

Redox Equilibrium of Antimony by Square Wave Voltammetry Method in CRT Display Glass Melts

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ABSTRACT

Fining and homogenization of melts during batch melting is closely related to the redox reaction of polyvalent element M (M: Sb, As etc), $M^{(x+n)+} + n/2O^{2-} \rightarrow M^{x+} + n/4O_2$. In this study, square wave voltammetry (SWV) measurements were performed to examine the redox behavior of an antimony ion in cathode ray tube (CRT) glass melts. According to results, well-separated two peaks are shown at low temperature while only one peak is shown at high temperature in voltammograms, which reveals that redox reaction of antimony consist of two steps: Sb^{5+}/Sb^{3+} and Sb^{3+}/Sb^0 , depending on the temperature. Based on the peak potential shown in the voltammogram, the thermodynamic data and the redox ratio for two redox couple were determined.

Key words : Fining, Redox reaction, Square wave voltammetry, Voltammogram, Thermodynamic data, Redox ratio

1. Introduction

Most fining chemical agents are polyvalent ion and undergo redox reactions through which an electron transfer from one polyvalent species to another occurs. This redox equilibrium state is very much involved with many physical properties of the melt as well as the final product. Fining behavior through redox reactions has been studied qualitatively and quantitatively using a voltammetric method.¹⁻⁷ In particular, Russel *et al.* investigated the redox behavior of various multivalent ions including antimony in simple ternary soda-lime silica^{1,3,6} and alkali borosilicate melts^{6,7} using square wave voltammetry (SWV). They suggested that in the resulting voltammogram, well-separated peaks are observed that were related to two reduction steps, Sb^{5+}/Sb^{3+} and Sb^{3+}/Sb^0 .

The chemical fining is highly important in the manufacture of cathode ray tube (CRT) glasses consisting of mixed alkali-mixed alkaline earth-silica because the glasses as a component of the display device permit virtually no bubble. Antimony oxide is one of the most frequently used chemical fining agents in the CRT glass industry. Thus far, there have been no voltammetric studies on CRT glass melts. Most studies have been carried out in primarily with soda-lime-silica and alkali-borosilicate glass melts. In the present work, the redox behavior of antimony was investigated in CRT model glass melts by SWV.

2. Redox Reaction and Square Wave Voltammetry (SWV)

SWV is one of the pulse technique in electrochemistry and directly related to the determination of redox-reaction equilibrium constants in glass melts containing various polyvalent ions. SWV is used for measurements of current-potential curves under potential control i.e., a definite potential that varies with time (for example, a step-like pulse) is applied to a working electrode of an electrochemical cell relative to a reference electrode, and the resulting current is registered at the counter electrode. The resulting current-potential curve is termed a voltammogram, as shown in Fig. 1. It provides valuable information regarding the behavior of the redox species. For example, in the δi -curve a maximum peak δi_{max} appears at the half-wave potential ($E_{1/2}$). Under several assumptions, the height of this current peak is given by⁸⁾

$$\delta i_{max} = \frac{0.3n^2 F^2 A C_{ox} \Delta E_p}{R_g T} \sqrt{\frac{D_{ox}}{\pi \cdot 1/2 t_p}} \quad (1)$$

In the equation, A represents the surface area of working electrode, C_{ox} denotes the concentration of oxidized ion at the initial potential, t_p is the pulse time, n is the amount of electron transferred, D_{ox} is the diffusion coefficient of oxidized ion, F is the Faraday constant, and ΔE_p is the step potential.

