

REDOX BEHAVIOR OF SULFUR IN SILICATE MELTS BY SQUARE WAVE VOLTAMMETRY

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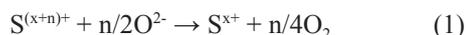
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Two types of alkali alkaline earth silicate melts (Flint and PDP) containing sodium sulfate or blast furnace slag were prepared and the sulfur redox equilibrium was studied by square wave voltammetry. Voltammograms at different frequencies in the temperature range from 1000°C to 1400°C were produced. The voltammograms of both melts showed two reduction peaks at high frequency but only one peak at low frequency. The peaks shown in the voltammogram of the melts prepared from the blast furnace slag were weak but their potentials were same as those of the melts from the sulfate. Based on the diffusion coefficients determined from the relation between peak current and pulse time, it was suggested that the first peak around -500 mV was due to the reduction of S^{4+} to S^0 and the second peak around -300 mV was related to the reduction of S^{6+} to S^{4+} .

INTRODUCTION

Sulfate (SO_4^{2-}) is introduced into glass melts as a fining agent or amber colorant with iron. The effectiveness of sulfur in glass melts depends on its valence states, S^{6+} , S^{4+} , S^0 and S^{2-} under 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. Therefore, it is very interesting to investigate the redox behavior of sulfur in situ in glass melt. In order to examine the redox behavior of multivalent ions in a glass melts various voltammetric methods [1-7] have been suggested and it seems to be a dominant opinion that square wave voltammetry (SWV) is the optimal technique to trace multivalent ions in situ in a melt [2-4]. A few studies on sulfur doped melts have been carried out by voltammetry [8-13]. But, the interpretation of the resulting voltammograms is still controversial.

In this study, two types of industrial model silicate melts called Flint and PDP containing sodium sulfate or blast furnace slag with sulfide were prepared under air atmosphere and the sulfur redox reaction was studied by SWV.

EXPERIMENTAL

The composition of Flint and PDP blank melt in mol% was $74.4SiO_2 \cdot 13.65Na_2O \cdot 1.18Al_2O_3 \cdot 10.77CaO$ and $69.1SiO_2 \cdot 9.0(Na_2O+K_2O) \cdot 13.0(MgO+CaO) \cdot 5.3SrO \cdot 1.1BaO \cdot 2.1ZrO_2 \cdot 0.4Al_2O_3$, respectively. One melts with sulfur was prepared from the batches (named sulfate batch) doped with 0.3 mol% SO_3 supplied from Na_2SO_4 . The other melts with sulfur were prepared from the batches (named slag batch) containing blast furnace slag in which sulfur exists in a sulfide state (S^{2-}), and the converted value to SO_3 corresponds to 0.03 mol% in the glass. 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 prepared for SWV measurements.

The voltammetry cell consists of three electrodes immersed into the melt and a potentiostat (Model 273A, EG & G, USA) connected to a computer. Platinum plate and wire were used as a counter electrode and a working electrode, respectively. The other platinum wire, called the reference electrode, was connected to O^{2-} conducting Y_2O_3 -stabilized ZrO_2 (YSZ) material which is in contact with the melts and flushed by reference air at a known oxygen partial pressure (p_{rO_2} : 0.21bar) during the SWV experiments. A detailed description of the cell construction is also shown elsewhere [14].

SWV is one of the pulse techniques in electrochemistry and directly related to the determination of redox reaction equilibrium constants in melts containing multivalent ions [15]. SWV is for the measurements of current-potential curves under a controlled potential consisting of a base and step potential, i.e. a definite potential varied with time is applied to a working electrode relative to a reference electrode and the resulting current is registered at the counter electrode. If the applied potential is enough to allow electron donation or acceptance between redox species, the recorded current-potential curve, called a voltammogram, gives valuable information on the behavior of the redox species by a characteristic peak current (I_p). For example, under several assumptions, this peak current is related with various parameters as follows [3, 15]:

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

In the equation, A represents the surface area of the working electrode, C denotes the concentration of oxidized ions at the initial potential, t is the pulse time (namely, reciprocal frequency), n has the same meaning as that in reaction (1), D is the diffusion coefficient of oxidized ions, F is the Faraday constant, and ΔE is the step potential.

