

# Sulfur Redox Equilibrium in Mixed Alkali Silicate Glass Melts

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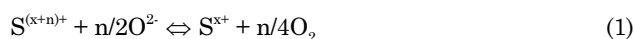
## ABSTRACT

The dependence of sulfur redox behavior and its diffusivity on temperature and composition was studied in mixed alkali silicate melts by means of square wave voltammetry (SWV) at different frequencies in a temperature range of 1000°C to 1400°C. The voltammograms showed two reduction peaks at high frequency but only one peak at low frequency. Irrespective of K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O), each peak potential due to reduction of S<sup>6+</sup> to S<sup>4+</sup> and S<sup>4+</sup> to S<sup>0</sup> moved toward a negative direction with temperature decrease, and the peak current showed a strong dependence on frequency at a constant temperature. However, the compositional dependence of the peak potential showed an inconsistent behavior with an increase of K<sub>2</sub>O. The mixed alkali effect was not observed in sulfur diffusion. This inconsistency of both peak potential and diffusion for compositional dependence may be derived from the strong volatilization of sulfur in melts.

**Key words :** Sulfur, Redox equilibrium, Diffusion, Voltammogram

## 1. Introduction

Sulfate (SO<sub>4</sub><sup>2-</sup>) is introduced into glass melts as a fining agent or amber colorant with iron in alkali lime silicate glass systems. The effectiveness of sulfur in glass melts depends on its valence states, S<sup>6+</sup>, S<sup>4+</sup>, S<sup>0</sup> and S<sup>2-</sup> in a reducing or oxidizing atmosphere. In glass melts, the following redox reaction for multivalent elements such as sulfur can be expected:



where n is the number of electrons transferred from one valence state of S to another.

In the last two decades, voltammetric methods proved to enable the determination of thermodynamic properties and diffusion coefficients of multivalent elements in glass melts. A few studies on sulfur doped melts have been carried out by voltammetry.<sup>1-6)</sup> However, the interpretation of the resulting voltammograms, especially the identification of peaks due to a sulfur redox reaction was controversial. Recently there was a new suggestion using the diffusivity comparison of two sulfur ions for peak identification in a voltammogram.<sup>7)</sup> There have been no investigations on the compositional dependence of sulfur redox equilibrium. Considering that the substrate glass for plasma display panels (PDP) consists of mixed alkali oxides and the sulfur fining is very important in those display glasses, it is very interesting to investigate the influence of the alkali oxide on the sul-

fur redox.

In this study, alkali-alkaline earth-silica PDP model glass melts doped with sulfate were prepared in an air atmosphere and the compositional dependence of the sulfur redox equilibrium was examined.

## 2. Experimental

The blank melts with the composition in mol% 69.1SiO<sub>2</sub>0.4Al<sub>2</sub>O<sub>3</sub> 9(Na<sub>2</sub>O+K<sub>2</sub>O)6.5MgO6.5CaO5.3SrO1.1BaO-2.1ZrO<sub>2</sub> in which K<sub>2</sub>O/(Na<sub>2</sub>O+ K<sub>2</sub>O) was varied from 0.25 to 0.75 and the same melts doped with 0.3 mol% SO<sub>3</sub> supplied from Na<sub>2</sub>SO<sub>4</sub> were prepared. The glass batches of about 300 g were melted at 1550°C in an electric furnace. High purity raw materials were used to exclude the effect of another multivalent impurity. The bubble free melts homogenized by stirring with a Pt/Rh rod were transferred to another electric furnace to perform the measurement of SWV.

