

Preparation of a hybrid solid glass electrolyte using a nano-porous sodium borosilicate glass membrane for lithium batteries

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Hybrid glass solid electrolytes are regarded as potential materials for application as electrolytes and separators in secondary lithium and lithium-ion batteries. Glass electrolyte membranes with nano-channels were prepared by spinodal decomposition and subsequent acid leaching. The phase-separated, alkali-rich phase was eluted by leaching for 1h at room temperature and a liquid electrolyte was infiltrated into the 3 dimensionally interconnected channels of the glass membrane to improve of ion mobility. The most suitable glass electrolyte membranes could be fabricated from 7.5Na₂O-46.25B₂O₃-46.25SiO₂ (mol%). The effects of leaching temperature, leaching time and acid type on the preparation of the membranes were investigated. The microstructure of the surface and cross-section of 7.5Na₂O-46.25B₂O₃-46.25SiO₂ glass electrolytes were examined with a scanning electron microscope. The channels interconnected throughout the membrane were confirmed to be formed and the channel size was in the range of 90-200 nm. For electrochemical investigates of the glass electrolyte, full cells were fabricated using a coin type cell by employing LiCoO₂ as a cathode and Mesocarbon Microbeads (MCMB) as an anode.

Key words: hybrid solid electrolyte, spinodal decomposition, glass electrolyte membrane, porous glass, Lithium batteries.

Introduction

In recent years much research to develop stable, safe, high energy density, light-weight, and shape-flexible lithium rechargeable batteries has been carried out in the field of all-solid-state batteries based on solid electrolytes [1]. To utilize a thin film battery, the electrolyte material must permit the repeated and rapid transfer of Li⁺ ions between the anode and cathode over the expected range of operating conditions (voltage, temperature, and current) as well as physical and electrochemical stability under contact with active materials.

Solid electrolytes for solid state thin film batteries are divided into inorganic and organic polymer electrolytes. Inorganic glass has been studied for a long time as a candidate for a solid state electrolyte material of a rechargeable thin film battery. 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 glass electrolytes to conventional bulk type batteries, hence, is impractical in spite of their merits and the research on this group of materials is diminishing recently [2].

As an alternative technique, to improve the shortcom-

ing of inorganic glass electrolytes hybrid electrolytes were developed in the form of organic-inorganic molecular hybridization and meso-scale hybridization by infiltration of a liquid electrolyte or gel electrolyte into a meso-porous membrane [3].

Phase separation is used in a well-known process for making special purpose porous and non-porous glasses. A homogeneous glass can be phase-separated to a glass former-rich phase and an alkali-rich phase, and the structure produced is a heterogeneous mixture of 3 dimensionally interconnected channels with different compositions [4]. Sodium borosilicate glasses are well known as materials in which an adequate heat treatment can induce phase separation by spinodal decomposition. Among glass systems, this glass system is believed to be the most suitable for a hybrid glass solid electrolyte due to its stable formability of a nano-porous interconnected structure with excellent mechanical strength, an inertness to moisture, and ease of fabrication.

Thermal treatment of alkali borosilicate glasses with a suitable composition in a temperature range between 550 and 700 °C initiates phase separation. Two different interconnected phases are obtained. The first one is an alkali borate-rich phase soluble in hot acids, water or alcohols and the second one is almost pure silica. Porous glasses consisting almost entirely of silica (96%) are obtained after the leaching procedure. The structural and textural properties of the porous glasses are determined by the initial glass composition, the conditions of heat treatment (temperature and time) and the leaching conditions (leachant type, leaching temper-

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ature, and leaching time) [5, 6].

In this interesting structure, hollow channels can be utilized as fast ion conducting routes while the solid skeleton maintains the solid external shape and mechanical strength. Also this inorganic skeleton reduces the flowing of the liquid electrolyte and supplements the low conductivity of the glass electrolyte.

In this paper, we report glass electrolyte membranes fabricated by the most suitable composition, heat treatment time, temperature and leaching conditions for lithium ion batteries. The electrochemical performance of these new materials will be discussed.

