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THE EFFECTS OF MOLTEN SALT AND ELECTRIC FIELD STRENGTH ON IONIC TRANSPORT IN GLASS UNDER THE FIELD-ASSISTED ION EXCHANGE

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The effects of the composition of molten salt and the electric field strength of the field-assisted ion-exchange treatment on the mixed-alkali glass were investigated. The commercial silicate glass of CRT glassware (Na_2O:K_2O=8:6 in mol%) was used as the sample, and the relation between the composition of $NaNO_3$+KNO_3 molten salt at the anode and the induced stress at the anode surface of the glass was examined. The same Na:K ratio in the salt as that in the glass was found not to induce the compression stress in the vicinity of the glass surface after the field-assisted treatment. Using this molten salt, the electric field strength applied to the glass was changed, and the apparent DC resistivity and the transport numbers in the glass were determined. The increasing field strength >300V/cm was found to increase the apparent resisitivity of the glass, and also reduced the transport number of K^+ in the glass.

(Key words: field-assisted ion exchange, molten salt, resistivity, transport number, electric field strength)

1. Introduction

Ion-exchange on glass has been investigated as a useful method to give optically or mechanically functional properties on glass substrate. For example, if the ions with a small electronic polarizability in the glass are replaced by the ions with a large polarizability, the refractive index of the glass surface increases and, for instance, an optical waveguide can be formed in glass substrate [1]. If the ions in the glass are exchanged for the ions with a larger ionic radius than the former one, the glass is chemically strengthened [2].

These above treatments are primarily carried out by the exchange between the monovalent cations, and there are two types of ion-exchange methods. One is the dipping method. The glass is dipped in a certain molten salt, and the monovalent cations in the glass and the molten salt are exchanged via the counter-diffusion process [2,3]. By this method, the glass surface contacting with the molten salt are exchanged uniformly, but it usually takes long time to make a deep ion-exchanged layer. A long treatment time in turn reduces the compression stress near the surface. The other is the electric field-assisted ion-exchange method. The electric field enforces the cations to move along the lines of electric force, and the cations are externally incorporated into the glass surface. The most advantageous point is that this method can attain the formation of the deep layer in much shorter period of time than the dipping method.

The cathode-lay tube of CRT glass is one of the examples of the glass products which are required to have the high mechanical strength. It have to not only maintain the vacuum inside against the atmospheric pressure, but also have high enough mechanical reliability for long term and against a certain abrasion. Such glasses usually contain more than 2 kinds of alkali ions (mixed alkali glasses) to have large electrical resistivity [5]. However, when such glasses are subjected to the field assisted ion-exchange treatment, we do not know enough knowledge on the ionic conduction mechanism in mixed alkali glasses; which ion becomes a major conducting carrier (transport numbers), how the field strength affects them and which models proposed previously [5,6,7] can be applies to the phenomena.

In this study, the field-assisted ion-exchange treatments were conducted on the commercial funnel glass (Na and K are mixed). The dependences of the composition of the molten salts of the anode and the electric field strength on the formation of the ion-exchanged layer and the transport numbers in glass were investigated.

2. Experimental

Figure 1 shows the schematic illustration of the apparatus for the field-assisted ion exchange on the glass samples. The examined glass was the commercial funnel glass with the composition of $65SiO_2$-$7.8PbO$-$3.5Al_2O_3$-$5.2CaO$-$3.4MgO$-$8.1Na_2O$-$6.2K_2O$-$0.8MO_x$ (in mol%). The glass plates with the dimension of 50 x 50 x t (t=3, 5, 6, 10) in mm were placed on the alumina tube with O.D.=28mm, and sandwiched and pressed by an another alumina tube with the same dimension. The anode salts of $NaNO_3$ + KNO_3 mixture with the composition of Na/K=0/1, 1/4, 2/5, 4/3 and 1/0, were placed inside the upper alumina tube. The cathode salt was $CsNO_3$ mixed with the Al_2O_3 paste (the mixture of $CsNO_3$, Al_2O_3 and propylene glycol). It was placed on a stainless plate (cathode electrode) and pressed onto the bottom surface of the glass inside the alumina tube. The glass samples were heated up to 450°C (=the strain point T_s of this glass) in the electric furnace, and held at this temperature in the accuracy of ±2°C. The anode electrode, Pt wire, was immersed in the anode molten salt and DC voltage of 300V and 500V was applied between the electrodes and the current conducting the circuit was monitored by the current meter, and the total charges were counted by the Coulomb meter. When the total charge reached 96C or 200C, the circuit and the electric furnace were simultaneously switched off and the glass samples were cooled to the room temperature. The cathode Al_2O_3 pastes were collected after the treatments and the included cationic elements were analyzed using the induction coupled plasma (ICP) spectroscopy. The stress induced in the vicinity of the anode glass surface was measured by the Berek method. Table 1 shows the conditions of the field-assisted ion exchange examined in this study.