During SWV measurements 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 study were performed under the following conditions: the applied potential and frequency range was 0~800 mV and 5~1000Hz, respectively. The final voltammogram of each melt at temperatures ranging from 1400°C to 1000°C was obtained by subtracting that of the blank melt from the original recorded voltammogram and analyzed with the aid of commercial software.

RESULTS AND DISCUSSION

Figure 1 shows the recorded voltammograms of Flint melts prepared from the sulfate batch at different frequencies in the temperature range of 1000°C~1400°C. The peak currents (I_p) strongly depend on the frequency. At low frequency, only one reduction peak at about -520 mV (first peak) is observed. However, with an increase of the frequency, another peak at -315 mV (second peak) occurs. According to Figure 1b, with temperature increase the peak potential corresponding to the peak current is shifted to a more positive value and the second peak is only observed at low temperature (<1300°C).

The voltammograms of PDP melts prepared from the sulfate batch at different frequencies at 1300°C were produced as shown in Figure 2. 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 -310 mV (second peak) appears and its peak potential shows a strong dependence on frequency. In Figure 3 the voltammograms of PDP melts at 100Hz are presented in the temperature range of 1100°C~1400°C. Figure 3 shows that the peak potentials (E_p) are shifted to more positive values with temperature increase and the second peak is weakened at high temperature. The behavior of the second peak in Flint and PDP melts is similar. Especially, the temperature dependence of the peak potential in both Flint and PDP melts means that with a temperature decrease the equilibrium state of reaction (1) shifts to the left, namely to an oxidation state. However, it seems to be difficult to identify the peak based on theoretical shape of voltammogram [8, 11] calculated using the number of electron transfer.

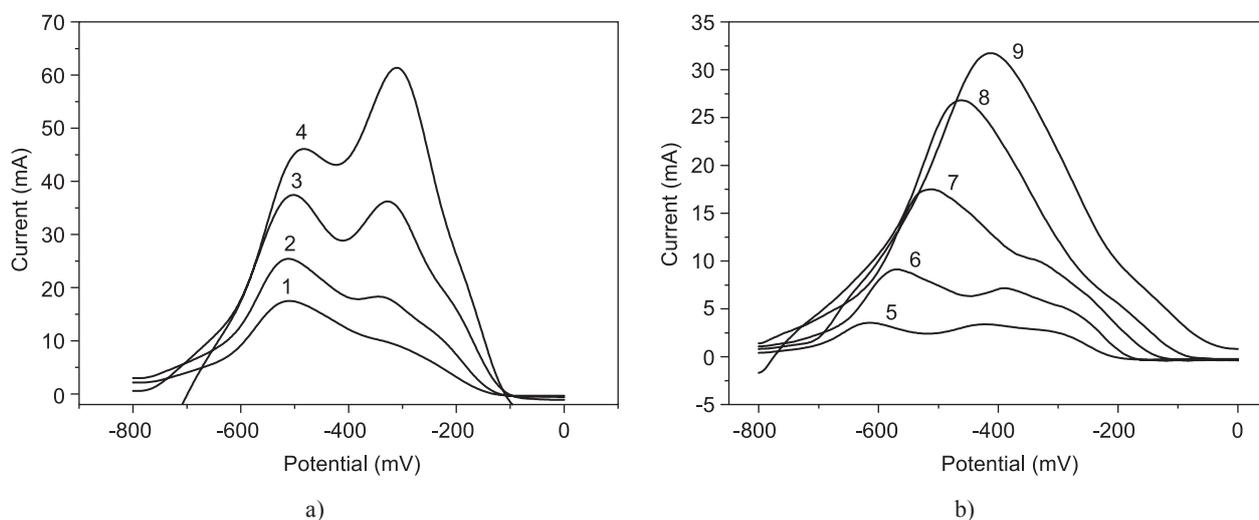


Figure 1. Voltammograms recorded in Flint melts containing 0.3 mol% SO_3 a) at 1200°C, 1: 100, 2: 200, 3: 500, 4: 1000 Hz and b) at 100 Hz, 5: 1000, 6: 1100, 7: 1200, 8: 1300, 9: 1400°C.

