Potential Sweep Voltammetry of Na₂O-SiO₂ Glass Melt by Stationary Platinum Electrodes*

Taketsugu HIRAI, Katsuaki TAKAHASHI**

Department of Synthetics Chemistry

(Received March 15, 1968)

Potential sweep voltammetries of $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$ at $730-1200°C$ were performed with the stationary platinum wire electrode and with the sweep rates of 40 and 120 mV/sec. Although current-potential relation of $Na_2O \cdot SiO_2$ at 1200°C gave stationary S-shape pattern, those of the rest were transient modes with hysteresis. From the voltammetric considerations, a reversible oxygen electrode process where diffuion of free oxygen anion or silicate anion may be a rate-determining stage was tentatively proposed. Approximate estimations of decomposition voltage supported that a sole reaction process such as the decomposition of Na_2O or indirect decomposition of SiO_2 in the melt was most probable.

§ 1. Introduction

Voltammetry, in which current (i)-potential (E) relations during electrolysis are determined, is an essential and fundamental procedure in electrochemical and electroanalytical studies. Because both stationary (time independent) and transient (time dependent) voltammetric techniques can be applicable to an electrolytic cell where mass transfer mode is controlled by sole or mixed process of diffusion, migration, convection, charge transfer or adsorption, the discussion of voltammetry requires a clear and quantitative understanding of mass transfer process. Well-known polarography, which is a form of stationary voltammetry with dropping mercury electrode, is based on the fact that, during electrolysis, the limiting current depends on the concentration of the solution. In accordance with the improvement in fused salt polarography using solid electrode, several polarographic investigations on various transition metals in molten silicates as the supporting electrolyte have

been performed by Lyalikov,[1] Delimarskii[2] and Baak,[3] and made clear the concentrations and valence states of metal oxides in the melt. On the contrary, recently quasi-steady state and transient voltammetries with linearly changing potential, namely "potential sweep method" have been highly developed in response to the remarkable improvement in electronic devices for electrochemical studies. This method is characterized by a wide availability and high sensitibity for some kinds of mass transfer modes under the adequate experimental conditions. On the other side, our preceding work[4] concerning decomposition voltage of Na_2O-SiO_2 system by commutator technique indidated that observed values contained some irreversible polarization such as concentration polarization in addition to reversible electromotive force. Therefore, voltammetry of alkalisilicate itself, in which current is carried completely by alkali cations, would be expected to be available for investigations on the diffusive behaviors of free oxygen anions or silicate anions and further on electrode processes of sodium cations in the melt. The present paper contains the result of several voltammetries of both sodium monosilicates and disilicates with stationary platinum wire electrode, and with comparatively

slow potential sweep such as the rates used in conventional polarography.

§2. Experimental procedure

a) Sample glass used $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$ sample glass was prepared from sodium carbonate (chemical reagent grade) and silica sand (99.8% purity). An uniform mixture of dry reagents was melted at 1200°C until well fined, quenched in air on the stainless steel plate, and crushed.

b) Apparatus and procedure i-E curves were determined using both conventional potentiostat and auxiliary electronic equipments of ultra-low frequency triangular wave generator, cathode-ray oscilloscope and electronic voltage recorder. In Fg. 1 is shown the schematic arrangement of these equipments, electrolytic cell and furnace. In the figure, electrolytic cell consists of platinum crucible as container, sample glass melt as electrolyte and three same smooth platinum wires (0.4 mm in diameter) designated as test electrode (T), counter electrode (C) and reference electrode (R) respectively. These three platinum

wires, covered with fine ceramic tubes separately except each end of about 1 cm in length, were inserted into a larger ceramic tube and fixed tightly with alumina cement adhesives. Electrode configuration was shown schematically in Fig. 1, where ohmic loss between T and R electrodes is intended to be minimized. Here R electrode is expected to act as an oxygen electrode. Potentiostat with current capacity of 150 mA supplies extermally programmed potential across T and R electrodes. Output of ultra-low frequency triangular wave generator with frequency range of $10^{-3} - 10^3$ c/s is electrically connected with auxiliary terminals named externally setting terminals on the potentiostat through the manual change-over switch. Cathode-ray oscilloscope, conventional type synchroscope, is used to monitor the wave form and to set a time when externally programmed triangular wave is introduced to potentiostat. Electronic voltage recorder gives the electrolytic current through T and C electrodes.

