

Short communication

Phase separation and electrical conductivity of lithium borosilicate glasses for potential thin film solid electrolytes

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Abstract

The ionic conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system was studied for potential application as a thin film electrolyte and compared with that of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass system. Among oxide glasses, these glass electrolytes are believed to be the most suitable for a thin film electrolyte due to the stable amorphous glass, its inertness to moisture and the ease of fabrication. The effect of spinodal decomposition on the ionic conductivity in the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system was also discussed. The ionic conductivity of phase-separated glass is dependent on the microstructure of the highly conductive phase. The structural analysis of the glass electrolyte was performed with various chemical compositions and the correlation to the ionic conductivity is discussed. The maximum conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system is $2.4 \times 10^{-8} \text{ S cm}^{-1}$, which is lower than that of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass system by almost one order of magnitude. However, despite low conductivity, the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system is still believed to be a strong candidate for a thin film electrolyte since its glass formability and chemical stability are excellent compared to other glass electrolyte systems.

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1. Introduction

Inorganic glass has been studied for long time as a candidate for a solid state electrolyte of a rechargeable thin film battery which applied to electronic devices such as by micro-electro-mechanical system, smart card, medical appliances and so on. It has been recognized that the major limitation of a glass electrolyte is the low lithium ion mobility while the electrochemical stability and the chemical inertness against the active materials employed in a lithium battery are regarded as major advantages. The application of the glass electrolytes to a conventional bulk type battery, hence, is impractical in spite of the merits and the research on this group of materials [1]. However, if the resistance of the electrolyte layer is reduced to a reasonable level, the glass electrolyte may become a candidate for a solid-state electrolyte. The reduction of resistance can be achieved by reducing the thickness of the electrolyte to a few micrometers range, which can be easily achieved by thin film fabrication technologies. In

thin film processes, inorganic solid electrolytes are generally regarded as more advantageous compared to a polymer based electrolyte since the film deposition and the subsequent process such as heat treatment and etching are more practical in common thin film processing facilities. Therefore, it is believed that the glass electrolyte can be a strong candidate when a solid-state thin film battery is considered. Among the various types of glass electrolytes, the oxide glasses are in general chemically and electrochemically more stable than the sulfide glasses and the compatibility with the equipment for thin film processing is excellent [2,3]. Thin films of amorphous oxides are easily deposited by conventional deposition equipment such as a sputterer or an evaporator.

Among the oxide glasses investigated for the electrolyte, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ are of considerable technological interest since a large amount of lithium can be incorporated and still yield stable glasses. Another interesting phenomenon observed in the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system is spinodal decomposition [4]. A homogeneous glass can be separated to a silica-rich phase and an alkali borate rich phase and the produced structure is a heterogeneous mixture of three-dimensionally interconnected channels with different composi-

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tions [5]. The interconnected structure of the two phases depends on the glass composition [6,7]. It is an interesting question that this spinodal decomposition is helpful for the conduction of a glass electrolyte. A thin sheet of glass electrolyte with three-dimensionally interconnected channels produced by the spinodal decomposition might be applicable as a matrix material for a hybrid electrolyte, which contains a conventional liquid electrolyte in the channels.

The present work discusses the ionic conductivity of a series of lithium borosilicates and the influence of phase separation (spinodal decomposition) on the electrical conductivity. The correlation to the structural variation to electrical conductivity is also discussed. The electrical conductivity and phase stability of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass are compared with $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass.