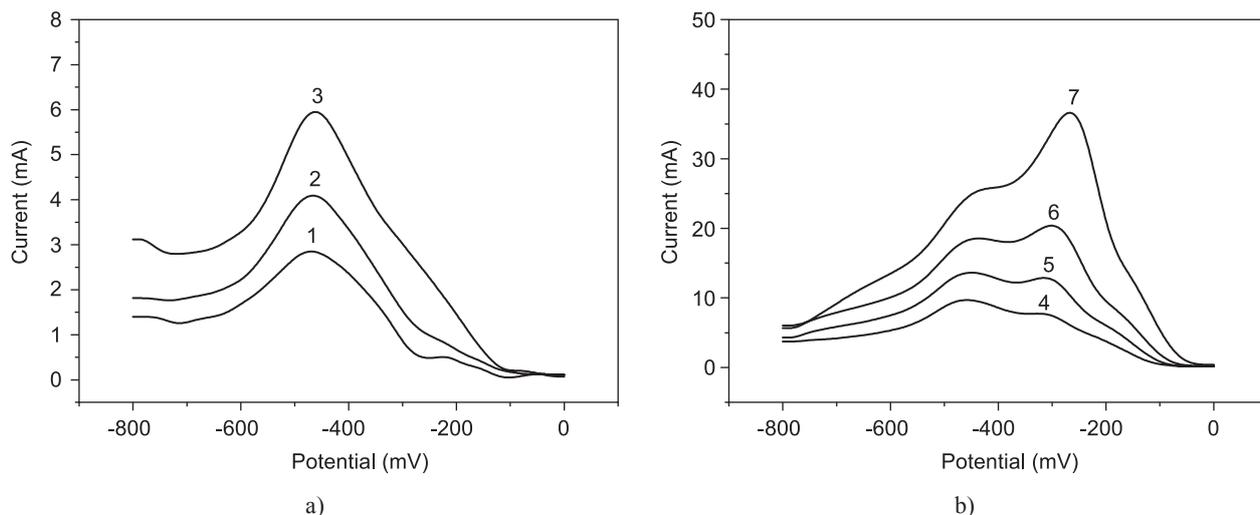


Figure 2. Voltammograms recorded in PDP melts containing 0.3 mol.% SO_3 for different frequency at 1300°C ; a) 1: 5, 2: 10, 3: 20 Hz, b) 4: 50, 5: 100, 6: 200, 7: 500 Hz.

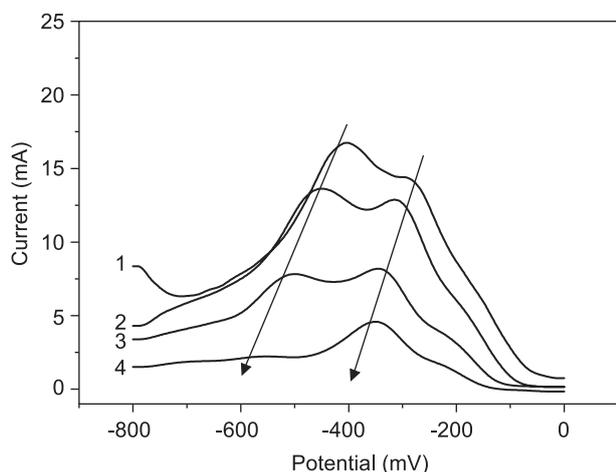


Figure 3. Voltammograms of PDP melts at 100 Hz, 1: 1400°C , 2: 1300°C , 3: 1200°C , 4: 1100°C .

