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Effect of Low-Cost Spodumene Sintering Aids on Electrical Properties for $Li_{0.25}La_{0.25}NbO_3$ Ceramic

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In this work, a low-cost natural mineral material, spodumene is used as novel sintering aids for $Li_{0.25}La_{0.25}NbO_3$ ceramics. $Li_{0.25}La_{0.25}NbO_3$ (LLNO) with improved electrical properties are synthesized by the spodumene-assisted sintering via high temperature solid state method. The effects of spodumene sintering aids on structure, microstructure and electrical properties for LLNO solid electrolyte were investigated by using XRD, SEM and AC-impedance, respectively. LLNO sintered at 1000 °C exhibits a pure perovskite structure while the samples with added spodumene sintering aids contain some impurities. LLNO with 5 wt.% spodumene sintered at 1000 °C presents an ionic conductivity of 4.96×10^{-5} $S\cdot cm^{-1}$ at 25 °C with an activation energy of 0.32 eV. The conductivity of LLNO-5% spodumene sample is one times magnitude higher than that of pure LLNO. The results indicate that the introduction of spodumene successfully acts as a sintering aid for LLNO ceramic solid electrolytes.

Keywords: *Spodumene, solid electrolyte, electrical property, natural mineral material.*

1. Introduction

Spodumene ($LiAl[Si_2O_6]$) is a low-cost natural mineral material, which is used as additives for metallurgy, glass and ceramics[1]. Spodumene can be used as a sintering aid to reduce ceramic sintering temperature, increase ceramic density, and thus improve ceramic properties[2,3]. Excessive sintering temperature is a huge challenge faced by oxide-type solid electrolytes for solid state lithium batteries. Co-sintering[4] of solid electrolyte with electrodes is a solid-state battery manufacturing technology with development prospects. The manufacture temperature of traditional electrode for lithium battery is about 600~900 °C (such as $LiMn_2O_4$, $LiFePO_4$ cathode and $Li_4Ti_5O_{12}$ anode)[5-7], as well as exceed 1100 °C for oxide-type solid electrolyte[8]. The high sintering temperature of solid electrolytes hinders the practical application of co-sintering technology in solid-state battery manufacturing[9].

$Li_{0.25}La_{0.25}NbO_3$ ceramic is a typical solid electrolyte for solid lithium battery. LLNO ceramics exhibit promising ionic conductivity and stability, but their high sintering temperatures lead to excessive energy consumption, lithium volatilization, and increased grain boundary resistance. LLNO possesses the perovskite-type A-site-deficient structure, high intrinsic vacancies concentration and larger lattice volume. LLNO has the potential to achieve high lithium-ion conductivity. The grain conductivity of LLNO ceramic solid elelctrolyte is 10^{-3} $S\cdot cm^{-1}$ as high as at room temperature[10].

The addition of sintering aids offers a viable pathway to simultaneously reduce sintering temperatures and enhance conductivity, particularly by mitigating grain boundary resistance[11-13]. Liu et al.[14] reported that the density of the electrolyte was improved after the addition of LiF. Specifically, at 500 °C, the addition of 4% LiF as a sintering flux resulted in a conductivity of 2.45×10^{-3} $S\cdot cm^{-1}$. At this point, the density and conductivity of the electrolyte were at their highest. Park et al.[15] showed that Li_2CO_3 is an effective sintering aid in $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolytes. It improves the density of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$, thereby enhancing ionic conductivity and battery performance. Liu et al.[16] synthesized a garnet-structured solid electrolyte $Li_{6.1}Ga_{0.3}La_3Zr_2O_{12}$ using a traditional solid-state method by introducing Al_2O_3 as a sintering aid. Adding a small amount of Al_2O_3 as a sintering aid reduced the sintering temperature from 1100 °C to approximately 1050 °C. At room temperature, the ionic conductivity can reach up to 1.28×10^{-3} $S\cdot cm^{-1}$. Spodumene presents a compelling alternative due to its ultra-low cost compared to synthetic sintering aids. Its efficacy in lowering sintering temperatures and improving properties in other ceramics[2,3], combined with its intrinsic lithium content, suggests significant potential for enhancing LLNO processability and performance cost-effectively. However, The application specifically to LLNO has not been systematically investigated.

