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To cite this article: XiaoZhen Liu *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **490** 062015

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Effect of lithium salts on room temperature ionic conductivity of W, Y and Al co-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte

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Abstract. $\text{Li}_{5.76}\text{La}_3\text{Zr}_{1.59}\text{W}_{0.35}\text{Y}_{0.06}\text{Al}_{0.2}\text{O}_{12}$ (W, Y, Al-LLZO) solid electrolyte was prepared using the solid-state reaction method. Effect of lithium salts (LiOH , LiNO_3 , Li_2CO_3 , $\text{Li}_2\text{C}_2\text{O}_2$) on the crystal structure, morphology, relative density and shrinkage, total ionic conductivity of the prepared solid electrolyte were studied, respectively. W, Y, Al-LLZO solid electrolytes of preparation with LiOH , LiNO_3 , Li_2CO_3 and $\text{Li}_2\text{C}_2\text{O}_2$ respectively are cubic phases at room temperature. The high the total ionic conductivity of $2.56 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 25°C is achieved in W, Y, Al-LLZO solid electrolyte of preparation with Li_2CO_3 .

1. Introduction

Lithium ion batteries are an alternative candidate which can store renewable energies in the future because of their high energy density, high power, and long cycle life ^[1]. Safety issue of the flammability of organic Li-ion salt electrolyte blocks their application in stationary energy storage systems. Hence, developing new electrolytes with higher safety to replace organic Li-ion salt electrolytes is urgent ^[1]. The safety of inorganic solid electrolytes is superior to the safety of conventional electrolytes. Garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) with excellent thermal performance, good chemical and electrical stability and high ionic conductivity has recently attracted significant attention ^[2]. LLZO has cubic and tetragonal crystalline phases. The priority is to stabilize its cubic phase in order to obtain highly conducting LLZO, due to the ionic conductivity of the cubic phase is two orders of magnitude higher than that of the tetragonal phase. Previous research indicated that elemental doping was a effective method for stabilizing the cubic phase ^[3]. Our research found that the room temperature ionic conductivity of LLZO could be improved significantly by the co-doping of W, Y and Al in LLZO ^[4].

In this paper, the W, Y and Al co-doped LLZO solid electrolyte was prepared using the solid-state reaction method. Effect of lithium salts (LiOH , LiNO_3 , Li_2CO_3 and $\text{Li}_2\text{C}_2\text{O}_2$) on the crystal structure, morphology, relative density and shrinkage, and total ionic conductivity of the prepared solid electrolyte were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) techniques, respectively.



2. Experimental

2.1. Preparation of the solid electrolyte sample

Samples of $\text{Li}_{5.76}\text{La}_3\text{Zr}_{1.59}\text{W}_{0.35}\text{Y}_{0.06}\text{Al}_{0.2}\text{O}_{12}$ (W, Y, Al-LLZO) were prepared using solid-state reaction method in the literature [4]. Stoichiometric amounts of LiOH [analytical reagent grade (AR), LiNO_3 (AR), Li_2CO_3 (AR), $\text{Li}_2\text{C}_2\text{O}_4$ (AR)], La_2O_3 (99.999 %), ZrO_2 (AR), WO_3 (AR), Y_2O_3 (99.999 %), Al_2O_3 (99.999 %) were mixed and ball-milled using a QM-BP planetary ball mill in isopropyl alcohol as the dispersing reagent with agate jar for 12 h. In order to compensate for the loss of lithium compounds in the high heating stage, 10 % excess of Li_2CO_3 was added. The mixed powder was dried in the oven at 105 °C for 2 h. The powder was then calcined in a muffle furnace at 900 °C for 6 h. Secondary mixed, dried and calcined at the same condition. The calcined powder was then pressed into pellets at 20 MPa with a diameter of 13 mm. The pellet was covered with the identical composition powder and sintered at 1160 °C for 10 h in air. The solid electrolyte sample was obtained.

2.2. Physical characterization

The crystal structures of the solid electrolyte samples were obtained by an X-ray diffractometer (Bruker AXS D8 Advance) using Cu Ka radiation at 40 kV and 30 mA with 2θ in range of 10~60° with 2°/min scanning rate.