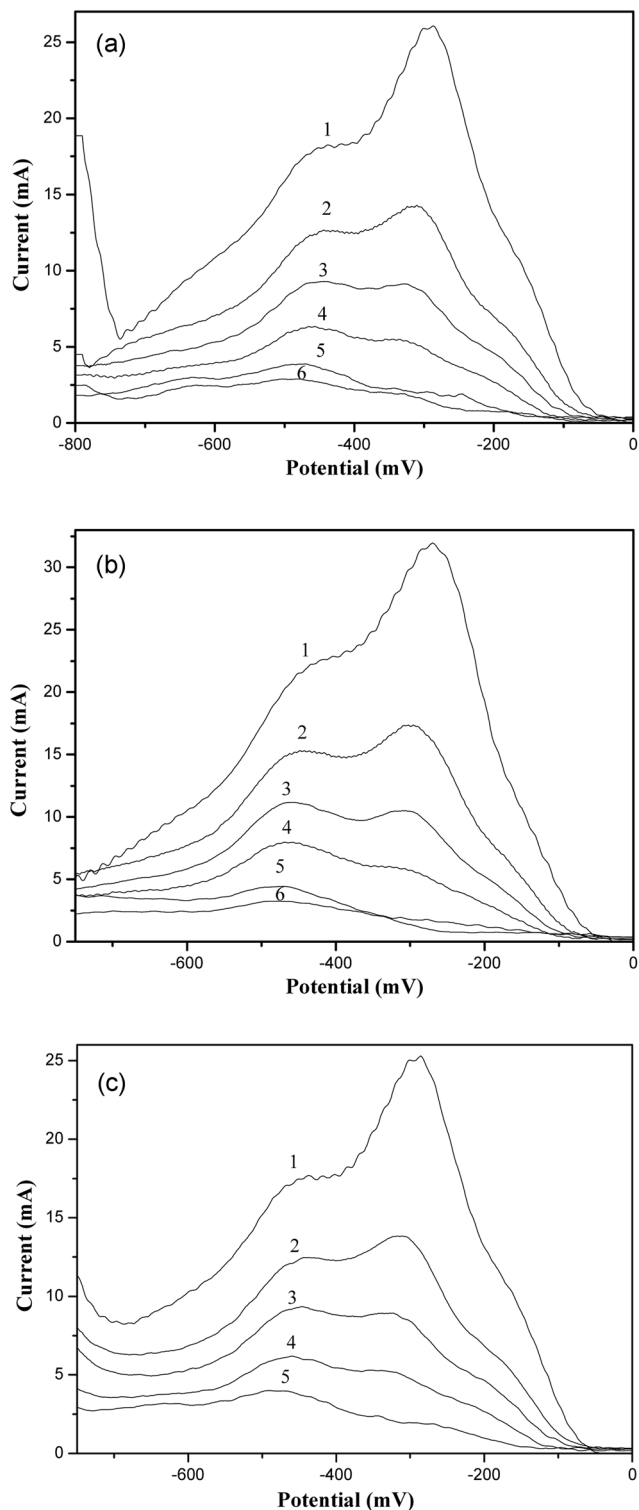
For the SWV measurement, while the prepared melts were maintained at 1400°C in the furnace, the electrodes of an electrochemical cell were dipped into the melts. The electrochemical cell for the SWV measurement consisted of three electrodes immersed into the melt in a Pt/Rh crucible and a potentiostat (Model 273A, EG&G, USA) connected to a computer. A platinum plate with 10×20 mm and a platinum wire with a diameter of 1 mm were used as a counter electrode and a working electrode, respectively. Another platinum wire called the reference electrode was connected with an O<sup>2-</sup> conducting Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) material which was contacted with melts and flushed by reference air with the known oxygen partial pressure (P<sub>r,O<sub>2</sub></sub>: 0.21 bar)

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during the SWV experiment. Both the experimental equipment and the procedure were described in detail in reference.<sup>8)</sup> During the SWV measurement at a given temperature



**Fig. 1.** Voltammograms of melts doped with 0.3 mol%  $\text{SO}_3$  at  $1300^\circ\text{C}$ , 1: 500, 2: 200, 3: 100, 4: 50, 5: 20, 6: 10 Hz: (a)  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.25$ , (b)  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.5$ , and (c)  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.75$ .

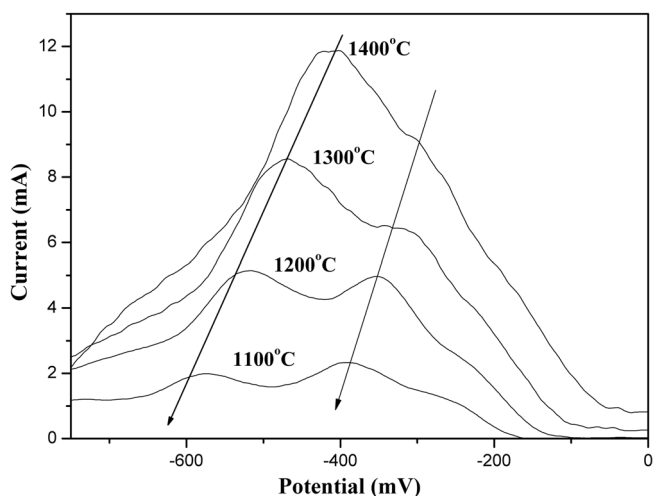
the furnace was switched off to avoid disturbance of the measured signal by the current of the heating elements. The SWV measurements in the present work were performed under following conditions: the range of the applied potential and frequency, 0 to  $-800$  mV and 5 to 1000 Hz. The final voltammogram of each melt at a temperature ranging from  $1400^\circ\text{C}$  to  $1000^\circ\text{C}$  was obtained by subtracting the voltammogram of the blank melt from the original recorded voltammogram.

