

The Effect of Lithia Addition on the Sodium Ion Conductivity of Vapor Phase Converted Na- β'' -alumina/YSZ Solid Electrolytes

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Abstract : Na- β'' -Al₂O₃ has been widely employed as a solid electrolyte for high-temperature sodium (Na) beta-alumina batteries (NBBs) thanks to its superb thermal stability and high ionic conductivity. Recently, a vapor phase conversion (VPC) method has been newly introduced to fabricate thin Na- β'' -Al₂O₃ electrolytes by converting α -Al₂O₃ into β'' -Al₂O₃ in α -Al₂O₃/yttria-stabilized zirconia (YSZ) composites under Na⁺ and O²⁻ dual percolation environments. One of the main challenges that need to be figured out is lowered conductivity due to the large volume fraction of the non-Na⁺-conducting YSZ. In this study, the effect of lithia addition in the β'' -Al₂O₃ phase on the grain size and ionic conductivity of Na- β'' -Al₂O₃/YSZ solid electrolytes have been investigated in order to enhance the conductivity of the electrolyte. The amount of pre-added lithia (Li₂O) precursor as a phase stabilizer was varied at 0, 1, 2, 3, and 4 mol% against that of Al₂O₃. It turns out that ionic conductivity increases even with 1 mol% lithia addition and reaches 67 mS cm⁻¹ at 350 °C of its maximum with 3 mol%, which is two times higher than that of the undoped composite.

Keywords : Na- β'' -alumina, Solid electrolyte, Vapor phase conversion, Lithia addition, Sodium-beta alumina batteries

1. Introduction

Sodium beta alumina (Na- β'' -Al₂O₃) is a sodium ion conducting solid electrolyte widely used in high-temperature sodium-sulfur (Na-S) and sodium-metal chloride (Na-MCl₂) batteries thanks to its fast sodium-ion conducting characteristics through loosely-packed conduction planes in its spinel blocks.¹⁻⁵⁾ There are two distinctive subgroups of sodium beta alumina, i.e., β - and β'' -Al₂O₃, with the nominal composition of (Na₂O):x(Al₂O₃); where the x is between 9 and 11 for β -alumina and 5 and 7 for β'' -Al₂O₃.⁶⁻⁸⁾ Na- β'' -alumina has been widely preferred among the polymorphs due to its

higher ionic conductivity resulting from higher Na-ion content.⁹⁾

Na- β'' -Al₂O₃ can be synthesized through various routes such as solid-state reaction, spark plasma sintering, or sol-gel process.¹⁰⁻¹³⁾ All the methods involve the use of a mixture of Na⁺ ion-containing precursors, Li⁺ or Mg⁺ ion-containing phase stabilizers, and Al₂O₃ sources. High-temperature sintering above 1,550 °C is generally required to densify the Na- β'' -Al₂O₃ solid electrolyte. However, the high-temperature firing causes Na-volatilization in the form of Na₂O and diminution in ionic conductivity.¹³⁾ Therefore, lithia (Li₂O) or magnesia (MgO) is used as phase stabilizers to balance the Na-loss through the charge-compensation mechanism.⁹⁻¹³⁾ The Li⁺ or Mg²⁺ ions partially substitute for Al³⁺

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ions in the spinel blocks. When doped with a monovalent cation (M^+), the Al^{3+} ions in the spinel blocks of $\beta''\text{-Al}_2\text{O}_3$ will be partially substituted by the M^+ ions ($[Al_{11-x}^{3+}M_x^{1+}]O_{16}^{2-}$), and the charge compensation is done with the introduction of an additional Na^+ ion in the conduction planes ($Na_{1+2x}^{1+}O_1^{2-}$).¹⁴⁾

Recently, a novel vapor phase conversion (VPC) approach has been introduced to obtain $Na\text{-}\beta''\text{-Al}_2\text{O}_3$ directly from $\alpha\text{-Al}_2\text{O}_3$.^{11,15)} The process involves the conversion of sintered $\alpha\text{-Al}_2\text{O}_3$ /yttria-stabilized zirconia (YSZ) composite into $Na\text{-}\beta''\text{-Al}_2\text{O}_3$ /YSZ at relatively lower temperatures of below 1,450 °C. This new technique effectively suppresses harsh Na_2O volatilization and $NaAlO_2$ aggregation, and restricts abnormal grain growth that frequently occurred at higher temperatures. The conversion is established by coupled diffusion of $2Na^+$ and O^{2-} ions from $Na_2O(g)$ source through converted sodium conducting $\beta''\text{-Al}_2\text{O}_3$ and oxygen conducting YSZ, respectively.¹⁶⁾ At the beginning of the VPC, Na_2O vapor from the atmospheric powder (pre-synthesized $Na\ \beta/\beta''\text{-alumina}$ powder) reacts with the $\alpha\text{-Al}_2\text{O}_3$ at the surface of the $\alpha\text{-Al}_2\text{O}_3$ /YSZ composite to form $Na\text{-}\beta/\beta''\text{-Al}_2\text{O}_3$. Subsequently, the Na^+ and O^{2-} ions from the vapor are transported through the converted $Na\text{-}\beta''\text{-Al}_2\text{O}_3$ and YSZ phases, respectively. The atmospheric powder is also to supply Li-or Mg-phase stabilizers during the conversion.

