

## A voltammetric approach to the redox behavior of S in flint glass melts doped with sulfate or sulfide

Ki-Dong Kim\*

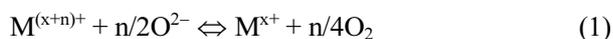
Department of Materials Science and Engineering, Kunsan National University, Chunbuk, Korea

Soda lime silicate flint glass melts 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 melts containing sodium sulfate showed two reduction peaks at high frequency but only one peak at low frequency. Based on the relation between peak current and pulse time, it was concluded that the second peak was nothing to do with the pure reduction of S<sup>4+</sup> to S<sup>0</sup> but might be related to sulfur adsorbed to an electrode. The peaks observed in the voltammograms of melts containing blast furnace slag with sulfide were located at similar potentials with those of sodium sulfate.

**Key words:** sulfate, sulfide, redox reaction, voltammogram

### Introduction

Sulfate (SO<sub>4</sub><sup>2-</sup>) 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<sup>6+</sup>, S<sup>4+</sup>, S<sup>0</sup> and S<sup>2-</sup> under a reducing or oxidizing atmosphere. In glass melts, the following redox reaction for multivalent elements such as sulfur can be expected:



where M is a multivalent ion, n is the number of electrons transferred from one valence state of M 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 SWV [8-13]. But, the interpretation of the resulting voltammograms is still controversial. The redox reaction in sulfate melts seems to be controlled by S<sup>4+</sup> and S<sup>0</sup> [11, 13].

In relation to the use of blast furnace slag (BFS) as a raw material in glass industry there have been reported benefits such as an improvement of the melting and refining [14-16]. It has been known that the decomposition of sulfate (SO<sub>4</sub><sup>2-</sup>) by a reaction with the sulfide (S<sup>2-</sup>) in the BFS improves the refining of melt. A sulfide alone may produce a refining action by reacting with oxygen to

generate SO<sub>2</sub>. However, a detailed investigation for a melt containing BFS has not been performed by voltammetry.

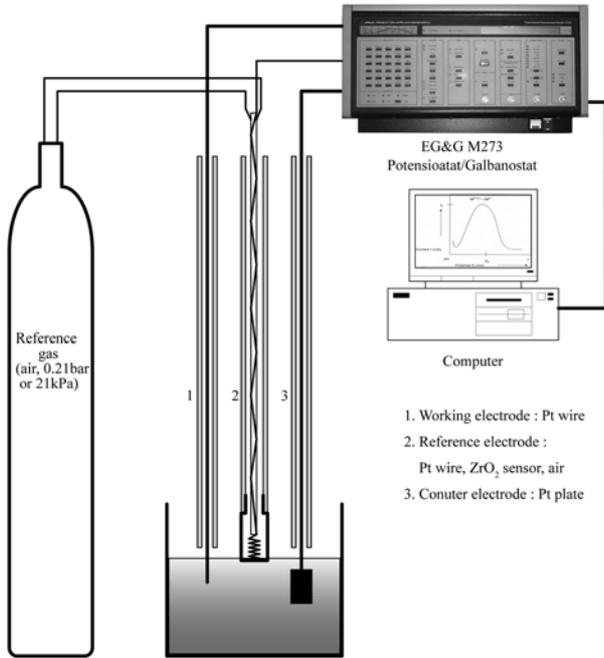
In this study, soda lime silicate flint glass melts containing sodium sulfate or BFS were prepared and the sulfur redox reaction was studied by SWV.

### Experimental

The blank melt composition in wt% was 74SiO<sub>2</sub>·2Al<sub>2</sub>O<sub>3</sub>·10CaO·14Na<sub>2</sub>O. Melts containing sulfur with the same composition were prepared by doping with 0.419 wt% SO<sub>3</sub> or 6% BFS (corresponding amount to 6 wt% of sand in glass batches). High purity raw materials were used to exclude the effect of another multivalent impurity. The glass batches of about 300 g were melted at 1450 °C in an electric furnace. The bubble free melts homogenized by stirring with a Pt/Rh rod were transferred to another electric furnace. While the prepared melts were maintained at 1400 °C in the furnace, the electrodes of an electrochemical cell were dipped into the melts to perform SWV measurements. The electrochemical cell as shown in Fig. 1 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<sup>2-</sup> conducting Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) material which is in contact with the melts and flushed by reference air at a known oxygen partial pressure (P<sub>r02</sub>: 0.21 bar or 21 kPa) during the SWV experiments. A detailed description of the cell construction is also shown elsewhere [17].