Experiment Procedure

Material preparation

A flow chart for the preparation of glass electrolyte membrane is shown Fig. 1. $x\text{Na}_2\text{O}-(1-x)(y\text{B}_2\text{O}_3-(1-y)\text{SiO}_2)$ glasses were prepared by a conventional melt and quenching technique. For the synthesis, the starting materials were well-dried powders of reagent grade Na_2CO_3 (99%), B_2O_3 (95%) and SiO_2 (99.8%), which were mixed in appropriate proportions to form 30 g batches. Each batch was melted at 1100°C for 5 h in Pt crucibles in an electrically-heated furnace and quenched in a stainless-steel mold.

A specimen was obtained in the state of a transparent and dense glass plate. Then, the prepared samples were cut and polished to discs with a diameter of 18 mm and a thickness of 0.5 mm to fit to a coin type cell. To form nano-sized channel by phase separation, the polished samples were heated to 600°C for 1 h and wet etched by an HF solution or H_2SO_4 solution at 25°C for 1 h. As a result of heat treatment, two phases, alkali-rich and glass former-rich phases, were formed in the glass and the color of these glasses became white due to the light scattering from these microstructures. After leaching, the glasses prepared were washed with distilled water at room temperature and dried thoroughly at 100°C for a long enough time. The alkali-rich phase formed during the thermal treatment was removed by leaching in acid. In consequence, inter-connected hollow channels were formed in the glass network [7].

Cell assembly

To fabricate full cells for electrochemical measurements of the porous glass electrolyte membrane, LiPF_6 liquid electrolyte was infiltrated into the etched glasses by dipping for two days in a glove box, and then these electrolytes were fabricated into 2032 coin type cells by the standard coin cell preparation technique where the prepared hybrid electrolytes were stacked up between a LiCoO_2 cathode and a MCMB (Mesocarbon Microbeads) anode.

Characterizations

The structures were characterized by XRD (Rigaku

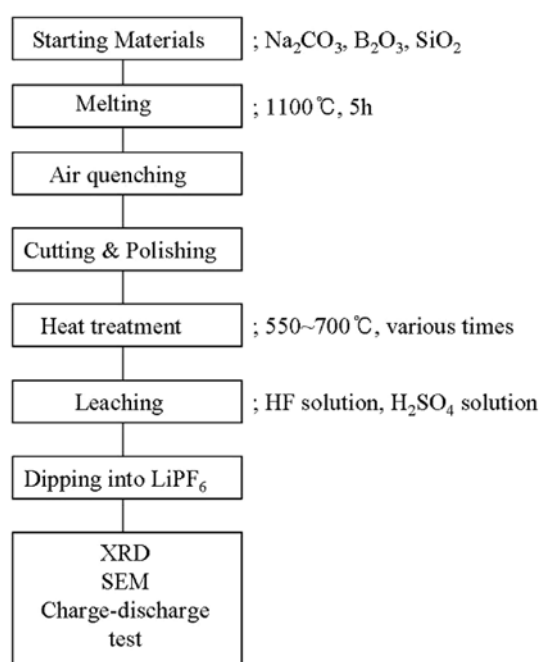


Fig. 1. Flow chart for the preparation and characterization of porous glass membranes.

M-2500 diffractometer) measurements using $\text{CuK}\alpha$ radiation with a graphite monochromator operating in the Bragg-Brentano (flat plate sample) geometry. XRD patterns of $x\text{Na}_2\text{O}-(1-x)(y\text{B}_2\text{O}_3-(1-y)\text{SiO}_2)$ glass after the heat treatment were obtained to confirm the amorphous state and phase separation.

To check the surface and cross sectional microstructure of the $x\text{Na}_2\text{O}-(1-x)(y\text{B}_2\text{O}_3-(1-y)\text{SiO}_2)$ glass membranes fabricated at various heat treatment temperature, time, and leaching conditions, a scanning electron microscope (SEM) was used.

The charge-discharge behavior of the cells was measured galvanostatically (current density = 0.5 mA/cm^2) in the 0.5-4.5 V range.