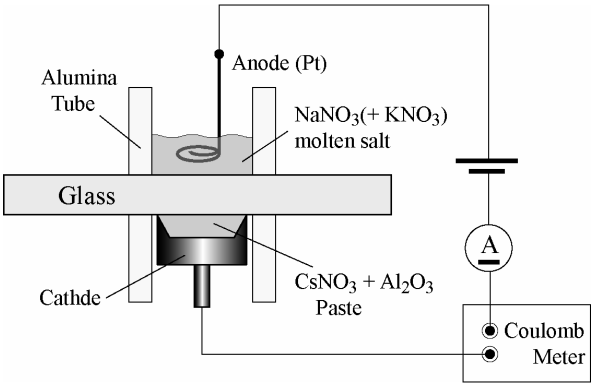

Fig.1 Schematic illustration of the field-assisted ion-exchange treatment.

Table 1. The conditions of the field-assisted ion-exchange treatments.

No.	1	2	3	4	5	6	7	8	9
Sample thickness t (mm)	10	10	10	10	10	10	5	3	3
Anode salt $NaNO_3/KNO_3$	0/1	1/4	2/5	4/3	1/0	4/3	4/3	4/3	4/3
DC voltage (V)	300	300	300	300	300	300	300	300	500
Electric field strength (V/cm)	300	300	300	300	300	300	600	1000	1667
Total charge (C)	96	96	96	96	96	200	200	200	200

3. Results

The compressive stress and the transport number using the molten salts with various Na:K ratio

The molar fractions of the alkali ions in the cathode salts were obtained by ICP analysis. No other cation of the glass components than alkali ions, Na and K, was detected. This means that the alkali ions were electrically extracted from the glass, not by the corrosion of the glass surface by $CsNO_3$ melt. Figure 1 shows the plots of these values as the transport numbers of g_{Na} and g_K in the glass samples under the electric field, and the compressive stresses of the anode surface measured by Berek method are also plotted in the upper graph. The transport numbers of g_{Na} and g_K of the glass are almost constant independent of the anode salt composition. g_{Na}'s are around 0.8 much larger than the fraction of Na^+ ions in the glass sample ($(Na/(Na+K))_{glass}=0.57$).

On the other hand, the compressive stress of the anode glass surface is strongly dependent on the composition of the anode salt. The compressive stress of the glass sample No. 4 was the smallest (nearly zero) when the anode salt with the same Na/K ratio as in the glass. In the case of the sample No. 5, on which the ion exchange using the anode salt with the fraction of Na/(Na+K)=1.0 was made, many clacks were observed on the anode glass surface due to the tensile stress.

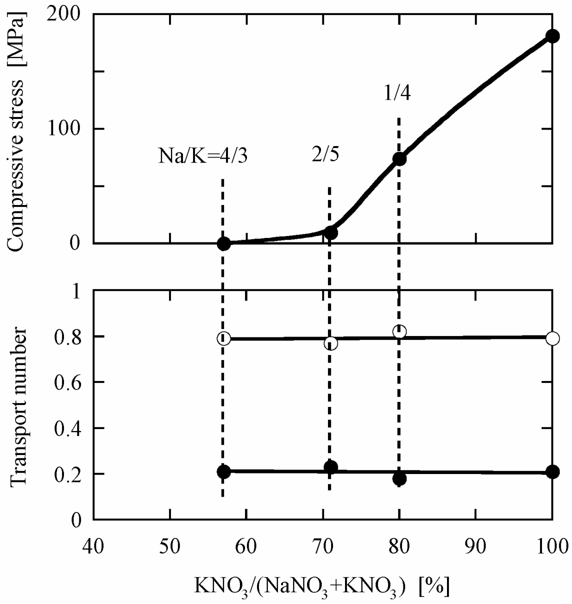

Fig. 2 Transport numbers of Na^+ and K^+ ions and the compression stresses induced in the glass surface at the anode side are plotted as a function of the composition of the anode salt.