Even though the role of phase stabilizer is evident in the conventional process, the effect of the phase stabilizer in the VPC has not been well studied yet. It was expected that Li_2O for the phase stabilization would be originated from the atmospheric powder.¹⁷⁾ Still, the incorporation of Li^+ in the spinel blocks of $Na\text{-}\beta''\text{-alumina}$ during the conversion would be very slow due to the poor diffusivity of Li^+ . If a precursor of lithia is added to the $\alpha\text{-Al}_2\text{O}_3$ /YSZ composite, before the phase conversion, it is expected that the addition of Li_2O no longer has to belong to the slow diffusion from the atmospheric powder. Therefore, the present study suggests the pre-addition of a Li_2O precursor into an $\alpha\text{-Al}_2\text{O}_3$ /YSZ mixture to increase sodium concentration after conversion and focuses on the effect of lithia concentration on the phase formation, microstructure, and ionic conductivity of vapor-

phase converted $Na\text{-}\beta''\text{-Al}_2\text{O}_3$ /YSZ composites. Since there are many reports regarding applying Li_2O as a sintering aid for various inorganic materials, the present research also investigates the other effects of the dopant in the VPC.^{18,19)} The concentration of YSZ is fixed at 30 vol.% to obtain both percolating O^{2-} ion conducting pathway and sufficient mechanical strength. The concentration of Li_2O is varied from 0 to 4 mol% against that of $\alpha\text{-Al}_2\text{O}_3$. The phase formation and electrical properties are systematically investigated through X-ray diffraction and AC impedance analysis.

2. Materials and Methods

2.1 Preparation of Li-stabilized $\alpha\text{-Al}_2\text{O}_3$ /yttria-stabilized zirconia (AY73Lx) composites

The precursor powder mixture consists of $\alpha\text{-Al}_2\text{O}_3$ (AES-11, Sumitomo, Japan), 3 mol% yttria-stabilized zirconia (YSZ) (TZ-3Y, Tosoh, Japan), and Li_2CO_3 (99.0%, Junsei Honsha, Japan). The mixture was homogeneously mixed with wet planetary milling (Pulverisette 5, Fritsch, Germany) at 500 rpm for 4h in ethanol (99.5%). $\alpha\text{-Al}_2\text{O}_3$ and YSZ were mixed in the volume ratio 7:3. Li_2CO_3 (99.0%, Junsei Honsha, Japan) was used as the phase stabilizer, and its concentration varied between 0 to 4 mol % with respect to $\alpha\text{-Al}_2\text{O}_3$. The dried powder mixtures were uniaxially pressed into pellets with 19 mm in diameter and 0.3–0.4 mm in thickness at 70 MPa. The green pellets were then sintered at 1,600 °C for 2 h to obtain $\alpha\text{-Al}_2\text{O}_3$ /YSZ composite discs. The $\alpha\text{-Al}_2\text{O}_3$ /YSZ composites are marked as AY73Lx, where x is the mole ratio of Li_2CO_3 against $\alpha\text{-Al}_2\text{O}_3$. (AY73Lx).

2.2 Synthesis of atmosphere powder for VPC

The atmosphere powder for VPC is made by mixing the synthesized $Na\text{-}\beta/\beta''\text{-Al}_2\text{O}_3$ powder, previously used $Na\text{-}\beta/\beta''\text{-Al}_2\text{O}_3$ powder, and $NaAlO_2$ in the weight ratio 50:40:10. $Na\text{-}\beta/\beta''\text{-Al}_2\text{O}_3$ powder used as the Na_2O source for the VPC contains ~10.26 wt.% Na_2O , ~0.83 wt.% Li_2O , and 88.9 wt.% Al_2O_3 . The precursors, $\alpha\text{-Al}_2\text{O}_3$, Na_2CO_3 (99.5%, Samchun chemical, Republic of Korea), and Li_2CO_3 , were dry-mixed and calcinated twice at 900 °C and 1,250 °C for 2h each to obtain $Na\text{-}\beta/\beta''\text{-Al}_2\text{O}_3$ atmosphere powder.

