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Effect of Calcining Time on the Room Temperature Ionic Conductivity of W, Y and Al Co-doped $Li_7La_3Zr_2O_{12}$ Solid Electrolyte

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Abstract. $Li_{5.76}La_3Zr_{1.59}W_{0.35}Y_{0.06}Al_{0.2}O_{12}$ (W, Y, Al-LLZO) solid electrolyte was prepared using the solid-state reaction method. Effects of calcining time (t) on the crystalline structure, morphology, relative density and shrinkage, the total ionic conductivity of the prepared W, Y, Al-LLZO solid electrolyte were studied, respectively. Controlling suitable calcining time can stabilize cubic phase W, Y, Al-LLZO at room temperature and improve the relative density and the ionic conductivity of the solid electrolyte samples. The relative density and the room temperature ionic conductivity of the W, Y, Al-LLZO solid electrolyte calcined at 900 °C for 6 h are 90.78 % and 2.31×10^{-4} S·cm^{-1} respectively.

1. Introduction

Due to potential safety risks such as volatilization, flammability and explosion of organic liquid electrolytes used in lithium-ion batteries, the demand for higher safety electrolytes is increasing [1, 2]. The safety of inorganic solid electrolytes exceeds significantly that of organic liquid electrolytes. Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) is considered to be the next generation of electrolytes, due to its high conductivity and good thermal stability [3, 4]. The ion conductivity of the cubic phase LLZO has much higher than that of the tetragonal phase LLZO. Element doping effectively stabilized the cubic LLZO [5-8]. Our research found that the co-doping of W, Y and Al in LLZO improved significantly the room temperature ionic conductivity of LLZO [9].

In this paper, the W, Y and Al co-doped LLZO were prepared using the solid-state reaction method. Effects of calcining time (t) on the crystalline structure, morphology, relative density and shrinkage, the total ionic conductivity of the solid electrolyte were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) techniques, respectively.

2. Experimental

2.1Preparation of the solid electrolyte sample

Samples of $Li_{5.76}La_3Zr_{1.59}W_{0.35}Y_{0.06}Al_{0.2}O_{12}$ (W, Y, Al-LLZO) were prepared using solid-state reaction method according to the literature [9]. Stoichiometric amounts of Li_2CO_3 [analytical reagent grade

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(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 with isopropyl alcohol as the dispersing reagent in agate jar for 12 h, 10 % excess of Li_2CO_3 was added to make up for the loss of lithium compounds in the following high heating stage. The mixed powder was dried in the oven at 105 ˚C for 2 h. The dried powder was calcined at 900 ˚C for 3, 6, 9, 12, and 15 h respectively. After mixture, drying and calcining at the same condition once more, the calcined powders were pressed into pellet with a diameter of 13 mm with 20MPa pressure. The pellet was covered with self-source powder and sintered at 1160 ˚C for 10 h in air. The solid electrolyte sample was obtained.

2.2Physical characterization

The crystalline structures of the prepared solid electrolyte samples were determined by a diffractometer (Bruker AXS D8 Advance) with Cu Ka radiation and $2\theta = 10° \sim 60°$.

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

The relative density of the prepared solid electrolyte samples was measured by the Archimedes method. The relative shrinkage is calculated with the diameter of pressed pellet and sintered pellet.

The ionic conductivity of the prepared solid electrolyte samples was determined using a solartron impedance analyzer (Solartron 1260 &1287) with100Hz～10MHz frequency range and 10 mV amplitude.

3. Results and discussion

3.1XRD studies

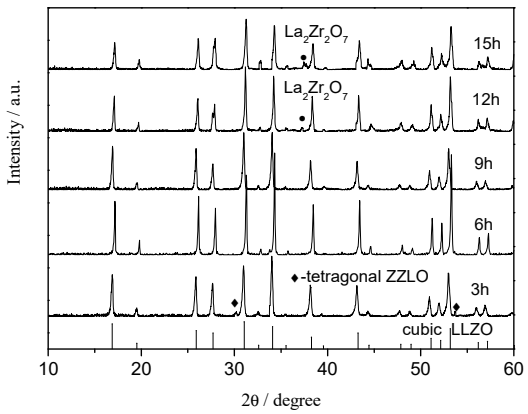

Figure 1. XRD spectra of the W, Y, Al-LLZO solid electrolyte samples for different t.