2. Experiments

Glass electrolytes with composition $x\text{Li}_2\text{O}-(1-x)(0.5\text{B}_2\text{O}_3-0.5\text{SiO}_2)$ and $x\text{Li}_2\text{O}-(1-x)(0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5)$ were prepared from SiO_2 (99.8%), B_2O_3 (95%), P_2O_5 (98%) and Li_2CO_3 (99%). The compositions of the studied glasses are listed in Table 1. The starting materials were mixed in proportions appropriate to form 20 g batches. The homogeneously mixed powders were then melted in Pt crucibles at 1000 °C for 5 h using an electric furnace and then quenched in a stainless-steel mold to give transparent glass plates of 1–2 mm thick. Samples were annealed for 2 h at 600–700 °C and the amorphous state of the glass electrolytes were confirmed at room temperature by X-ray diffraction (XRD). Then, to check the microstructure, a piece of glass was chemically etched in 1 mol% HF solution at 25 °C for 3 min and then dried at 120 °C for 3 h. A scanning electron microscope (SEM) was employed to observe the morphology of spinodal decomposition.

For lithium ion conductivity measurement, Pt was sputtered on both sides of the glass electrolyte as an ion blocking electrode. Conductivity measurements were performed by complex impedance methods using a Solartron impedance analyzer with an ac voltage of low amplitude over the frequency range 1 Hz to 1 MHz at room temperatures. And the comparison between the different ionic conductivities before and after spinodal decomposition was also done by using impedance analyzer.

Table 1
The compositions of glass electrolytes studied

Sample no.	Li_2O	B_2O_3	SiO_2
1	5	47.5	47.5
2	7	46.5	46.5
3	9	45.5	45.5
4	10	45	45
5	15	42.5	42.5
6	20	40	40
7	25	37.5	37.5
8	30	35	35
9	35	32.5	32.5
10	40	30	30
11	45	27.5	27.5
12	50	25	25

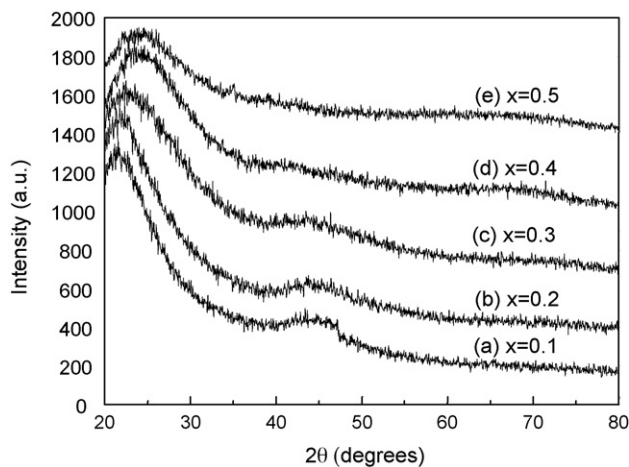


Fig. 1. X-ray diffraction pattern of prepared glass electrolytes with the compositions of $x\text{Li}_2\text{O}-(1-x)(0.5\text{B}_2\text{O}_3-0.5\text{SiO}_2)$.

3. Results and discussions

The prepared glass specimens were all in the amorphous state as shown in the X-ray diffraction pattern of Fig. 1. At a low Li_2O concentration, small broad peaks were observed at $2\theta \sim 45^\circ$ and these peaks are produced by the heterogeneous microstructure generated by the spinodal decomposition. The phase separation became undetectable by X-ray diffraction patterns beyond a 40 mol% Li_2O concentration. The produced microstructures of a phase-separated specimen are shown in Fig. 2. It is known that the details of microstructure, more specifically the separation type (spinodal channel type or precipitate type) and the feature size of separated phase, are generally determined by the concentration of the added network modifier [8]. As illustrated in Fig. 2(d), the microstructure produced in the region of low concentration of Li_2O , denoted by “A,” was usually composed of a lithium rich channel and a network forming rich matrix. An example of this type of structure is shown in Fig. 2(a). The microstructures shown in Fig. 2 are that of the specimen after the acid wet etching which removes the lithium rich phases. Therefore, the residual skeletons shown in the figure are network former rich phases. In Fig. 2(a), three-dimensionally interconnected channels were etched out by a wet etching and interconnected holes were left. This microstructure was inverted into a lithium rich matrix and a network former rich channel in the specimen with a high concentration of Li_2O , denoted by “C.” An example of this type of structure is shown in the Fig. 2(c).