For SWV measurements, a three-electrode system was used, as shown in Fig. 2. A platinum plate (3) and wire (1) were used as a counter electrode and a working electrode, respectively. Another platinum wire (2) termed a reference electrode, was connected with an O^{2-} conducting Y_2O_3 -stabilized ZrO_2 (YSZ) material,⁹⁾ which was in contact with melts

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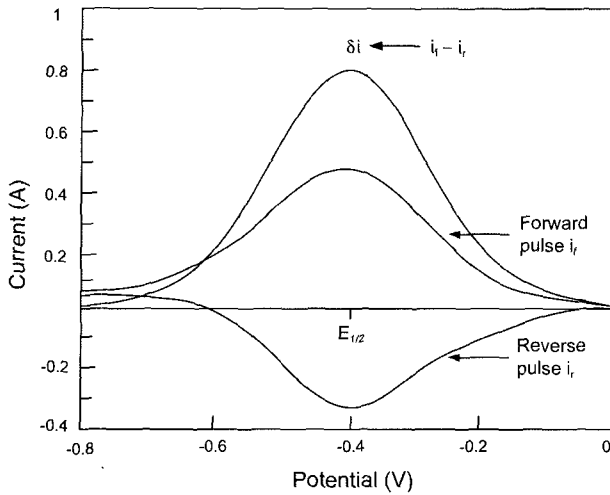


Fig. 1. An arbitrary voltammogram for a redox reaction with a half-wave potential of -400 mV with regard to the reference electrode.

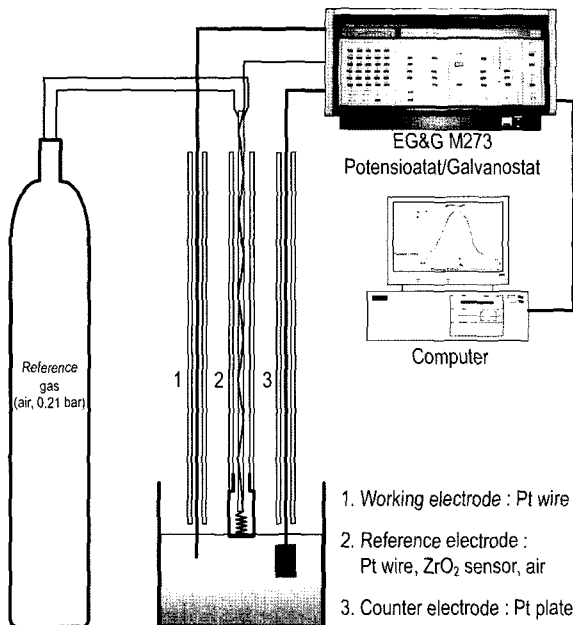
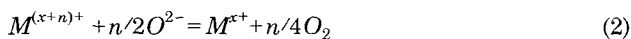


Fig. 2. Three-electrode system for square-wave voltammetry measurements.

and flushed by reference air with a known oxygen partial pressure (P_{rO_2} : 0.21 bar) during the SWV experiment. The varying potential E was applied between the working and the reference electrodes, while an electrical current accompanied by this potential flowed between the working and the counter electrodes. This current was primarily caused by the redox reactions in the electrolyte if the potential difference was sufficient to allow an electron donation or acceptance. The redox reaction of a polyvalent ion in CRT glass melts proceeds as follows:



Here, M is a polyvalent ion (Sb, Ce, As etc), n is the number

of electrons transferred from one valence state of M to another. Electrons are provided or occupied by oxygen during the reaction. The resulting voltammogram reveals a characteristic peak current (δi_{max}) at $E_{1/2}$ known as the half-wave potential. The equilibrium constant at temperature T of the reaction (2), $K(T)$ can be simplified, with a small number of assumptions, to Eq. (3).

$$K(T) = \frac{[M^{x+}] \cdot P_{O_2}^{n/4}}{[M^{(x+n)^+}]} = \exp\left[\frac{n \cdot F \cdot E_{1/2}}{R_g \cdot T}\right] \quad (3)$$