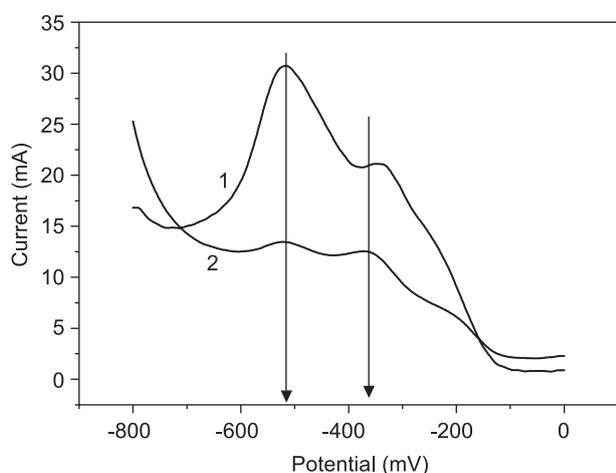


Figure 4. Voltammograms of Flint melts at 1200°C and 300 Hz, 1: sulfate batch, 2: slag batch.

Figure 4 shows voltammogram recorded at 1200°C and 300 Hz of two Flint melts produced from the sulfate and the slag batches, respectively. The peak current (I_p) showed a dependence on sulfur concentration. But the position of two peaks for both melts is located almost at the same potential. PDP melts produced from the slag batches showed also the same behavior in the peak position as the melts from sulfate.

In Figure 5, the peak currents (I_p) of the first and the second peak for Flint and PDP melts based on in Figure 1 and Figure 2 are plotted as a function of $\tau^{-1/2}$. According to the relationship between I_p and $\tau^{-1/2}$ as indicated in Equation (2), linearity can be expected under the diffusion controlled reaction. Both melts show a relative good linearity in spite of some scattering in the first peak of Flint melts. Comparing the slope of the first with that of the second peak, a great difference in diffusion coefficient between two redox pairs inducing the peaks is anticipated.

Although several voltammetric studies [8-13] on sulfur doped melts have been carried out, there are various interpretations for the redox pair due to the reduction at a peak shown in voltammogram. Based on theoretical curve for electron transfer and linearity between I_p and $\tau^{-1/2}$ some studies [9, 11] concluded that the second peak was due to S^{4+}/S^0 and the first peak was attributed to S^0/S^{2-} . Three peaks were found in the voltammogram of Lafage et al. [10] who proposed the presence of two kinds of S^{4+} complex and S^0/S^{2-} . In the study of Yamashita et al. [13] there were also three peaks which were assumed due to $\text{S}^{6+}/\text{S}^{4+}$, S^{4+}/S^0 and S^0/S^{2-} . Tilquin et al. [12] suggested that the second peak was due to adsorption of sulfur by the relation between the double layer capacitance and potential, and thus the second peak was nothing to do with S^{4+}/S^0 but the first peak was related to S^{4+}/S^0 . In some works [8, 16] it was suggested that the second peak was associated with $\text{S}^{6+}/\text{S}^{4+}$ in terms

of SO_3^{2-} solubility. A recent work in which the valence state of sulfur in silicate glasses was determined at room temperature using X-ray absorption near edge structure spectroscopy reported that the S^{6+} was clearly identified but the presence of S^{4+} was unclear [17]. No difference in the peak potential between two melts as shown in Figure 4 of the present study means that S^0/S^{2-} is not possible even in the melts produced from the slag batches. According to several studies [18, 19], it has been known that sulfide ions (S^{2-}) contained in blast furnace slag are oxidized to SO_2 during batch melting by following reaction under oxidation atmosphere: $\text{S}^{2-}(\text{melt}) + 3/2\text{O}_2 \rightarrow \text{SO}_3^{2-}(\text{melt}, \text{S}^{4+})$. Since the existence of S^{2-} in the melts is not possible under oxidation atmosphere, sulfur can exist in a state of S^{6+} (sulfate, SO_4^{2-}), S^{4+} (sulfite, SO_3^{2-}) and probably S^0 .