However, the total conductivty of LLNO ceramic is only 10^{-5} $S\cdot cm^{-1}$ at room temperature, which is almost two orders of magnitude lower than that of grain conductivity. So, there is a clear room for improvement of the total conductivity of LLNO ceramic solid electrolyte. Furthermore, the traditional sintering temperature of LLNO is exceed 1100 °C[17]. Such a high sintering temperature is unfavorable for the practical applications of LLNO ceramic solid electrolyte. Adding sintering aids is an effective method to reduce the sintering temperature of solid electrolytes and enhance their

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conductivity. The process of sintering is known to result in an improvement in the density of ceramic particles, thereby lowering the sintering temperature and enhancing electrical conductivity[9,14]. Currently, there have been limited studies on improving the performance of LLNO through the addition of sintering aids.

In this work,$Li_{0.25}La_{0.25}NbO_3$ ceramic solid electrolyte with different contents of spodumene as sintering aids were prepared by solid-state reaction method. The structure, microstructure and electrical properties of the LLNO ceramic solid electrolytes with or without spodumene sintering aids were investigated and compared by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and AC-impedance method, respectively. The effect of low-cost spodumene sintering aids on electrical properties for $Li_{0.25}La_{0.25}NbO_3$ solid electrolyte was disscused.

2. Materials and Methods

LLNO solid electrolytes were synthesized via a solid-state reaction method and then sintered at high temperature. The stoichiometric weighed of anhydrous La_2O_3 (99.9%, Sinopharm Chemical Reagent Co., Ltd), Li_2CO_3 (99.8%, Aladdin Chemical Reagent Co., Ltd), Nb_2O_5 (99.5%, Sinopharm Chemical Reagent Co., Ltd) and spodumene (Natural mineral powder, Fengfeng Shun stone powder factory) powder were used as the raw materials. The spodumene content was 0%, 1%, 3%, 5%, and 8%, and the corresponding ceramic samples were named LLNO-SP0, LLNO-SP1, LLNO-SP3, LLNO-SP5, and LLNO-SP8, respectively. 10 wt.% Li_2CO_3 powder were added into the raw materials to avoid the loss of lithium caused by the evaporation of Li_2O during high temperature synthesis. The raw materials were mixed by using ball-milling method for 8 hours. After ball-milling, the mixed powder was calcined at 900 °C for 12 h in air with an alumina crucible. After calcine, the powder was reground and pressed into pellets with 15 mm diameter at 10 MPa. Finally, all pellets were sintered at 1000-1100 °C for 12 h in air.

The phase composition of samples was obtained using X-ray diffraction (XRD) on a Bruker D8 device with Cu Kα radiation. The cross-section surface microstructure of pellets was characterized via scanning electron microscope (SEM) on a S-3000N device. The conductivity of the samples was determined by AC impedance spectroscopy (1 Hz~1 MHz, CHI660E) between room temperature and 100 °C. The electronic conductivity of samples were measured using an CHI660E electrochemical station device via DC-polarization method at room temperature. Before the electrical property characterization, the surface of samples was coated with soft graphite electrode as the ion-blocking electrode.

3. Results and Discussion

Figure 1 shows the XRD images of spodumene and ceramic samples. All solid electrolyte ceramic samples display the typical perovskite structure. The positions of the main diffraction peaks remain consistent. LLNO sintered at 1100 °C have a pure perovskite structure. Samples with added spodumene sintering aids at 1000 °C remain the perovskite structure but contain some impurities such as $LiNbO_3$, La_2O_3, and $LaNbO_4$. The characteristic peaks of spodumene disappeared in solid electrolyte ceramics. The main diffraction peaks of all samples remain in the same position, indicating that no doping occurred. The role of spodumene during sintering for LLNO ceramic is not dopants but sintering additives.

