

# Electrochemical Approach in Plasma Display Panel Glass Melts doped with Sulfate and Sulfide II. Square Wave Voltammetry

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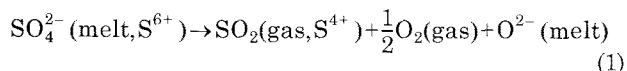
## ABSTRACT

Redox behavior was observed in alkali alkaline earth silicate PDP (Plasma Display Panel) glass melts doped with sulfate and sulfide by square wave voltammetry (SWV). According to voltammograms produced at a temperature range of 1100 to 1400°C and frequency range of 5 to 1000 Hz, both melts showed the same behavior in which there is one reduction peak at low frequency but another peak at an increase of frequency. Based on the frequency dependence of the peak current, self diffusivity of S<sup>4+</sup> was determined. Based on the temperature dependence of the peak potential, standard enthalpy ( $\Delta H^0$ ) and standard entropy ( $\Delta S^0$ ) for the reduction of S<sup>4+</sup> to S<sup>0</sup> were calculated.

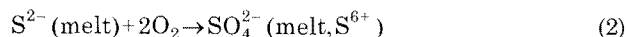
**Key words :** Sulfate, Sulfide, Voltammogram, Redox reaction, Diffusivity

## 1. Introduction

In the manufacture of display glasses by batch melting, fining is one of the most important processes because they permit almost no bubble inducing optical defects. In general, fining in the manufacture of plasma display panel (PDP) glass is completed chemically by redox reaction of sulfate ions (SO<sub>4</sub><sup>2-</sup>) supplied by Na<sub>2</sub>SO<sub>4</sub> under oxidation atmosphere. During the fining process these ions theoretically undergo the following reduction of S<sup>6+</sup> to S<sup>4+</sup> by generation of SO<sub>2</sub> and O<sub>2</sub> participating in bubble growth.<sup>1-3)</sup>



In several studies,<sup>4-6)</sup> it has been found that sulfide ions (S<sup>2-</sup>) contained in blast furnace slag (BFS) can contribute to fining during batch melting by the following reaction under oxidation atmosphere:



Since reaction (2) is irreversible under oxidation atmosphere, sulfur (S) can exist in the fined melts as S<sup>6+</sup> (sulfate, SO<sub>4</sub><sup>2-</sup>), S<sup>4+</sup> (sulfite, SO<sub>3</sub><sup>2-</sup>) and S<sup>0</sup>. Recently, both reactions (1) and (2) were confirmed indirectly during first fining by work in which oxygen equilibrium pressure of melts after first fining was detected quantitatively.<sup>7)</sup> However, the measurement of oxygen equilibrium pressure has a limit since it cannot give any detailed information about sulfur state in

melt. Hence, square wave voltammetry (SWV) has been used to examine the redox reaction of the polyvalent ions.

The redox behavior of sulfur ions in melts has been studied qualitatively by SWV for soda lime silica glasses.<sup>8-11)</sup> Although the interpretation of the voltammogram by SWV is still controversial, the redox reaction in melts seems to be controlled by S<sup>4+</sup> and S<sup>0</sup>.<sup>10,11)</sup> However, there have been no SWV studies for melts of PDP glass consisting of alkali-alkaline earth silica. Considering that the redox reaction of polyvalent ions depends on the glass composition, it is very interesting to investigate the redox behavior of sulfur in situ in glass melts, especially doped with sulfate. In the present work, PDP display glass melts containing sodium sulfate or blast furnace slag were prepared. SWV was performed in the melt state by means of zirconia solid electrodes and the resulting voltammograms were analyzed from the viewpoint of sulfur state, diffusivity and thermodynamics.

## 2. Experimental Procedures

### 2.1. Preparation of glass melts

The blank composition of PDP glass in mol% was 69.1SiO<sub>2</sub>, 9.0(Na<sub>2</sub>O+K<sub>2</sub>O), 13.0RO(MgO+CaO), 5.3SrO, 1.1BaO and a small amount of ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> in which the Na<sub>2</sub>O/K<sub>2</sub>O and the MgO/CaO mole ratios were fixed at 1. Additionally, the blank melts were doped (1) with 0.3 mol% SO<sub>3</sub> supplied from Na<sub>2</sub>SO<sub>4</sub>, (2) with 0.03 mol% SO<sub>3</sub> from 6% BFS (a corresponding amount to 6 wt% of the sand in glass batches) and (3) with mixing of both materials, respectively. Each experimental melt was named (1) sulfate melt, (2) BFS6 melt and (3) sulfate+BFS6 melt. The composition of the melt and the preparation procedure of melts by batch melting are detailed elsewhere.<sup>7)</sup>