XRD spectra of the W, Y, Al-LLZO solid electrolyte samples for different t are shown in Figure 1. The peaks are labeled with the cubic phase LLZO (ICSD 422259, the vertical lines in the bottom). As shown in Figure 1, when t = 3 h, in addition to the peaks of the cubic phase LLZO, the diffraction peak at $2\theta = 30.5°$change to 2 peaks, number of the diffraction peaks in $50° \leq 2\theta \leq 55°$ are four, which indicate the existence of the tetragonal phase in the solid electrolyte samples [10]. When t = 6 or 9 h, the diffraction peaks can match well with the diffraction peaks of the cubic LLZO, which indicates that the solid electrolyte samples are the cubic phase. When t = 12 or 15 h, in addition to the peaks of the cubic phase LLZO, the diffraction peak of $La_2Zr_2O_7$ is appeared, which indicate the existence of $La_2Zr_2O_7$ impurity in the solid electrolyte samples.

3.2SEM images

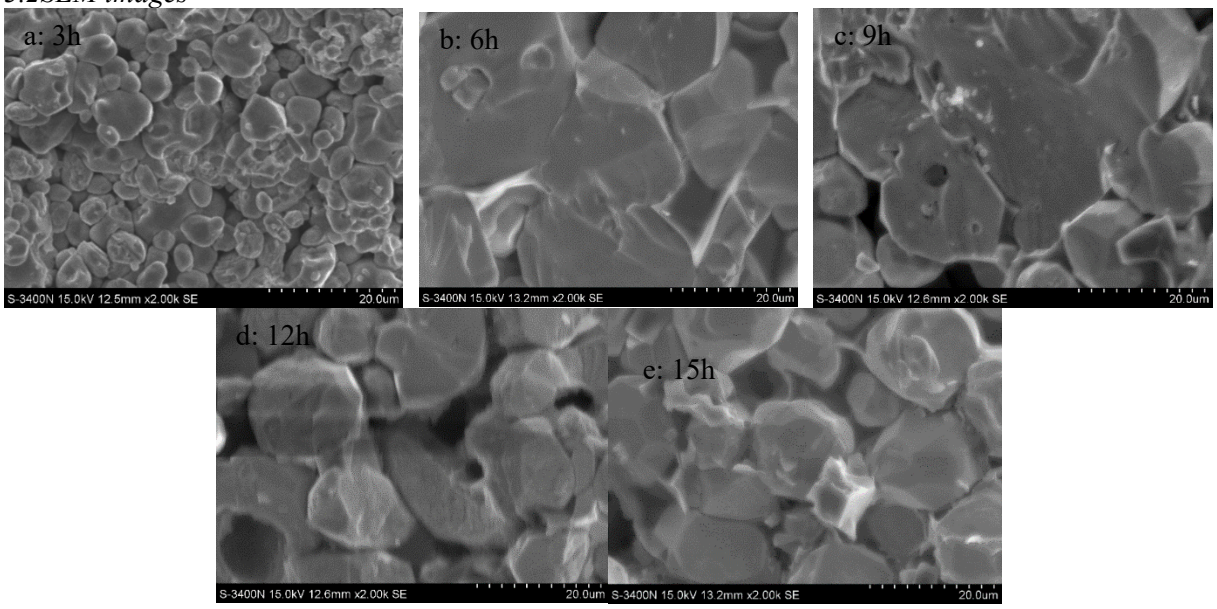

Figure 2. SEM images of the cross-section of the W, Y, Al-LLZO solid electrolyte samples for different t.

