Among redox pairs in borate and silicate melts, $\text{Pb}^{2+}/\text{Pb}^0$ is important; the reduced species are metallic and reactive with the Pt in the solid in linear sweep voltammetry. Since Pb metal is soluble in solid Pt, and any excess deposit of Pb over the solid solubility limit yields a liquid alloy on the electrode, the current-potential curve bends at that point. A computer simulation of the process confirmed this interpretation. The application of this technique seems quite valuable to compare the basicity of various melts. The effect of alumina on the basicity of sodium silicate melts is discussed.

INTRODUCTION
Linear sweep voltammetry has been applied to oxide melts for redox equilibrium measurements (1-4). The usefulness of this technique in spite of difficulties due to high operating temperature lies evidently in this direct measurement compared with chemical analyses of reduced and oxidized species in quenched melts. Thus, $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ equilibria in sodium borate melts were measured as functions of solvent basicity and temperature (3,4). In the course we met with the problem when the couple $\text{Pb}^{2+}/\text{Pb}^0$ was to be measured. The current-potential curve showed an abrupt bending and a large anodic peak which was characteristic of a system of the reduced species adsorbing on the electrode. In this report, the electrode process is discussed and the application to sodium aluminosilicate melts is described.

EXPERIMENTAL
Linear sweep voltammetry. The working electrode is a platinum wire of 0.4 mm diameter whose end has been coiled in order to provide a large surface area. This electrode is assumed to be reversible with respect to the reaction

$$\text{Pb}^{2+} + 2e = \text{Pb} \quad (1)$$

The current due to the unavoidable reaction

$$1/2\text{O}_2 + 2e = \text{O}_2^- \quad (2)$$

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at the gas-electrode-oxide melt coexisting phases was minimized and disregarded. The reference electrode is a folded platinum wire of 0.4 mm diameter and was positioned to just contact the melt surface. It is reversible with respect to the reaction (2). The platinum crucible functioned as the counter electrode. The measurement was carried out in pure oxygen.

**Sample melts.** The sample melts were prepared in the following procedure. Sodium, lead and aluminum nitrates of nominal compositions were dissolved in nitric acid, and ethyl silicate with ethanol is added. The latter was hydrolyzed by adding ammonium hydroxide solution. The resultant gel mixture was dried and heated to powder aggregate. It was finally melted in a platinum crucible, then the cell assembly was immersed. The content of lead oxide was fixed to one mole % in finally established runs.

**Experimental results.** Examples of the current-potential curves are shown in Fig.1. It is noted that the curves are quite different from those in ordinary redox couples. Thus, The cathodic current rises abruptly after being low and the anodic curve shows a large peak characteristic of adsorption of reduced species on the electrode.

**Computer simulation of l.s.v. process.** The mode of the voltammetry will be described as follows.

1. Before the bending point is reached, Pt-Pb solid solution is formed on the electrode. The current is very low because of the low diffusivity and the low concentration of Pb in the solid solution.
2. When the concentration of Pb reaches the solubility limit, a liquid metal phase starts to appear. The current increases because the diffusivity of Pb is quite high and Pt dissolves in the liquid keeping the activity of Pb constant at the solid-liquid boundary, and the current is governed by the diffusivity of Pb^{2+} in the oxide melt.
3. In the reverse sweep, a large cathode peak appears because the reduced species is concentrated near the electrode surface and because of the large diffusivity of Pb in the liquid alloy.
4. The current suddenly approaches zero when the liquid phase disappears.
5. The electrode reaction is reversible and Nernst equation gives the activity ratio at the electrode surface.

The computer simulation was carried out to solve the difference equation in place of the differential equation of Fick's 2nd law. The system is divided into sufficiently small parts (1×10^{-5} cm in the melt and 2×10^{-7} cm in the electrode) in the direction perpendicular to the electrode.
The concentration of each part is calculated at each time increment of $1 \times 10^{-5}$ sec. An example of the simulated current-potential curve is shown in the left part of Fig. 2. The agreement is satisfactory. Instead of the simplified Laplace transform method, where the concentration at the electrode surface is given, the concentration profile near the surface is visualized. The right side of Fig. 2 shows the concentration profiles at the times denoted on the voltammogram. Here the vertical axis is the concentration of Pb$^{2+}$ or of Pb in a conventional scale. The far right side of the figure shows those of the liquid alloy phase, whose height is much lowered for drawing convenience.

Fig. 2 shows that at the bending point the Pb$^{2+}$ concentration is not much lower than the original level (the straight line) and the Pb content in the liquid alloy is approximated by that in solid-liquid equilibrium of Pt-Pb system at the experimental temperature. The activity of lead in this system has been measured by Schwerdtfeger (5). Therefore, at the potential of the bending point, $E_{dep}$, the following reaction is in equilibrium,

$$\text{Pb}^{2+} + \frac{1}{2} \text{O}_2 = \text{Pb(liquid alloy)}$$  \hspace{1cm} (3)

where $\Delta G^0(3)$ is the standard free energy change of reaction (3). One must note that the standard state of the left hand side is not pure PbO, since $\text{O}_2^-$ here is the component of the solvent.

If the activity of Pb$^{2+}$ is a function of only the basicity of the solvent irrespective of the solvent component and if the basicity is properly expressed by the activity of Na$_2$O, $E_{dep}$ will be a function of the latter. Fig. 3 shows an example of the potential in silicate and aluminosilicate melts, where alumina content ranged 5 to 15 mole %. The activity of Na$_2$O in these melts has been measured previously (6,7). Fig. 3 shows the above prediction is fulfilled. The experimental results including those of other redox pairs will be discussed in more detail.

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Figure 1. Linear sweep voltammogram in sodium aluminosilicate melts.

50 \( \left( \frac{1}{2} \text{Na}_2\text{O} \right) \cdot X \left( \frac{1}{2} \text{Al}_2\text{O}_3 \right) \cdot (50 - X) \text{SiO}_2 \)

1473 K
scan rate 0.4 (V/s)

- anodic current
- cathodic current

40 mA
-850 mV

\( X = 0 \)
\( X = 5 \)
\( X = 10 \)
\( X = 15 \)
Figure 2. Computer simulation of voltammogram and concentration profile
Figure 3. Potential at the bending point in sodium silicate and aluminosilicate melts as function of their basicity.