Figure 2 shows the SEM images of fracture surface for ceramic samples. The size of the sample was roughly measured with a ruler. Grain sizes of the ceramic pellets were determined to be 38 μm. All samples are relatively dense but same pores can be observed due to the loss of lithium caused by the evaporation of Li_2O during high temperature synthesis. The grain boundaries of LLNO samples are clear. There are obvious melting marks at the grain boundaries of LLNO-SP1, LLNO-SP3, LLNO-SP5 and LLNO-SP8 ceramics, which were caused by the assisting sintering effect of spodumene as sintering aids. This indicates that the introduction of spodumene acts as a sintering aid for ceramics. Wrinkle and crack were observed in all samples, which was caused by the thermal stress during rapid cooling process after sintering. The emergence and intensification of impurity peaks with increasing spodumene content are attributed to side reactions during sintering[18]. Spodumene ($LiAlSi_2O_6$) decomposes above 900 °C, releasing reactive Li_2O_3 and SiO_2-Al_2O_3 components. $Li_2O + Li_{0.25}La_{0.25}NbO_3 \rightarrow 2LiNbO_3 + La_2O_3$ (lithium excess triggers $LiNbO_3$ precipitation), $SiO_2 + La_2O_3 \rightarrow La_2SiO_5$ (silica consumes lanthanum, forming silicate intermediates), $Al_2O_3 + Nb_2O_5 \rightarrow LaNbO_4$ (aluminum facilitates niobium oxide segregation). Higher spodumene loads amplify these reactions, leading to stronger impurity peaks in XRD. This aligns with observations in Al_2O_3-spodumene systems, where ≥5% additives induce secondary phases proportional to dosage. Spodumene undergoes partial melting above 1000 °C. Decomposed spodumene components react with LLNO or surface oxides, as confirmed by the emergence of $LaNbO_4$ and $LiNbO_3$.

Figure 3(a) shows the AC-impedance spectra of LLNO while Figure 3(b) gives the AC-impedance spectra of LLNO-SP0, LLNO-SP1, LLNO-SP3, LLNO-SP5, and LLNO-SP8. The conductivity (σ) of samples were calculated by the following Formula 1.

$$\sigma = \frac{d}{R \times S} \tag{1}$$

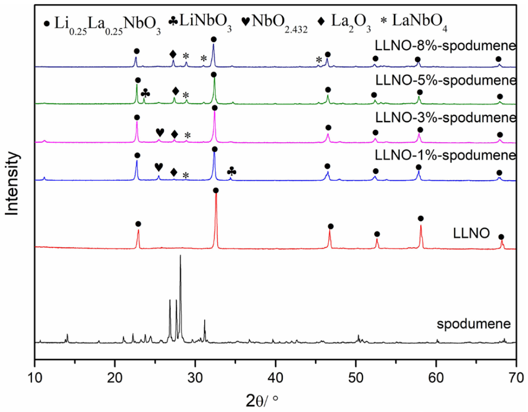

Figure 1. XRD pattern of ceramic pellets.