### 3. Results and Discussion

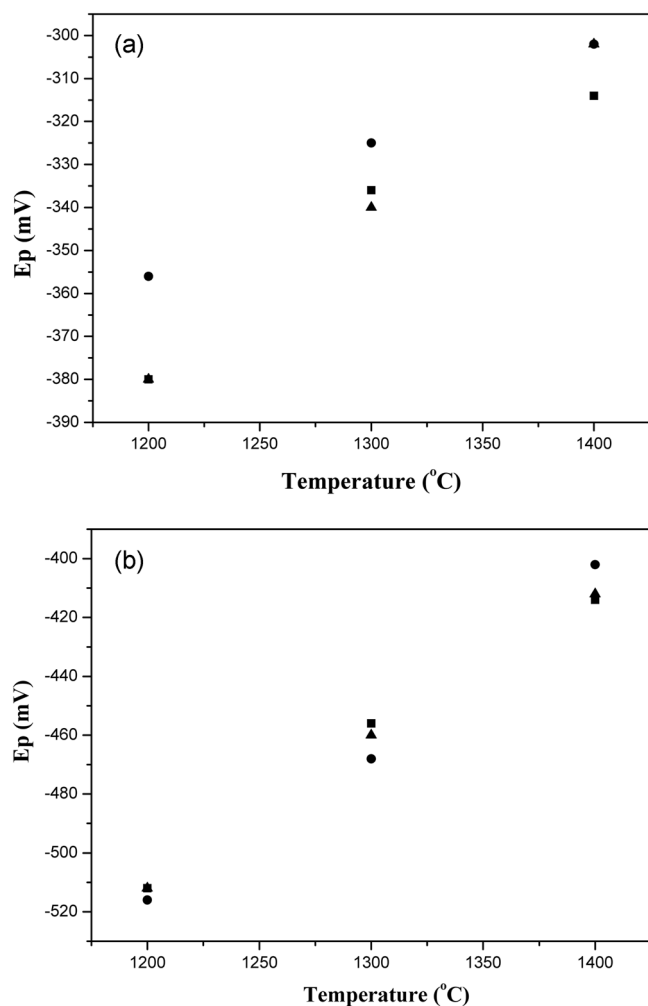
#### 3.1. Voltammograms

Fig. 1 shows the recorded voltammograms of the melts with  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.25, 0.5$  and  $0.75$  at different frequencies at  $1300^\circ\text{C}$ . The peak currents ( $I_p$ ) strongly depended on the frequency irrespective of the  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$  value. At a low frequency, only one reduction peak at about  $-480$  mV (first peak) was observed. However, with an increase of the frequency, another peak at around  $-310$  mV (second peak) occurred. According to recent study<sup>7)</sup> in which sulfur redox in sulfate and sulfide doped silicate melts was investigated by SWV the first peak was due to the reduction of  $\text{S}^{4+}$  to  $\text{S}^0$  (expressed as  $\text{S}^{4+}/\text{S}^0$ ) and the second peak was attributed to the reduction of  $\text{S}^{6+}$  to  $\text{S}^{4+}$  (expressed as  $\text{S}^{6+}/\text{S}^{4+}$ ).

In Fig. 2 the voltammograms of the melt with  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.5$  at 50 Hz are presented in a temperature range of  $1100^\circ\text{C}$  to  $1400^\circ\text{C}$ . Fig. 2 shows that the peak potentials ( $E_p$ ) were shifted to more negative values with a temperature decrease as marked by an arrow and the second peak was weakened at a high temperature. The other two melts with  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.25$  and  $0.75$  showed the same behavior. In particular, the temperature dependence of  $E_p$  means that with a temperature decrease the equilibrium state of reaction (1) shifts to the left, namely to an oxidation state. The temperature dependence based on the  $E_p$ -value shown in Fig. 2 is presented in Fig. 3. The plot of  $E_p$