The apparent ionic conductivity of the phase-separated specimen was dependent on the microstructure discussed above. In general, the formation of the phase with a high alkali content in a form of interconnected three-dimensional network tends to increase the conductivity as long as its volume ratio is not too small. Another factor to be considered is the alkali content of the alkali-rich phase. Since the alkali content directly determines the ionic conductivity and the total conductivity is determined by the simple rule of mixture, $\sigma_{\text{tot}} = v_c\sigma_c + v_m\sigma_m$ (where v_i is the volume fraction, σ_i is the conductivity of i phase, and the subscripts c and m denote the channel and matrix), the conductivity of the specimen increases only if the increased conductivity of alkali-

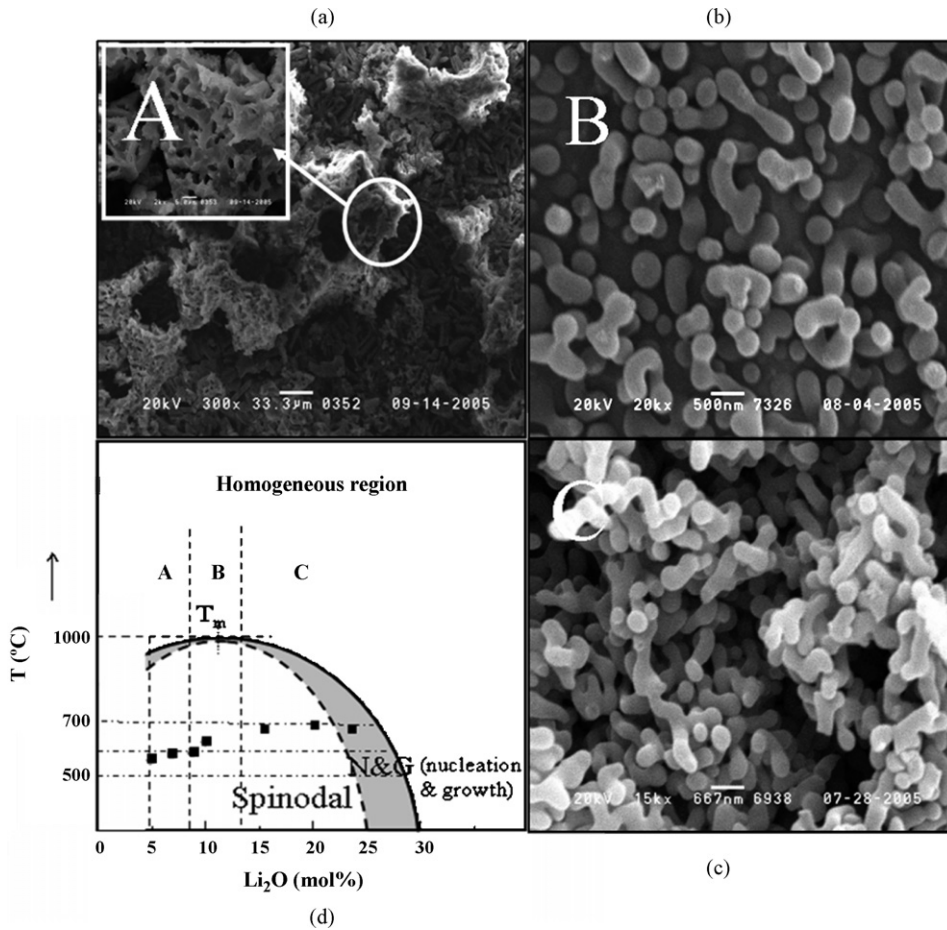


Fig. 2. The variation of microstructure of the glass specimen produced by the spinodal decomposition with Li_2O content of (a) 7 mol%, heat-treated at 600°C for 2 h, (b) 9 mol%, heat-treated at 650°C for 2 h, (c) 15 mol%, heat-treated at 700°C for 2 h. All specimens were etched in HF of 25°C for 3 min. The residual skeleton is the network former rich phase and (d) immiscibility dome of $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--SiO}_2$ system [4] and the compositions and heat treatment temperatures studied in the present study (denoted by solid square dots).