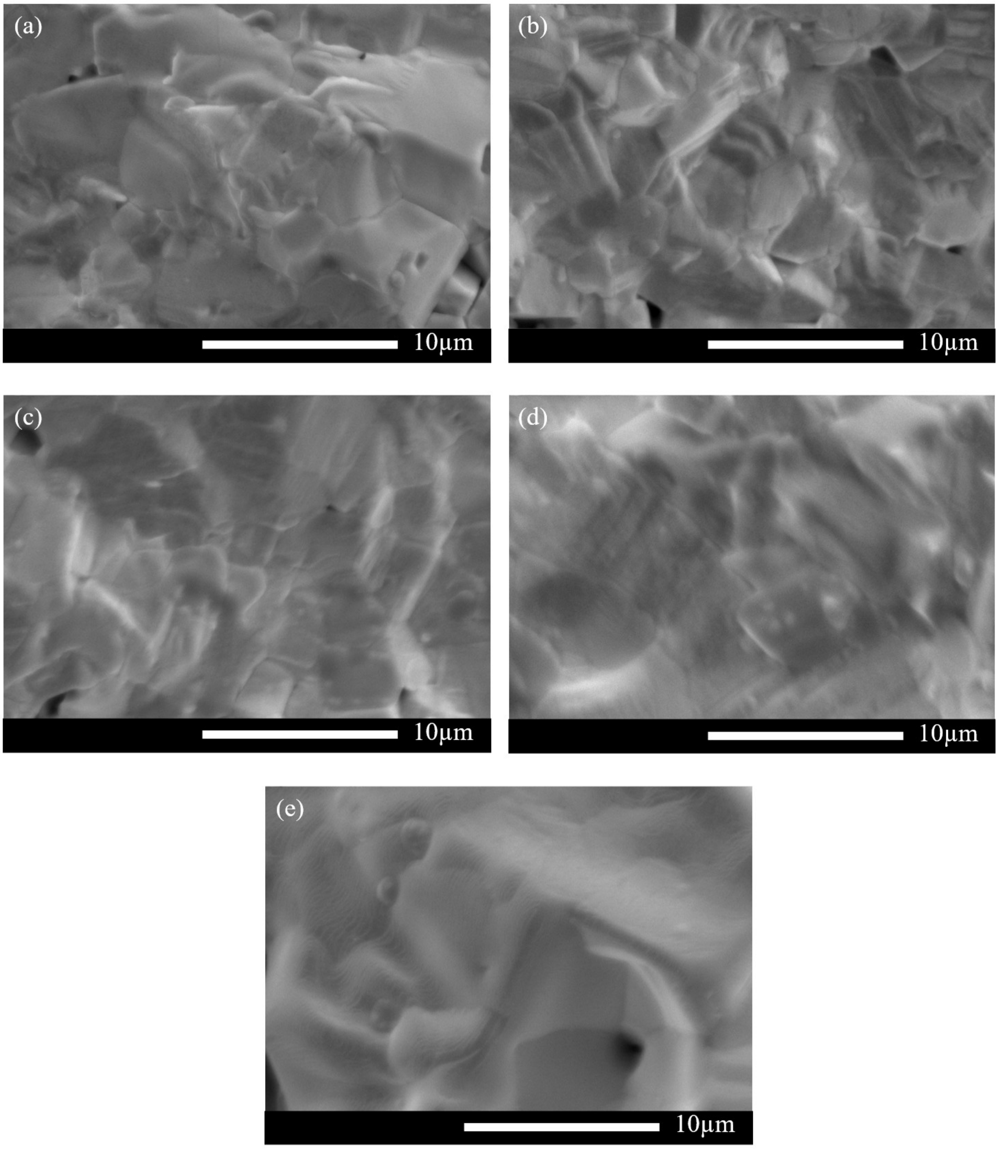

Figure 2. SEM images of LLNO (a), LLNO-SP1 (b), LLNO-SP3 (c), LLNO-SP5 (d), LLNO-SP8 (e).