The order of experimental procedure is as follows: Platinum crucible containing sample cullet is heated in the furnace to 1200°C or more where no volatilization substantially occurs, followed by inserting assembled platinum wire electrodes vertically into the melt to a certain depth, determined experimentally as mentioned below, along the vertical steel guide attached to the furnace wall. After the cell is allowed to cool to a given temperature, it is checked that the spontaneous potential across T and R electrodes is to be essentially zero by manipulating the knob of the rest potential reading. Then monitoring the triangular wave form on the Braun tube of the oscilloscope, half cycle of the wave having given frequency and magnitude in peak-to-peak voltage was introduced to the potentiostat by the timely change-over of the switch. The potential sweep rates of 40 and 120 mV/sec used in this experiment, corresponded to the operation in the frequency of 0.0033 and 0.01 c/s respectively for the same peak-to-peak voltage of 6V. At the same time, time dependence of electrolytic current through T and C electrodes was observed by the recorder. Because elapsed time is

T : Test electrode

C : Counter electrode

R : Reference electrode

Electrode configuration.

PC : Platinum crucible

G : Glass melt

E : Platinum wire electrode

C : Ceramic tube

PS : Potentiostat

U : Ultra-low frequency
   triangular wave generator

S : Manual change-over switch

CRO : Cathode-ray oscilloscope

R : Electronic voltage recorder

TC : Thermocouple

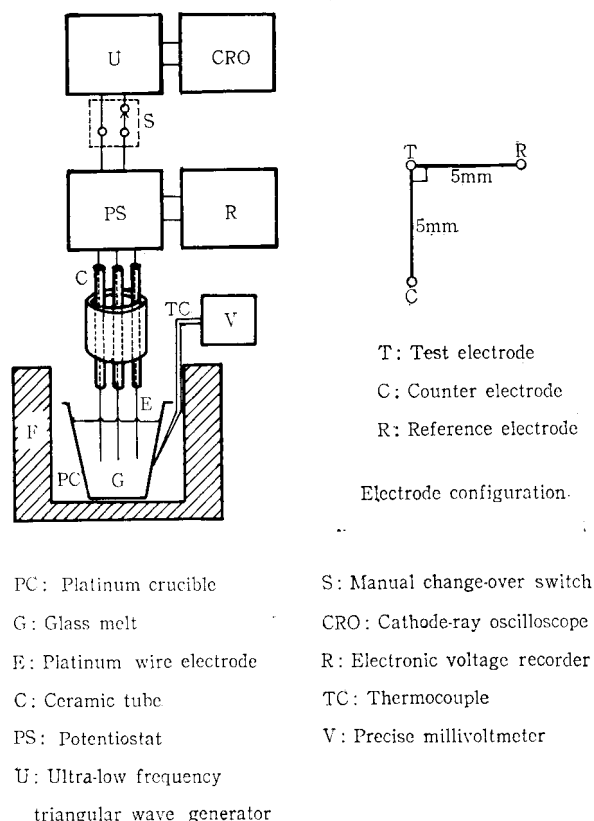V : Precise millivoltmeter

Fig. 1 Schematic representation of the measuring apparatus

directly proportional to the applied potential, voltammetry with linearly changing potential, in other words, i-E curve by potential sweep method was finally obtained from above i-t curve. Appropriate operation below the current capacity of the potentiostat can be attained by adjusting the immersion depth of platinum electrodes. Experiments were conducted by the following combined conditions, i. e., sample glasses of $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$, potential sweep rates of 40 and 120 mV/ sec and temperatures of 730, 840, 980 and 1200°C.