rich phase compensates the reduced volume fraction. Overall, the ionic conductivity increased with increasing Li_2O content and it is very well known that this increase is due to the increase of both the mobility and number of charge carrier. Increase of charge carrier number is not linearly proportional to the Li_2O content since the oxide glasses with alkali ions are generally weak electrolytes [9]. The estimation of ionization fraction of lithium added is not a routine measurement and the method for indirect determination has been suggested previously [10]. The increase in lithium ion mobility is due to the formation of non-bridging oxygens or broken bonds within the glass network. Non-bridging oxygen sites are known to offer hopping sites for ionic conduction in oxide glass networks where a cation such as Li^+ easily jumps into or out due to the relatively weak bonding or the shallow energy well [1]. The formation of non-bridging oxygen is also contributing to the relatively open network structure with a large free volume for ion drift. The combination of these two effects increases the ionic mobility of the glass electrolyte.

The ionic conductivities of glasses are summarized in Fig. 3 as functions of the concentration of alkali oxide added to glass. The effect of spinodal decomposition on the ionic conductivity is also shown in Fig. 3, where the conductivities measured after

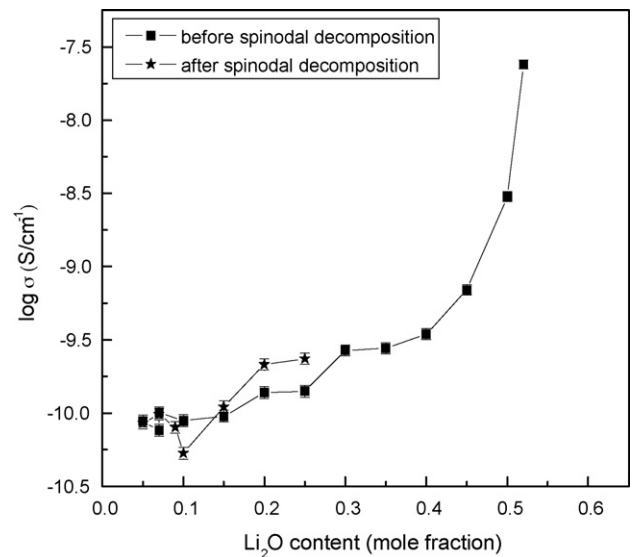


Fig. 3. The variation of ionic conductivity as functions of Li_2O content in $x\text{Li}_2\text{O}\text{--}(1-x)(0.5\text{B}_2\text{O}_3\text{--}0.5\text{SiO}_2)$ glass electrolyte.

the spinodal decomposition is denoted by star symbols. It is clear in this figure that the conductivity variation by phase separation is categorized into three regions; the region with $\text{Li}_2\text{O} < 9 \text{ mol}\%$, $10\text{--}15 \text{ mol}\%$, and $>20 \text{ mol}\%$. In the region with $\text{Li}_2\text{O} < 9 \text{ mol}\%$, there is no evidence that the ionic conductivity was enhanced, while in the region with $\text{Li}_2\text{O} > 20 \text{ mol}\%$ it is certain that the ionic conductivity increased noticeably. The microstructure of the region with $\text{Li}_2\text{O} < 9 \text{ mol}\%$ is the type “A” shown in Fig. 2(a); the fast ion conducting (lithium rich) channels with the low conductivity (glass former rich) matrix. The microstructure of the region with $\text{Li}_2\text{O} > 20 \text{ mol}\%$ is the type “C” shown in Fig. 2(b); the low conductivity (glass former rich) channels embedded in the fast ion conducting (lithium rich) matrix. Therefore, it is certain from the result in Fig. 3 that at least in a lithium borosilicate glass electrolyte the formation of the fast ion conducting (lithium rich) matrix is more beneficial for enhancing the conductivity. Overall, however, the enhancement of the conductivity by phase separation is not great compared to the natural increase by the addition of lithium into the glass network. Therefore, it can be said that the effect of phase separation on the apparent conductivity is rather limited from a practical viewpoint.