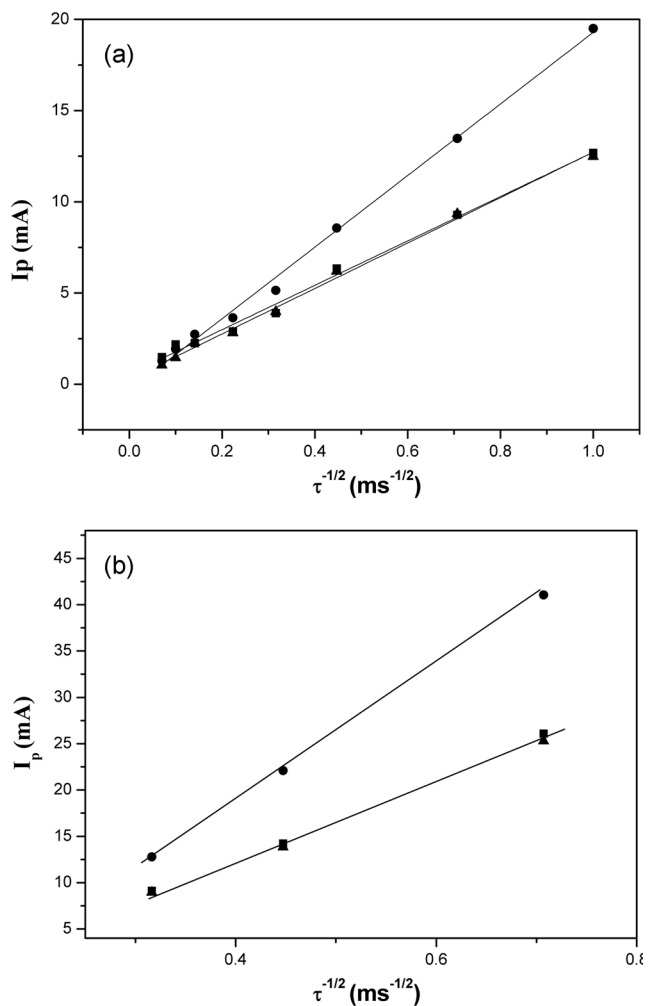
**Fig. 2.** Voltammograms of  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.5$  melt doped with 0.3 mol%  $\text{SO}_3$  at 50 Hz.



**Fig. 3.** Experimental plot of the peak potential ( $E_p$ ) at 50 Hz for (a)  $S^{6+}/S^{4+}$  and (b)  $S^{4+}/S^0$  as a function of temperature:  $K_2O/(Na_2O+K_2O)=0.25$ (■), 0.5(●), and 0.75(▲).

versus T showed a linear relationship by which the calculation of the standard enthalpy ( $\Delta H^0$ ) and the standard entropy ( $\Delta S^0$ ) for the reaction (1) was possible. In relation to the compositional dependence, with an increase of  $K_2O/(Na_2O+K_2O)$  the  $E_p$ -values of both redox pairs at a constant temperature showed no consistency. This tendency is presented in detail in Fig. 6 in which the  $E_p$ -values at different temperature are presented as a function of  $K_2O/(Na_2O+K_2O)$ .

According to the relationship between  $I_p$  and  $\tau^{-1/2}$  ( $\tau=1/f$ ,  $\tau$ : pulse time,  $f$ : frequency), linearity is expected in a diffusion-controlled reaction and thus the diffusion coefficient ( $D$ ) can be calculated from the slope. On the basis of the results shown in Fig.1 the  $I_p$  of the three melts at 1300 $^{\circ}$ C is plotted as a function of  $\tau^{-1/2}$  in Fig. 4. Table 1 contains the diffusion coefficients ( $D$ ) at three different temperatures for reduction of  $S^{6+}/S^{4+}$  and  $S^{4+}/S^0$  in the melt.  $D$  is plotted as a function of temperature in Fig. 5. Although the present values of Table 1 belong to a range similar to the data of the recent investigated sulfur diffusion coefficients in silicate melts<sup>9</sup> the tem-



**Fig. 4.** Peak current ( $I_p$ ) for (a)  $S^{6+}/S^{4+}$  and (b)  $S^{4+}/S^0$  as a function of  $\tau^{-1/2}$  at 1300 $^{\circ}$ C for the melts with  $K_2O/(Na_2O+K_2O)= 0.25$ (■), 0.5(●), and 0.75(▲).