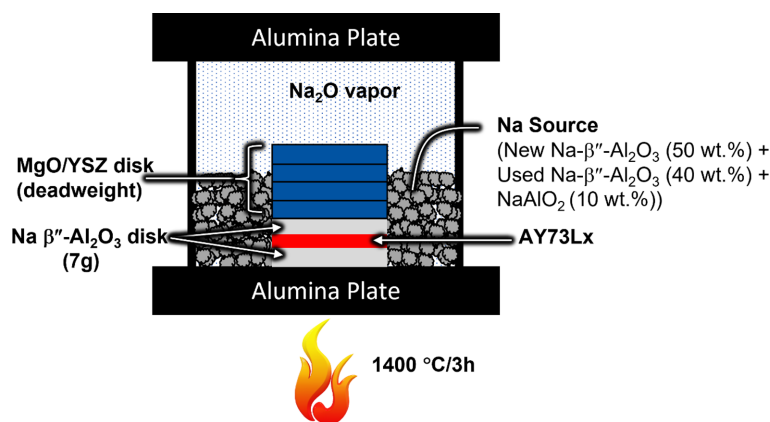


Fig. 1. Schematic setup for vapor phase conversion of AY73Lx into BY73Lx.

2.3 Vapor phase conversion to prepare Na-β''-Al₂O₃/YSZ (BY73Lx) composite

The schematic of the VPC process is shown in Fig. 1. The sintered AY73Lx disks were packed in the atmosphere powder with dead weights (sintered MgO/YSZ flat disks) ($> 50 \text{ g/cm}^2$) to minimize warpage, and then encapsulated in a dense α -Al₂O₃ crucible. To avoid sodium loss, the α -Al₂O₃ crucible was pre-reacted with the atmosphere powder at a temperature of 1,550 °C for 3h. The VPC process was carried out at 1,400 °C for 3 h. The converted Na-β''-alumina/YSZ composites are marked as BY73Lx, where x is the mole ratio of Li₂CO₃ against α -Al₂O₃.

2.4 Characterization of AY73Lx and BY73Lx

The microstructure of the fractured cross-sections of the sample was analyzed with a scanning electron microscope (SEM, XL30S FEG, Philips Electron optics B.V., Netherlands). Thermal etching at 1,500 °C for 10 min was conducted after micro-polishing for the grain size analysis of the AY73Lx. The density of the sample was estimated by Archimedes' method. X-ray diffraction analysis (D8 Advance A25, Bruker, Germany) using Cu-K α radiation was used for the phase analysis and structural transformation. The conversion of α -Al₂O₃/YSZ composites into Na-β''-Al₂O₃/YSZ was verified by analyzing the decrease in intensity of α -Al₂O₃ peaks ((104) and (113)), and the increase in intensity of Na-β''-Al₂O₃ peaks ((1011) and (0210)).

The ionic conductivity measurements were carried

out between 200 °C and 350 °C with an impedance analyzer (SP240, Bio-Logic Science Instruments, France) using two-probe 'across-to-plane' mode. Circular Au patterns of a diameter of 8 mm were sputtered on the sample's surface and further brush-painted with commercial Ag paste as blocking electrodes. A piece of wires-connected Pt mesh was also attached to the electrode on each face as a current collector. The samples were then fired at 600 °C for 7 min to remove binders and sinter the Ag particles. A 2h dwell is allocated in the heating schedule to obtain thermal equilibrium for the impedance measurement at each temperature. The impedance spectra were obtained within the frequency range from 10 Hz to 5 MHz.

3. Results and Discussion

3.1 Phase identification

Fig. 2(a) shows the results of the XRD analysis of the AY73Lx samples sintered at 1,600 °C for 2 h. As shown in the figure, no secondary phases are formed during sintering. All the peaks are matched well with the α -Al₂O₃ [PDF#46-1212] and 3 mol% YSZ [PDF#83-0113]. No diffraction peaks corresponding to Li₂O were identified in the spectrum. The first and second strongest peaks of all patterns belong to the (111) peaks at $2\theta = 30^\circ$ and (220) peaks at $2\theta = 34.77^\circ$ of TZ-3Y, respectively. The (220) planes of TZ-3Y and (104) planes of α -Al₂O₃ share common peak positions at $2\theta = 34.77^\circ$. A sharp decrease in intensity of (104) peak shown

