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# Physical Chemistry

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## Abstract

## Full Text

## Physical Chemistry

**V. N. Boronenkov, O. A. Esin, P. M. Shurygin**

# Cathodic Processes at a Disk Electrode in Oxide Melts

*(Presented by Academician A. N. Frumkin, April 18, 1963)*

Polarization in molten silicates, in particular in metallurgical slags, usually has a concentration character. Quantitative interpretation of the results, however, is difficult, since convective diffusion to the electrodes is often not controlled. In this connection A. N. Frumkin ([1]) recommends using a rotating disk electrode ([2]). In recent years it has been used in the study of salts ([3],[4]). In our experiments the disk electrode was the end face of an iron wire tightly sheathed in a corundum tube. The reference electrode and the anode were made of the same wire, which made it possible to measure the polarization directly ($\eta$). The measurements were carried out by the commutator method ([5]) in a silite furnace at temperatures of 1300–1470°. Slags of two compositions were used as the supporting electrolyte: 40% CaO, 40% $SiO_2$, 20% $Al_2O_3$ (No. 1) and 49% CaO, 51% $Al_2O_3$ (No. 2). Iron oxide was added to them. Figure 1 shows polarization curves at different disk rotation speeds. The curves exhibit two reduction waves —at polarizations of 120–150 mV and 350 mV. Subsequently, the dependences of the current values at these polarizations on the cathode rotation speed were recorded. As can be seen from Fig. 2, the experimental results are described rather well by the formula of V. G. Levich ([2]):

$$i_{\text{pr}} = 0.62zFD^{2/3}\nu^{-1/6}\sqrt{\omega}C_0, \tag{1}$$

in which $z$ is the number of electrons in the elementary act, $D$ is the diffusion coefficient, $C_0$ is the bulk concentration of the ions discharged at the cathode, $\nu$ is the kinematic viscosity of the slag, and $\omega$ is the angular velocity of rotation of the disk. The appearance of two deposition waves in slag of similar composition was also noted in ([5]). There it was associated with two stages of reduction of trivalent iron ions:

$$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}, \tag{2}$$

$$\text{Fe}^{2+} + 2e \rightarrow \text{Fe}^{0}. \tag{3}$$

For the first of these to proceed with appreciable currents in our case, the presence of $Fe^{3+}$ ions near the iron cathode is necessary, which is unlikely. It is known that slags equilibrated with metallic iron practically do not contain $Fe^{3+}$ ions. The presence here of $Fe^{3+}$ cations is possible only for kinetic reasons, when the rate of the reaction

$$Fe^{3+} + Fe \rightarrow 2Fe^{2+} \tag{4}$$

is less than the rate of supply of $Fe^{3+}$ to the iron cathode ($^6$). But in the case of the kinetic regime of reaction (4), its rate will not depend on stirring of the slag. Experiments convince us of the opposite (Fig. 2). Thus, step (2) is not realized under our conditions, and the first reduction wave proves to be associated with process (3). The second step apparently corresponds to the discharge of silicon:

$$Si^{4+} + 4e \rightarrow Si^0 \tag{5}$$

or

$$Si^{4+} + 2e \rightarrow Si^{2+}. \tag{6}$$

Indeed, for slag (2), which contains no $SiO_2$, the polarization curve of the background (Fig. 3) does not have the characteristic break at $\eta = 230$ mV. Addition of $SiO_2$ up to 10% leads to the appearance of a current plateau (curve b). At the same time, $SiO_2$ increases the viscosity of the slag from 3 to 6 poise [8], owing to which a decrease in currents is observed.

**Fig. 1.** Polarization curves for slag No. 1, $t = 1400$°C.
*a*—background at $n = 60$ rpm, *b*—background at $n = 750$ rpm, *v*—with addition of 1% iron oxides at $n = 1200$ rpm.

**Fig. 2.** Dependence of the limiting current on the disk rotation rate and $\lg D$ on $1/T$ in slag No. 1 with addition of 2.88% $Fe_2O_3$ and 1.44% FeO;
$a$—$\eta = 150$ mV, $t = 1350°$; $b$—$\eta = 150$ mV, $t = 1400°$; $v$—$\eta = 150$ mV, $t = 1450°$; $g$—$\eta = 350$ mV, $t = 1400°$; $d$—$\lg D - 1/T$ for silicon; $e$—$\lg D - 1/T$ for iron.

decrease in currents. Additions of iron oxides increase the values of $i$ without the appearance of a second reduction wave. Finally, the increase in current at polarizations greater than 0.4-0.5 V is due to the discharge of other ions that make up the background; these are probably $Al^{3+}$ ions. The appearance of aluminum in the products of cathodic deposition at current densities of 1-1.5 A/cm$^2$ was noted previously [7].

