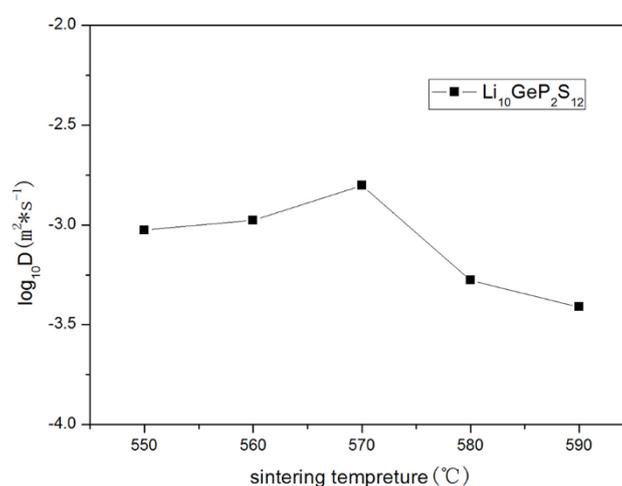


Figure 3. The ionic conductivities of LGPS samples fabricated under different sintering temperature.

Table 1. The ionic conductivities of LGPS samples fabricated under different sintering temperature

Temperature(°C)	Thickness(mm)	Ionic conductivit(mS/cm)
550	4	0.94
560	4	1.1
570	4	1.6
580	4	0.527
590	4	0.38

3.3. EIS test at room temperature of the different samples

To further investigate the effects of the temperature on the ionic conductivity of the LGPS samples fabricated under 570 °C, the EIS test under different temperature was performed. As shown in Fig. 4, the ionic conductivity of the sample change significantly in the temperature range of 30-125 °C. Namely, the ionic conductivity of 125 °C (2.8 mS/cm) of the sample is nearly two times as that of 30 °C (1.6 mS/cm). This enhanced ionic conductivity at higher temperature is ascribed to the accelerated transfer rate of Li at a high temperature. The above results suggest that a better crystalline is beneficial to the

higher lithium ion conductivity, high temperature environment is helpful to accelerate the rapid transfer of the lithium ions in the crystal lattice, thus further improves the ionic conductivity of LGPS solid electrolyte.

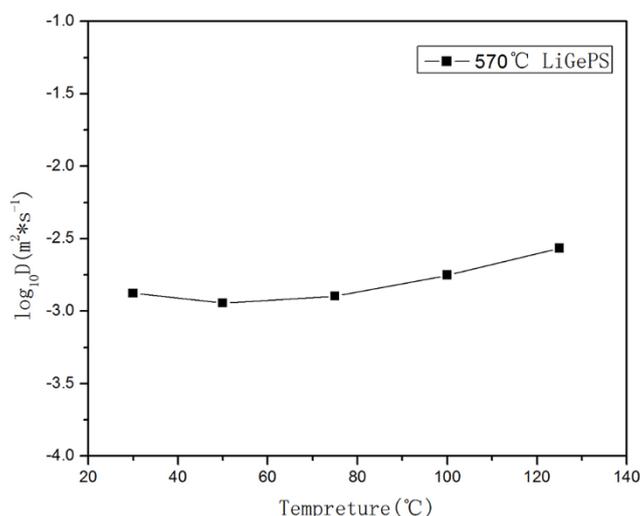


Figure 4. The ionic conductivities of LGPS samples fabricated under different sintering temperature.

