Original article

Improving the Li-ion conductivity and air stability of cubic $Li_7La_3Zr_2O_{12}$ by the co-doping of Nb, Y on the Zr site

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ABSTRACT

The elements Nb and Y were simultaneously substituted to the Zr sites of an $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte to improve its Li-ion conductivity and air stability. Samples of $Li_7La_3Zr_{2-2x}Nb_xY_xO_{12}$ were fabricated using a solid-state reaction method. The results show that the introduction of Nb and Y can stabilise cubic-phase LLZO. The total conductivity of $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ electrolyte can reach $8.29 \times 10^{-4}\,S\,cm^{-1}$ at 30 °C when sintered at 1230 °C for only 15 h. Surprisingly, the conductivity of $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ can be maintained at $6.91 \times 10^{-4}\,S\,cm^{-1}$ after exposure to air for 1.5 months, indicating excellent air stability. Furthermore, a $LiFePO_4/Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}/Li$ cell displayed stable charge/discharge and cycling performance at ambient temperature, suggesting there is potential to use $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ electrolyte in Li-ion batteries. Additionally, the effects of varying the co-doping amount and dwelling time on the Li-ion conductivity of $Li_7La_3Zr_{2-2x}Nb_xY_xO_{12}$ were investigated.

1. Introduction

Recently, increasing amounts of attention have been given to all-solid-state lithium ion batteries (LIBs) because they are less hazardous than commercialised liquid-based LIBs [1–3]. The properties of solid electrolytes and their interfaces with electrodes are critical to the performance of all-solid-state LIBs. High Li-ion conductivity and excellent stability are essential properties for solid electrolytes used in all-solid-state LIBs. So far, various types of inorganic solid electrolytes with conductivities higher than $10^{-4}\,S\,cm^{-1}$ at room temperature have been developed, including cubic garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) [4–6], NASICON type $LiM_2(PO_4)_3$ (M = Ti, Ge, Zr, Hf) [7,8] and sulfide-based series [9–11]. Among these solid electrolytes, cubic-phase LLZO has been widely studied because of its excellent stability against cathodes [12] and lithium metal anodes [13]. Their specific capacity can be as high as 3860 mAh g^{-1}.

Many efforts have been made to enhance the Li-ion conductivity and stability of cubic LLZO. The conductivity (σ) of LLZO can be described by Eq. (1):

$$\sigma = e.n_c\mu \tag{1}$$

where e is the elementary charge, n_c is the concentration of mobile Li ions, and μ is the mobility of Li^+. Therefore, improvement of Li-ion conductivity can be achieved by enhancing the mobility and concentration of Li ions. The former was usually achieved by the introduction of an element with lower valence on the Zr site, while the latter can be obtained by increasing the lattice parameter or introducing vacancies, which can be realised by doping the elements with larger ion diameters or higher valences, respectively [4,14–20]. It has been reported that the substitution of an element with a larger ion diameter can enlarge the size of the Li-ion migration pathway and increase the mobility of Li ions [20]. Additionally, supervalent cation substitution on the Zr^{4+} site can increase the vacancy concentration, which can improve Li-ion conductivity by lowering the activation energy of Li ions [19]. The partial substitution of Li^+ sites by Al^{3+}, Ge^{4+} and Ga^{3+} can also enhance Li-ion conductivity by activating Li ions, because the columbic repulsion between them and Li^+ is stronger than that between Li ions [5,6,21,22]. Furthermore, Li-ion conductivity can also be improved by tailoring the microstructures. Grain structures with high density, few boundaries and good connectivity help reduce intergranular impedance, which can be achieved by adding sintering aids [23–25].

Recently, it was found that LLZO electrolyte can be aged in air by reacting with CO_2/H_2O [26,27]. Jin et al. [26] pointed out that the reaction initially took place at the grain boundaries. By contrasting the air stability of LLZO fabricated in alumina and Pt crucibles, Xia et al. [27] reported that high density and Li content also benefit the air stability. As we know, sintering aids can improve the density of LLZO, and a high amount of lower valence element substitution at the Zr sites of LLZO can increase its Li content. So, the introduction of sintering aids and lower valence elements might be useful for improving the air stability of LLZO.