§ 3. Experimental result

In the couse of the experiments was there found the deposition of dark grey substance on the T electrode after cathodic half cycle sweep as well as on C electrode after anodic same sweep, and innermost melt layers adjacent to these electrodes were also faintly contaminated in foggy state. These deposits may be recognized as metallic silicon or further alloy of Pt-Si from the analogous feature in the preceding work.[4] As a result, each experiments were carried out by using fresh platinum wire electrodes except R electrode. In Fig. 2 and 3 are shown summarily typical i-E curves of $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$ at 840 and

1200°C. In the figures, effect of potential sweep rates was omitted due to the less difference in the patterns as compared with the reproducibility in the same repeated experiments. The patterns at 980°C were almost same as those at 840°C. The patterns at 730°C were fairly obscure because of the less sensitivity of the recorder. In Fig. 2 only i-E curve of $Na_2O \cdot SiO_2$ at 1200°C showed polarographic stationary S-shape pattern with a slight maximum wave, but the rest curves showed transient patterns with hysteresis, having one anodic peak in the latter half respectively. Wholly same tendency was detected in the case of cathodic half cycle sweep as shown in Fig. 3, although the shape of each cathodic peak in the first half of the half cycle sweep becomes generally more sharp. Thus voltammetry of relatively high Na_2O content sample at higher temperature transfers to stationary mode from transient one.

§ 4. Discussion

Recently Gileadi[5] predicted that the slow method with sweep rates in the range of 1-100 mV/sec is a quasi-steady state method and aim of such measurements is to evaluate the steady state mechanism of the reaction concerned. Therefore, if now interesting reaction
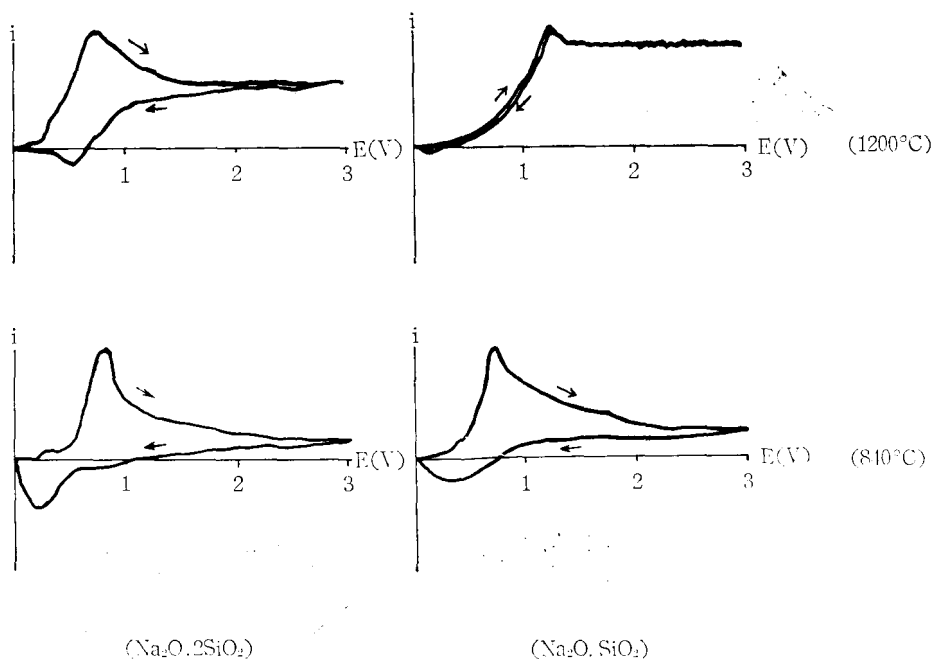