**Table 1.** Diffusion Coefficients ( $D$ ) at Different Temperature for Reduction of  $S^{6+}/S^{4+}$  and  $S^{4+}/S^0$  in Melts with  $K_2O/(Na_2O+K_2O)=0.25, 0.5$  and  $0.75$

Temperature (K)	Redox pair	$K_2O/(K_2O+Na_2O)$		
		0.25	0.5	0.75
1673	$S^{6+}/S^{4+}$	$1.03558 \times 10^{-8}$	$9.63602 \times 10^{-9}$	$1.06641 \times 10^{-8}$
	$S^{4+}/S^0$	$6.524 \times 10^{-10}$	$6.323 \times 10^{-10}$	$5.889 \times 10^{-10}$
1573	$S^{6+}/S^{4+}$	$2.02689 \times 10^{-8}$	$2.42774 \times 10^{-8}$	$1.85535 \times 10^{-8}$
	$S^{4+}/S^0$	$4.165 \times 10^{-10}$	$6.541 \times 10^{-10}$	$4.213 \times 10^{-10}$
1473	$S^{6+}/S^{4+}$	$7.71571 \times 10^{-9}$	$7.50252 \times 10^{-9}$	$4.59257 \times 10^{-9}$
	$S^{4+}/S^0$	$7.526 \times 10^{-11}$	$1.339 \times 10^{-10}$	$6.357 \times 10^{-11}$

perature dependence of  $D$  for both  $S^{6+}$  and  $S^{4+}$  does not follow Arrhenius behavior but shows a great deviation from the linearity. Unlike other multivalent ions, sulfur could be volatilized strongly.<sup>6,10</sup> The change in total sulfur concentration due to such a strong volatilization may be a reason for the above non Arrhenius behavior of Fig. 5.

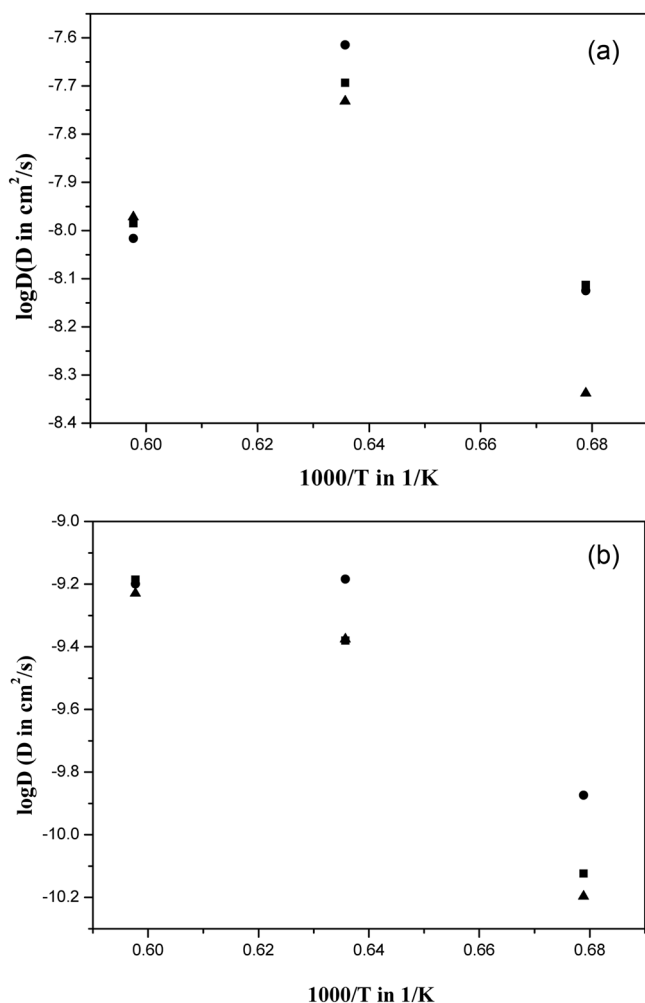


Fig. 5. Temperature dependence of the diffusion coefficient ( $D$ ) of (a)  $S^{6+}$  and (b)  $S^{4+}$  for the melts with  $K_2O/(Na_2O+K_2O)=0.25$  (■), 0.5 (●), and 0.75 (▲).

