Influence of sintering aids and excess Lithium on the conductivity of perovskite-type

$\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ solid electrolyte

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Abstract

Perovskite-structured $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ solid-state Lithium-conductors were prepared by conventional solid-state reaction method. Influence of sintering aids (Al_2O_3 , B_2O_3) and excess Lithium on structure and electrical properties of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ (LSNZ) has been investigated. Their crystal structure and microstructure were characterized by X-ray diffraction analysis and scanning electron microscope, respectively. The conductivity and electronic conductivity were evaluated by AC-impedance spectra and potentiostatic polarization experiment. All sintered compounds are cubic perovskite structure. Optimal amount of excess Li_2CO_3 was chosen as 20 wt. % because of the total conductivity of LSNZ-20% was as high as $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C and $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C, respectively. Electronic

conductivity of LSNZ-20% is $2.93 \times 10^{-8} \text{ S cm}^{-1}$, nearly 3 orders of magnitude lower than ionic conductivity. The density of solid electrolytes appears to be increased by the addition of sintering aids. The addition of B_2O_3 leads to a considerable increase of the total conductivity and the enhancement of conductivity is attributed to the decrease of grain-boundary resistance. Among these compounds, LSNZ-1wt% B_2O_3 has lower activation energy of 0.34 eV and the highest conductivity of $1.98 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C .

Key words: sintering, perovskite, ionic conductivity, electrical properties

1. Introduction

Li-ion batteries have been widely used in digital cameras, laptop computers and other portable electronic equipment. [1] However, liquid organic electrolytes in today's conventional Li-ion battery are flammable. [2] This disadvantage limits the application of Li-ion batteries to electric vehicles. [3] Solid state Li-ion conductors are attracting more and more attentions due to their excellent safety performance. [4] Moreover, solid state electrolytes have lots of advantages including large potential window, no leakage and environmental-friendly. [5] Solid state Lithium ion conductors include Sulfide, Garnet, NASICON-type and Perovskite-type solid state electrolytes. [6] Among those mentioned solid electrolytes, perovskite-type Li-La-Ti-O (LLTO) electrolytes had attracted much attention due to the high bulk Li-ion conductivity ($10^{-3} \text{ S cm}^{-1}$). However, the syntheses of LLTO need high sintering temperature (1350°C). [7] Furthermore, Ti^{4+} in LLTO electrolytes can be reduced to Ti^{3+} when LLTO is in contact with Li metal and then induce electronic conductivity. [7,8] In order to solve these problems, Thangadurai et al

[8] designed and prepared new Li-ion conductors with the general formula $\text{LiSr}_{1.65}\square_{0.35}\text{B}_{1.3}\text{B}'_{1.7}\text{O}_9$ ($\square$ =vacancy; B=Ti, Zr; B'=Nb, Ta). Among these solid electrolytes, $\text{LiSr}_{1.65}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$ has the highest conductivity. $\text{LiSr}_{1.65}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$ is likely to be used as solid electrolytes in all-solid-state Li-ion battery.

Chen et al [9] investigated [perovskite-structured Li–Sr–Ta–Zr–O solid electrolytes](#). $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ exhibited a bulk lithium-ion conductivity of 0.2 mS cm^{-1} at 30°C . Otherwise, Li–Sr–Ta–Zr–O solid electrolytes were stable above 1.0 V against lithium metal. Inada et al [10] synthesized $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ solid electrolyte by using “powder-bed sintering” method. Impurity phase were reduced significantly and the conductivity at 27°C is approximately 3 times higher than previously result.

Kimura et al [11] synthesized $\text{Li}_{2x-y}\text{Sr}_{1-x}\text{Ta}_y\text{Zr}_{1-y}\text{O}_3$ (LSTZ, $x=0.75y$) solid electrolytes with various Ta contents ($y=0.60, 0.70, 0.75, 0.77$ and 0.8). The lattice parameters of LSTZ samples were increased with increasing Ta contents. But LSTZ with higher Ta contents included impurity phases. Optimal Ta contents is $y=0.75$. Huang et al [12] prepared perovskite-type electrolytes with general formula $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Hf}_{1/4}\text{O}_3$ (LSHT). At least 15 wt % excess Li_2CO_3 was added to account for the Li_2O loss at high-temperature. Li-ion conductivity of LSHT is $3.8 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C , with activation energy of 0.36 eV. However, Ta-containing raw materials are too expensive for industrial application. Nb-based compounds are much cheaper than Ta-based compounds and, their properties are similar. Yu et al [13] designed and synthesized perovskite-type Li–Sr–Zr–Nb–O (LSNZ) solid electrolytes. Sample with the optimal composition of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Nb}_{3/4}\text{Zr}_{1/4}\text{O}_3$ has total ionic conductivity of $2.0 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C . It is important that adding excess Lithium to account for the Li_2O loss at high-temperature and improve performance of solid Li-ion conductors. [12, 13, 14, 15] Moreover, the application of sintering aids can increase conductivity of solid electrolytes. [16, 17]