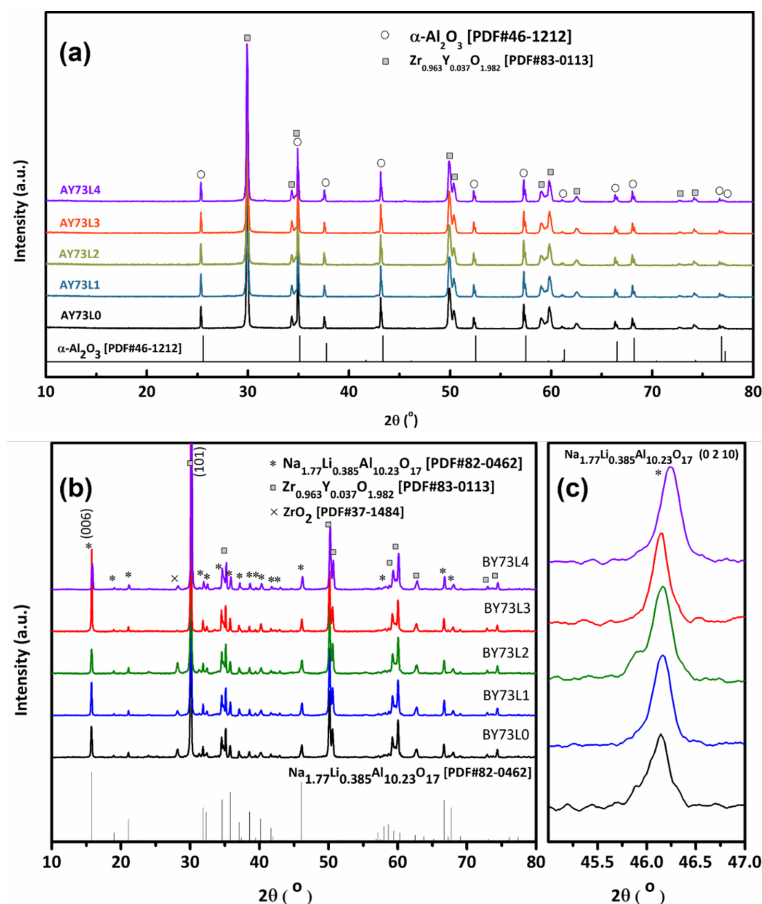


Fig. 2. (a) XRD pattern of the AY73Lx samples sintered at 1,600 °C for 2 h. (b) XRD patterns of the BY73Lx samples vapor phase converted at 1,400 °C for 3h and phase-stabilized with 0, 1, 2, 3, and 4 mol % of Li₂O. (c) XRD patterns of BY73Lx enlarged between 45° and 47° to check the presence of Na β-Al₂O₃. No peak was detected corresponding to Na-β-Al₂O₃.

in Fig. 2(b) after conversion of AY73Lx is due to the conversion of α-Al₂O₃ into Na-β"-Al₂O₃. Moreover, the reduction in intensity of the α-Al₂O₃ peaks at 2θ=25° and 2θ=43° also confirms the conversion of α-Al₂O₃ into Na-β"-Al₂O₃¹⁴⁾. Regardless of Li₂CO₃ contents, patterns in Fig. 2(b) are identical and well matched with the ICDD patterns of β"-alumina [PDF No. 01-082-0462], 3 mol% YSZ [PDF No. 01-083-0113], and partially transformed monoclinic zirconia [PDF#37-1484]. No secondary peaks are observed in the converted BY73Lx samples other than the monoclinic zirconia. The evolution of the tetragonal-to-monoclinic (t-to-m) transition in the converted samples is due to the martensitic transformation in YSZ.²⁰⁾ Generally, the t-to-m transi-

tion during crack propagation is the main strengthening mechanism in YSZ-containing ceramics.^{20,21)}

Moreover, it is clear from Fig. 2(b) that the 3 mol% Li₂O stabilized sample has a stronger β" (006) orientation compared to the others. The lattice parameters were calculated from the (0210) peaks of BY73Lx to understand the effect of Li concentration on the phase formation of Na-β"-Al₂O₃ during conversion, which is given in Table 1. As shown in Fig. 2(c), all the peaks at (0210) coincide; therefore, it is clear that there is no significant change in the lattice parameters, even though a lattice parameter increase due to Li⁺ doping (0.76 Å) in the Al³⁺ site (0.535 Å) was expected. The result indicates minimal incorporation of Li⁺ in

Table 1. Lattice parameter and orientation degree of BY73Lx

Sample ID	Lattice parameter $\beta''\text{-Al}_2\text{O}_3$ [Å]		Orientation degree (C-axis/crystal face)			
	a	c	0° (006)	33.3° (104)	60° (110)	90° (1010)
BY73L0	5.593	33.659	0.59	0.09	0.10	0.22
BY73L1	5.590	33.643	0.60	0.09	0.10	0.22
BY73L2	5.590	33.643	0.52	0.11	0.12	0.20
BY73L3	5.591	33.651	0.79	0.10	0.10	0.22
BY73L4	5.590	33.643	0.57	0.11	0.09	0.16
PDF#82-0462 ($\text{Na}_{1.77}\text{Li}_{0.385}\text{Al}_{10.23}\text{O}_{17}$)	5.603	33.621	0.45	0.19	0.14	0.22

the α - or β'' -phase during sintering and conversion. Instead, the Li might have resided at the grain boundaries as a glassy phase since the densification in the conventional $\beta''\text{-Al}_2\text{O}_3$ synthesis process involves the existence of an eutectic reaction among the ternary $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-Li}_2\text{O}$ system. If there are any secondary phases of Li at the grain boundary, it will block the Na^+ conduction across the grain boundary.