Results and Discussion

A glass system in a metastable state generates phase separation by appropriate heat treatment. Fig. 2 shows two types of phase separation mechanisms which are determined by the concentration of Na_2O and heat treatment temperature. The first one is spinodal decomposition which phase-separates the glass to 3 dimensionally inter-connected channels with two different compositions without nucleation. The second one is a nucleation and growth mechanism called binodal decomposition when the microstructure is composed of dispersed spherical glass particles in a matrix. To obtain inter-connected porous glasses for hybrid glass solid electrolytes, it is necessary to heat below T_c . In this study, glasses with the composition $7.5\text{Na}_2\text{O}-46.25\text{SiO}_2-46.25\text{B}_2\text{O}_3$ were heat-treated in the range of $550-700^\circ\text{C}$, as presented in Fig. 2.

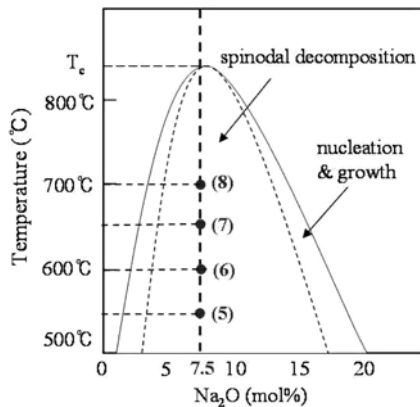


Fig. 2. The immiscibility dome of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system. The points denoted by filled dots are the compositions and temperatures of the specimens studied in this study.

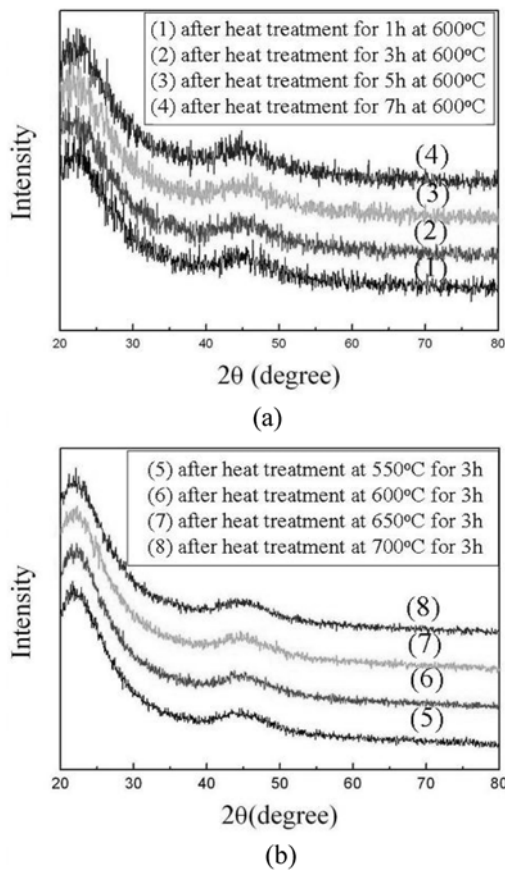


Fig. 3. XRD patterns of the $7.5\text{Na}_2\text{O}-46.25\text{B}_2\text{O}_3-46.25\text{SiO}_2$ glass prepared at various (a) heat treatment time and (b) heat treatment temperatures.

In principle, the microscopic features of a spinodally decomposed glass such as channel shape, size, and surface roughness are determined by the composition and heat treatment temperature. However, acid leaching is also another practical factor to consider for successful preparation. Therefore, the optimum conditions to achieve the desired channel size, channel connectivity, and surface smoothness have to be determined by test-

ing various specimens prepared with various conditions.

Glass specimens prepared at various heat treatment times and temperatures were all in a typical amorphous state and phase-separated as shown in the X-ray diffraction patterns of Fig. 3. By heat treatment in the range of 550–700 °C for 1–7 h, an additional small broad peaks was observed at $2\theta \sim 45^\circ$ and this peak is produced by the heterogeneous microstructure generated by the spinodal decomposition. Devitrification was not observed and stable porous glasses were obtained without cracks or crystallization [8].

