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Oxygen Pressure Dependence of Lead Ion Transport in PbO-SiO₂ Melts

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The diffusivity of lead in a PbO-SiO₂ melt was determined as a function of oxygen pressure from kinetic data for the oxidation of liquid lead covered by a layer of lead silicate melt which is short-circuited to facilitate electronic transport. The diffusivity-oxygen pressure relation thus obtained agreed well with the corresponding prediction based on definitions of the fluxes of Pb^{2+} and electron holes and an appropriate equilibrium relation.

TRANSPORT properties of crystalline substances frequently can be related to the point-defect structure of the solid. Therefore, predictable changes in the transport property of the components of such solids can be accomplished by either changing their chemical potentials or by adding dopants. Generally, the transport properties of a liquid phase are less amenable to point defect analysis since they are usually viewed as a continuum. The purpose of the present report is to demonstrate that for the PbO-SiO₂ melt the variation of diffusivity of lead with oxygen pressure can be explained by writing an appropriate model based on its nonstoichiometry.

Thermogravimetric experiments were conducted to determine the oxidation rate of a layer of liquid lead covered by a layer of molten lead silicate ($x_{PbO}=0.55$, $x_{SiO_2}=0.45$). It was found that the oxidation rate was inversely proportional to the thickness of the slag layer (Fig. 1). The foregoing observation indicated that the oxidation

process was diffusion-controlled.[1,2] The transport of lead ions in such a system is accompanied by the motion of electron holes in the opposite direction maintaining electrical neutrality,[3,4] as depicted schematically in Fig. 2.

The oxidation rate of liquid lead in such experiments was found to be very low. However, when Ir wires were used to short circuit the slag/gas and slag/metal interfaces the oxidation rate was observed to increase by an order of magnitude, as shown in Fig. 3. It is proposed that the Ir wire establishes a fast electronic transport $(t_3=1)^{3,4}$ and therefore increases the oxidation rate of lead. From Fig. 3 it is possible to determine the specific rate constant, k_r, as a function of P_{O_2} using the following expression:

$$(1/A)\,(dn/dt)=(k_r/x) \tag{1}$$

where dn/dt is the oxidation rate in electronic equivalents/s, A the slag/metal interface area in cm², and x the slag height in cm. The plot of k_r as a function of P_{O_2} is shown in Fig. 4.

Based on the present experimental

conditions, i.e. electronic short circuiting of the slag, the specific rate constant k_r can be expressed as[5]:

$$k_r=|Z_2|C_2\int_{a_2'}^{a_2''}\left(\frac{Z_1}{|Z_2|}D_1+D_2\right)\,d\ln a_2\,\Bigg|_{t_3=1} \tag{2}$$

where Z_i is the absolute charge, a_i the thermodynamic activity, D_i the self-diffusion coefficient in cm²/s, and C_i the concentration in terms of gram atoms/cc. The i values 1, 2, and 3 represent Pb^{2+}, O^{2-}, and electrons, respectively. The superscript single prime indicates the activity at the metal/oxide interface whereas the superscript double prime indicates the activity at the gas/oxide interface.

In most cases one of the ions has a much higher diffusivity than the other. Therefore in the present work it is assumed that $D_{Pb}(D_1)$ is $\gg D_2$. Thus, Eq. (2) can be written as:

$$k_r=|Z_2|C_2\int_{a_2'}^{a_2''}\left(\frac{Z_1D_{Pb}}{|Z_2|}\right)\,d\ln a_2 \tag{3}$$

Substituting $Z_1C_1=|Z_2|C_2$ and changing integration limits to oxygen pressures we have:

$$k_r=\frac{Z_1^2C_1}{2|Z_2|}\int_{P'_{O_2}}^{P''_{O_2}}D_{Pb}\,d\ln P_{O_2} \tag{4}$$

Differentiating k_r with respect to $\ln P_{O_2}$ in Eq. (4), we have:

$$\frac{dk_r}{d\ln P_{O_2}}=\frac{Z_1^2C_1}{2|Z_2|}D_{Pb} \tag{5}$$

Thus the slope of the plot of k_r versus $\ln P_{O_2}$ will be equal to the right-hand side expression of Eq. (5). Utilizing the slopes of the plot of k_r versus $\ln P_{O_2}$ (Fig. 4), the cationic diffusivity D_{Pb} as a function of P_{O_2} can be determined.