$(Na_2O.2SiO_2)$ $(Na_2O.SiO_2)$

Fig. 2 Anodic voltagrams of the Pt|Na₂O·SiO₂ and Pt|Na₂O·2SiO₂ half-cell systems at 840°C and 1200°C
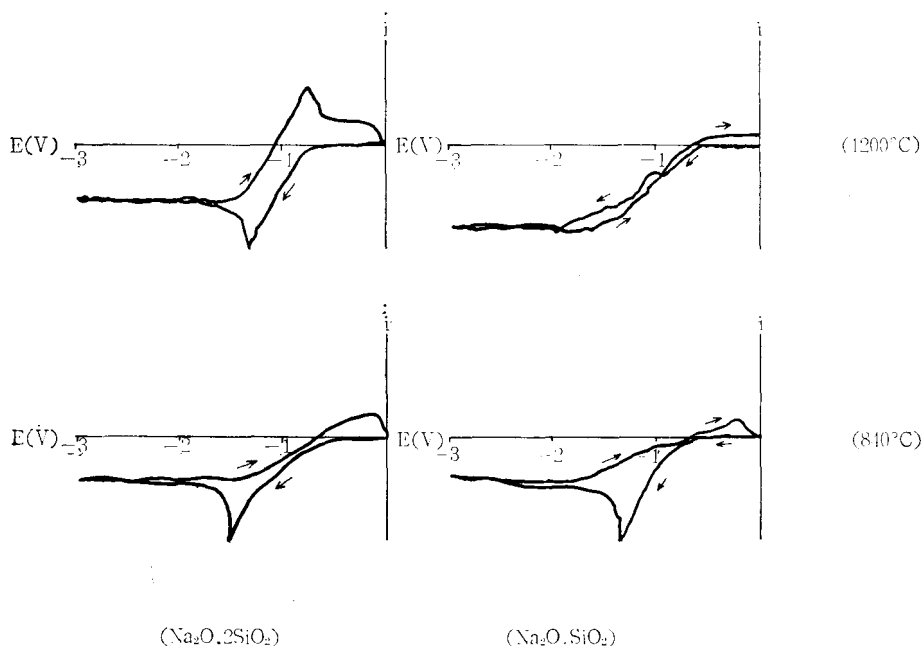
Fig. 3   Cathodic voltagrams of the Pt|Na$_2$O·SiO$_2$ and Pt|Na$_2$O·2SiO$_2$ half-cell systems at 840°C and 1200°C

is partially or completely controlled by diffusion, the corresponding theory given by Delahay as well as that in polarography would be available to evaluate above experimental results.

In the anodic sweep, free oxygen anion or silicate anion, which participates oxygen electrode reaction, may move under the diffusion-controlled mode, because sodium ion, a major charge carrier in the melt, acts as the supporting electrolyte. Now S-shape i-E relation obtained experimentally in the anodic sweep of Na$_2$O·SiO$_2$ at 1200°C is satisfied by either of following two equations, namely

$$E = {}_r E_{1/2} + \frac{RT}{nF} \ln \frac{(i_a - i)}{i}$$

(reversible process)   (1)

$$E = {}_{ir} E_{1/2} + \frac{RT}{\beta nF} \ln \frac{(i_a - i)}{i}$$

(totally irreversible process)   (2)

E: potential
${}_r E_{1/2}$, ${}_{ir} E_{1/2}$: half-wave potentials for reversible and irreversible process respectively
i: current
i_a: limiting current
T: absolute temperature
R: gas constant

F: Faraday's constant
n: number of electrons involved in electrode process
β: transfer coefficient

As above equations are of same form, n for reversible process or βn for totally irreversible process is easily calculated from the gradient of E-$\ln (i_a - i)/i$ plot as shown in Fig. 4. But
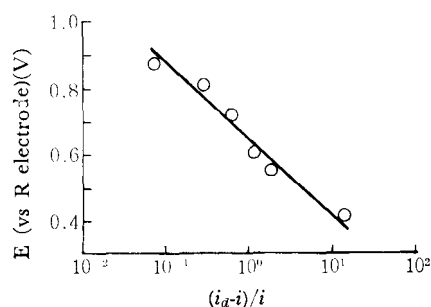

Fig. 4 E-$\ln (i_a$-$i)/i$ plot of Pt|Na$_2$O · SiO$_2$ half-cell system at 1200°C

these experimental values were extremely less in reproducibility. For example, several values between 2.5 and 1.2 were obtained as shown in Table 1. Taking round number of 2 for n, a reversible oxygen electrode, where diffusion of oxygen or silicate anion is a rate-determining stage, may be proposed. On the contrary, for the irreversible process further discussion is

Table 1 *n* or *βn* values of the several half-cell systems.