The microstructures of phase-separated $7.5\text{Na}_2\text{O}-46.25\text{B}_2\text{O}_3-46.25\text{SiO}_2$ glasses after leaching are presented in Fig. 4. The glass membrane has nano-size pores and no micro-cracks were observed after the leaching treatment. Below 600 °C, the spinodal decomposition was not fully developed, while above this temperature the tendency of an oversized pore size was observed. As expected from the kinetics of spinodal decomposition, the control of the channel size was more efficiently done by the heat treatment temperature than time.

Another interesting phenomenon is the specific separation type (spinodal channel type or precipitate type) [9]. For example, in Fig. 4(b), the microstructure was formed by leaching out interconnected channels with the sodium-rich phases and the network former-rich matrix was retained. In the figure, the dark portions are the etched channels, while the remaining portion is the network former-rich skeleton survived after leaching. However, this microstructure was inverted into a sodium-rich matrix and a network former-rich channel in Fig. 4(d). For the purpose of a hybrid solid glass membrane, it is desirable to achieve a structure with a network former-rich skeleton, such as Fig. 4(b), because of its excellent mechanical strength. From a practical viewpoint, the channel size has to be determined for the convenience of the infiltration process. Too small a channel size, such as in Fig. 4(e), will prevent the complete infiltration of the liquid electrolyte into whole length of channels. Too small a channel size also will make it difficult to fabricate a completely interconnected channel since it is hard for the leachant to penetrate into the center of the specimen and the products of etching are hard to remove from the etching front. Too large a channel size, such as in Fig. 4(h), will weaken the mechanical strength of the membrane by increasing the probability of forming micro-cracks within the specimen. The variation of the average channel size of porous glass membranes by heat treatment time is presented in Fig. 4(B). The channel size was in the range of 90–240 nm and it increased with increasing heat treatment time. By a trial-and-error method, the optimized porous glass membrane was prepared at a heat treatment temperature of 600 °C and heat treatment time of 3 h, which is shown in Fig. 4(f). The channel size was 160 nm.