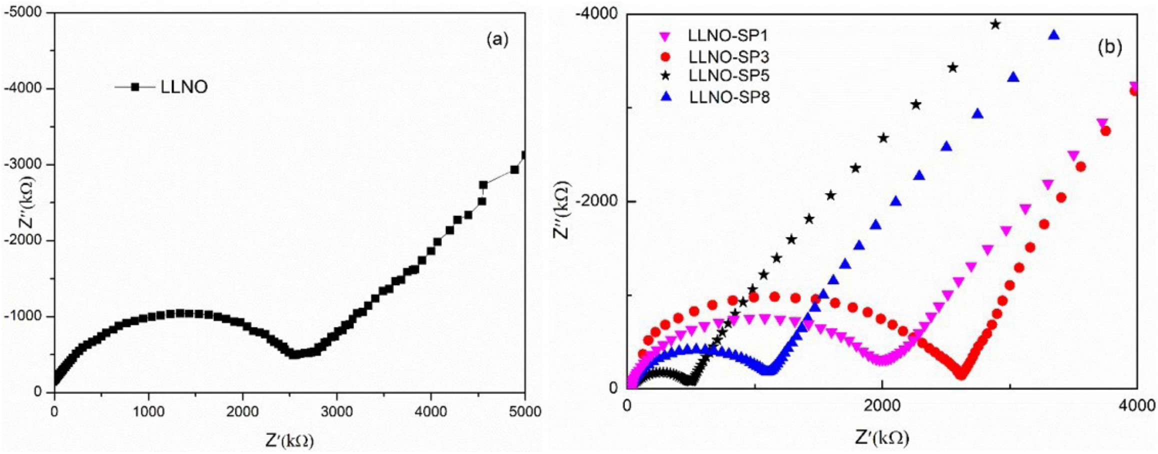

Figure 3. AC-impedance images of ceramic pellets.

where σ is the conductivity ($S \cdot cm^{-1}$) of pellets, S is the surface area (cm^2) and d is the thickness (cm) of ceramic pellet. The total resistance (R, Ω) of ceramic pellets is the intercept of semicircles as shown in Figure 3 on the real axis (Z′).

According to the calculation results, LLNO without spodumene exhibits a low conductivity of 2.38×10^{-6} $S \cdot cm^{-1}$. The conductivity of samples increased after adding spodumene as sintering aids. LLNO-SP5 (5% spodumene) sintered at 1000 °C presents an ionic conductivity of 4.96×10^{-5} $S \cdot cm^{-1}$ at 25 °C. The conductivity of LLNO-5% spodumene sample is 10 times higher than that of pure LLNO sintered at 1100 °C without spodumene. All samples exhibit only one well-defined semicircle in the high-frequency region, indicating that grain boundary resistance is negligible compared to bulk resistance. This occurs because high-purity LLNO with relative density minimizes grain boundary scattering sites, merging grain and grain boundary contributions into a single semicircle. In Figure 3(a) and Figure 3(b), the intercept of the semicircle's left end on the Z′ axis defines R.

Figure 4 shows the temperature dependence of the conductivity (σ) of LLNO ceramics. The conductivity, electronic conductivity and activation energy of each sample were calculated and shown in Table 1. As can be seen, the activity energy deceased when spodumene was added as sintering additives. The activation energy of LLNO-SP5 is 0.32 eV, which was lower than pure LLNO. It is worth noting that the Arrhenius curve of LLNO-SP3 exhibits a scattered characteristic, which means that the conductivity activation energy of LLNO-SP3 does not extremely conform to the Arrhenius equation. These results indicate that adding spodumene is benefit to lithium conduction in LLNO ceramics. The relative density of LLNO increases and ion blockage interfaces caused by porosity are reduced when 5% spodumene is heated to 1000 °C[19]. The addition of sintering aid was inadequate, resulting in ineffectiveness. Conversely, an excess of combustion aid led to non-conductivity in the sample. Ying et al.[20] calculated that the conductance activation energy is directly related to the defect concentration and type introduced by the impurity. The sudden drop in the conductivity and Ea value of LLNO-SP8 could be caused by the sintering aids being added in excessive amounts[21]. When the amount of spodumene added exceeds a certain level, more impurities are produced through additional side reactions. As shown in Figure 1, excessive sintering aid affects the conductivity and Ea of the sample.

Figure 5 shows the DC-polarization spectra of samples. The electronic conductivity of samples was calculated and listed in Table 1. As can be seen, the electronic conductivity calculated based on DC-polarization curves is about 4-orders lower than the corresponding ionic conductivity for all samples. This means that LLNO ceramics with spodumene sintering aids is still an ionic-conductor. Ionic conductivity arises from the migration of charged ions through lattice defects or grain boundaries. It dominates in solid electrolytes where ions are the primary charge carriers. Electronic conductivity involves the movement of electrons or holes through the material. While essential for electrodes, uncontrolled σ_e in electrolytes causes self-discharge and capacity loss in batteries by creating internal short circuits. A high σ_i/σ_e ratio ($>10^3$) is crucial in solid-state electrolytes[22]. Our results meet this requirement, ensuring minimal electron leakage during operation. It is conceivable that fluctuations in the sodium feldspar composition of the samples may have precipitated the emergence of impurities. In the sample designated LLNO-SP5, the densification process that was found to be optimal resulted in the separation of the impurity phase, thereby reducing σ_e to a minimum[23]. In the sample designated LLNO-SP8, the presence of excessive lithium feldspar resulted in the promotion of the formation of $LaNbO_4$. In this phase, the reduction of the aforementioned phase is exhibited through mixed ionic-electronic conductivity, which is evidenced by an increase in σ_e to 2.95×10^{-9} $S \cdot cm^{-1}$.