The morphologies of the cross-section of the solid electrolyte samples were measured with a scanning electron microcopy (HITACHI S3400N).

The relative density of the solid electrolyte samples were measured by the Archimedes method. The relative shrinkage is calculated using the equation (Relative shrinkage = $(d_0 - d_1) / (d_0) \times 100\%$, d_0 and d_1 represent the diameter of pressed pellet and sintered pellet respectively.).

Electrochemical impedance spectroscopy measurements of the solid electrolyte samples were measured using a solartron impedance analyzer (Solartron 1260 & 1287) to measure the ionic conductivity in the frequency region from 100Hz to 10MHz with 10 mV amplitude.

3. Results and discussion

3.1. XRD studies

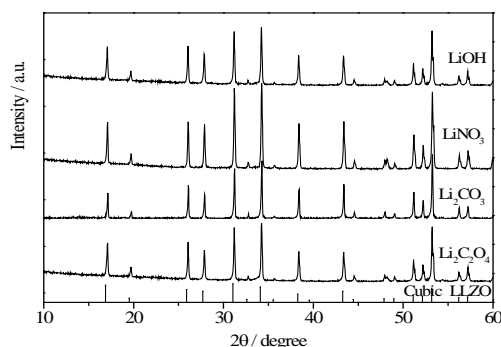


Figure 1. XRD spectra of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt. Figure 1 shows XRD spectra of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt. The peaks are labeled with the cubic phase LLZO (ICSD 422259, the vertical lines in the bottom). According to Figure 1, with LiOH, LiNO_3 , Li_2CO_3 , $\text{Li}_2\text{C}_2\text{O}_4$, respectively, all diffraction peaks can match well with the diffraction peaks of the cubic LLZO, which indicates that the samples are a single cubic phase.

3.2. SEM images

Figure 2 shows the morphologies of the cross-section of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt. According to Figure 2, with LiNO_3 , LiOH, Li_2CO_3 , $\text{Li}_2\text{C}_2\text{O}_4$, respectively,

order of grain size (D) are $D\text{-Li}_2\text{CO}_3 > D\text{-Li}_2\text{C}_2\text{O}_4 > D\text{-LiNO}_3 > D\text{-LiOH}$. Pores among grains were observed in the samples, order of pore size (A) among grains are $A\text{-Li}_2\text{C}_2\text{O}_4 > A\text{-LiOH} > A\text{-LiNO}_3 > A\text{-Li}_2\text{CO}_3$. With Li_2CO_3 , the grain size is the biggest and the grains are the best contact with each other, which is beneficial to enhancement of densification.

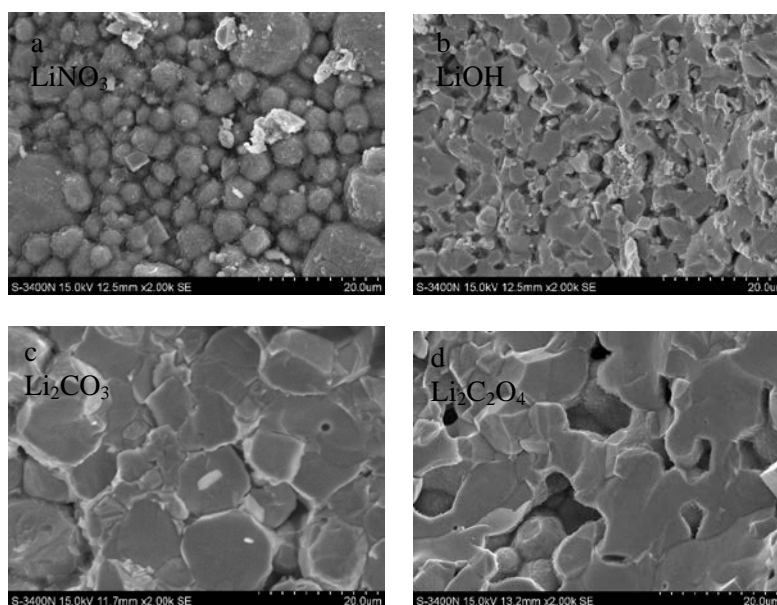


Figure 2. SEM images of the cross-section of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt.