In contrary to other regions, the conductivity decreased in the intermediate region. In this intermediate region, the structure of spinodal decomposition transformed from the “A” type to “C” type. As shown in Fig. 2(b), the microstructure of the lithium rich phase in this intermediate region is rather discontinuous and isolated. Therefore, the fast conducting channels are disconnected and the pathways for ion drift are blocked, which results in reduced apparent conductivity.

The ionic conductivity of $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--P}_2\text{O}_5$ and $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--SiO}_2$ are compared as functions of Li_2O content in Fig. 4. The room temperature conductivities of these glass electrolytes exhibited a large difference of almost one order of magnitude. Conductivity of $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--P}_2\text{O}_5$ glass electrolyte, however, saturated at 45 mol% of Li_2O , while that of $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--SiO}_2$

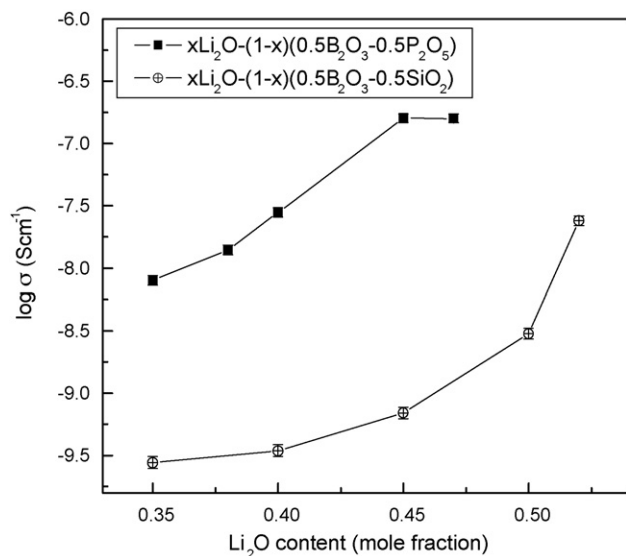


Fig. 4. The comparison of the conductivity of $x\text{Li}_2\text{O}\text{--}(1-x)(0.5\text{B}_2\text{O}_3\text{--}0.5\text{SiO}_2)$ and $x\text{Li}_2\text{O}\text{--}(1-x)(0.5\text{B}_2\text{O}_3\text{--}0.5\text{P}_2\text{O}_5)$ glass electrolyte as functions of Li_2O content.

kept increasing to 52 mol% Li_2O . The different behavior of these two glass electrolytes are attributed to the difference in the glass forming abilities. It was observed that in $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--SiO}_2$ glass system a homogeneous glass electrolyte was more easily fabricated even at a high Li_2O content, $>47 \text{ mol}\%$, while the tendency for crystallization in the $\text{Li}_2\text{O}\text{--B}_2\text{O}_3\text{--P}_2\text{O}_5$ glass system rapidly increased at this level of Li_2O content and it was almost impossible to obtain a glass specimen without a crystalline phase at 50 mol% Li_2O .