Considering the results of foregoing studies it is inferred that two peaks shown in the voltammograms are only attributed to $\text{S}^{6+}/\text{S}^{4+}$ and S^{4+}/S^0 . Additionally, the diffusion coefficient of S^{6+} and S^{4+} must be different

each other as shown in Figure 5. Table 1 contains diffusion coefficients (D) calculated using equation (2) under the assumption that n is 2 ($\text{S}^{6+}/\text{S}^{4+}$) or 4 (S^{4+}/S^0) in conjunction with the first and second peak, and C is constant (sulfur evaporation is neglected). The resulting D values lie in the range of the recent investigated sulfur diffusion coefficients in silicate melts [20]. However, in order to confirm the peak identification it is necessary to know the relative magnitude in diffusion coefficient between S^{6+} and S^{4+} . Since the diffusion of multivalent ion is strongly dependent on the number of transferred electrons ($D \propto n^{-4}$), D for S^{4+}/S^0 will be much smaller than that for $\text{S}^{6+}/\text{S}^{4+}$. Comparison of D values in table 1 implies that the first peak indicating the minimum value may be due to S^{4+}/S^0 and thus the second peak with maximum value corresponds to $\text{S}^{6+}/\text{S}^{4+}$. Figure 6 shows an Arrhenius relationship between diffusion coefficient and temperature plotted on the basis of the above suggestion.

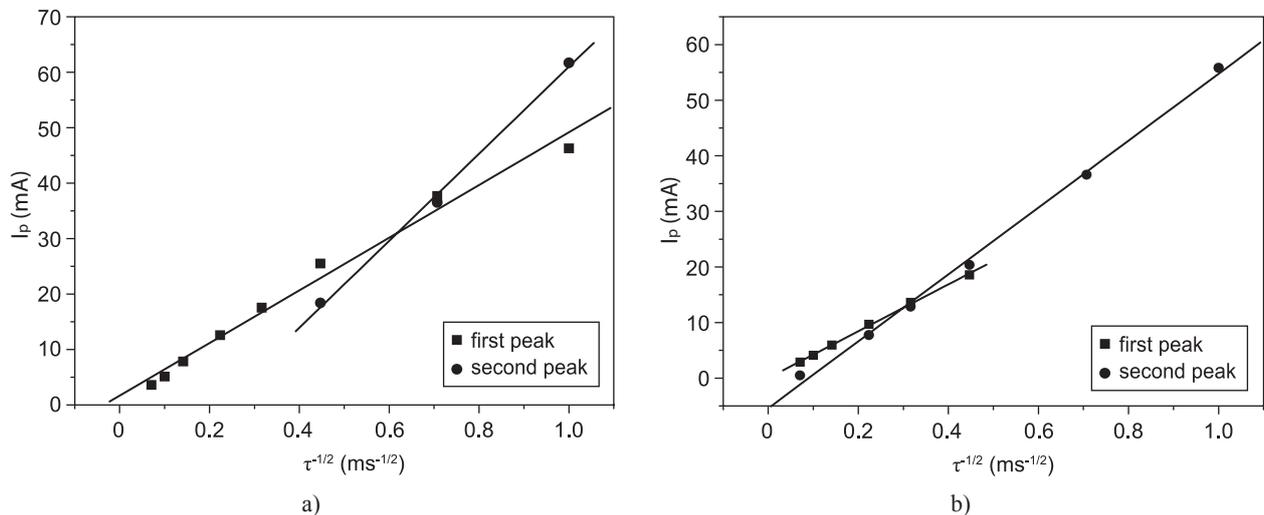


Figure 5. Peak current (I_p) as a function of the reciprocal square root of the pulse time (τ) in a) Flint melts at 1200°C, b) PDP melts at 1300°C.