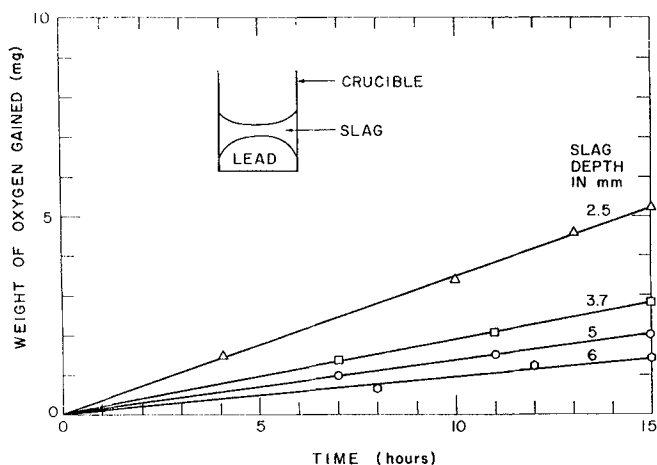The D_{Pb} values at $P_{O_2}=21.3$ KPa,

Fig. 1. Oxidation plots of liquid Pb covered by liquid slag ($x_{PbO}=0.55$, $x_{SiO_2}=0.45$) at 1173 K; partial pressure of oxygen=101 kPa.
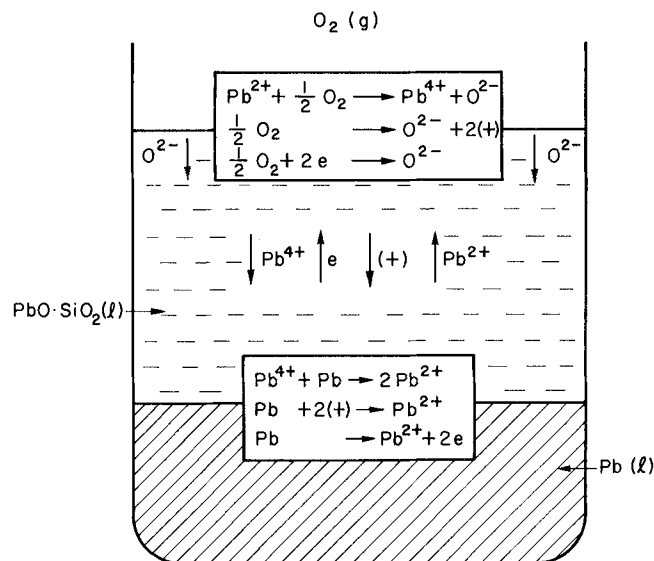

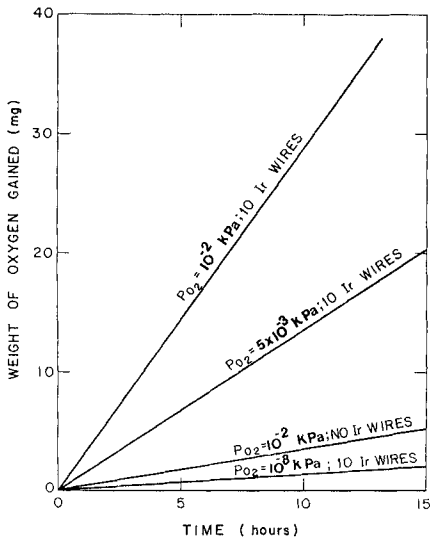Fig. 2. Conceptual model for oxidation of lead underlying liquid PbO-SiO₂ melt.

Fig. 3.   Oxidation plots at 1173 K of liquid lead covered by 2.5 mm slag ($x_{PbO}=0.55$, $x_{SiO_2}=0.45$), indicating the effect of short-circuiting slag/gas and slag/metal interfaces with Ir wires.

2.03 KPa, 5.06×10^{-3} KPa, and 2.02×10^{-7} KPa were calculated to be 3.36×10^{-7} cm^2/s, 1.50×10^{-7} cm^2/s, 2.82×10^{-8} cm^2/s, and 3.0×10^{-9} cm^2/s, respectively. The value of D_{Pb} obtained by Langanke and Schmalzried[6] for the slag of the same composition at $P_{O_2}=21.3$ KPa was 3.58×10^{-7} cm^2/s; this value agrees well with the corresponding value of $D_{Pb}=3.36\times10^{-7}$ cm^2/s obtained in the present work. The plot of ln D_{Pb} versus ln P_{O_2} was found to be a straight line, as shown in Fig. 5. From the slope of the plot in Fig. 5 it was found that $D_{Pb}\propto P_{O_2}^{1/4}$.
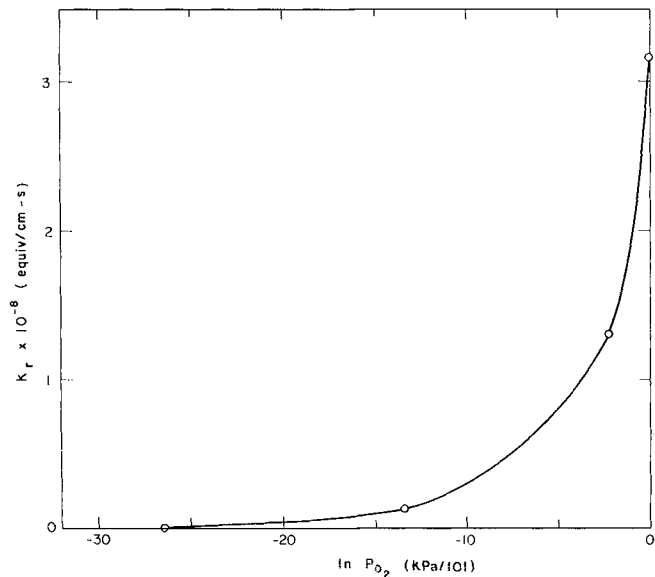
The aforementioned observation may be quantitatively interpreted by considering a mechanistic scheme for oxidation illustrated in Fig. 2. Note that the formation and transport of SiO_4^{4-} and its polymers are ignored since they contribute little to the transport of charge in the melt. It was demonstrated earlier[3] that of the possibilities depicted in Fig. 2, oxidation takes place by counter transport of holes (+) and Pb ions. The transport to Pb^{2+} ions can be quantified as:

$$J_{Pb^{2+}}=D_{Pb^{2+}}\Delta C_{Pb^{2+}}/L \qquad (6)$$

where $J_{Pb^{2+}}$, $D_{Pb^{2+}}$, and $\Delta C_{Pb^{2+}}$ are the flux, diffusivity, and the concentration difference (between the gas-slag and the slag-metal interface) of Pb^{2+} ions and L is the thickness of the slag layer. If the concentration of (+) at the slag-metal interface is assumed to be small, $J_{(+)}$ can be represented as:

$$J_{(+)}=kC_{(+)} \qquad (7)$$

where k is a constant and $C_{(+)}$ is the concentration of positive holes (+) at the slag-gas interface. At the gas-slag interface the chemical reaction is represented by:

$$\tfrac{1}{2}O_2=O^{2-}+2(+) \qquad (8)$$

$$k_{eq}=\frac{(a_{O^{2-}})(f_{(+)}C_{(+)})^2}{P_{O_2}^{1/2}} \qquad (9)$$

where $a_{O^{2-}}$ is the activity of O^{2-} ions in the melt and $f_{(+)}$ is the activity coefficient of positive holes (+) in the PbO-SiO$_2$ melt. Since the slag is electrically neutral:

$$2J_{Pb^{2+}}=J_{(+)} \qquad (10)$$

Rearranging Eqs. (6), (7), and (10) gives:

$$C_{(+)}=\frac{2D_{Pb^{2+}}\Delta C_{Pb^{2+}}}{kL} \qquad (11)$$

We now combine Eqs. (9) and (11) to obtain:

$$D_{Pb^{2+}}=\left(\frac{kk_{eq}^{1/2}L}{2f_{(+)}a_{O^{2-}}^{1/2}\Delta C_{Pb^{2+}}}\right)P_{O_2}^{1/4} \qquad (12)$$

When the slag-metal and slag-gas interfaces are electrically short circuited by means of Ir wires, k may be relatively high to yield high values of $J_{(+)}$ according to Eq. (7). However, if we assume k, $a_{O^{2-}}$ and $C_{Pb^{2+}}$ to be constants, we obtain $D_{Pb^{2+}}$ to be proportional to $P_{O_2}^{1/4}$. Our data indicate that the factor within the square bracket on the right-hand side of Eq. (12) is insensitive to changes in P_{O_2}.

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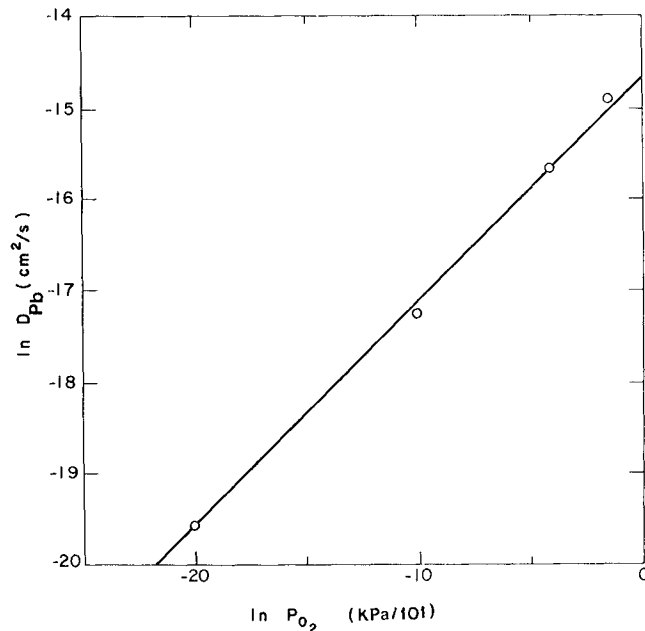

Fig. 4.   Variation of k_r as a function of P_{O_2} during oxidation of liquid lead covered with slag ($x_{PbO}=0.55$, $x_{SiO_2}=0.45$) at 1173 K.

Fig. 5.   Plot of ln p_{O_2} vs ln D_{Pb} in slag ($x_{PbO}=0.55$, $x_{SiO_2}=0.45$) at 1173 K.