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Abstract

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ON THE POLARIZATION OF CERTAIN GAS ELECTRODES CONTACTING SOLID ELECTROLYTES

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The question of electrode polarization in the case of solid electrolytes has apparently not yet been investigated at all. However, the study of this range of phenomena as applied to solid electrolytes is undoubtedly of interest.

As the electrolyte we chose a solid solution containing 85 mole % zirconium oxide and 15 mole % calcium oxide. According to the literature data ($^{1-4}$), this electrolyte, at the temperatures of our experiments, is an ionic conductor. Its electrical conductivity is due mainly to the motion of oxygen ions, owing to the presence of a larger number of vacant oxygen sites that arise in the formation of the solid solution, and is substantially higher than that of a number of other solid electrolytes. Free oxygen sites arise because, in the formation of the solid solution, the lattice of cubic (stabilized) zirconium oxide is retained, and calcium ions occupy part of the sites intended for zirconium ions ($^{5-7}$).

The solid electrolyte was prepared by a method already described in the literature (^{4}). In view of the nature of the electrolyte chosen, it was decided to study the behavior of the oxygen electrode. For this purpose the following electrochemical cell was investigated:

$$\mathrm{Pt}, \mathrm{O}_2 \left| \begin{matrix} \text{solid electrolyte} \\ 85 \text{ mole } \% \ \mathrm{ZrO}_2 + 15 \text{ mole } \% \ \mathrm{CaO} \end{matrix} \right| \mathrm{O}_2, \mathrm{Pt}. \qquad \text{(I)}$$

The construction of such a cell did not differ in principle from that described in detail in one of our papers (^{4}). Here we shall note only that the electrodes consisted of thin porous layers obtained by applying to the electrolyte a suspension of platinum powder in a solution of rubber in benzene, followed by ignition.

Experiments with cell (I) were carried out in the following manner. Both platinum electrodes were in an atmosphere of air. A constant current was passed through the cell from an external source. One of the oxygen electrodes served as the anode, the other as the cathode. For each current value, the potential difference between the electrodes of the cell was measured by means of a potentiometer. The cell was located in an electric furnace, the temperature of which

Fig. 1

Figure 1: Fig. 1

was maintained by a thermoregulator to an accuracy of ±2°. The temperature was measured with a Pt—PtRh thermocouple. Before the start of the measurements and after their completion, the ohmic resistance of the electrolyte was measured by means of an alternating-current bridge (frequency 3000 Hz).

The measurements were carried out at temperatures of 900, 1000, and 1100°C. The resistances of the electrolyte at the indicated temperatures were, respectively: 23, 90; 7.93; 3.80 Ω.

The relationship between the current strength and the voltage at the electrodes of the cell, obtained in direct-current measurements, is shown graphically for the three indicated temperatures in Fig. 1. It is evident from the figure that the voltage and current strength are linearly related. The electrolyte resistances found—

obtained from the slopes of the straight lines in Fig. 1, are, at 900, 1000, and 1100° C, respectively: 25.2; 8.3; 3.86 Ω. Comparison of these figures with the values of the electrolyte resistance measured directly makes it possible to assert that, at the indicated temperatures, within the range of current variation investigated by us, the overvoltage at the oxygen electrodes is insignificant; the possibility of a small overvoltage is not excluded, especially at 900° C. However, it should be borne in mind that we measured the total effect at both oxygen electrodes. For one oxygen electrode this effect will probably be still smaller. Thus, it should be considered that the overvoltage, if it exists at the oxygen electrode, is sufficiently small, and therefore at the indicated temperatures it can in a number of cases be neglected. It is obvious that the oxygen pressure must not be very small. Indeed, the results of experiments carried out by us analogously to those described above, but with the replacement of air by argon contaminated with oxygen ($P_{\mathrm{O2}} = 5 \cdot 10^{-4}$ atm), lead to the conclusion that there is a considerable polarization of the electrodes, apparently mainly due to concentration effects.

Fig. 1

In connection with the small magnitude of the overvoltage at the oxygen electrode, it became possible to study the overvoltage at another electrode by replacing one of the oxygen electrodes in cell (I) with it. In order not to complicate the phenomenon under study by the deposition of some solid substance at one of the electrodes, we decided to investigate another gas electrode, choosing as the latter a CO electrode; and we settled on the following cell:

$$\mathrm{Pt, CO + CO_2} \left| \begin{array}{c} \text{solid electrolyte} \\ 85\ \text{mol.\%} + 15\ \text{mol.\%} \end{array} \right| \mathrm{O_2, Pt.} \qquad \text{(II)}$$

Fig. 2

Figure 2: Fig. 2

Cell (II) was constructed in the same way as cell (I). Since, in contrast to cell (I), it gave a noticeable electromotive force, the measurements could be carried out without an external source of electromotive force. The cell was closed through a resistance box, in series with which was connected an instrument measuring the current strength; by changing the resistance of the box, the current strength was changed. In this way the anodic polarization of the CO electrode was studied.