Here, P_{O_2} represents the oxygen equilibrium pressure between the reference and working electrodes before application of the artificial potential, F is the Faraday constant and R_g is the gas constant. Modification of Eq. (3) using the relationship $K(T) = \exp\left[\frac{-\Delta H}{R_g T} + \frac{\Delta S}{R_g}\right]$ allows the following Eq. (4):

$$\ln K(T) = \frac{-\Delta H}{R_g T} + \frac{\Delta S}{R_g} = \frac{n \cdot F \cdot E_{1/2}}{R_g \cdot T} \quad (4)$$

The redox reaction enthalpy (ΔH) and entropy (ΔS) at T are calculated from the slope and interception derived by plotting $\ln K$ versus $1/T$.

$$\Delta H = R_g \left\{ \frac{\delta \ln K(T)}{\delta T} \right\} \quad (5)$$

$$\Delta S = R_g \left\{ \frac{1}{T} \cdot \frac{\delta \ln K(T)}{\delta T} + \ln K(T) \right\} \quad (6)$$

If P_{O_2} in the glass melts is different from P_{rO_2} before applying the artificial potential, a potential difference (ΔE_m) between the reference and working electrodes arises, and it is expressed as the following Nernst equation:

$$\Delta E_m = \frac{R_g \cdot T}{4F} \ln \frac{P_{O_2}}{P_{rO_2}} \quad \text{or} \quad P_{O_2} = P_{rO_2} \cdot \exp\left[\frac{4 \cdot F \cdot \Delta E_m}{R_g \cdot T}\right] \quad (7)$$

If P_{O_2} in Eq. (3) is replaced by Eq. (7), the redox ratio is also calculated from $E_{1/2}$ and ΔE_m as follows:

$$\frac{[M^{x+}]}{[M^{(x+n)^+}]} = \frac{1}{P_{O_2}^{n/4}} \exp\left[\frac{n \cdot F \cdot E_{1/2}}{R_g \cdot T}\right] = \frac{1}{P_{rO_2}^{n/4}} \exp\left[\frac{n \cdot F \cdot \left(E_{1/2} - \frac{4}{n} \Delta E_m\right)}{R_g T}\right] \quad (8)$$

3. Experimental Procedure

3.1. Glass Preparation

The composition of CRT model glass is $74.5SiO_2 \cdot 1.4Al_2O_3 \cdot 10RO \cdot 14R'_2O$, in which R is Sr and Ba and R' is Na and K in mol%. $0.07Sb_2O_5$ was added as a fining agent. High-purity raw materials were used to exclude the effect of multivalent impurities. Approximately 300 g of the batch was melted at $1500^\circ C$ in a platinum crucible for 2 h, and the bubble-free melts were homogenized by stirring using a Pt/Rh rod and transferred to another electric furnace. While the prepared melts were maintained at $1400^\circ C$ in the fur-

nance, the electrodes of an electrochemical cell were dipped into the melts to perform the SWV measurement. To exclude the influence of the glass matrix on the SWV measurements, a blank glass containing no antimony was also prepared.

3.2. SWV Measurements

An electrochemical cell consists of three electrodes that are immersed into glass melts, as shown in Fig. 2. The furnace was heated to 1400°C and three electrodes were subsequently lowered until the reference electrode made slight contact with the melt, the counter electrode was completely submerged and the working electrode was approximately 1 cm into the glass melt. It was very important that the dip-in length during the measurements of the blank melts was identical to the melts containing the polyvalent ion, as the peak height in a voltammogram is linearly proportional to the dip-in length of the working electrode, as indicated in Eq. (1). Under this careful treatment of electrodes, the measured voltammogram of the blank melts is subtracted from that of the melt containing antimony, resulting in a final voltammogram with peaks caused only by the polyvalent ion of interest.

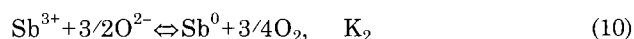
During SWV measurements, the furnace was switched off to avoid disturbance of the measured signal by the current in the heating elements. However, the glass melt did not cool quickly due to its higher heat capacity, although the temperature of the furnace will cool by nearly 25°C during the measurement. The set-up of the SWV measurements was fixed, as follows, and the measurements were performed at a temperature range of 1400°C to 800°C.