3.3. The relative density and shrinkage

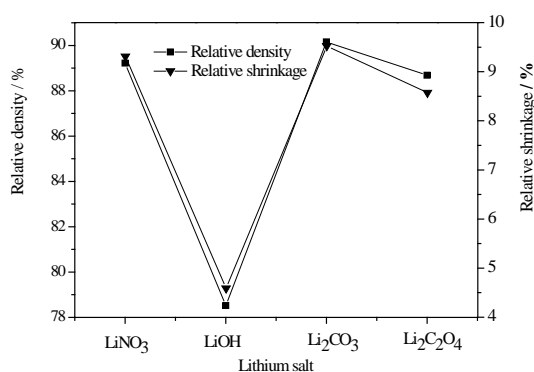


Figure 3. Relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt.

Figure 3 shows the relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt. According to Figure 3, with LiNO_3 , LiOH , Li_2CO_3 , $\text{Li}_2\text{C}_2\text{O}_4$, respectively, the relative densities are 89.22 %, 78.52 %, 90.16 % and 88.69 % respectively, the relative density is the biggest with Li_2CO_3 . Effect of the lithium salts on the relative shrinkage and the relative density are similar. The relative shrinkage reaches maximum (9.06 %) with Li_2CO_3 .

3.4. The ionic conductivity

Figure 4 shows the impedance spectra of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt measured at 25 °C in air. All the plots of the solid electrolyte samples show a single semicircle at high frequency region and a remarkable diffusion tail at the low frequency region. The total ionic conductivities were obtained by analyzing the impedance data with ZsimpWin software for simulation. The total ionic conductivity values of the samples are shown in Table 1. From Table 1,

with LiNO_3 , LiOH , Li_2CO_3 and $\text{Li}_2\text{C}_2\text{O}_4$, respectively, σ are 1.86×10^{-4} , 3.18×10^{-5} , 2.56×10^{-4} and $1.45 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ respectively, the σ is the biggest with Li_2CO_3 . With Li_2CO_3 , the grain size is the biggest and the grains are the best contact with each other, and the relative density is the biggest, so the σ is the biggest.

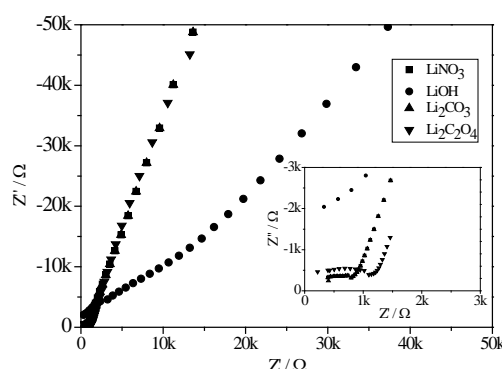


Figure 4. Impedance spectra of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt.

Table 1. Conductivity of the W, Y, Al-LLZO solid electrolyte samples with different lithium salt

lithium salt	LiNO_3	LiOH	Li_2CO_3	$\text{Li}_2\text{C}_2\text{O}_4$
$\sigma / \text{S}\cdot\text{cm}^{-1}$	1.86×10^{-4}	3.18×10^{-5}	2.56×10^{-4}	1.45×10^{-4}

4. Conclusion

W, Y, Al-LLZO solid electrolytes of preparation with LiOH , LiNO_3 , Li_2CO_3 and $\text{Li}_2\text{C}_2\text{O}_4$ respectively are cubic phases at room temperature. The high relative density of 90.16 % and total ionic conductivity of $2.56 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C are achieved in W, Y, Al-LLZO solid electrolyte of preparation with Li_2CO_3 .

Acknowledgments

This work was financially supported by the Program for National Natural Science Foundation of China (51572176), Shanghai Municipal Education Commission (Plateau Discipline Construction Program, 0817), Collaborative Innovation Fund of Shanghai Institute of Technology (XTCX2017-5).

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