$\text{Na-}\beta''\text{-Al}_2\text{O}_3$ has a rhombohedral structure consisting of three spinal blocks separated by conduction slabs partially filled with Na^+ ions. It is well understood that the grain growth in $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ occurs parallel to the basal plane (along the conduction plane), which leads to the formation of elongated grains with platelet morphology²⁰. The ionic conduction occurs through the diffusion of Na^+ ions through the conducting slab. However, the conduction of the polycrystalline $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ is anisotropic due to the irregular orientation of the conduction planes. Therefore, the degree of crystal orientation in BY73Lx is to be determined to explain the effect of Li_2O addition on ionic conductivity.²² The crystal orientation is determined using the Lotgering factor, f_{001} , which is given as²³:

$$f_{001} = \frac{\left(\frac{\sum I_{00l}}{\sum I_{hkl}}\right) - \left(\frac{\sum I_{00l}^0}{\sum I_{hkl}^0}\right)}{1 - \left(\frac{\sum I_{00l}^0}{\sum I_{hkl}^0}\right)} \quad (1)$$

where, I_{00l} is the intensity of 00l peak and I_{hkl} is the peak intensities of all the planes within the

measured 2θ range; and I_{00l}^0 and I_{hkl}^0 are the corresponding intensities of the reference sample without any preferred orientation.^{20,22,24} As shown in Fig. 2(b), the relative intensity of (006) reflection of BY73L3 is stronger than that of other compositions, indicating a higher phase orientation of BY73Lx grains along the (006) direction. The degree of orientations calculated using Equation 1 for various peaks are shown in Table 1; the corresponding angle between the crystal plane and c-axis is also shown in the table. It is clear from Fig. 2(b) and Table 1 that the (006) planes of BY73L3 - which are perpendicular to the c-axis (0°) - have a higher orientation with $f_{001} = 0.79$ compared to other compositions. However, the orientation along other reflections (104), (110), and (1010) are comparatively lower and have almost identical values. Hence it can be summarized that the 3 mol% Li doping enables a higher phase orientation for the BY73Lx samples along the direction of conduction planes.

3.2 Microstructure

The microstructure of the sintered AY73Lx (x = 0–4 mol%) after thermal etching is shown in Figs. 3(a) and 6(a–d). The 70:30 ratio provides a percolating uniformly distributed equiaxed grains of $\alpha\text{-Al}_2\text{O}_3$ and YSZ for all the compositions; the white shade represents YSZ, and the grey shade indicates $\alpha\text{-Al}_2\text{O}_3$. As shown in the figures, the grain size of the AY73Lx composites increases with the dopant concentration. Moreover, the SEM images indicate complete densification with negligible

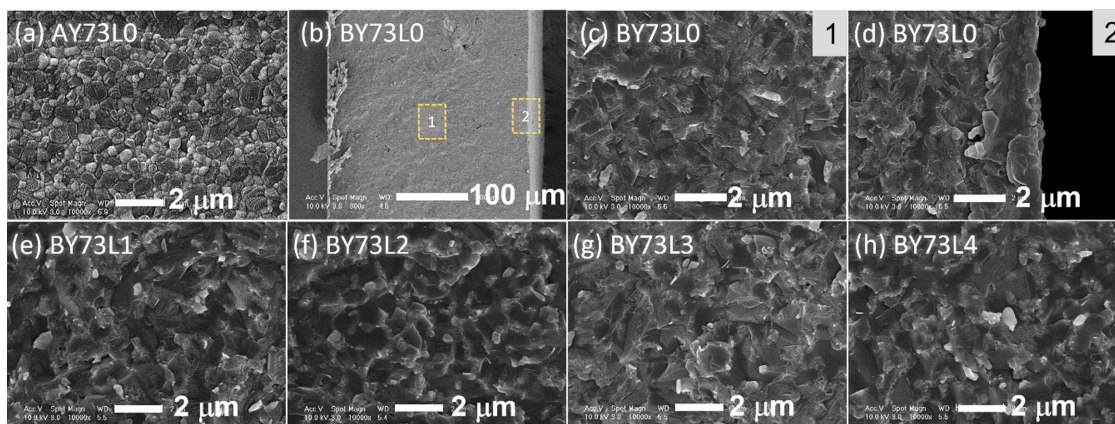


Fig. 3. Cross-sectional SEM micrographs of (a) AY73L0 sintered at 1,600 °C, (b–d) BY73L0, (e) BY73L1, (f) BY73L2, (g) BY73L3, and (h) BY73L4 sintered at 1,600 °C and vapor phase converted at 1,400 °C.