As far as we know, influence of sintering aids and excess Lithium on the electrical properties of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Nb}_{3/4}\text{Zr}_{1/4}\text{O}_3$ has never been reported. In this study, we attempt to research the influence of sintering aids (Al_2O_3 , B_2O_3) and excess Lithium on the structure and conductivity of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ (LSNZ). We found that the total conductivity of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ Li-ion conductor achieve the highest value by the addition of 20 wt. % excess Lithium. Furthermore, sintering aids could increase conductivity of LSNZ solid electrolytes and the addition of B_2O_3 leads to a considerable increase of the total conductivity ($1.98 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C).

2. Experimental

$\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ (LSNZ) samples with different wt. % excess Li_2CO_3 (marked as LSNZ-x%, $x=0, 10, 20$ and 30) were prepared via a conventional solid-state reaction route. Samples with different sintering aids (marked as LSNZ-1wt% Al_2O_3 and LSNZ-1wt% B_2O_3) were prepared base on LSNZ-20%. Stoichiometric reagent-grate of Li_2CO_3 (99%, AR), SrCO_3 (99.9%, AR), Nb_2O_5 (99.9%, AR), ZrO_2 (99%, AR), Al_2O_3 (99%, AR) and B_2O_3 (99%, AR) were used as starting materials. These reagents were weighted accurately and mixed by ball-milling in anhydrous alcohol at a rotation speed of 300rpm for 12 hours. Then evaporate the solvent at 150°C for 10 hours to get mixtures. The mixtures were calcined at 1100°C for 12 hours in alumina crucible. After calcination, the powders were reground and pressed into pellets (15mm in diameter) at a pressure of 200Mpa by cold isostatic pressing. In the end, ceramic pellets were sintered at 1250°C for 15 hours in ZrO_2 crucible in air.

The crystal structure of solid electrolyte samples were characterized by X-ray diffraction (XRD) using Cu K α ($\lambda=0.15418\text{nm}$) radiation on Rigaku Ultima IV. The measurement angle (2θ) was ranged from 5° to 90° with a step size of 0.02° . The density of ceramic pellets was determined by the weight and

volume of pellets using Archimedes method. Microstructure was measured by field emission scanning electron microscopy (SEM) on FEJ-250.

Ion conductivity of all samples was characterized by AC-impedance on Solartron 1260 Impedance/Grain-Phase analyzer. Both sides of pellets were coated with a conducting Pt ink layer (dry at 900 °C for 2h) as blocking electrode for testing. The frequency was ranged from 1 Hz to 10 MHz with a polarization voltage of 100 mV over the temperature ranging from 30 °C to 140 °C. Electronic conductivity was evaluated by potentiostatic polarization experiment on Princeton V3 electrochemical workstation at 30 °C. The scanning time is 600 seconds with applied voltage of 4 V.

3. Results and discussion

3.1 Crystal structure

Fig. 1 shows the XRD patterns of LSNZ-x% samples with the standard pattern of SrZrO_3 . It can be seen that perovskite-structured $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ solid electrolytes had been synthesized successfully by using solid state reaction method at high temperature. However, impurity phases of $\text{Sr}_6\text{Nb}_{10}\text{O}_{30}$ and ZrO_2 was detected due to the usage of a large number of Li/Nb to replace Sr/Zr elements. Furthermore, the diffraction peaks shift to higher angles obviously since the ionic radii of Li^+ and Nb^{5+} is smaller than Sr^{2+} and Zr^{4+} . As can be seen in Fig. 1, impurity phase $\text{Sr}_6\text{Nb}_{10}\text{O}_{30}$ is conspicuously when adding 0 wt. % excess Li_2CO_3 (LSNZ-0% Sample). The intensity of impurity phase $\text{Sr}_6\text{Nb}_{10}\text{O}_{30}$ diffraction peaks is decreased by the addition of excess Li_2CO_3 (LSNZ-10%, LSNZ-20% and LSNZ-30%). This phenomenon demonstrates that the presence of impurity phase is partially due to the severe evaporation of Li_2O at high temperature. Impurity phase can be reduced by adding excess Li_2CO_3 . Combined with impedance spectroscopy, LSNZ-20% sample was selected for further study due to high conductivity.