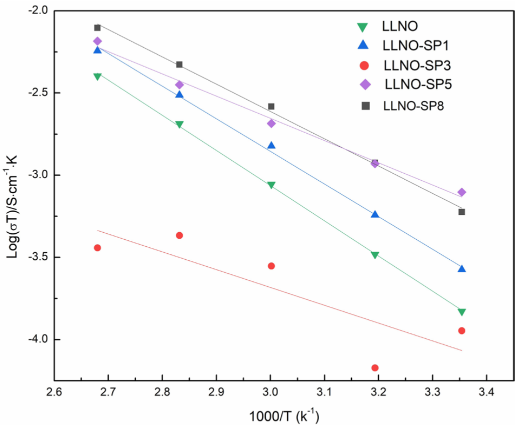

Figure 4. Arrhenius plots of ceramic samples.

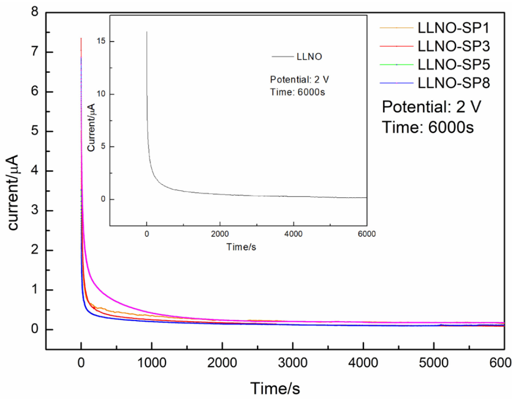

Figure 5. DC-polarization spectra of ceramic samples.

Table 1. Conductivity and activation energy of the spodumene composite LLNO ceramics.

Sample	$\sigma_{25°C}$/$S \cdot cm^{-1}$	σ_{ele}/$S \cdot cm^{-1}$	Ea/eV
LLNO	2.38×10^{-6}	3.69×10^{-9}	0.42
LLNO-SP1	2.45×10^{-6}	0.74×10^{-9}	0.39
LLNO-SP3	8.96×10^{-7}	2.95×10^{-9}	non
LLNO-SP5	4.96×10^{-5}	0.54×10^{-9}	0.32
LLNO-SP8	3.81×10^{-5}	0.90×10^{-9}	0.38

4. Conclusions

In conclusion, $Li_{0.25}La_{0.25}NbO_3$ ceramic solid electrolyte with different contents of spodumene as sintering aids were synthesized succesfully by solid-state reaction method. SEM images revealed distinct melting marks at the grain boundaries of ceramic pellets, attributed to the sintering-enhancing effect of spodumene. The sample LLNO-SP5 sintered at 1000 °C exhibited the best performance, achieving the highest ionic conductivity of 4.96×10^{-5} $S \cdot cm^{-1}$ at 25 °C, a significant increase from 2.38×10^{-6} $S \cdot cm^{-1}$ for the baseline material. Furthermore, LLNO-SP5 demonstrated a low activation energy of 0.32 eV. The electronic conductivity of LLNO-SP5 is four orders of magnitude lower than its ionic conductivity, demonstrating that LLNO-SP5 is a pure ionic conductor. Therefore, the natural spodumene mineral proves to be a feasible and effective sintering aid for enhancing the properties of LLNO solid electrolyte ceramics.

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Data Availability

All data are provided within the manuscript.