On the basis of the limiting currents found, as well as the viscosities and densities of slags taken from works [8–10], and the results of chemical analysis, the diffusion coefficients ($D$) of iron and silicon ions were calculated by formula (1) (Table 1). The temperature dependences of the values $D$ were well described by exponential equations (see straight lines $d$ and $e$ in Fig. 2). In this case the activation energies in slag (1) are: $E_{\mathrm{Si}} = 110$ kcal/mol and $E_{\mathrm{Fe}} = 59$ kcal/mol. At $\eta = 150$ mV the current is governed by the diffusion of two types of ions: $\mathrm{Fe}^{2+}$ and $\mathrm{Fe}^{3+}$. This leads to a certain uncertainty in the values of $z$ and $D$ in equation (1). The total limiting current in this case will be equal to:

$$i_{\mathrm{lim}} = i_{\mathrm{lim}}^{\mathrm{Fe}^{2+}} + i_{\mathrm{lim}}^{\mathrm{Fe}^{3+}} =$$

$$= 0.62 F \nu^{-1/6} \sqrt{\omega D_{\mathrm{e}}^{2/3}} \left( 2C_0^{\mathrm{Fe}^{2+}} + 3C_0^{\mathrm{Fe}^{3+}} \right),$$

where

$$D_{\mathrm{e}} = \left( \frac{2C_0^{\mathrm{Fe}^{2+}} D_{\mathrm{Fe}^{2+}}^{2/3} + 3C_0^{\mathrm{Fe}^{3+}} D_{\mathrm{Fe}^{3+}}^{2/3}}{2C_0^{\mathrm{Fe}^{2+}} + 3C_0^{\mathrm{Fe}^{3+}}} \right)^{3/2}$$

is the effective diffusion coefficient. ($D_{\mathrm{e}}$) is intermediate between $D_{\mathrm{Fe}^{2+}}$ and $D_{\mathrm{Fe}^{3+}}$, and is closer to each of them the greater the concentration of the corresponding ion. In our experiments $D_{\mathrm{e}}$, apparently—

**Fig. 3.** Polarization curves for slag No. 2, $t = 1470°$;
$a$—background at $n = 60$ rpm, $b$—addition of 10 $\mathrm{SiO}_2$ at $n = 60$ rpm, $v$—addition of 7% iron oxides at $n = 60$ rpm, $g$—addition of 7% iron oxides at $n = 750$ rpm.

presumably closer to $D_{\mathrm{Fe}^{3+}}$. The values of $D$ for silicon were determined on the assumption that $z = 4$, i.e., only process (5) takes place. The calculated values of $D_{\mathrm{Fe}}$ and $E_{\mathrm{Fe}}$ are close to those obtained by other methods (11). The data in Table 1 show that $D_{\mathrm{Fe}}$ increases as the content of iron oxides in the slag increases, which is associated with a decrease in the viscosity of the slag. The diffusion coefficients of silicon are an order of magnitude smaller than those of iron, which is probably due to greater energetic difficulties in the movement of $\mathrm{Si}^{4+}$ ions, since $E_{\mathrm{Si}} > E_{\mathrm{Fe}}$. Similar results were obtained by other methods (12). The diffusion coefficients of complex-forming ions ($\mathrm{Si}^{4+}$, etc.) proved to be substantially smaller than those of modifier ions ($\mathrm{Fe}^{2+}$, etc.). The comparatively high concentrations of iron oxides in our experiments, which noticeably changed the viscosity of the slag, caused a nonlinear dependence of the limiting current on concentration, i.e., a nonconstant value of

$$\frac{i_{\mathrm{Fe}}}{\sqrt{\omega} C_0}$$

(Table 1) and, as a consequence, a dependence of the diffusion coefficients of iron on its content in the slag.

Table 1

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Diffusion coefficients of iron and silicon ions in molten oxides

| Melt No. | FeO, wt. % | $Fe_2O_3$, wt. % | $t$, °C | $\frac{i^{150}}{\sqrt{\omega}}$ | $\frac{i^{350}}{\sqrt{\omega}}$ | $D_{\mathrm{e}}^{\mathrm{Fe}}$ | $D_{\mathrm{Si}}$ | $\frac{i^{150}}{\sqrt{\omega}} C_{\mathrm{Fe}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.48 | 0.21 | 1400 | 0.0057 | 0.061 | $3 \cdot 10^{-6}$ | $4 \cdot 10^{-7}$ | 0.95 |
| 1 | 0.48 | 0.21 | 1350 | 0.017 | 0.046 | $8.7 \cdot 10^{-7}$ | $6.2 \cdot 10^{-8}$ | |
| 1 | 1.49 | 2.88 | 1400 | 0.027 | 0.11 | $1.9 \cdot 10^{-6}$ | $2 \cdot 10^{-7}$ | 0.58 |
| 1 | 1.49 | 2.88 | 1450 | 0.038 | 0.29 | $2.7 \cdot 10^{-6}$ | $7.7 \cdot 10^{-7}$ | |
| 1 | 2.05 | 5.17 | 1400 | 0.061 | – | $2.5 \cdot 10^{-6}$ | – | 0.87 |
| 2 | 1.3 | 2.48 | 1470 | 0.151 | – | $1.8 \cdot 10^{-5}$ | – | – |
| 2 | 3.73 | 4.34 | 1470 | 0.24 | – | $1.3 \cdot 10^{-5}$ | – | – |

The results presented indicate the applicability of the rotating-electrode method for studying concentration polarization in molten oxides.

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