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## 2.2. Measurement of SWV

The electrochemical cell for SWV measurement consists of three electrodes immersed in the melt in a Pt/Rh crucible and potentiostat (Model 273A, EG&G, USA) connected to a computer. A platinum plate and a wire were used as counter electrode and working electrode, respectively. The other platinum wire called the reference electrode was connected with  $O^{2-}$  conducting  $Y_2O_3$ -stabilized  $ZrO_2$  (YSZ) material which was in contact with melts and flushed by reference air with known oxygen partial pressure ( $P_{O_2}$ : 0.21 bar) during the SWV experiment. The detailed description of the cell construction is shown in the literature.<sup>12,13</sup>

SWV was for the measurements of current-potential curves under controlled potential consisting of base and step potential. When a definite potential varied with time is applied to a working electrode by potentiostat, the resulting current is registered at the counter electrode. The measured current-potential curve is called a voltammogram which gives valuable information on the behavior of the redox species. If the applied potential is enough to allow electron donation or acceptance between redox species, the voltammogram reveals a characteristic peak current ( $I_p$ ). For example, under several assumptions this peak current is related with various parameters as in the following equation (3).<sup>14</sup>

$$I_p = \frac{0.3n^2F^2A \cdot C \cdot \Delta E}{R_g T} \sqrt{\frac{D}{\pi \cdot \tau}} \quad (3)$$

In the equation,  $A$  represents the surface area of the working electrode,  $C$  denotes the concentration of oxidized ion at the initial potential,  $\tau$  is the pulse time (namely, reciprocal frequency),  $n$  is the amount of electron transferred,  $D$  is the diffusion coefficient of oxidized ions,  $\Delta E$  is the step potential,  $R_g$  is the gas constant and  $F$  is the Faraday constant. The corresponding potential to  $I_p$  in voltammogram is called peak potential ( $E_p$ ). The equilibrium constant at temperature  $T$  of redox reaction,  $K(T)$  can be simplified with a few assumptions as equation (4):

$$K(T) = \frac{[M^{x+}] \cdot P_{O_2}^{n/4}}{[M^{(x+n)+}]} = \exp\left[\frac{n \cdot F \cdot E_p}{R_g \cdot T}\right] \quad (4)$$

Here,  $M$  is polyvalent ion as  $S^{4+}$  and  $P_{O_2}$  is oxygen equilibrium pressure between reference and working electrode before application of artificial potential. According to equation (4),  $K(T)$  is determined by  $E_p$  in the voltammogram. Modification of equation (4) allows the following equation (5):

$$\ln K(T) = \frac{-\Delta H^0}{R_g T} + \frac{\Delta S^0}{R_g} = \frac{n \cdot F \cdot E_p}{R_g \cdot T} \quad (5)$$

From equation (5) standard enthalpy ( $\Delta H^0$ ) and standard entropy ( $\Delta S^0$ ) of reaction can be directly calculated.

During SWV measurement at a given temperature the furnace was switched off to avoid disturbance of the measured signal by the current of the heating elements. SWV measurements in the present work were performed under

the following conditions: the applied potential and frequency range was 0~-800 mV and 5~1000 Hz, respectively. The final voltammogram of each melt at the temperature ranging from 1400°C to 1100°C was obtained by subtracting that of the blank PDP melt from the original recorded voltammogram and analyzed with aid of commercial software.

## 3. Results and Discussion

The voltammogram of sulfate melt (a PDP glass melt containing 0.3 mol%  $SO_3$ ) for different frequencies at 1300°C was produced as shown in Fig. 1. The first peak is located at the same potential (about -480 mV) irrespective of the frequency. But the peak currents ( $I_p$ ) strongly depend on the frequency. For low frequency, only one reduction peak at about -480 mV (first peak) could be observed. However, with an increase in frequency, another peak at -300 mV