Dependences of the ion conduction on electric field intensity

Figure 3 shows the examples of the observed current changes conducting the glass samples under the field-assisted ion exchange at 300V. The annotated numbers in the figure show the thickness *t* of the glass samples. When the glass thickness *t* becomes one third (10? 3mm), the currents through the glass didn't show tripled value. This suggests that Ohm's law would not be held in these experiments. Figure 4 shows the plots of the transport numbers g_{Na} and g_K against the sample thickness *t*. It is clearly seen that g_{Na} increases with decreasing *t*. The increasing electric field strength suppresses the transport of K^+ ions in glass.

Figure 5 shows the calculated volume resisitivity ρ of the glass samples at T_s under various electric field strengths. The increase of the electric field strength gradually increases the calculated resistivity of the glass. Compared with the resistivity obtained by the impedance measurement (shown by the broken line), the electric field more than 300V/cm increases the resistivity of the glass apparently.

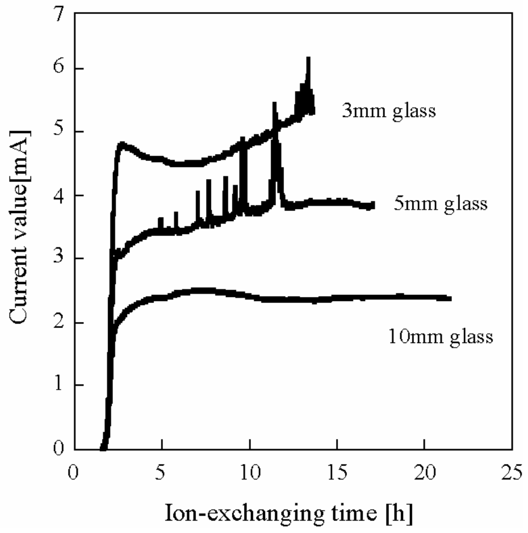

Fig.3 The observed current conducting the circuit during the field-assisted ion-exchange treatment of 200C.

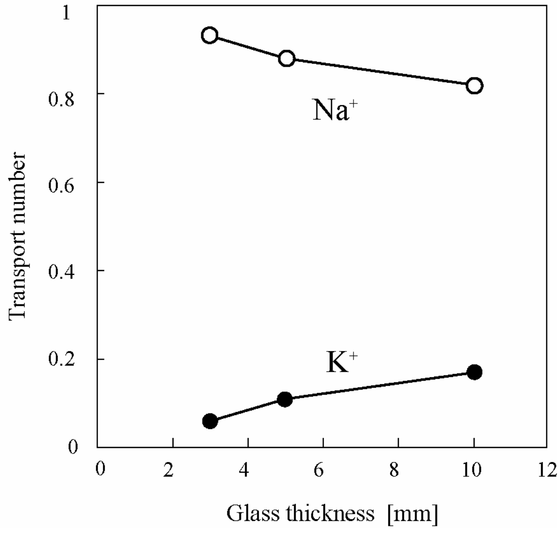

Fig.4 Transport numbers of Na^+ and K^+ ions of the glass samples with different thickness. The applied DC voltage was 300V.

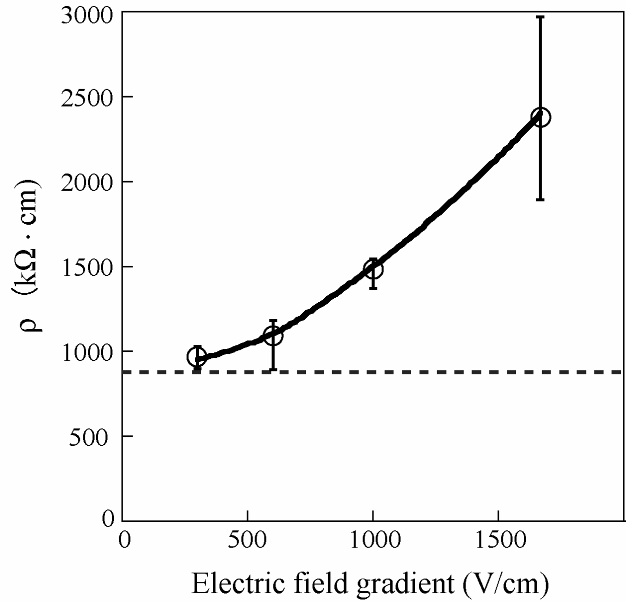

Fig.5 Plots of the apparent volume resistivity calculated using the current and the applied voltage as a function of the applied electric field strength. The broken line represents the DC resistivity obtained by 2-electrode impedance measurement.