4. Conclusion

In this paper, the LGPS solid electrolyte with a high ionic conductivity is prepared by the mechanical ball grinding and pressing sintering process under an inert environment of isolated oxygen and water. And the influences of different sintering temperatures (550 °C, 560 °C, 570 °C, 580 °C, 590 °C) on crystallinity and ionic electrochemical properties of the prepared LGPS powder were investigated. All the LGPS samples fabricated under different temperature show good crystallinity, and the sample fabricated under 570°C owns a much better crystallinity since excessive sintering temperatures may cause the loss of sulfur. This improved crystallinity is favourable to the rapid transfer of Li. Moreover, the ionic conductivities of the LGPS samples fabricated under 550 °C, 560 °C, 570 °C, 580 °C, 590 °C are 0.94 mS/cm, 1.1 mS/cm, 1.6 mS/cm, 0.527 mS/cm, 0.38 mS/cm, respectively. And the LGPS fabricated under 570°C shows the highest the ionic conductivities. This work demonstrate that the tenability of crystallinity and ionic electrochemical properties of the prepared LGPS via the sintering temperatures to improve the electrochemical properties of the rechargeable batteries for Li ion batteries.

Acknowledgments

This work was financially supported by high density power laboratory fund.

References

- [1] X.F. Li, J. Liu, and M. N. Banis et al. Atomic layer deposition of solid-state electrolyte coated cathode materials with superior high-voltage cycling behavior for lithium ion battery application, *ENERG ENVIRON SCI*, 7.2 (2014) 768-778.
- [2] W.S. Tang, A. Unemoto, and W. Zhou et al. Unparalleled Lithium and Sodium Superionic Conduction in Solid Electrolytes with Large Monovalent Cage-like Anions, *ENERG ENVIRON SCI*, 8.12 (2015): 3637.
- [3] N. Kayama, K. Homma, Y. Yamakawa, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto and A. Mitsui, A lithium superionic conductor, *Nat. Mater.*, 10.9 (2011) 682
- [4] M. Xu, J. Ding, and E. Ma, One-dimensional stringlike cooperative migration of lithium ions in an ultrafast ionic conductor, *Appl. Phys. Lett*, 101.3 (2012) 19.

- [5] Y. Mo, S. P. Ong, and G. Ceder, First Principles Study of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ Lithium Super Ionic Conductor Material, *J. Chem. Mater.* 24.1 (2012) 15–17.
- [6] S. Adams, R. P. Rao, Structural requirements for fast lithium ion migration in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, *J. Mater. Chem.* 22.16 (2012) 7687-7691.
- [7] F. Du, X. Ren, J. Yang, J. Liu, W. Zhang, Nanocasted Synthesis of Mesoporous LaCoO_3 Perovskite with Extremely High Surface Area and Excellent Activity in Methane Combustion, *J. Phys. Chem. C.* 112.39 (2014) 15293-15298.
- [8] O. Kwon, M. Hirayama and K. Suzuki et al. Synthesis, structure, and conduction mechanism of the lithium superionic conductor $\text{Li}_{10+d}\text{Ge}_{1+d}\text{P}_{2-d}\text{S}_{12}$, *J. Mater. Chem. A.* 3.1 (2014) 438-446.
- [9] P. Bron. et al. $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$: An Affordable Lithium Superionic Conductor. *J. Am. Chem. Soc.* 135 (2013) 15694-15697.
- [10] A. Kuhn, O. Gerbig, C. Zhu, F. Falkenberg, J. Maier, and B. V. Lotsch, A new ultrafast superionic Li-conductor: ion dynamics in $\text{Li}_{11}\text{Si}_2\text{PS}_{12}$ and comparison with other tetragonal LGPS-type electrolytes, *Phys. Chem. Chem. Phys.* 16.28 (2014) 14669-146734.
- [11] S.P. Ong, Y. Mo, and W. D. Richards et al. Phase stability, electrochemical stability and ionic conductivity of the $\text{Li}_{10\pm 1}\text{MP}_2\text{X}_{12}$ ($\text{M} = \text{Ge, Si, Sn, Al or P, and X} = \text{O, S or Se}$) family of superionic conductors, *ENERG ENVIRON SCI.* 6.1 (2012) 148-156.
- [12] J. Hassoun et al. A structural, spectroscopic and electrochemical study of a lithium ion conducting $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, solid electrolyte, *J. Power Sources.* 229 (2013) 117-122.