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Effect of calcining temperature 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 by the solid-state reaction method. Effect of calcining temperature (T) on the crystal structure, morphology, relative density and shrinkage, total ionic conductivity of the prepared solid electrolyte were studied, respectively. Suitable T can stabilize cubic phase W, Y, Al-LLZO at room temperature, accelerate densification and improve the ionic conductivity respectively. The high total ionic conductivity of $2.31 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C is achieved in W, Y, Al-LLZO solid electrolyte calcined at 900 °C for 6 h.

1. Introduction

At present, the most advanced electrolytes used in lithium-ion batteries still use organic lithium ion salt electrolytes. The organic lithium ion salt electrolyte has led to security issues as a result of dendrite formation and flammability. There is an urgent need to develop new electrolytes with higher safety to replace organic electrolytes [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) has recently been attracting significant attention, due to its excellent thermal performance and high conductivity [2]. LLZO has cubic and tetragonal crystalline phases. The lithium ion conductivity of the cubic phase LLZO is higher about 2 or 3 orders of magnitude than that of the tetragonal phase LLZO. Elements doping is an effective method to stabilize the cubic LLZO [1]. 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 [3].

In this paper, the W, Y and Al co-doped LLZO were prepared by the solid-state reaction method. Effect of calcining temperature (T) on the crystal structure, morphology, relative density and shrinkage, total ionic conductivity of the prepared solid electrolyte were investigated, respectively. The solid electrolyte samples were characterized with 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 W, Y, Al-LLZO (the composition: $\text{Li}_{5.76}\text{La}_3\text{Zr}_{1.59}\text{W}_{0.35}\text{Y}_{0.06}\text{Al}_{0.2}\text{O}_{12}$) were prepared by solid-state reaction method in the literature [3]. Stoichiometric amounts of Li_2CO_3 [analytical reagent



grade (AR)], La₂O₃ (99.999 %), ZrO₂ (AR), WO₃ (AR), Y₂O₃ (99.999 %), Al₂O₃ (99.999 %) were mixed and ball-milled by planetary ball-milling (QM-BP planetary ball mill) with agate jar for 12 h with isopropyl alcohol as the dispersing reagent, 10 % excess of Li₂CO₃ was added to compensate for the loss of lithium compounds in the subsequent high heating stage. The homogeneously mixed powder was dried in the oven at 105 °C for 2 h. Then the dried powder was moved into a corundum crucible, and calcined at 700, 800, 900, 1000, 1100 °C, respectively, for 6 h in a muffle furnace and cooled down to room temperature. After secondary mixture, drying and calcining at the same condition, the calcined powders were putted into $\Phi = 13\text{mm}$ model of stainless steel, pressed into pellet with 20MPa pressure. The pellet was covered with mother powders 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 determined with a Bruker AXS D8 Advance diffractometer with Cu K α radiation at 40 kV and 30 mA in the 2θ ranges from 10° to 60° with 2°/min scanning rate.

The morphologies of the cross-section of the solid electrolyte samples were measured with HITACHI S3400N scanning electron microscopy.

The relative density of the solid electrolyte samples were measured by the Archimedes method. The relative shrinkage is calculated using equation of Relative shrinkage = $(d_0 - d_1) / (d_0) \times 100\%$. In the equation, 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 applied by a solartron impedance analyzer (Solartron 1260 & 1287) to measure the ionic conductivity. The applied frequency range was 100Hz~10MHz with 10 mV amplitude.

3. Results and discussion

3.1. XRD studies

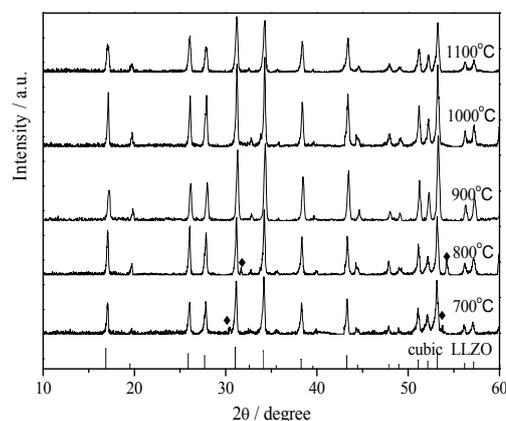


Figure 1. XRD spectra of the W, Y, Al-LLZO solid electrolyte samples at different T.

Figure 1 shows XRD spectra of the W, Y, Al-LLZO solid electrolyte samples at different T. The peaks are labeled with the cubic phase LLZO (ICSD 422259, the vertical lines in the bottom). According to Figure 1, with T being in the range of 700~800 °C, except for the peaks of the cubic phase LLZO, diffraction peak at $2\theta = 30.5^\circ$ split into 2 peaks, and there are four diffraction peaks in $50^\circ \leq 2\theta \leq 55^\circ$, the diffraction peaks indicate the existence of the tetragonal phase in the solid electrolyte samples^[4]. The solid electrolyte samples are a mixture phases of cubic phase and tetragonal phase. With T being in the range of 900~1100 °C, 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