The ionic conductivity in the glass electrolyte is closely related to the network structure and the local environment where a lithium ion is located, and especially on the existence and the structure of the non-bridging oxygens. It is very well known that the number of non-bridging oxygens in a silicate glass is simply proportional to the added alkali content while that of a borate glass is rather complicated. In borate glasses, the non-bridging oxygen is generated by the conversion of a BO_4 unit (four coordinated boron) to $[\text{BO}_3]^-$ (three coordinated boron with a non-bridging oxygen). Therefore, the formation of $[\text{BO}_3]^-$ units promotes the ionic mobility and increases the ionic conductivity. The structural variation of borosilicate glass electrolytes prepared in this work was characterized by Raman spectroscopy, which is shown in Fig. 5. The peaks at 480, 1250, and 1450 cm^{-1} are assigned to $\text{Si}\text{--O}\text{--Si}$, $[\text{B}_2\text{O}_5]^{4-}$, and $\text{B}\text{--O}$ [11,12], respectively. No noticeable changes in these peaks were observed since these peaks are related to the molar ratios of glass formers which were fixed to 1:1 in this work. The peak at 803 cm^{-1} (boroxol ring) was observed only for low Li_2O and gradually disappeared with increasing Li_2O , while the peak 760 cm^{-1} ($[\text{BO}_4]$, four coordinated boron) grew instead [13]. The peak at 760 cm^{-1} ($[\text{BO}_4]$, four coordinated boron) also gradually decreased from medium Li_2O content, 25 mol% and the peak at 967 cm^{-1} ($[\text{BO}_3]^-$, three coordinated boron with a non-bridging oxygen) grew instead. The peak at 1100 cm^{-1} ($[\text{O}\text{--Si}\text{--O}]^-$, four coordinated silicon with a non-bridging oxygen) [14] exhibited similar behavior to the peak at 760 cm^{-1} .

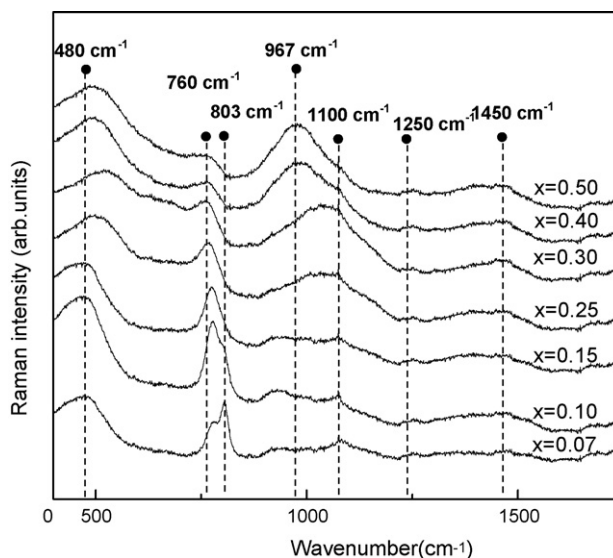


Fig. 5. Raman spectra of $x\text{Li}_2\text{O}\text{--}(1-x)(0.5\text{B}_2\text{O}_3\text{--}0.5\text{SiO}_2)$ glass electrolyte at various Li_2O concentrations.

In overall, the main feature of boron changed in the following sequence, boroxol \rightarrow $[\text{BO}_4] \rightarrow [\text{BO}_3]^-$. The major source of non-bridging oxygen also changed from $[\text{O}-\text{Si}-\text{O}]^{-1}$ to $[\text{BO}_3]^-$, which suggests that the lithium ions are preferentially associated with boron rather than silicon and this tendency helps to increase the mobility of lithium ions.

4. Conclusions

In the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system, the maximum ionic conductivity was achieved with $2.4 \times 10^{-8} \text{ S cm}^{-1}$ at room temperature and the conductivity was not high enough for application as a bulk type electrolyte. Compared to the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ system, the conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system was lower by almost two orders of magnitude. The phase separation by a spinodal decomposition tended to increase the apparent conductivity in the range of $20 \text{ mol}\% < \text{Li}_2\text{O} < 25 \text{ mol}\%$ by the formation of a highly conductive phase, while in the transitional range, $8 \text{ mol}\% < \text{Li}_2\text{O} < 15 \text{ mol}\%$, the conductivity was reduced due to the disconnected highly conducting channels. The effect of phase separation was rather limited and turned out to be not enough to increase the conductivity to a practical level.

However, the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system is believed to be a good candidate for a thin film solid electrolyte due to its stable glass forming ability and stable chemical properties. The resistance to moisture is much better than the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ system and the authors' preliminary experiments have demon-

strated that the deposition of a thin film electrolyte is easily done in the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system. Therefore, the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system is believed to be still worthwhile for the fabrication of thin film electrolytes.

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