In this paper, Y_2O_3 and Nb_2O_5 were used to achieve co-doping of Y^{3+} and Nb^{5+} on Zr^{4+} sites in LLZO. The larger diameter of Y^{3+} (0.9 Å) compared to Zr^{4+} (0.72 Å) and Nb^{5+} (0.69 Å) might be beneficial for the diffusion of Li^+ [19,20] and is expected to enhance the Li^+ conductivity. Furthermore, Y_2O_3 is also a well-known sintering aid [23] and might be useful for enhancing the stability of LLZO in air. In addition, the valence of Y (+3) is lower than that of Zr (+4), which can compensate for the Li loss caused by the introduction of Nb^{5+}, thereby improving the air stability.

2. Experimental

Bulk $Li_7La_3Zr_{2-2x}Nb_xY_xO_{12}$ (x = 0, 0.125, 0.25, 0.5) samples were prepared by solid-state reaction. Stoichiometric amounts of Li_2CO_3 (99%, 15 wt% excess), La_2O_3 (99.99%), ZrO_2 (99.9%), Y_2O_3 (99.99%) and Nb_2O_5 (99.99%) were selected as original materials. $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ samples (called 0.25Nb in the following description) were also prepared for comparison. The starting materials were ball-milled for 8 h, then heat treated at 900 °C for 8 h and then ball-milled again for 8 h. Then, the obtained powders were pressed into pellets and calcined at 1100 ~ 1230 °C for 10 ~ 24 h in an alumina crucible. The mother powders were used to cover the pellets to reduce possible Li loss.

An X-ray diffractometer (XRD) with Cu Kα radiation (Bruker-AXS Microdiffractometer D8 Advance) was used to identify the phase composition of the as-prepared samples. The microstructures of the samples were detected using a scanning electron microscope (SEM, HITACHI S-4800), equipped with an energy-dispersive spectroscopy (EDS) system. An impedance analyser (CHI 660E) with a frequency range of 10 Hz to 1 MHz was used to test the Li-ion conductivity of garnet pellets in air at 21 ~ 110 °C. Two sides of the LLZO samples were ground with SiC paper up to 2000 grit and then sputtered with Au for use as Li-ion blocking electrodes for AC impedance measurement. For the air-exposed sample, Au was not erased during the exposure. The humidity in the lab is 10–40% from March to May and 40–90% from July to October. The sample exposed in the lab for 7.5 months between March 16 and October 31. To evaluate the chemical stability between $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ and a Li-metal anode, the charge-discharge behaviour of $LiFePO_4/Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}/Li$ was investigated on a battery test station (Arbin BT-2000) between 2.8 and 4.2 V. The $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ sample used in the cell was 0.4 mm in thickness. A small amount of liquid electrolyte was introduced at both sides of the LLZO electrolyte (two drops each side) to reduce the interface resistance. The liquid electrolyte was prepared by dissolving lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) in ionic liquid (N-methyl, butylpiperidinium bis-(trifluoromethylsulfonyl)imide (PP14TFSI)) to satisfy the safety requirements for the battery.

3. Results and discussion

3.1. Effect of various co-doping amounts on LLZO electrolyte properties

Fig. 1 shows the XRD patterns of $Li_7La_3Zr_{2-2x}Nb_xY_xO_{12}$ samples prepared at 1230 °C for 15 h. Fig. 1a is the diffraction pattern of undoped LLZO after such treatment. The clear splitting peaks indicate the existence of a tetragonal phase of garnet. However, nearly all the peaks