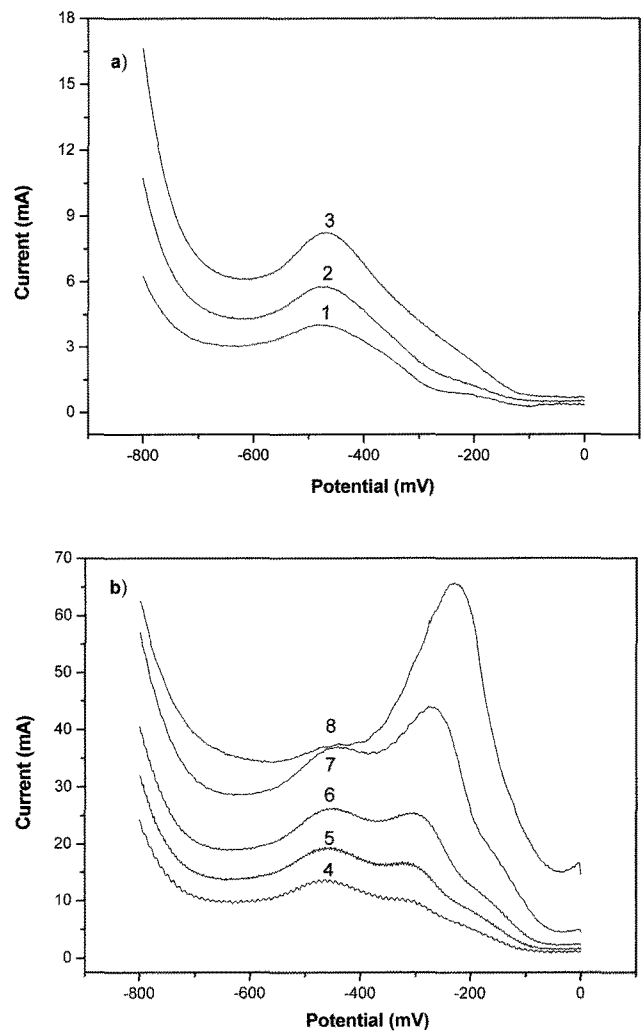


Fig. 1. Voltammograms in sulfate melt for different frequencies at 1300°C, (a) Curve: 1=5 Hz, 2=10 Hz, 3=20 Hz, (b) Curve: 4=50 Hz, 5=100 Hz, 6=200 Hz, 7=500 Hz, 8=1000 Hz.

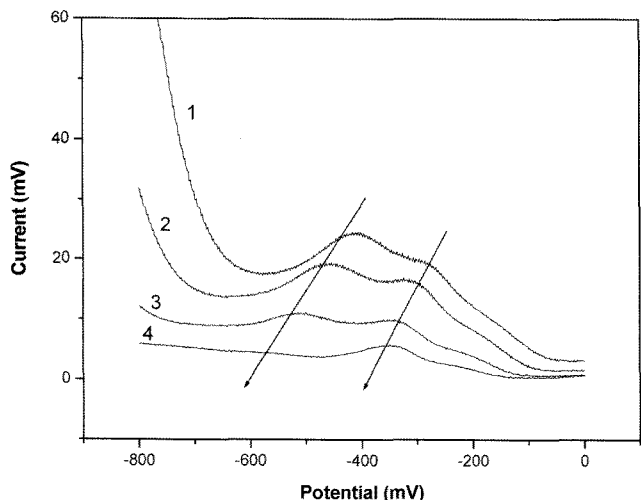


Fig. 2. Voltammograms in sulfate melt at 1: 1400°C, 2: 1300°C, 3: 1200°C, 4: 1100°C (frequency=100 Hz).

(second peak) took place and its peak potential shows a strong dependence on frequency. In Fig. 2 the voltammogram at 100 Hz is presented in the temperature range of 1100°C~1400°C. Fig. 2 shows that the peak potentials ( $E_p$ ) are shifted to more positive values with increasing temperature and the second peak is weakened at high temperature. The dependence of the voltammogram of sulfate melt on frequency and temperature in Figs. 1 and 2 is similar to that of flint melt containing sulfate.<sup>11)</sup> In relation to the identification of peaks shown in the voltammogram, some attempts<sup>8-11)</sup> have been undertaken based on the theoretical curve for electron transfer. It was concluded that the first peak was due to the reduction of  $S^{4+}$  to  $S^0$  ions ( $SO_2 + 4e^- \leftrightarrow S^0 + 2O^{2-}$ ) and the second peak is attributed to adsorption of sulfur.<sup>10)</sup>