- Initial potential E_i : 0 V
- Final potential E_{end} : -0.8 V
- The frequency: 100 Hz
- The height of the potential pulse of ΔE_b : 0.002 V and ΔE_p : 0.1 V

4. Results and Discussion

Fig. 3(a) shows a voltammogram of a melt doped with Sb_2O_5 . The curves in the temperature range 1400-1100°C show one peak. However, at 1000°C, an occurrence of a new peak is shown, and finally at 900°C two well-separated peaks were found, as shown in Fig. 3(b), where the original peak exists at -318 mV and the other new one at nearly -76 mV.

The voltammogram suggests that the antimony undergoes two different reaction steps with equilibrium constants K_1 and K_2 , as follows:



At temperatures above 1100°C, only one peak exists in the voltammogram. A comparison with the theoretical curve for a three-electron transfer indicates that the curves in Fig.

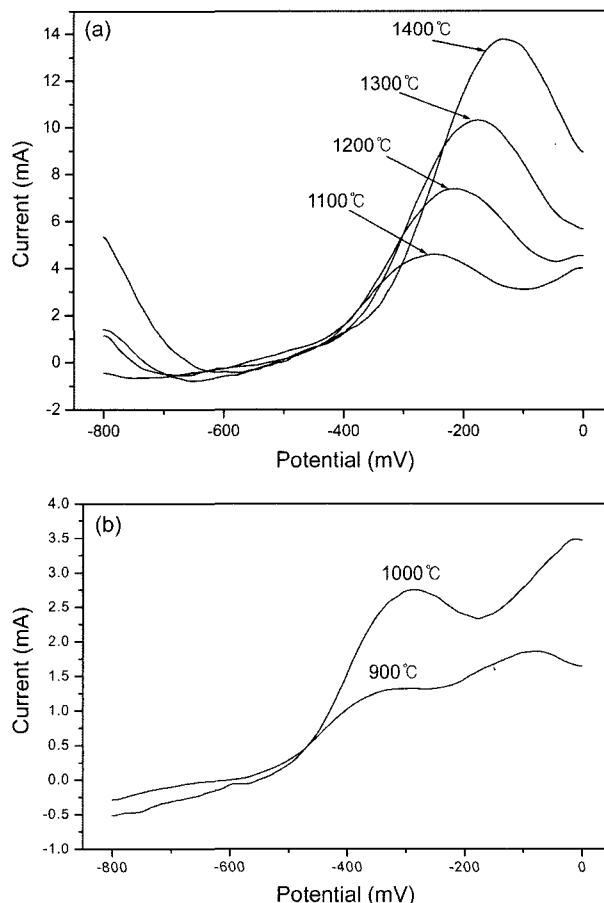


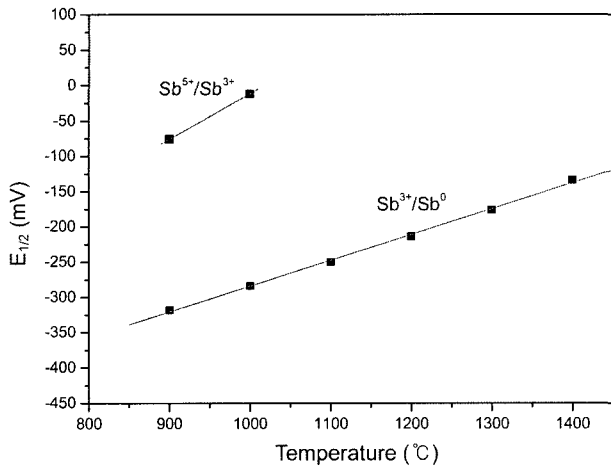
Fig. 3. Voltammogram of a CRT glass melt doped with 0.07 mol% Sb_2O_5 in a temperature range of 1400°C to 900°C.