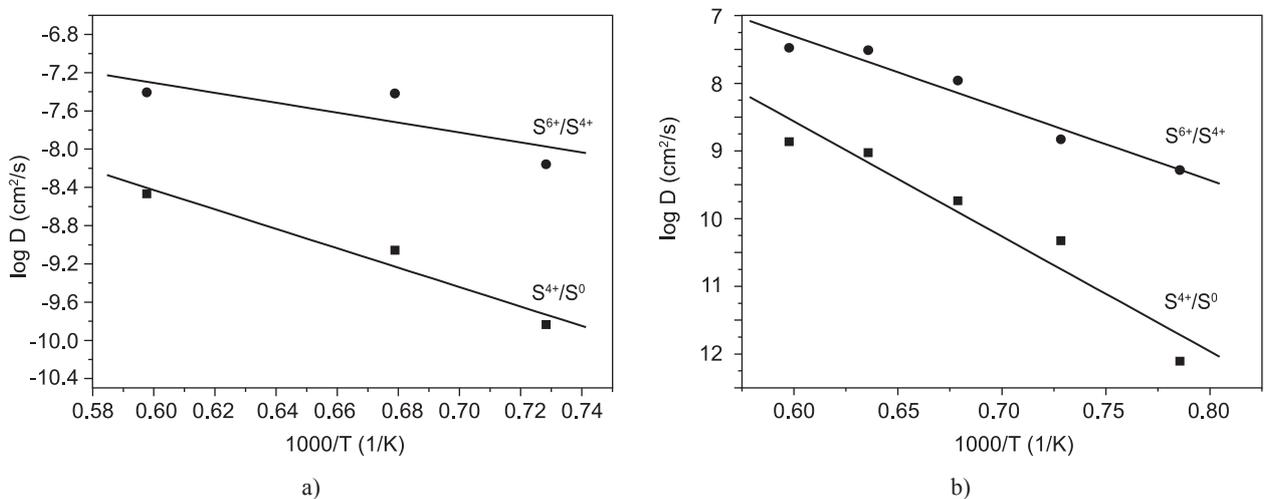


Figure 6. Diffusion coefficient (D) of sulfur ion as a function of reciprocal temperature in a) Flint melts, b) PDP melts.

Table 1. Diffusion coefficient (D) of sulfur ion for the first and the second peak in Flint and PDP melts derived from the slope between I_p and $\tau^{-1/2}$ shown in Figure 5.

Melts	Peaks	D (cm ² /s)	
		$n = 2$ (S ⁶⁺ /S ⁴⁺)	$n = 4$ (S ⁴⁺ /S ⁰)
Flint at 1200°C	First	1.39869×10^{-8}	8.74179×10^{-10}
	Second	3.81495×10^{-8}	2.38434×10^{-9}
PDP at 1300°C	First	1.50876×10^{-8}	9.42975×10^{-10}
	Second	3.07782×10^{-8}	1.92364×10^{-9}

CONCLUSION

Sulfur redox equilibrium in Flint and PDP melts was studied by square wave voltammetry. In the recorded voltammograms for both melts prepared from the sulfate batches, two peaks named first peak and second peak were observed depending on the frequency and temperature. The peak potentials in the voltammograms of both melts prepared from the slag batches showed almost the same value as those of the melts from the sulfate batches indicating that the reduction of S⁰ to S²⁻ is absent. The peak current (I_p) was strongly dependent on frequency (or pulse time: τ), but the slope between I_p and $\tau^{-1/2}$ for two peaks in one melt was different each other. Based on the diffusion coefficient calculated by applying the number of the transferred electron to the slope, it was suggested that the first peak is due to the reduction of S⁴⁺ to S⁰ and the second peak is attributed to the reduction of S⁶⁺ to S⁴⁺.

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