SWV is one of the pulse techniques in electrochemistry and directly related to the determination of redox reaction equilibrium constants in melts containing multivalent

\*Corresponding author:  
Tel : +82-63-469-4737  
Fax: +82-63-469-4731  
E-mail: kdkim@kunsan.ac.kr



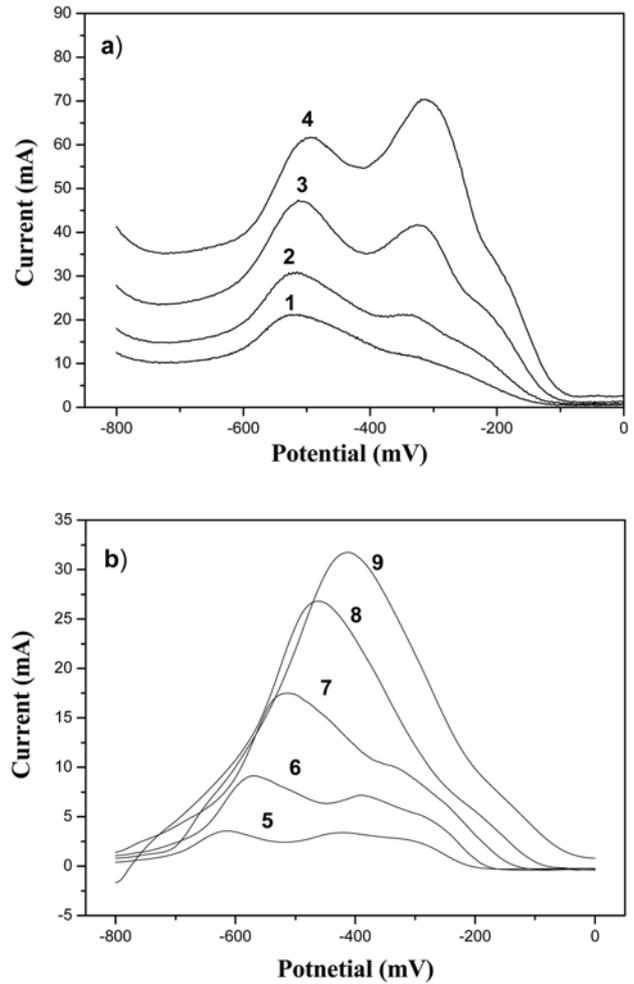
**Fig. 1.** Three electrode system for square wave voltammetry measurement.

ions [18]. 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 [8, 9]:

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

In the equation,  $A$  represents the surface area of the working electrode,  $C$  denotes the concentration of oxidized ions at the initial potential,  $\tau$  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  $\Delta E$  is the step potential.

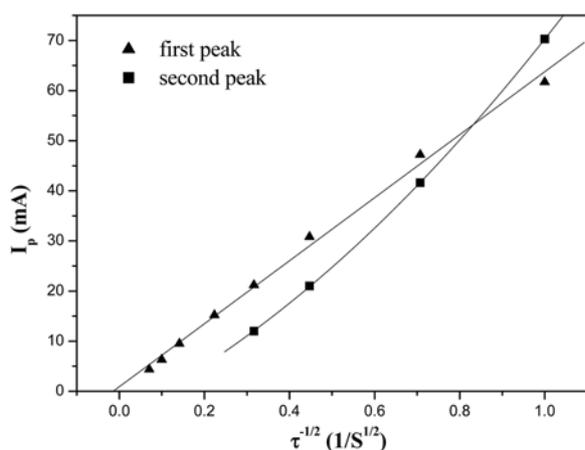
During SWV measurements at a given temperature the furnace was switched off to avoid disturbance of the measured signal by the current of the heating elements. SWV measurements in the present study were performed under the following conditions: the applied potential and frequency range was 0~800 mV and 5~1000 Hz, 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.



**Fig. 2.** Square wave voltammograms recorded in a flint glass melt containing 0.419 wt%  $\text{SO}_3$  supplied from sodium sulfate 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.

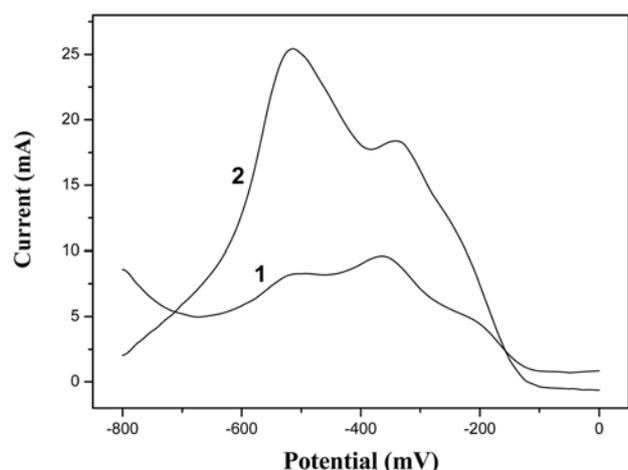
## Results and Discussion

The voltammograms of flint glass melts containing sulfate at different frequencies in the temperature range of 1000 °C~1400 °C were produced and shown in Fig. 2. 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 Fig. 2(b), the peak potential corresponding to the peak current is shifted to a more positive value with an increase in the temperature and the first peak is only observed at high temperature ( $\geq 1300$  °C). This temperature dependence of the peak potential means that the equilibrium state of reaction (1) shifts to the right, namely to a reducing state with a temperature increase. In Fig. 3, the currents ( $I_p$ ) of the first and the second peak in Fig. 2(a) 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 is