of the co-doped samples can be assigned a cubic garnet structure except for a small amount of $Li_{0.9}Y_{0.9}Zr_{0.1}O_2$ (marked with "I"), indicating that the co-doping of Nb and Y can stabilise cubic-phase LLZO. Thompson et al. [28] reported that vacancies, usually caused by the substitution of higher valence cations, contribute to the stabilisation of cubic LLZO. So, the existence of substitutional Nb^{5+} here may cause the formation of Li^+ vacancies, which stabilises the cubic LLZO. This has been demonstrated by a previous study [18]. When lower-valence Y (3 +) was introduced, the concentration of Li^+ could be increased for electric compensation. So, one could expect a tuning effect, caused by vacancy formation and Li^+ introduction, on the stability and conductivity of the LLZO host. Additionally, all the diffraction peaks of the LLZO vary according to the amounts of Nb and Y doping, indicating changes in the lattice parameter. The change of a typical diffraction peak located at 16.5—17° is shown in Fig. 1b. Compared with $Li_7La_3Zr_2O_{12}$, the peak of $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ shifts to a higher angle, indicating a decrease in the lattice parameter. This phenomenon should be attributed to the ionic diameter of Nb^{5+} (0.69 Å), which is smaller than that of Zr^{4+} (0.72 Å). Analogously, the lower diffraction angle of $Li_7La_3Zr_{1.75}Nb_{0.125}Y_{0.125}O_{12}$ compared to $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ can be ascribed to the larger diameter of Y^{3+} (0.9 Å) compared to Nb^{5+} and Zr^{4+}.

The Nyquist plots of $Li_7La_3Zr_{2-2x}Nb_xY_xO_{12}$ samples measured at 30 °C are illustrated in Fig. 2. All the plots of co-doped samples show only a single semicircle at the medium frequency region and a remarkable diffusion tail at the low-frequency region. The semicircle represents the grain boundary impedance and the straight line corresponds to Warburg-type impedance, which originates from the diffusion of Li ions in the gold blocking electrodes. The bulk resistance, usually appearing at high frequency, cannot be detected because of the limitation of sweeping frequency. The intercept of the semicircle on the real axis at the low-frequency region can be considered as the total resistance [4]. It can be seen that when x is 0.5, the impedance is much smaller than the others. The bulk and grain boundary resistances can be obtained by fitting the impedance spectra with an equivalent circuit model of $R_g(R_{gb}CPE1)$ (CPE2), where R_g is the grain resistance, R_{gb} is the grain boundary resistance and CPE is a constant phase element. Subsequently, the ionic conductivity of LLZO electrolyte was estimated using the following equation: $\sigma_t = (1/R_t)·(l/S)$, where σ_t, R_t, l and S represent total ionic conductivity, total resistance, thickness and the effective area of LLZO electrolyte, respectively. The calculated ionic conductivities of LLZO electrolytes measured at 21 and 30 °C are summarised in Table 1. The total conductivity of the undoped LLZO is only 7.34×10^{-6} S cm^{-1} at 30 °C. As expected, all the co-doped samples show conductivities of more than 10^{-4} S cm^{-1}, which satisfies the requirements of all-solid-state LIBS [29]. In addition to the cubic phase, the high density (shown in Table 1) of the co-doped samples should be another reason for increased conductivity. The high density should be attributed to the existence of Y_2O_3 as a sintering aid. Furthermore, the higher density of the co-doped samples compared to the 0.25Nb-doped sample shown in Table 1 also indicates that the existence of Y_2O_3 can increase the density of LLZO. Surprisingly, when x is 0.5, the corresponding ionic conductivity is 8.29×10^{-4} S cm^{-1} at 30 °C, which is comparable to the highest conductivity of single Nb (8×10^{-4} S cm^{-1} at 25 °C) [18] or Y doped (8.1×10^{-4} S cm^{-1} at 25 °C) [24] samples. The much lower conductivity for the 0.25Nb doped sample in our work (4.28×10^{-4} S cm^{-1}) might be ascribed to the lower density resulting from the much shorter sintering time (only 15 h) than the reported one (36 h). It should be noted that even when the testing temperature is 21 °C, the conductivity of $Li_7La_3ZrNb_{0.5}Y_{0.5}O_{12}$ can be as high as 6.53×10^{-4} S cm^{-1}. The reason for the conductivity enhancement will be further explained in the following sections.

To further determine the cause of the improved conductivity observed in the co-doped samples, the microstructures of polished (Fig. 3a-d) and chemical etched (Fig. 3a–d) surfaces were investigated.