4. Discussion

Dependences of transport number and compressive stress on the compositions of molten salts

The compressive stress induced in the anode glass surface was strongly dependent on the composition of the anode salt. The increase of Na^+ fraction in the salt drastically decreased the compressive stress of the glass. Na:K fraction of the salt by which the compressive stress became zero corresponded well with that of the mother glass. On the other hand, the transport numbers obtained from the extracted Na^+ and K^+ from the cathode surface did not coincide with Na:K fraction of the mother glass. Na^+ ions are transported as major charge carriers in this glass at 300V/cm and extracted largely than K^+ ions. Their independence of the composition of the anode salt can be reasonably understood because the salt would affect only the vicinity of the anode glass surface, but not the ionic conduction over whole of the glass. Larger extraction of Na$^+$ than K$^+$ at the cathode means larger migration of Na$^+$ than K$^+$ from the anode salt. The drastic reduction of the compressive stress with the addition of $NaNO_3$ into the anode salt can be explained from the aspect of the transport numbers. However, as seen in the sample 5, 100% Na$^+$ in anode salt might promote the replacement K$^+$ with Na$^+$ (because g_{K}?0) and induce clacks due to the tensile stress. Therefore, the choice of the composition of the anode salt is important to control the induced compressive stress for chemical tempering of the mixed alkali glasses. The electric field strength, in addition, should be taken into account, because the transport numbers are also affected by the field strength as shown in Fig. 4.

Dependences of the ionic conduction on electric field strength

The most interesting results in this work are the dependences of the transport number and the apparent volume resisitivity on the electric field strength. The field assistance for the migration of the alkali ions into the glass surface is one of the advantageous points of the field-assisted ion-exchange method to carry out, for instance, the chemical tempering in a short period of time. The increase of the electric field is usually one of the parameters to accelerate the speed of the ion-migration. However, the increasing apparent volume resisitivity with the field strength shows that it is not so simple. As shown in Fig. 4, the increase of the field strength decreases the transport number g_{K} and the total carrier concentration is considered to decrease; only Na$^+$ ions can move. This would qualitatively explain the increase of the apparent resistivity of the glass. Kuroki *et al.*[8] reported the EPMA (electron probe microscope analysis) results of the ion-exchanged layers of the same glass samples in this study. One of the most typical features of the ion-exchanged layer by the field-assisted ion-exchange method is the step function-type concentration profiles. The frontier region of the ion exchange has a sharp interface with the thickness of the order of micrometer size, and the concentrations of the alkali ions are drastically changed in the progress of the ion exchange. In this work, we employed the anode salt which does not form the ion-exchanged layer at 300V/cm, and there is not such interface apparently. This means that the transports of Na$^+$? Na$^+$ and K$^+$? K$^+$ should proceed in the ratio given by the transport number g_{Na} and g_{K}. However, the large field strength decreases g_{K}, and K$^+$? Na$^+$ would be necessarily caused. This is a quite important point to use the filed-assisted ion-exchange treatment on the mixed alkali glasses. The electric filed strength is usually not uniform in the glass subjected to the treatment, and the ‘local’ transport numbers depend on the field strength there. When we consider the chemical tempering process using KNO_3 on Na$^+$/K$^+$ mixed silicate glasses [8,9], the progress of the ion-exchange layer depends on the electric filed strength. In the glass under the large field strength, K$^+$? K$^+$ process would be suppressed, and K$^+$? Na$^+$ would proceed. As a result, the depth of the ion-exchanged layer would be thicker than the part of the glass under smaller field strength. As seen in the results by Yano *et al.* [9], the transport properties are important to design the ion-exchanged layer in the glasses, and the electric field strength should be one of the factors of the ion-exchange treatment taken into consideration.

5. References

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