3(a) are in good agreement with the theoretical curves. According to Russel^{1,6)} this peak is due to the reduction of Sb^{3+} to Sb^0 , as described in reaction (10). The peak related to reaction (9) is positioned at positive potentials to those temperature levels; consequently it is not shown in the voltammogram, whereas at temperatures lower than 1000°C, the second peaks become more visible because the half-wave potential is positioned in the applied potential region. Considering the fitting results,¹⁾ the second peak is caused by the reduction of Sb^{5+} to Sb^{3+} .

Table 1 shows the half-wave potential values for the present glass melts containing antimony. As shown in Table 1, the half-wave potential value of the Sb^{3+}/Sb^0 reaction shifts in a negative direction as the temperature decreases, indicating that the equilibrium state of reaction (10) shifts toward the left. Therefore, at a low temperature it is more apt to exist in the form of a higher valence state. On the other hand, with the increase in temperature, a reduced state is favored. In all temperature ranges, the half-wave potential for reaction (10) shifts more in a negative direction compared to that of reaction (9), indicating that a larger negative potential is needed in reaction (10) to be sufficient to convert the oxidized state to a reduced state.

Table 1. Half-Wave Potentials Measured in a Glass Melt Containing Sb_2O_5

	Half-wave potential ($E_{1/2}$, mV)	
	$\text{Sb}^{3+} \rightarrow \text{Sb}^0$	$\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$
1400°C	-134	
1300°C	-176	
1200°C	-214	
1100°C	-250	
1000°C	-284	-12
900°C	-318	-76

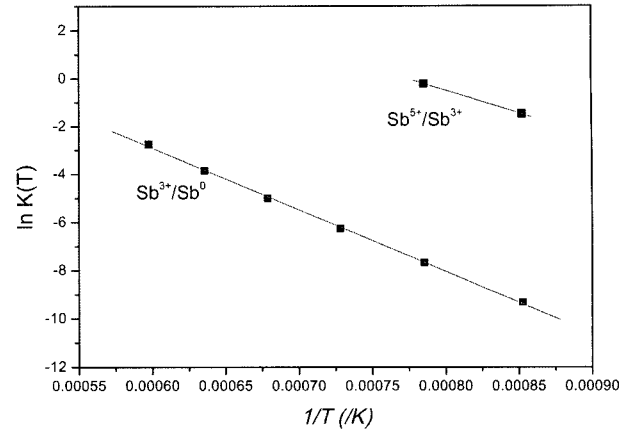
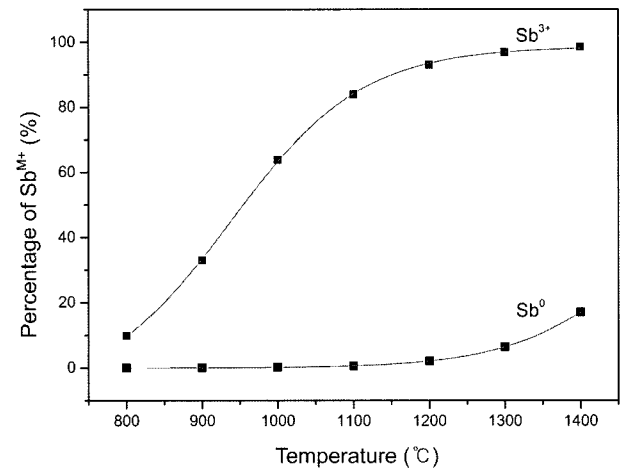
**Fig. 4.** Experimental plot of the half-wave potential ($E_{1/2}$) as function of temperature.