### 3.2. Compositional dependence

Since the present PDP model glasses with 9 mol% total alkali concentration consist of  $Na_2O$  and  $K_2O$  they belong to typical mixed alkali glasses. The mixed alkali glasses exhibit interesting characteristics, in particular a nonlinear dependence of their properties on the relative concentration of two network-modifying alkali oxides. The properties of an alkali oxide glass, which depend upon the mobility of alkali ions such as electrical resistivity, show a strong maximum at an intermediate mixed-alkali composition when one alkali is replaced by another. This behavior is known as the mixed alkali effect and many relevant experimental data were reviewed in three outstanding papers.<sup>11-13</sup> According to the review papers, the magnitude of the effect increases with an increase of the radius difference (or difference of the ionic field strength) of the alkali ion pair and depends on the temperature, and no mixed alkali effect occurs at a low alkali concentration of less than 10 mol%. Although several theories and models have been developed for the theoretical

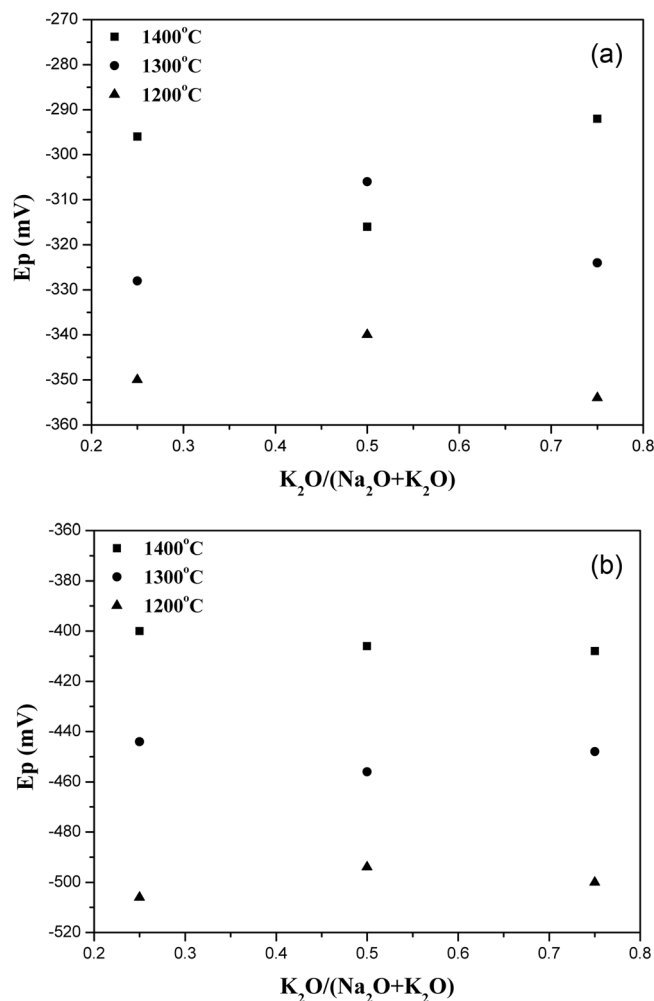


Fig. 6. Dependence of peak potential ( $E_p$ ) at 100 Hz for (a)  $S^{6+}/S^{4+}$  and (b)  $S^{4+}/S^0$  at different temperature on  $K_2O/(Na_2O+K_2O)$ .

approach, none of the existing theories has received universal acceptance.

In Fig. 6  $E_p$ -values at different temperatures are presented as a function of  $K_2O/(Na_2O+K_2O)$ . The compositional dependence of  $E_p$ -values showed no consistent behavior.  $E_p$ -values for both redox pairs at 1200°C showed maxima but an opposite behavior between  $S^{6+}/S^{4+}$  and  $S^{4+}/S^0$  occurred at 1300°C. In principle, the extreme value is not inevitable in the compositional dependence of  $E_p$  because the mixed alkali effect is limited in kinetic properties. As mentioned above,  $E_p$  is an indicator of a redox reaction: the shift of  $E_p$  to the positive value means that the reduction is dominant. However, Fig. 6 shows that at a constant sulfur concentration the equilibrium of the redox reaction (1) proceeds to the right or the left hand side with an increase of  $K_2O$  content depending on temperature. Since this behavior does not agree with that of Duffy<sup>14</sup> based on basicity which increases with an increase of  $K_2O$  content in alkali silicate glasses, such a compositional dependence of  $E_p$  in the present study