The anodic overvoltage at the CO electrode was determined from the following elementary equation:

$$\eta = E_0 - Ir - IR, \tag{1}$$

where η is the absolute value of the anodic overvoltage at the CO electrode, E_0 is the absolute equilibrium value of the electromotive force of cell (II), I is the current strength, r is the resistance of the electrolyte, which was measured repeatedly during the experiment, always when passing from one current strength to another, and IR is the potential drop in the external circuit (measured directly with a potentiometer).

The oxygen electrode was washed with a stream of pure oxygen, and the CO electrode with a stream of a mixture of composition: 66 vol.% CO + 34 vol.% CO_2. The flow of this gas mixture was maintained so large that any further increase in it no longer affected the measurement results. The emf of such a cell was sufficiently stable, and its value at temperatures above 900° was practically equal to the thermodynamic value. This once again confirms that the chosen electrolyte is an ionic conductor and shows that the electrodes used at the temperatures indicated above are reversible gas electrodes.

To isolate the measured effect in a purer form, the surface of the CO electrode was made 20 times smaller than the surface of the oxygen electrode.

The resistance of the solid electrolyte, measured on an alternating-current bridge, decreases somewhat as the current increases. It is possible that this is due to improved contact of the electrodes with the solid electrolyte as the current strength increases. However, we did not investigate the cause of this phenomenon specially, since the ohmic potential drop in the electrolyte does not play a particularly large role: at the maximum current strength it amounts to no more than 30% of the magnitude of the overvoltage, and for medium currents only about 6% of the overvoltage. The range from the smallest to medium currents contains more than half of all measurements. Thus, even a not very accurate determination of the ohmic resistance of the electrolyte does not introduce a substantial error into the magnitude of the overvoltage.

Fig. 2

In Fig. 2, for three temperatures, the dependence of the overvoltage on the logarithm of the current density at the CO electrode is presented graphically. As is seen from this graph, at all three temperatures the dependence of η on $\lg i$ is expressed by straight lines, i.e.

$$\eta = a + b \lg i. \tag{2}$$

Two electrons take part in the anodic process at the CO electrode; in connection with this, it may be assumed that $b = \dfrac{2.3RT}{2F\alpha}$. Table 1 gives the values of b, α, and a for three temperatures.

Table 1

	900°	1000°	1100°
b	0.258	0.250	0.260
α	0.45	0.51	0.52
a	1.068	0.953	0.866

It seems to us inadvisable to speak of the temperature dependence of the quantities b, α, and a, since the accuracy of our measurements is insufficient to establish it quite reliably in the relatively small temperature interval in which we worked.

On examining Fig. 2, attention is drawn to the fact that at small currents the experimental points deviate very appreciably from the straight line. It may be assumed, for example, that at small overvoltages the reverse current is not suppressed and must be taken into account. In view of the fact that the value of α differs little from 0.5 (see Table 1), for the direct current, on the basis of equation (2), one may write:

$$\vec{i} = Ke^{\frac{\eta F}{RT}}. \tag{3}$$

The constant K can be expressed, using (2), through the constants a

and b. Let us define the reverse current $\overleftarrow{i}$ by an expression symmetric to equation (3):

$$\overleftarrow{i} = Ke^{-\frac{\eta F}{RT}}. \tag{4}$$

In the region of comparatively small overvoltages,

$$\vec{i} = i + \overleftarrow{i}. \tag{5}$$

Here i is the measured current, while $\vec{i}$ and $\overleftarrow{i}$ are, respectively, the forward and reverse currents.

In the region of large overvoltages, $\vec{i} \simeq i$.

Using equation (4), for the points deviating from the straight line in Fig. 2, the values of $\overleftarrow{i}$ were calculated, and then, from (5), the values of $\vec{i}$. After this, the indicated points were shifted in Fig. 2 by changing their abscissas from $\lg i$ to $\lg \vec{i}$. The displacement of these points is indicated by arrows, and the new positions of the points by circles. After displacement, the points fit well on straight lines. The foregoing suggests that the reverse process at small overvoltages is described by equation (4).

In conclusion, we note that in the case of the CO electrode there is a large overvoltage, the presence of which indicates a slow electrode reaction despite the comparatively high temperatures of the experiments. To substantiate the mechanism of the phenomenon, a further series of investigations must be carried out.

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