Fig. 3 shows the voltammogram of sulfate, BFS6 and sulfate+BFS6 melts recorded at 1300°C and 100 Hz. The peak current ( $I_p$ ) showed a great dependence on sulfur con-

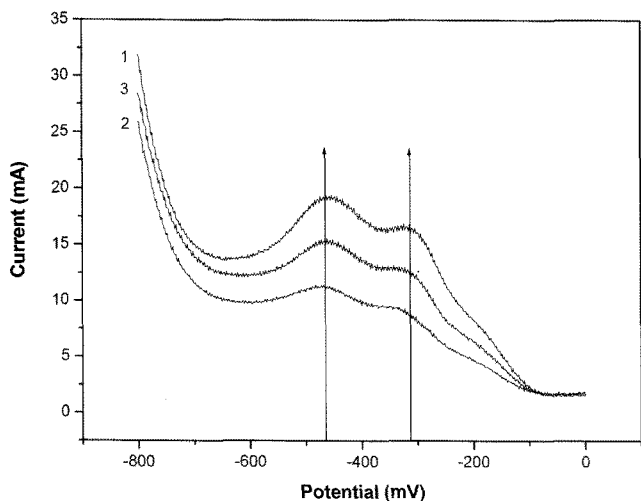


Fig. 3. Voltammograms at 1300°C and 100 Hz. 1: sulfate melt, 2: BFS6 melt 3: sulfate+BFS6 melt.

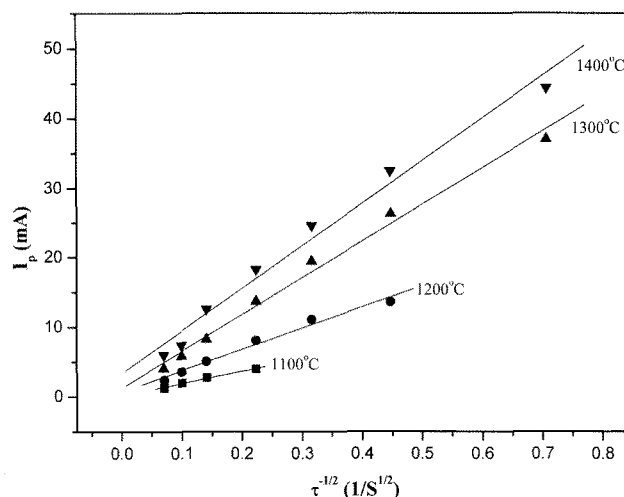


Fig. 4. First peak-current as a function of the reciprocal square root of the pulse time ( $\tau$ ) in sulfate melt.

centration. But the peak position is located at almost the same potential. The same peak potential of three melts means that the sulfide compound of BFS finally plays the same role as sulfate during the fining process.

According to the relationship between  $I_p$  and  $\tau^{-1/2}$  as indicated in equation (3), linearity is expected under diffusion-controlled reaction. The  $I_p$  of the first peak in Fig. 1 is plotted as a function of  $\tau^{-1/2}$  in Fig. 4. Table 1 contains diffusion coefficients ( $D$ ) for reduction of  $S^{4+}/S^0$  in the sulfate melt cal-

Table 1. Self Diffusion Coefficient of  $S^{4+}$  in Sulfate Melt

Temperature (K)	Self diffusivity, $D$ ( $cm^2/s$ )
1673	$4.782 \times 10^{-8}$
1573	$3.144 \times 10^{-8}$
1473	$9.181 \times 10^{-9}$
1373	$2.597 \times 10^{-9}$

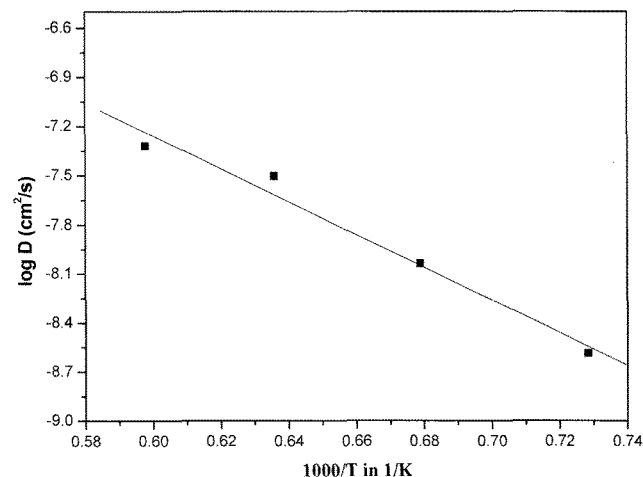


Fig. 5. Temperature dependence of diffusion coefficient ( $D$ ) for  $S^{4+}$  at reaction  $S^{4+} + 4e^- \rightarrow S^0 + 2O^{2-}$  in sulfate melt.