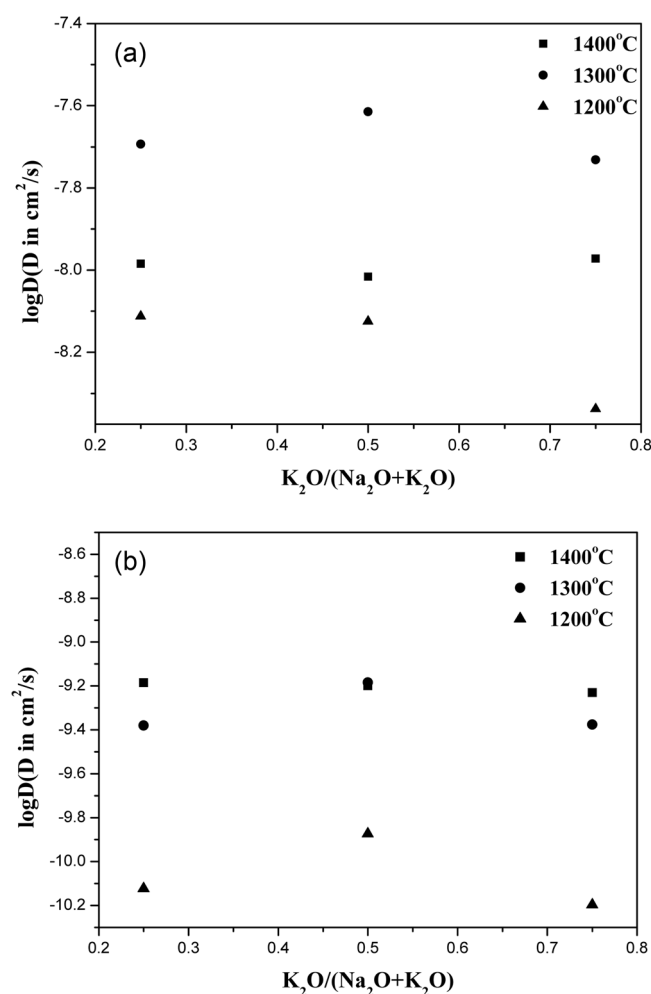


Fig. 7. Dependence of diffusion coefficient (D) of (a) S<sup>6+</sup> and (b) S<sup>4+</sup> at different temperature on K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O).

cannot be explained by the glass basicity. Finally, this inconsistent behavior implies again that it is due to the volatilization of sulfur in melts as indicated in the previous discussion. A similar inconsistent behavior was also observed in the compositional dependence of the diffusion coefficient as shown in Fig. 7. The diffusion coefficient D is a property that depends on ion mobility and thus the occurrence of the mixed alkali effect (minima in D) was expected in the present melts. However, most of the results in Fig. 7 show maxima rather than minima. A recent study in which the compositional dependence of Fe<sup>3+</sup>/Fe<sup>2+</sup> was investigated showed a linear increase of  $E_p$  and minima in diffusion against K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O).<sup>15</sup> Under the assumption that the sulfur volatilization did not occur in the present melts, a linear increase of  $E_p$  for S<sup>(x+n)+</sup>/S<sup>x+</sup> could also be expected. If this assumption for  $E_p$  could be applied to the compositional dependence of S<sup>6+</sup>/S<sup>4+</sup>, [S<sup>6+</sup>O<sub>4</sub>]<sup>2-</sup>-2Na<sup>+</sup> and [S<sup>4+</sup>O<sub>3</sub>]<sup>2-</sup>-2K<sup>+</sup> would be dominant respectively at each end member, in other words, K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)=0 and 1, and in the mixed alkali range the two types would be mixed.

## 4. Summary

Redox behavior and diffusivity of sulfur was studied in mixed alkali silicate melts with K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)=0.25, 0.5 and 0.75 by means of square wave voltammetry (SWV). According to the voltammograms, in all the melts two reduction peaks due to S<sup>6+</sup>/S<sup>4+</sup> and S<sup>4+</sup>/S<sup>0</sup> were observed and each peak potential moved toward a negative direction, namely an oxidation state with a temperature decrease and the peak current showed a strong dependence on frequency at a constant temperature. In relation to the compositional dependence, the shift of the peak potential and the diffusion coefficient was inconsistent with an increase of K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O), and its probable cause was regarded as sulfur volatilization. Under the assumption that volatilization was absent, sulfur coordination and bonding with alkali ion was suggested.

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