Fig. 2 shows the XRD patterns of LSNZ-20%, LSNZ-1wt% Al₂O₃ and LSNZ-1wt% B₂O₃. The diffraction peaks of all samples shift to higher angles. As shown in Fig. 2, impurity phases such as Sr₆Nb₁₀O₃₀ and ZrO₂ was detected too. For LSNZ-1wt% Al₂O₃, diffraction peaks of Al₂O₃ were also observed. The impurity phases can not be removed completely by the addition of sintering aids or excess amount of Li₂CO₃. In general, impurity phase can decrease conductivity of solid electrolytes, phase purity of perovskite-type LSNZ electrolytes could be further decreased by optimizing synthesis process. So there is a room for further improvement in conductivity for LSNZ solid electrolytes.

For all samples, the diffraction peaks observed in XRD patterns belongs to cubic perovskite structure with a space group of Pm-3m. The cubic lattice parameter of LSNZ-20% sample was determined to be $a = 3.982 \text{ \AA}$. All of samples have similar lattice parameter and no significant change was observed.

3.2 Microstructure

Fig. 3 shows the cross-section SEM images of solid electrolyte pellets. As can be seen, the particle distribution is uniform. Good linkage of LSZN grains was observed. The grain size increases slightly with the increase in excess Lithium contents. There are still pores in pellets. But pellets sintered with sintering aids have much bigger grain size and denser structure. Furthermore, the segregation of possible impurity phase at the grain-boundaries for LSZN-1wt% Al₂O₃ is evidenced through the SEM images of Fig. 3(e).

The density of LSZN pellets was assessed by Archimedes method. $\rho = \frac{m_1}{m_1 - m_2} \times \rho_{\text{water}}$. Here,

ρ is the density of pellets; ρ_{water} is density of water, m_1 is the weight of pellets in air while m_2 is the weight in deionizer water. Increasing excess Lithium contents lead to an increment in the density from 3.67 g cm^{-3} to 3.99 g cm^{-3} . Furthermore, density of LSZN pellets was improvement by the addition of

sintering aids. Among all of the samples, LSZN samples with the addition of 1 wt. % B_2O_3 have the highest density of 4.09 g cm^{-3} .

3.3 AC-impedance analysis

Figure 4 (a) shows typical AC-impedance plots of LSZN-x% samples at 30°C and Fig. 4 (b) shows Nyquist plots of LSZN samples with the addition of Al_2O_3 and B_2O_3 at 30°C . The semicircle and straight line tail were obtained in high frequency and low frequency regions, respectively. All of the impedance data was fitted with the equivalent circuit with a combination of bulk, grain-boundary and Warburg resistance, as shown in Fig 4 (a). Bulk resistance (R_{bulk}), grain-boundary resistance (R_{gb}) and total resistance (R_{total}) of LSZN samples were obtained from this equivalent circuit. The contributions of R_{bulk} and R_{gb} to R_{total} are listed in Table 1.

For LSZN-x% samples, LSZN-20% exhibits the highest conductivity. Further increasing in excess Li_2CO_3 up to 30wt% leads to the decrease of conductivity. This phenomenon may be attributed to the blocking of the pathways for Li^+ transporting because that there are too many non-crystalline Li_2O (insulating phase) in ceramic pellets.

For LSZN samples containing different sintering aids, all of the samples have similar bulk resistance. LSZN-1wt% B_2O_3 has higher total conductivity and lower grain-boundary resistance. This indicates that the enhancement for total conductivity is attributed to the reduction of grain-boundary resistance. B_2O_3 could be helpful to facile Li^+ transporting through grain-boundary. No significant reduction in the grain-boundary and total resistance was observed for LSZN-1wt% Al_2O_3 samples. This result can be attributed to the presence of impurity phase in the solid electrolytes prepared with Al_2O_3 , as shown in XRD patterns. Furthermore, melting point of Al_2O_3 (2054°C) is much higher than B_2O_3 (450°C), the

sintering temperature (1250°C) may be too low to melt Al_2O_3 and hence they separate from the perovskite solid electrolytes. So Al_2O_3 could not benefit to decrease the grain-boundary resistance. B_2O_3 has better performance in LSN solid electrolytes compare to Al_2O_3 .