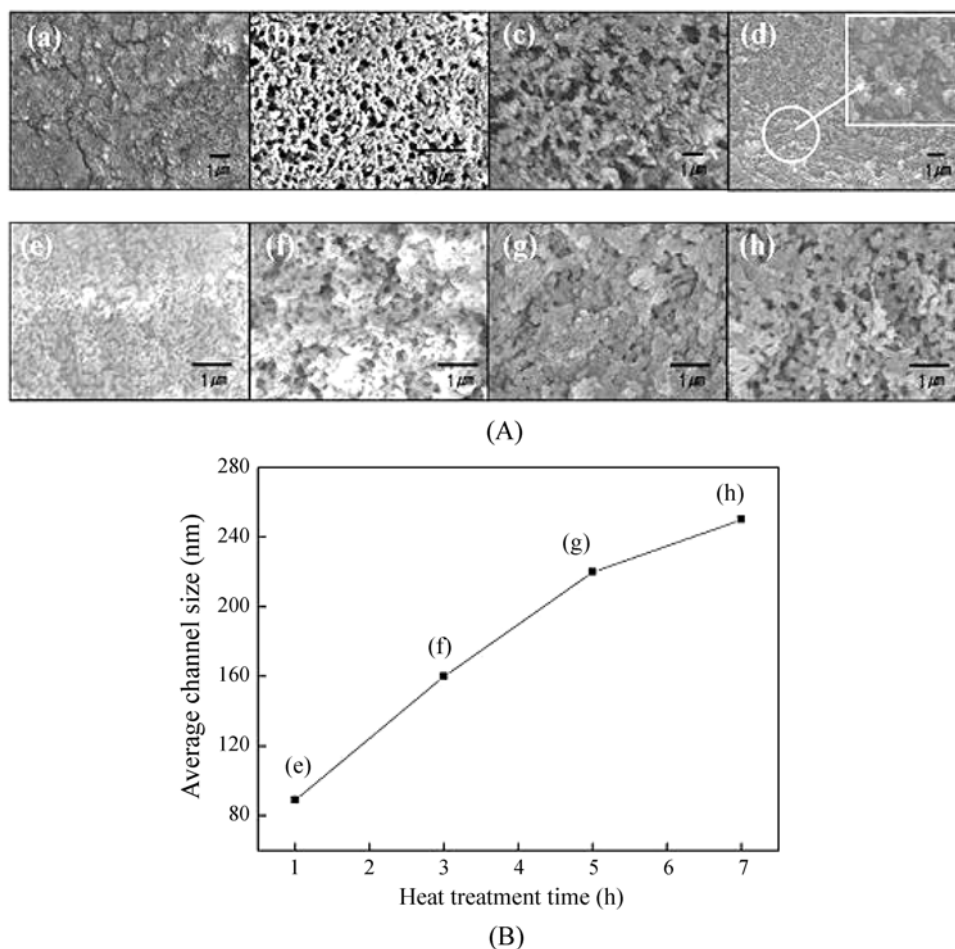


Fig. 4. (A) SEM photographs of phase separated $7.5\text{Na}_2\text{O}-46.25\text{B}_2\text{O}_3-46.25\text{SiO}_2$ glass heat-treated at (a) 550°C , (b) 600°C , (c) 650°C , and (d) 700°C for 3 h and heat-treated for (e) 1 h, (f) 3 h, (g) 5 h, and (h) 7 h at 600°C . The photographs were taken after acid leaching. (B) Variation of average channel size of porous glass membranes by heat treatment time.

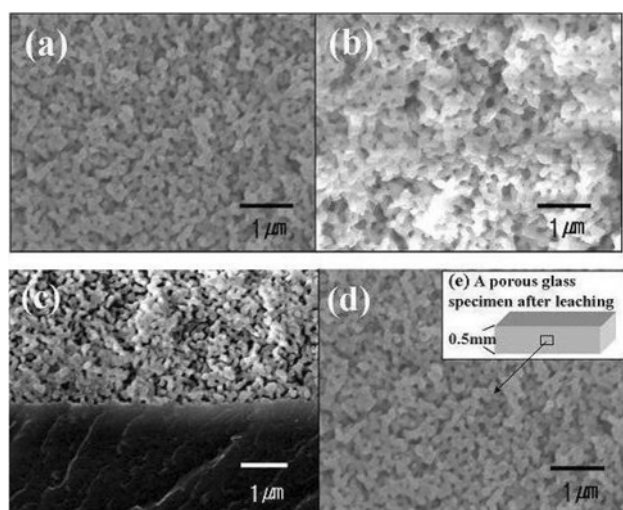


Fig. 5. SEM micrograph of cross section of porous glass membrane leached by (a) HF solution, (b) H_2SO_4 solution leachant at 25°C for 1 h and leached for (c) 30 minutes, (d) 1 h at 25°C by HF solution (e) Schematic representation of a section of a porous glass measured by SEM after leaching.

Figure 5(a) and (b) show cross section SEM micrograph of the center of porous glass membrane produced

by leaching using HF solution or H_2SO_4 solution. The mechanical strength of etched $7.5\text{Na}_2\text{O}-46.25\text{B}_2\text{O}_3-46.25\text{SiO}_2$ glass membranes was better for HF leachant than for H_2SO_4 . This is probably due to the better etching selectivity of HF to the alkali-rich phase and the resulting channels then have smoother etched surfaces.

Figure 5(c) and (d) show microstructures of the cross sections produced by changing the leaching time. To ensure the channels run through the specimen from the top to bottom, the interconnected sodium-rich channel has to be perfectly etched at the center of the specimen. Figure 5(c) shows the cross section of the center of a 0.5 mm thick specimen etched for 30 minutes. One can see that the center of the specimen was not completely etched and this would block the ionic drift. By considering the mechanical strength of the membrane, the optimum leaching condition for the fabrication of a porous glass membrane was determined to 25°C for 1 h.

