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A. I. Sotnikov, O. A. Esin, Yu. P. Nikitin

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Abstract

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CHEMICAL POLARIZATION AT HIGH TEMPERATURES

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Since the hydrogen overvoltage decreases by 2 mV/deg (^{1}), it would seem that at temperatures above 1000°C one could hardly expect substantial activation difficulties. However, oxygen in melts may be bound so strongly in certain complexes that its anodic evolution will be accompanied by a considerable overvoltage. On the other hand, during the discharge of oxygen from oxide-fluoride melts, chemical polarization is observed (^{2,3}), due mainly to the decomposition of its surface compounds with graphite. In this case part of the polarization is caused (^{3}) by processes of restructuring of the double layer.

We studied the kinetics of the reduction of FeO in an aluminate melt (45 mol.% CaO; 42 mol.% SiO_2; 13 mol.% Al_2O_3) by carbon dissolved in liquid iron. Metal droplets were moved electrocapillarily in the aluminosilicate with increasing velocity u. The reduction process was thereby accelerated, since mass transfer of FeO and C to the reaction surface was facilitated. At $u = 2.5$ cm/sec, a further increase in the reaction rate ceased, which indicated the transition of the process to a kinetic regime.

In this case the dependence of the reaction rate V_C on the concentrations of FeO (0.25-6.5 wt.%) and C (0.6-3 wt.%), as well as on temperature (1740-1850°K), is described by the equation

$$V_C = 2.2 \cdot 10^{-2} [\% C]^{0.65} (\% \mathrm{FeO})^{0.4} \exp\left\{-\frac{32000}{RT}\right\}. \tag{1}$$

The latter can easily be derived if it is assumed that, far from equilibrium, the reaction is composed of two stages:

$$\mathrm{C} + \mathrm{O}^{2-} = \mathrm{CO} + 2e, \tag{2}$$

$$\mathrm{Fe}^{2+} + 2e = \mathrm{Fe}, \tag{3}$$

proceeding only from left to right.

Under stationary conditions their rates are equal, which makes it possible (1) to eliminate the potential and obtain the expression

$$V_C = k \cdot (\mathrm{Fe}^{2+})^{\frac{\alpha_2}{\alpha_2+\beta_3}} [\mathrm{C}]^{\frac{\beta_3}{\alpha_2+\beta_3}}, \tag{4}$$

which agrees with the experimentally found one. In both cases the exponents are fractional, and their sum is equal to unity. Since stage (3) proceeds without substantial activation difficulties (4), a retardation of stage (2) should be expected.

In order to determine whether stage (2) is retarded, the anodic polarization of liquid iron saturated with carbon was studied in oxide melts at 1630-1800°K. The potential was measured with the aid of a commutator (current-pulse duration $\sim 6 \cdot 10^{-3}$ sec, pause $\sim 3 \cdot 10^{-3}$ sec) and an EO-7 electronic oscillograph. The latter made it possible to determine that part of the polarization which decays faster than in 10^{-3} sec.

The reference electrode was the same Fe—C alloy, forming with the anode the cell:

Fe—C	oxide	C or Al_2O_3	oxide	Fe—C
anode	melt		melt	reference electrode

After a 15-20-minute hold, the potential difference in the absence of current was sufficiently stable and close to zero.

The anodic current of Fe^{2+} ions under conditions of constant potential rapidly (5 min) becomes very small. Indeed, the dependence of the diffusion flux i_{diff} from a stationary source on time t is described by equation (1)

$$i_{\text{diff}} = \frac{A}{\sqrt{t}} (C_{\text{surf}} - C_{\text{bulk}}). \tag{5}$$

Hence, at $\varphi = \text{const}$, the difference between the measured current densities for two moments of time $i^{(t)}$ will be

$$i^{(t_1)} - i^{(t_2)} = A(C_{\text{surf}} - C_{\text{bulk}}) \left(\frac{1}{\sqrt{t_1}} - \frac{1}{\sqrt{t_2}} \right),$$

$$i_{\text{diff}} = \frac{i^{(t_1)} - i^{(t_2)}}{(1/\sqrt{t_1} - 1/\sqrt{t_2})\sqrt{t}}. \tag{6}$$

The diffusion current, calculated from equation (6), did not exceed 2-3% of the total at $t > 5$ min.

Fig. 1. Dependence of the polarization of the liquid Fe—C anode on the logarithm of the current density. 1 —1800°K, 2 —1720°K, 3 —1630°K, 4 — temperature dependence of the exchange current

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Figure 1 gives, in semilogarithmic coordinates, curves for the dependence of the anodic polarization η on the current density at different temperatures. The electrolyte was the same melt as in the experiments on the kinetics of the FeO reduction reaction.

In accordance with expectations, at $\eta > 100$ mV the usual equation for retarded discharge proved valid:

$$i = i_0 \exp\left\{\frac{\alpha n F}{RT}\eta\right\}. \tag{7}$$

Here the exchange current (i_0) at a temperature of 1720°K is 15 mA/cm^2, which agrees with data (^{5}) obtained by another method.

The temperature dependence of i_0 (Fig. 1, 4) is described by the expression

$$i_0 = B \exp\left\{-\frac{E}{RT}\right\} \tag{8}$$

with activation energy $E \simeq 40$ kcal/mole.