The morphologies of the cross-section of the W, Y, Al-LLZO solid electrolyte samples for different t are shown in Figure 2. As shown in Figure 2, when t = 3 h, the grain sizes are in the ranges of 1 ~ 6 μm, the contact between particles is not close, which means a low density. When t = 6 h, the grain sizes become the bigger, and the contact between particles is better, which is beneficial to enhancement of densification. With t being in the range of 6 ~ 15 h, the grain sizes become the smaller and the contact between particles is worse with t increasing, which is not beneficial to enhancement of densification.

3.3The relative density and shrinkage

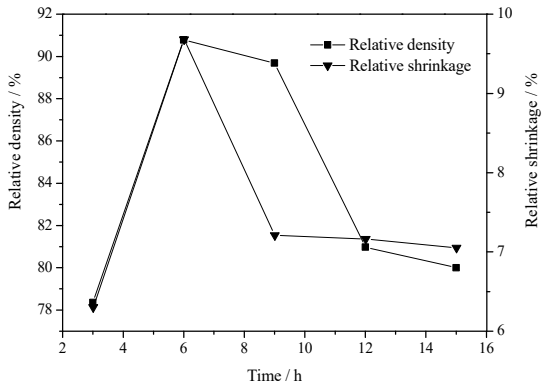

Figure 3. Relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples for different t.

The relative density and shrinkage of the W, Y, Al-LLZO solid electrolyte samples for different t are shown in Figure 3. As shown in Figure 3, as t increase, the relative density increases from 78.36 % for t = 3 h to 90.78 % for t = 6 h. Then, the relative density decreases to 80.00 % for t = 15 h. Similarly, for t = 6 h, the relative shrinkage is 9.03 %, the value is maximum.

3.4The ionic conductivity

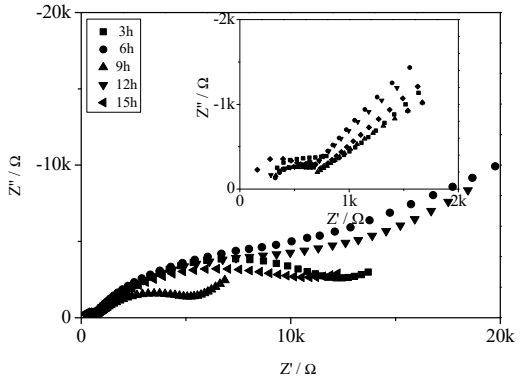

Figure 4. Impedance spectra of the W, Y, Al-LLZO solid electrolyte samples for different t.

Table 1 Conductivity of the W, Y, Al-LLZO solid electrolyte samples for different t

t / h	3	6	9	12	15
σ / S·cm^{-1}	8.66×10^{-6}	2.15×10^{-4}	2.05×10^{-5}	1.41×10^{-5}	1.17×10^{-5}

The impedance spectra of the W, Y, Al-LLZO solid electrolyte samples for different t measured at 25 ˚C in air are shown in Figure 4. As shown in Figure 4, a single semicircle and a remarkable diffusion tail are observed in the high frequency region and the low frequency region respectively in the plots of all the samples. The total ionic conductivities (σ) were gotten using ZsimpWin software for simulation to analyzing the impedance data. Table 1 show the total ionic conductivity values of the solid electrolyte samples. From Table 1, the σ increase significantly from 8.66×10^{-6} S·cm^{-1} for t = 3 h to 2.15×10^{-4} S·cm^{-1} for t = 6 h. The relative density increases significantly with t increasing in the range of 3 ~ 6 h, thus the ionic conductivity increases significantly. When t is in the range of 6 ~ 15 h, the σ decreases from 2.15×10^{-4} S·cm^{-1} to 1.17×10^{-5} S·cm^{-1}. The results indicate that controlling t can control the ionic conductivity of the solid electrolyte samples.

4. Conclusions

Controlling suitable calcining time can stabilize cubic phase W, Y, Al-LLZO at room temperature and improve the relative density and the ionic conductivity of the solid electrolyte samples. The relative density and the room temperature ionic conductivity of W, Y, Al-LLZO solid electrolyte calcined at 900 °C for 6 h are 90.78 % and 2.31×10^{-4} S·cm^{-1} respectively.

Acknowledgements

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