porosity. Furthermore, a relative density of ~95% is achieved for all the AY73Lx samples. Mordekovitz et al. reported that Li-addition enhances sinterability and grain growth.²⁵⁾

The cross-sectional SEM images of the BY73Lx (x = 0–4 mol%), vapor phase converted at 1,400 °C for 3 h, is shown in Figs. 3(b–h). All of the BY73Lx compositions were converted entirely. The variation of Li concentration doesn't seem to have a significant effect on the conversion kinetics, except for the higher orientation degree of the 3 mol% Li₂O doped Na-β"-Al₂O₃ grains as evident from the XRD patterns. A contiguous Na-β"-Al₂O₃ and YSZ phase is visible in the SEM images, as would be required for the complete conversion to occur through the coupled transport of 2Na⁺ through the α-Al₂O₃ phase and O²⁻ through the YSZ phase.^{15,26)} Typical Na-β"-Al₂O₃ grains are platelet-shaped; therefore, polygonal morphology of α-Al₂O₃ grains changed into platelets during conversion. Since the grain growth and conversion direction are identical, the platelet grains will be elongated towards the conversion direction.

3.3 The effect of Li doping on the Na⁺ conduction

The impedance spectra of the BY73Lx are shown in Figs. 4(a,b). Fig. 4(a) shows the high-frequency EIS spectra of BY73Lx measured at a constant temperature of 352±2 °C over the frequency range from 10 Hz to 5 MHz. Extrapolation of the high-

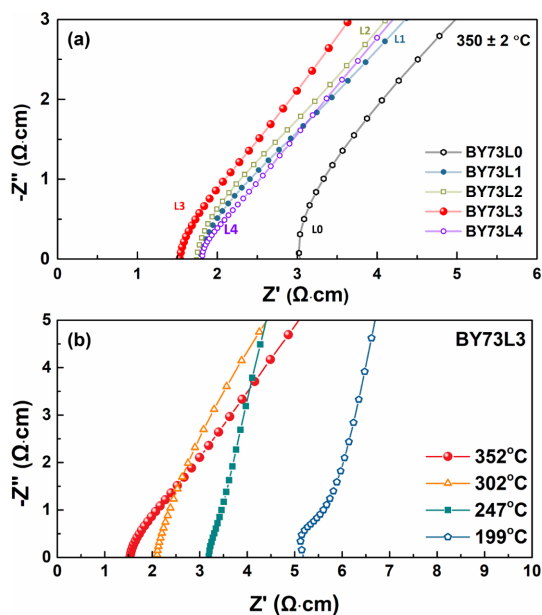


Fig. 4. Electrochemical impedance spectra of (a) the BY73Lx as a function of lithium content (0–4 mol%) measured at 350 °C, and (b) the BY73L3 (t = 290 μm) in the temperature range 199 to 352 °C.

frequency intercept to the x-axis gives the resistance contribution of the grains. As shown in Fig. 4(a), the area-specific resistance (ASR) of BY73Lx decreases with an increase in Li concentration initially and reaches the lowest value of 1.5 Ω·cm for the 3 mol% Li₂O doped sample. With a further rise

in Li_2O , the ASR starts to decrease. The highest ASR is obtained for the sample without Li_2O doping, which means that a small amount of Li_2O addition helps increase the ionic conductivity of the electrolyte. The increase in resistance of the 4 mol% Li_2O doped sample can be due to the blocking effect of the Li_2O -containing secondary phase present at the grain boundaries. Fig. 4(b) shows the high-frequency impedance spectra of BY73L3 measured at temperatures 199, 247, 302, and 352 °C in the frequency range 10 Hz to 5 MHz. The lowest ASR of 1.5 $\Omega\cdot\text{cm}$ is obtained at 352 °C. As the temperature decreases, ASR increases, and the highest value is obtained at 199 °C. The Arrhenius plot of the conductivity of the BY73Lx is given in Fig. 5(a). From the Arrhenius plot, the activation energy can be obtained by taking the slope of the linear fit and using the following equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_a}{k_b T}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, T is the temperature in Kelvin, E_a is the activation energy, and k_b is the Boltzmann constant.