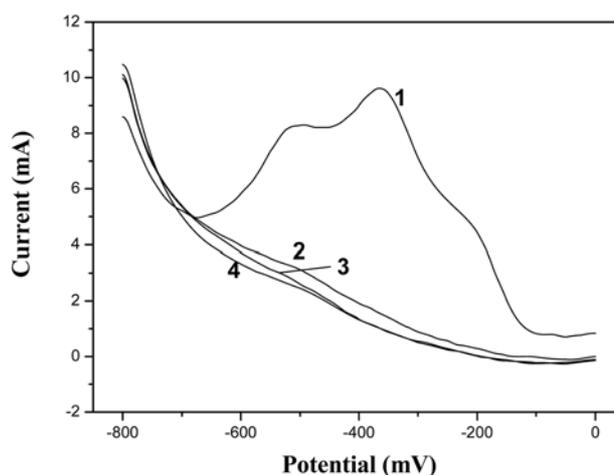


**Fig. 3.** First and second peak-current as a function of the square root of the pulse time ( $\tau$ ) at 1200 °C in a flint glass melt containing 0.419 wt%  $\text{SO}_3$ .

expected under a diffusion controlled reaction. But the linearity is observed only for the first peak. Although several voltammetric studies [8-12] 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 some studies [9, 10] concluded that the second peak is due to  $\text{S}^{4+}/\text{S}^0$  and the first peak is attributed to  $\text{S}^0/\text{S}^{2-}$ . However, it was proved that the second peak occurring at the right hand side of voltammogram was due to adsorption of sulfur by the relation between the double layer capacitance and potential [11], and the dependence of  $I_p$  on  $\tau^{-1/2}$  for various sulfur concentrations in the literature [10] showed clearly no linearity. Therefore, it can be concluded that the peak at  $-315$  mV named the second peak in the present study is nothing to do with  $\text{S}^{4+}/\text{S}^0$ . According to the study in which the exact theoretical curve for 4 electron transfer was compared with those peaks [11], the first peak at about  $-520$  mV seems to be related to  $\text{S}^{4+}/\text{S}^0$ .



**Fig. 4.** Voltammograms recorded in flint glass melts containing 1 : 6% BFS (calculated in terms of  $\text{SO}_3$  : 0.0366 wt%) and 2 : 0.419 wt%  $\text{SO}_3$  at 1200 °C and 100 Hz.



**Fig. 5.** Voltammograms recorded in flint glass melts containing 1 : 6% BFS, 2 :  $\text{Fe}_2\text{O}_3$ , 3 : MnO and 4 :  $\text{TiO}_2$  at 1200 °C and 100 Hz.

Fig. 4 shows a comparison between voltammograms of flint glass melts containing  $\text{SO}_3$  and 6% BFS. Although the peak current shows a strong dependence on the sulfur concentration, the peaks observed in the voltammogram of the melt containing the BFS are located at similar potentials, about  $-522$  mV and  $-355$  mV, to those of sodium sulfate. In order to examine the influence of other polyvalent ions existing in the BFS on both peak potentials, SWV measurements of glass melts containing 0.0131 wt%  $\text{Fe}_2\text{O}_3$ , 0.0122 wt% MnO and 0.0268 wt%  $\text{TiO}_2$  corresponding to 6% BFS were conducted as shown in Fig. 5. In voltammograms 2, 3 and 4, no characteristic peaks were observed. Therefore, peaks observed in voltammogram 1 of glass melt containing BFS are caused by reaction of sulfur only. These results indicate that sulfide compound of BFS behaves the same as that of sodium sulfate during the batch melting process.

## Conclusions

Square wave voltammetry measurements were carried out in flint glass melts containing sulfate and sulfide. Two peaks were shown at high frequency and low temperature in voltammograms of melts containing the sulfate. Based on the linearity of the plot for  $I_p$  versus  $\tau^{-1/2}$  in the present study and some results in the cited literature [11] it can be concluded that the first peak is only due to reduction of  $\text{S}^{4+}$  to  $\text{S}^0$ . In the voltammograms of melts containing sulfide, the location of peaks was very similar to that of melts containing sulfate. Therefore, it is concluded that the sulfide contained in BFS shows the same behavior as the sulfate during a batch melting process.

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