Analogous measurements with oxide melts of another composition confirmed the validity of equation (7). The values of the transfer coefficients α and exchange currents are given in Table 1.

Replacing CaO by BaO somewhat increases the exchange current, while an increase in the concentration of Al_2O_3 substantially decreases it. This is evidently due, respectively, to a decrease and an increase in the binding energy of the oxygen ion with the electrolyte. Confirmation of this may be the larger value of the surface tension for Al_2O_3 in comparison with SiO_2 (^{6}).

From the polarization decays on the oscilloscope screen one can estimate (^{1}) the capacitance C of the double layer.

The decay curve in our case is described by the equation:

Fig. 2. Dependence of polarization on current density (1) and of the double-layer capacitance C on η (3) for a platinum anode, as well as of the value C' for the Fe–C alloy on η (2)

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$$-C\frac{d\eta}{dt} = i_A^C - i_{\text{diff}}^{\text{Fe}^{2+}}, \tag{9}$$

where $i_{\text{diff}}^{\text{Fe}^{3+}}$ is the diffusion current of Fe^{2+} ions arising when η decreases. As $t \to 0$, the anodic current of carbon oxidation i_A^C is equal to the total i, and $i_d^{\text{Fe}^{2+}} = -nF\delta\, d(\text{Fe}^{2+})/dt$, where δ is the effective thickness of the reaction layer. Expressing $d(\text{Fe}^{2+})/dt$ in terms of $d\eta/dt$ by differentiating the Nernst formula, we have

$$-C\left|\frac{d\eta}{dt}\right|_{t\to 0} = i + \delta\,\frac{u^2F^2}{RT}\,(\text{Fe}_*^{2+})\,e^{\frac{nF}{RT}\eta}\left|\frac{d\eta}{dt}\right|_{t\to 0}. \tag{10}$$

Denoting $i\big/\left(-\left|d\eta/dt\right|_{t\to 0}\right)$ by C' and taking into account that the concentration of iron ions at the comparison electrode is $(\text{Fe}^{2+}) = 5.5\cdot 10^{-5}$ g-ion/cm^3 (7), we obtain, for 1720° K,

$$C' = C + 150\,\delta e^{13.5\eta}. \tag{11}$$

The experimental dependence of C' on η is shown in Fig. 2, 2. With increasing η, the quantity C' increases; in the interval 550-750 mV it remains practically constant. It is possible that, beginning at 550 mV, along with the increase in $e^{13.5\eta}$, the capacitance of the double layer C decreases. At $\eta = 750$ mV it reaches a minimum. Taking $C_{750\text{ mV}} = 20\,\mu\text{F/cm}^2$, we obtain $\delta = 10^{-4}$ cm. The thickness of the diffusion layer in analogous systems has the same order of magnitude (8). In other words, the character of the initial portions of the polarization decay in time does not contradict the assumption of a slow discharge of oxygen ions.

Fig. 2. Dependence of polarization on current density (1) and of the double-layer capacitance C on η (3) for a platinum anode, as well as of the value C' for the Fe–C alloy on η (2)

The results of measurements of the anodic polarization of a platinum electrode in melt No. 1 (see Table 1) are presented in Fig. 2, 1. They show that equation (7) is also applicable here over a fairly wide interval of overvoltages. True, at $\eta = 1100$ mV a bend is observed, the occurrence of which is possibly connected with oxidation of the platinum surface. The exchange current is 1.6 mA/cm^2 at $T = 1690^\circ$ K, i.e., it is an order of magnitude smaller than i_0 for the Fe–C electrode. In other words, the process $O^{2-} = O + 2e$ is accompanied by greater activation difficulties than stage (2), in which carbon is a strong depolarizer.

Table 1

Exchange currents and transfer coefficients at $T = 1720^\circ$K

No.	Electrolyte composition, mol. %	i_0, mA/cm^2	α
1	45% CaO; 42% SiO_2; 13% Al_2O_3	15	0.5
2	45% BaO; 42% SiO_2; 13% Al_2O_3	24	0.5
3	45% CaO; 29% SiO_2; 26% Al_2O_3	3	0.4

The capacitance of the platinum electrode, found from equation (9) at $i_d = 0$ with the aid of measurements of $|d\eta/dt|_{t\to0}$, is presented in Fig. 2, 3. The elevated values of C are due to the difference between the true surface of the electrode and the geo-

metric effect and the adsorption of oxygen atoms on platinum^(1). In the latter case, the value of C is determined not by the capacity of the double layer, but by the rate constant of desorption or molization. Experiment has shown, however, that the addition to the electrolyte of a small amount of surface-active anions substantially shifts the potential η_m of the capacitance minimum in the negative direction. Thus, in the presence of 0.15 wt.% ferric oxide in the electrolyte, $\eta_m = 600$ mV instead of 830 mV in the absence of Fe_2O_3. In other words, the polarization of the platinum electrode is likewise caused mainly by the retarded discharge of oxygen ions.

The nucleation of a new phase (bubbles of O_2 or CO) evidently proceeds without substantial difficulty in both cases, since otherwise the coefficient α would be equal to unity^(1).

Ural Polytechnic Institute
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