As shown in Fig. 5(a), the ionic conductivity of BY73Lx measured at 350 °C increases with Li concentration and reaches the highest value of 67 mS cm^{-1} for 3 mol% doped samples, which was more than double that of the BY73L0 (32 mS cm^{-1}) measured at the same temperature. Moreover, there is an

abrupt increase in the ionic conductivity when Li concentration changes from 0 to 1 mol%. The ionic conductivity starts to decrease with a further increase in the Li_2O doping after 3 mol%. The conductivity of every composition increases with temperature, and the highest value is reported at 350 °C for all compositions. Therefore, Li_2O doping is beneficial for increasing the ionic conductivity of Na- β'' - Al_2O_3 solid electrolytes. The activation energy of all the compositions was calculated using Equation (2), and it varied between 0.20 eV for BY73L0 and 0.28 eV for BY73L4. The activation energy for the BY73L3 was calculated as 0.25 eV. The ionic conductivity and the activation energy of BY73Lx were compared with the reported values of Na- β'' - Al_2O_3 /YSZ compositions were prepared at a 70:30 ratio using VPC, as shown in Table 2.

To elucidate the reason for the higher ionic conductivity of the BY73L3, we have determined the relative β and β'' fraction of the samples after conversion from the XRD data of Fig. 2(b). The calculations were done using the following equations²⁷⁻²⁹:

$$f(\beta) = \frac{1}{3} \left\{ I_{\beta(102)} \times \frac{10}{3} + I_{\beta(206)} \times \frac{10}{3.5} + I_{\beta(107)} \times \frac{10}{5.5} \right\} \quad (3)$$

$$f(\beta'') = \frac{1}{2} \left\{ I_{\beta''(102)} \times \frac{10}{4} + I_{\beta''(102)} \times \frac{10}{8} \right\} \quad (4)$$

where $I_{\beta(102)}$, $I_{\beta(206)}$, and $I_{\beta(107)}$ are the peak X-ray intensities of (102), (206), and (107) planes of Na

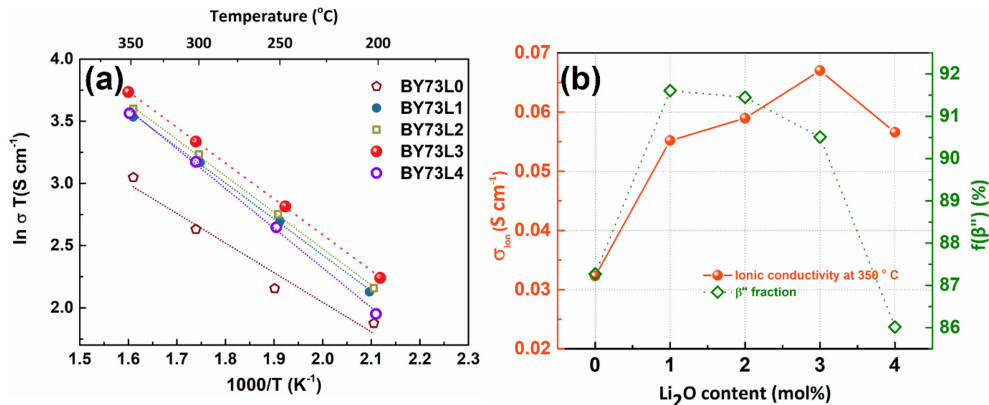


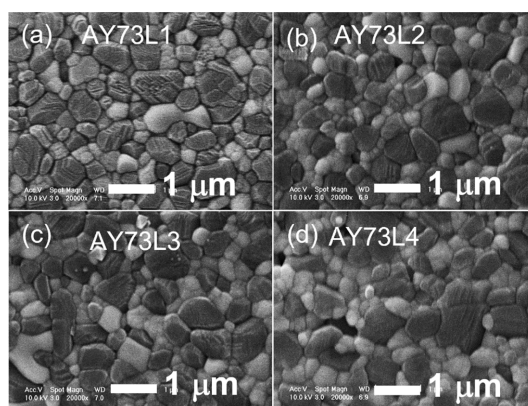
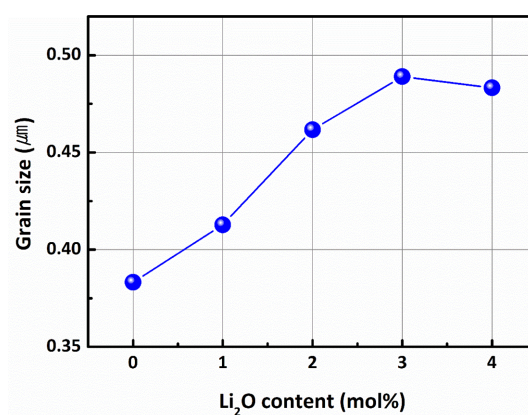
Fig. 5. (a) Arrhenius plots of BY73Lx as a function of lithium content (0–4 mol%). (b) The variation of measured ionic conductivity, and β'' phase fraction of BY73Lx at different Li_2O concentrations. The ionic conductivity data is taken at 350 °C.