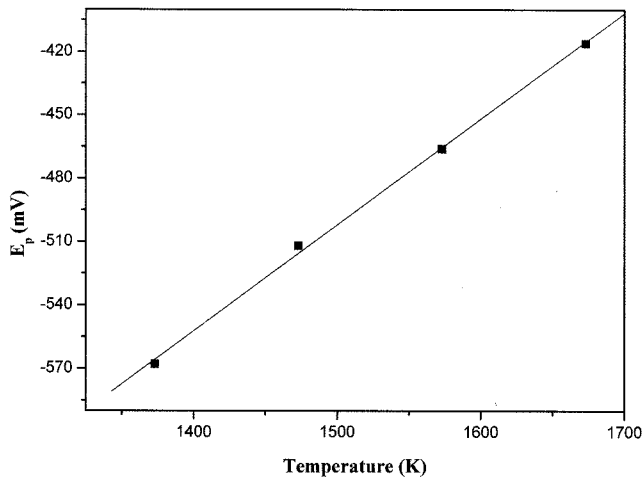


Fig. 6. Experimental plot of  $E_p$  as a function of temperature in sulfate melt.

Table 2. Peak Potential ( $E_p$ ) at 1673 K, Enthalpy ( $\Delta H^0$ ) and Entropy ( $\Delta S^0$ ) for the Reduction of  $S^{4+}/S^0$  in Sulfate Melt

$E_p$ (mV) at 1673 K	-416
$\Delta H^0$ (KJ·mole <sup>-1</sup> )	491
$\Delta S^0$ (J·mole <sup>-1</sup> ·K <sup>-1</sup> )	199

culated from the slope between  $I_p$  and  $\tau^{-1/2}$ .  $D$  is plotted as a function of temperature in Fig. 5. Within the limits of error, the values can be fitted to an Arrhenius-type equation. Although diffusion coefficients of various polyvalent ions in melts have been determined by SWV<sup>15-17</sup> there are no data for sulfur diffusion using SWV. Comparing the present values of Table 1 with the recent data<sup>18</sup> determined by trace diffusion, both results belonged to a similar range.

In Fig. 6 the peak potentials ( $E_p$ ) for  $S^{4+}/S^0$  in sulfate melt are plotted as a function of temperature.  $E_p$  decrease with decrease of temperature and their temperature dependence shows a good linearity.  $E_p$  values shift toward the negative direction as the temperature decreases. This indicates that the equilibrium state of reaction (1) shifts toward the left, namely to the oxidation state. Therefore, at low temperature it is favorable to exist in the form of a higher valence state. On the other hand, with an increase of temperature the reduced state is favored. According to equation (5), the linearity in Fig. 6 indicates that standard enthalpy ( $\Delta H^0$ ) and standard entropy ( $\Delta S^0$ ) are constant within the investigated temperature range. Peak potential at 1400°C and the calculated enthalpy and entropy for  $S^{4+}/S^0$  are summarized in Table 2. Compared with the thermodynamic data for  $Fe^{3+}/Fe^{2+}$ ,  $Sb^{3+}/Sb^0$  and  $Zn^{2+}/Zn^0$  of alkali alkaline earth silicate melts determined by SWV<sup>13</sup> it is recognized that  $\Delta H^0$  and  $\Delta S^0$  for  $S^{4+}/S^0$  indicate relatively high values.

#### 4. Summary

SWV measurements were conducted in three PDP glass

melts doped with 1) sulfate, 2) BFS, and 3) sulfate+BFS. In the recorded voltammograms for three melts two peaks were observed depending on frequency. The peak current was strongly dependent on sulfur concentration, but the peak potential showed almost the same value meaning that the sulfide of BFS gives the same influence to the fining process as sulfate. Based on the frequency dependence of the peak current and the temperature dependence of the peak potential, self diffusivity of  $S^{4+}$ , standard enthalpy and entropy for the reduction of  $S^{4+}/S^0$  were determined.

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