In Fig. 4, the half-wave potential ($E_{1/2}$) in Table 1 is plotted as a function of the temperature. The temperature dependence in both cases shows good linearity, which indicates that reaction enthalpy and entropy are temperature independent in the relevant temperature range. The plotting of $\ln K(T)$ versus $1/T$ presents also a linear relationship, as shown in Fig. 5. The calculated standard enthalpy (ΔH) and standard entropy (ΔS) of reactions (9) and (10) based on Eqs. (5) and (6) are summarized in Table 2 with those of soda-lime silicate and alkali borosilicate melts.^{6,7)}

The redox ratio in glass melts was calculated using the following modification of Eq. (8) under the assumption that the melt is equilibrated with air (0.21 bar), specifically $\Delta E_m = 0$ and that the relationship for $\text{Sb}^{5+}/\text{Sb}^{3+}$ in Fig. 5 is extrapolated linearly.

Table 2. The Standard Enthalpy (ΔH) and Entropy (ΔS) for Reduction of Sb^{3+} to Sb^0 and Sb^{5+} to Sb^{3+} in CRT, Soda-Lime Silica (SLS)⁶⁾ and Alkali Borosilicate (ABS)⁶⁾ Glass Melts

	CRT		SLS*		ABS**	
	$\text{Sb}^{3+} \rightarrow \text{Sb}^0$	$\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$	$\text{Sb}^{3+} \rightarrow \text{Sb}^0$	$\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$	$\text{Sb}^{3+} \rightarrow \text{Sb}^0$	$\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$
ΔH (kJ/mol)	213	157	244	286	291	207
ΔS (J/mol·K)	103	122	120	206	127	147

*74SiO₂16Na₂O10CaO**57SiO₂12B₂O₃17Na₂O11Li₂O3MgO**Fig. 5.** Experimental plot of the equilibrium constant ($\ln K$) as function of the reciprocal temperature.**Fig. 6.** Percentage of Sb^{3+} and Sb^0 as function of temperature based on Eqs. (11) and (12).

$$\% \text{Sb}^{3+} = 100x \frac{[\text{Sb}^{3+}]}{[\text{Sb}^{3+}] + [\text{Sb}^{5+}]} = 100x \frac{K_1(T)}{K_1(T) + 0.21^{1/2}} \quad (11)$$

$$\% \text{Sb}^0 = 100x \frac{[\text{Sb}^0]}{[\text{Sb}^0] + [\text{Sb}^{3+}]} = 100x \frac{K_2(T)}{K_2(T) + 0.21^{3/4}} \quad (12)$$

Fig. 6 shows the percentages of Sb^{3+} and Sb^0 . The percentage of antimony in the Sb^{3+} state varies from 63% at 1000°C to 98% at 1400°C. Even if there is a slight numerical error, the percentage of the reduced antimony Sb^{3+} increases as

the temperature increases. The total concentration of antimony must be, however, a sum of Sb^{5+} , Sb^{3+} , and metallic antimony (Sb^0). As the temperature increases, the concentration of Sb^{5+} decreases while the concentration of metallic antimony increases up to only 13%. However, the existence of metallic antimony (which causes a defect in glass products) is scarcely found in the industrial melts, as the production is a non-equilibrium process. Through the results of the calculated redox ratio in Fig. 6, it was confirmed that reaction (9) is dominant at high temperatures and contributes strongly to the fining of the melts.

5. Summary

Square wave voltammetry (SWV) measurements were performed for CRT glass melts containing Sb_2O_5 . Two well-separated peaks were shown at low temperatures while only one peak appeared at a high temperature in voltammograms. This reveals that the redox reaction of antimony is composed of two different steps depending on the temperature. The thermodynamic data for each step are $\Delta H=157$ kJ/mole, $\Delta S=122$ J/mole·K for $\text{Sb}^{5+}/\text{Sb}^{3+}$ and $\Delta H=213$ kJ/mole, $\Delta S=103$ J/mole·K for $\text{Sb}^{3+}/\text{Sb}^0$. The antimony percentage in the Sb^{3+} state varies from 63% at 1000°C to 98% at 1400°C. Based on the results of the redox ratio, it is confirmed that the fining in the CRT glass melts was mostly due to the reduction reaction of Sb^{5+} to Sb^{3+} .

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