With the increase of measuring temperature, it is difficult to distinguish bulk and grain-boundary resistance of samples, since there is only one semicircle in high frequency region. So this semicircle represents total resistance of samples. [18] The straight line indicates that LSNZ is ionic conductor naturally. The intercept point of straight line with real axis in low frequency region corresponds to the total resistance of samples nearly. The conductivity of all samples was calculated using the following equation $\sigma = \frac{d}{A \times R}$, where σ is the total conductivity, d is thickness of sample, A is the surface area of electrode, and R is the total resistance obtained by AC-impedance spectra. As a result of calculation, $\sigma(\text{LSNZ-20\%}) > \sigma(\text{LSNZ-10\%}) > \sigma(\text{LSNZ-30\%}) > \sigma(\text{LSNZ-0\%})$. LiSNZ_{20wt%} has the highest Total conductivity of $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C and $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C, respectively. This can be attributed to the decrease of impurity phase with the addition of excess Li_2CO_3 . Furthermore, it has been reported that excess Li_2CO_3 can improve grain-boundary ionic conductivity of solid electrolytes. [13]

Conductivity of LSNZ was improved by the addition of sintering aids. LSNZ-1wt% B_2O_3 has higher total conductivity than LSNZ-1wt% Al_2O_3 . The conductivity of LSNZ-1wt% B_2O_3 is as high as $1.9 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C and $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C, respectively. As can be seen in XRD patterns, the addition of Al_2O_3 introduced impurity phase, which could decrease conductivity of solid electrolytes. At the same time, addition of B_2O_3 would not produce impurity phase. This can explain the result that $\sigma(\text{LSNZ-B}_2\text{O}_3) > \sigma(\text{LSNZ-Al}_2\text{O}_3)$.

Figure 5 shows the temperature dependence of total conductivity in the temperature range from 30°C

to 140 °C. The activation energy was calculated from Arrhenius equation $\sigma T = \sigma_0 \exp(-Ea / k_B T)$.

Here, Ea is activation energy, T is absolute temperature, σ_0 is pre-exponent constant and k_B is

Boltzmann constant ($=1.381 \times 10^{-23} \text{ J K}^{-1}$). Activation energy can be calculated from slope of

corresponding straight line. Values of σ and Ea of all samples are summarized in Table 2. The

activation energy of LSNZ-20% sample is 0.36 eV, which is very close to Ea of typical fast ionic

conductor like garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (0.35 eV) and NASICON-type $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ (0.31 eV).

[19, 20, 21, 22] LSNZ-1wt%B₂O₃ and LSNZ-1wt%Al₂O₃ samples have lower activation energies than

LSNZ-20%.

3.4 Electronic conductivity

Electronic conductivity of LSNZ solid electrolytes was investigated by potentiostatic polarization measurement. Fig. 6 shows the potentiostatic polarization current. Due to the usage of ion blocking electrode for testing, the steady state current shown in Fig. 6 can be attributed to electronic conduction of samples. Electronic conductivity can be calculated using the equation $\sigma_e = \frac{d \times I}{A \times U}$. Here, σ_e is electronic conductivity, d is thickness of samples, A is surface area and U is applied DC voltage. As a result, electronic conductivity of LSNZ-20% sample is $2.93 \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$, nearly 3 orders of magnitude lower than its ionic conductivity. The electronic conductivity contribution to total conductivity is very small. This result demonstrates that LSNZ is a good ionic conductor. The σ_e of LSNZ-1wt%Al₂O₃ and LSNZ-1wt%B₂O₃ samples is $6.24 \times 10^{-8} \text{ S cm}^{-1}$ and $5.6 \times 10^{-8} \text{ S cm}^{-1}$, respectively. An increment for σ_e after adding Al₂O₃ and B₂O₃ was observed. However, electronic conductivity is still much lower than ionic conductivity. This demonstrates that LSNZ-1wt%Al₂O₃ and LSNZ-1wt%B₂O₃ are excellent ionic conductors as well as LSNZ-20%.