For the electrochemical investigations, full cells prepared in the form of 2032 coin cells using LiCoO_2 as a cathode material and MCMB (Mesocarbon Microbeads) as an anode material were tested for their charge-

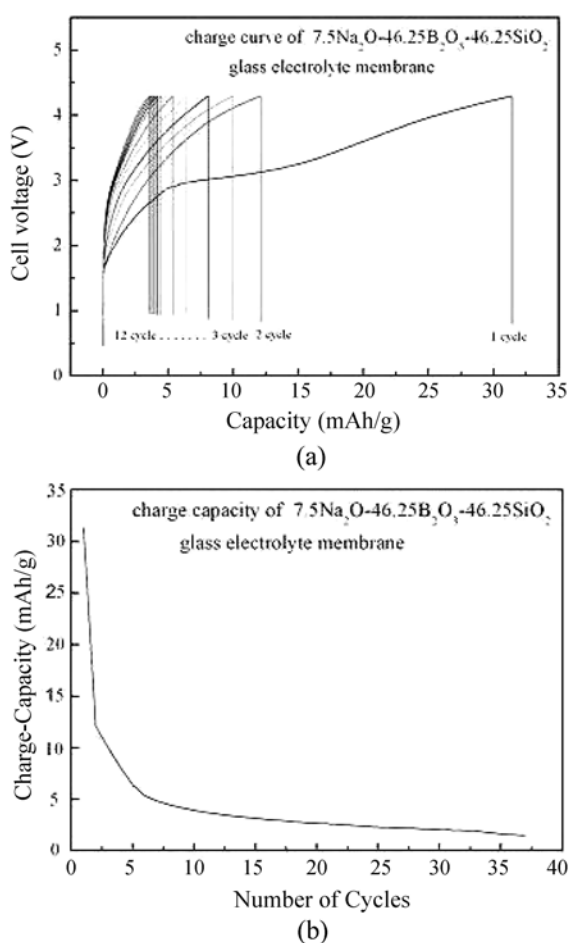


Fig. 6. (a) Charge-discharge curves of full-cells using porous glass electrolyte membranes. (b) cycling performance of full-cells using porous glass electrolyte membranes.

discharge behavior and the results are shown in Fig. 6. The charge curves showed the normal initial increase with a subsequent decrease in cell voltage and the total capacity did not reach the maximum which is normally 140 mAh/g. Also, a discharge curve did not appear. One reason of this incomplete charging and discharging curves might be that the glass electrolyte membrane has an unstable interface contact with the electrode materials causing interfacial polarization resistances in the hybrid solid electrolyte.

Another possible reason might be that the liquid electrolyte (LiPF_6) had not completely infiltrated into the porous glass membranes because of an imperfect dipping method. For successful charge-discharge, it is necessary to improve the interfacial contact with the electrode materials and the dipping method. Therefore, the authors are developing the technique to improve the contact and the dipping method.

Conclusions

Glass membrane was obtained by leaching phase-separated $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass produced by spinodal decomposition. XRD patterns of all glass specimens after heat treatment in the range 550-700 °C and for 1-7 h proved that the prepared glass membranes were in an amorphous state without devitrification. The control of the pore size was more efficiently achieved by heat treatment temperature than time. For preparation of a porous glass electrolyte membrane, the optimum heat treatment temperature and time seem to be 600 °C for 3 h. The mechanical strength of etched $7.5\text{Na}_2\text{O}-46.25\text{B}_2\text{O}_3-46.25\text{SiO}_2$ glass membranes was better for HF solution leachant than for H_2SO_4 . To improve ion mobility, the interconnected sodium-rich channels were perfectly etched and then LiPF_6 was infiltrated into these channels.

The hybrid solid electrolyte composed of this glass membrane and LiPF_6 was installed into a coin cell. Although charge-discharge curves indicated that the interfacial contact with the electrodes needed improvement, it has been shown that the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ hybrid electrolyte membrane might be applied as a hybrid electrolyte in lithium secondary batteries due to its stable glass forming ability and nano-scale channel structure.

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