Table 2. Comparison table of BY73L3 and other BY73 fabricated using vapor phase conversion technique

Conversion condition	Doping agent	σ [mS cm ⁻¹]	T [°C]	E _a [eV]	Reference
1,250 °C for 108 h	-	137	350	-	26)
1,250 °C for 20 h	5 mol% Fe ₂ O ₃	16.3	350	0.2	14)
1,450 °C for 10 h	-	181	350	-	20)
1,500 °C for 4 h	-	8.8	350	-	27)
1,250 °C for 36 h	-	94	350	-	26)
1,400 °C for 3 h	3 mol% Li ₂ O	67	350	0.25	This work

β -Al₂O₃, respectively: and $I_{\beta''(1011)}$ and $I_{\beta''(2010)}$ are peak intensities of the Na β'' -Al₂O₃, respectively. Generally, VPC leads to the formation of both β and β'' phases: however, ionic conductivity of the β phase is one order smaller than that of β'' phase. Therefore, the relative fraction between β and β'' will determine the conductivity of the final product. As shown in Fig. 5(b), the highest β'' phase fraction, 91.5%, is obtained for the BY73L1. With further increase in Li concentration, the β'' phase in the composite decreased and reached the lowest measured value of 86% for the BY73L4. Therefore, it is evident that the higher ionic conductivity of BY73L3 is not due to the β'' phase in the sample. Moreover, the higher amounts of Li⁺ doping, > 3 mol% is detrimental to the ionic conductivity because of the lower conversion rate to β'' phase and the formation of a glassy phase assumed at the grain boundaries.

The higher ionic conductivity of the BY73L3 sample can be due to two possible factors: one can be the higher orientation degree of the (006) planes of the Na- β'' -Al₂O₃, as shown in Table 1. The grain size effect can be another factor that possibly affects the ionic conductivity. Therefore, using the line intercept method, we further examined the grain size of the AY73Lx composites from the SEM images in Figs. 2(a) and 6(a–d). The grain size in Fig. 7 is the average of the two phases, α -Al₂O₃ and YSZ. The grain size of the AY73Lx increases with Li⁺ doping, as shown in Fig. 7, and the highest value of 0.49 mm is obtained for AY73L3. The smallest grain size of 0.38 mm was observed for the undoped BY73L0. With further doping, the grain size decreased; for AY73L4, the grain size was 0.48 mm. As shown in Figs. 5(b)

**Fig. 6. SEM images of the cross-section of sintered a-Al₂O₃/YSZ with Li₂O concentration (a) 1 mol%, (b) 2 mol%, (c) 3 mol%, and (d) 4 mol%.****Fig. 7. Variation of grain size of AY73Lx with Li₂O concentrations.**

and 7, the variation of ionic conductivity of BY73Lx and grain size of AY73Lx with Li₂O concentration have a similar trend. The grain size and ionic conductivity have the highest value at 3

mol% Li doping. It is well understood that the final grain size of the converted BY73Lx composites depends on the grain sizes of the AY73Lx composite, and the ionic conductivity will be higher for larger-grained samples.

4. Conclusions

Na- β'' -Al₂O₃/YSZ (BY73Lx) composites were prepared by vapor phase conversion of α -Al₂O₃/YSZ (AY73Lx) composites at 1,400 °C for 3 h. To investigate the effect of phase stabilizer in the vapor phase conversion process, Li₂O was pre-added with the AY73 powder mixture as a phase stabilizer, and their concentration varied from 0 mol% to 4 mol%. The effect of phase stabilizer concentration on the structure, microstructure, and ionic conductivity of vapor phase converted Na- β'' -Al₂O₃/YSZ composite was systematically investigated. No obvious change in the crystal structure parameters hardly indicates the substitution of Li⁺ onto the Al³⁺ site in the spinal block. A phase pure BY73Lx composite was obtained after conversion except for the minor secondary phase of the tetragonal-to-monoclinic transitioned YSZ. A higher orientation degree is observed for (006) planes of Na- β'' -Al₂O₃ than other compositions. There was considerable grain growth observed with an increase in Li₂O concentration. The largest grain size of 0.49 μ m was obtained for 3 mol% doped BY73Lx. The effect of Li₂O concentration on the Na ion conductivity of BY73Lx was also investigated. The conductivity was enhanced with Li₂O, and a maximum value of 67 mS/cm was obtained for 3 mol% doped BY73Lx. The ionic conductivity of BY73L3 was more than double that of BY73L0. The higher ionic conductivity of the 3 mol% doped BY73Lx can be due to the higher crystal orientation of Na- β'' -Al₂O₃ grains and the larger grain size of α -Al₂O₃/YSZ composites. This result indicates that even a small amount of pre-added lithia effectively promotes ionic conduction.

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Conflicts of Interest

The authors declare no conflict of interest.

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