4. Conclusions

Solid electrolytes $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ with the addition of sintering aids and excess lithium were synthesized successfully by conventional solid-state reaction method at high temperature. The influence of sintering aids and excess Lithium on the structure and electrical properties was investigated. All of samples present a cubic perovskite structure. However, impurity phases were also detected and can not be removed completely by adding sintering aids or excess amount of Li_2CO_3 . Adding excess Li_2CO_3 can improve total conductivity of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ solid electrolytes, optimal amount of the excess Li_2CO_3 is 20 wt. % since the total conductivity of LSNZ-20% sample is the highest of $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C. Electronic conductivity of LSNZ-20% sample is 3 orders of magnitude lower than its ionic conductivity. Sintering aids can improve density and conductivity of LSNZ solid electrolytes. LSNZ with the addition of 1 wt. % B_2O_3 has the highest density and conductivity of $1.9 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Enhancement of conductivity by the addition of B_2O_3 is attributed to the decrease of grain-boundary resistance. In summary, our results indicate that $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{1/4}\text{Nb}_{3/4}\text{O}_3$ is a promising solid Li-ion conductor. The addition of sintering aids and excess lithium is very beneficial for improving conductivity of LSNZ solid electrolytes.

Acknowledgements

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Figure captions:

Fig. 1. XRD patterns of LSNZ-x%.

Fig. 2. XRD patterns of LSNZ with the addition of sintering aids.

Fig. 3. Cross-section SEM images of (a) LSNZ-0%, (b) LSNZ-10%, (c) LSNZ-20%, (d) LSNZ-30%, (e) LSNZ-1wt% Al₂O₃, (f) LSNZ-1wt% B₂O₃.

Fig. 4. AC-impedance spectra of (a) LSNZ-x% at 30°C, (b) LSNZ with the addition of sintering aids at 30°C.

Fig. 5. Arrhenius plots of (a) LSNZ-x%, (b) LSNZ with the addition of sintering aids.

Fig. 6. Potentiostatic polarization patterns of LSNZ-20%, LSNZ-1wt% Al₂O₃ and LSNZ-1wt% B₂O₃.

Table 1 R_{bulk} , R_{gb} , R_{total} at 30 °C of LSNZ-x%, LSNZ-1wt% Al_2O_3 and LSNZ-1wt% B_2O_3 .

Samples	$R_{\text{total}}/\Omega\cdot\text{cm}$	$R_{\text{bulk}}/\Omega\cdot\text{cm}$	$R_{\text{gb}}/\Omega\cdot\text{cm}$	$R_{\text{gb}}/R_{\text{total}}$
LSNZ-0%	1.92×10^5	6.35×10^4	1.28×10^5	67%
LSNZ-10%	6.67×10^4	1.67×10^4	5.00×10^4	75%
LSNZ-20%	6.25×10^4	1.75×10^4	4.50×10^4	72%
LSNZ-30%	1.72×10^5	4.66×10^4	1.25×10^5	73%
LSNZ-1wt% Al_2O_3	6.25×10^4	1.76×10^4	4.49×10^4	72%
LSNZ-1wt% B_2O_3	5.05×10^4	1.77×10^4	3.28×10^4	65%

Table 2 Density, total conductivity and activation energies of LSNZ-x%, LSNZ-1wt% Al_2O_3 and LSNZ-1wt% B_2O_3 .

sample	Density/g cm^{-3}	$\sigma(30^\circ\text{C})/\text{S cm}^{-1}$	$\sigma(100^\circ\text{C})/\text{S cm}^{-1}$	Ea/eV
LSNZ-0%	3.67	5.2×10^{-6}	1.9×10^{-5}	0.28
LSNZ-10%	3.73	1.5×10^{-5}	6.99×10^{-5}	0.31
LSNZ-20%	3.97	1.6×10^{-5}	1.1×10^{-4}	0.36
LSNZ-30%	3.99	5.8×10^{-6}	6.0×10^{-5}	0.41
LSNZ-1% Al_2O_3	4.07	1.6×10^{-5}	1.11×10^{-4}	0.35
LSNZ-1% B_2O_3	4.09	1.98×10^{-5}	1.12×10^{-4}	0.34