Sample Glass (mole %)	Temperature (°C)	*n* or *βn*
50 Na₂O·50 SiO₂	1200	1.3
40 Na₂O·60 SiO₂	1070	1.8
40 Na₂O·60 SiO₂	950	1.3
35 Na₂O·65 SiO₂	1280	1.9
35 Na₂O·65 SiO₂	1280	1.2
35 Na₂O·65 SiO₂	1250	1.7
33 Na₂O·67 SiO₂	1250	2.4

impossible for lack of β value. It should be noted, however, that obrerved half-wave potential $_{ir}E_{1/2}$ is more anodic than $_rE_{1/2}$. Thus oxygen electrode reaction of Na₂O · SiO₂ at 1200°C would be explained as a reversible or an irreversible process having n or βn of 2 and $_rE_{1/2}$ or $_{ir}E_{1/2}$ of approx. +0.5V vs R electrode respectively. In the same manner, whole transient i-E relations having on peak in current may also be explained as the diffusion-controlled process. The potential E_p corresponding to the maximum current is theoretically introduced by Randles,[6] Sevik[7] and Delahay.[8]

$$_rE_p = {}_rE_{1/2} + 1.1\frac{RT}{nF} \text{ (reversible process)} \tag{3}$$

$$_{ir}E_p = E_i + \frac{RT}{\beta nF}\left[Q + \frac{1}{2}\ln\frac{\beta nF}{RT}\,v \right]$$
(totally irreversible process) (4)

E_i : initial potential

v : rate of potential sweep

Q : constant

According to the equation (3) and (4) $_rE_p$ is $1.1\frac{RT}{nF}$ volt more anodic than the potential $_rE_{1/2}$, but quantitative comparison of $_{ir}E_p$ with $_{ir}E_{1/2}$ is obvously impossible. Thus observed peak potential E_p of approx. +0.5V vs R ele-

ctrode may be slightly more anodic than $_rE_{1/2}$ for the reversible process.

In the cathodic sweep, i-E relataon of Na₂O ·SiO₂ at 1200°C was same S-shape pattern as shown in the anodic sweep and those of the rest were also transient patterns with hysteresis. But in this case it is obviously impossible to explain approximate value of −1.3V vs reference electrode as theoretical $E_{1/2}$ or E_p from the standpoint of the diffusion-controlled procees, because the sodium ions transfer by migration as well as by diffusion.

As a result, it was concluded that one anodic reaction and one cathodic reaction were detected in the electrolysis of the melt by stationary platinum electrode. Furthermore, the value of 1.8V, potential difference between anodic and cathodic values of $E_{1/2}$ or E_p, proposed that decomposition reaction of Na₂O or the indirect decomposition of SiO₂ in the melt was most probable, although they may be less in physical meaning.

Acknowledgement

References

1) Yu. S. Lyalikov, Zavodsk. Lab., **18**, (1952) 1070.

2) Yu. K. Delimarskii, S. S. Ognyanik, Zh. Neorgan. Khim., 7, (1962) 1757.

3) T. Baak, R. L. Frederick, J. Amer. Ceram. Soc., **50**, (1967) 38.

4) T. Hirai, Y. Miura, T. Yoshio, K. Takahashi, This Memoirs 2, (1967) 62.

5) S. Srinivasan, E. Gileadi, Electrochim. Acta, **11**, (1966) 321.

6) J. E. B. Randles, Trans Faraday Soc., **43**, (1948) 327.

7) A. Sevik, Collection Czechoslov. Chem. Communs., **13**, (1948) 349.

8) P. Delahay, J. Am. Chem. Soc. **75**, (1953) 1190.