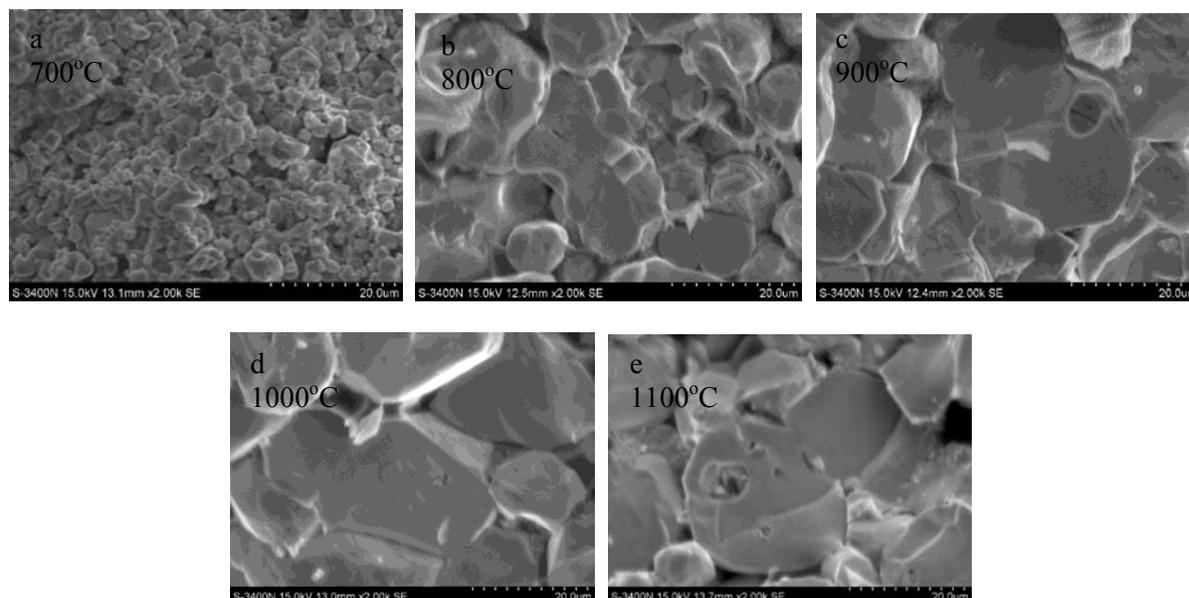


Figure 2. SEM images of the cross-section of the W, Y, Al-LLZO solid electrolyte samples at different T.

Figure 2 shows the morphologies of the cross-section of the W, Y, Al-LLZO solid electrolyte samples at different T. According to Figure 2, with T being at 700 °C, the grain sizes lie in the ranges from 1 to 4 µm, the grains are not in good contact with each other, which means a low density. With T being in the range of 700~900 °C, the grain sizes become the bigger and the grains are the better contact with each other with T increasing, which is beneficial to enhancement of densification. With T being in the range of 900~1100 °C, the grain sizes become slightly the smaller with T increasing.

3.3. The relative density and shrinkage

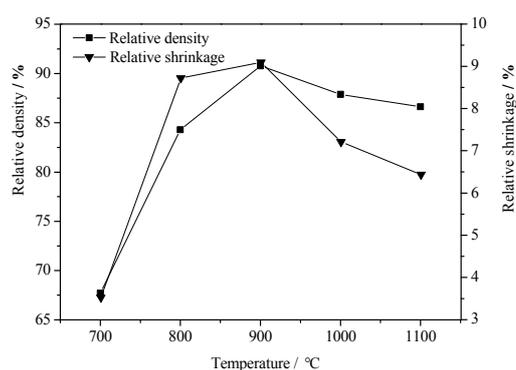


Figure 3. Relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples at different T.

Figure 3 shows the relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples at different T. As T rises, the relative density firstly increases from 67.71 % at T = 700 °C to 90.78 % at T = 900 °C. Then, the relative density decreases to 86.63 % at T = 1100 °C. Effect of T on the relative shrinkage and the relative density are similar. The relative shrinkage reaches maximum (9.03 %) at T = 900 °C.

3.4. The ionic conductivity

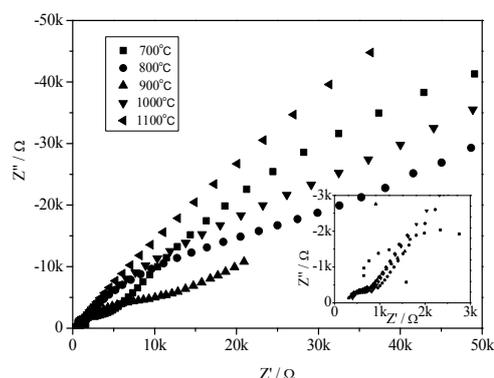


Figure 4. Impedance spectra of the W, Y, Al-LLZO solid electrolyte samples at different T.

Table 1. Conductivity of the W, Y, Al-LLZO solid electrolyte samples at different T

T / °C	700	800	900	1000	1100
$\sigma / \text{S}\cdot\text{cm}^{-1}$	5.5×10^{-5}	2.14×10^{-4}	2.31×10^{-4}	2.26×10^{-4}	2.19×10^{-4}

Figure 4 shows the impedance spectra of the W, Y, Al-LLZO solid electrolyte samples at different T 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 solid electrolyte samples are shown in Table 1. From Table 1, it can be seen that σ increase significantly from $5.5\times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at T = 700 °C to $2.31\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at T = 900 °C. With T increasing, the relative density increases, so the ionic conductivity increases. As T being from 900°C to 1100 °C, the σ slightly decreases from $2.31\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ to $2.19\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. The results indicate that the higher conductivity in the samples can be obtained by controlling T.

4. Conclusion

Suitable calcining temperature can stabilize cubic phase W, Y, Al-LLZO at room temperature, accelerate densification and improve the ionic conductivity. The high relative density of 90.78 % and total ionic conductivity of $2.31\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C are achieved in W, Y, Al-LLZO solid electrolyte calcined at 900 °C for 6 h.

Acknowledgments

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