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Abstract

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The Behavior of a Platinum Electrode Washed by a Mixture of Oxygen and Carbon Dioxide in Molten Carbonates

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A platinum electrode washed by oxygen has been used by a number of authors in studying the electrochemistry of molten oxygen-containing salts ([1]-[6]). In the cited works it was shown that, under these conditions, platinum behaves as an oxygen electrode reversible with respect to the oxygen-containing anion. The behavior of the platinum electrode in molten carbonates has been very little covered in the literature. Baur and co-workers ([7]) used platinum as the material of the oxygen electrode of a fuel cell, while in a paper by American authors ([9]) platinum was used as a reference electrode in the study of anodic polarization. Japanese investigators ([8]) employed platinum as the material of the oxygen electrode and as a reference electrode in studying a fuel cell. There are no special studies in the literature on the nature and reversibility of a platinum electrode washed simultaneously by oxygen and carbon dioxide.

The subject of the present work was the study of the dependence of the e.m.f. of gas concentration cells in molten carbonates on the composition of the gas washing the platinum electrode. It was established that the surface of an electrode made of platinum sheet, in the course of operation in molten carbonates, becomes covered with a relatively thin but dense layer of oxides, protecting the metal from further oxidation. As a result, the oxidized platinum surface behaves as a sufficiently indifferent electrode. It should be noted that an attempt to use silver as an indifferent electrode was not successful. In this case it was found that silver, washed by oxygen or by a mixture of oxygen and carbon dioxide, dissolves appreciably in molten carbonates with the formation of silver ions.

The electrodes consisted of small rectangular plates of platinum sheet with current leads of platinum wire welded to them. The electrode was fixed in an alumina tube through which the required mixture of gases, dried by passage through bottles with sulfuric acid, was fed into the melt. The mixtures were prepared in advance by mixing the corresponding gases in cylinders. Nitrogen served as an inert diluent for oxygen and carbon dioxide. Both electrodes of the gas cell were located in one large corundum crucible without any separating diaphragm, since preliminary experiments had established that, with the chosen geometry of arrangement and the dimensions of the crucible, the gases of one electrode exert no noticeable influence on the other electrode.

As the electrolyte in all experiments, a ternary mixture of carbonates of potassium (30 mol.%), sodium (40 mol.%), and lithium (30 mol.%) with a melting temperature of 390° ([10]) was used. Before each experiment, dried carbon dioxide was bubbled through the melt for 30 min to suppress the thermal dissociation of the carbonates and remove traces of moisture. The temperature of the experiments was maintained constant within 720 ± 5° by an automatic regulator. The e.m.f. of the gas concentration cells was measured with a high-resistance d.c. potentiometer of type P-307.

The dependence of the emf on the gas composition was studied for the following three concentration cells:

$$\mathrm{Pt}\ (p_{\mathrm{CO2}} = 0.2;\ p_{\mathrm{O2}} = 0.2)\,|\,\mathrm{CO}_3^{2-}\,|\,({'p}_{\mathrm{O2}} = x;\ {'p}_{\mathrm{CO2}} = 0.2)\ \mathrm{Pt}, \qquad \text{(I)}$$

$$\mathrm{Pt}\ (p_{\mathrm{CO2}} = 0.2;\ p_{\mathrm{O2}} = 0.2)\,|\,\mathrm{CO}_3^{2-}\,|\,({'p}_{\mathrm{O2}} = 0.2;\ {'p}_{\mathrm{CO2}} = x)\ \mathrm{Pt}, \qquad \text{(II)}$$

$$\mathrm{Pt}\ (p_{\mathrm{CO2}} = 0.67;\ p_{\mathrm{O2}} = 0.33)\,|\,\mathrm{CO}_3^{2-}\,|\,({'p}_{\mathrm{O2}} = x;\ {'p}_{\mathrm{CO2}} = 1 - x)\ \mathrm{Pt}. \qquad \text{(III)}$$

The study by the emf method of the first concentration cell was intended to determine the effect of changing the partial pressure of oxygen at the electrodes of this cell. For more effective suppression of the thermal dissociation of carbonates, occurring according to the equation

$$\mathrm{M_2CO_3} \rightarrow \mathrm{CO_2} + \mathrm{M_2O} \qquad (1)$$

or, what is the same thing,

$$\mathrm{CO}_3^{2-} \rightarrow \mathrm{CO_2} + \mathrm{O}^{2-},$$

the partial pressure of carbon dioxide was chosen to be comparatively high (0.2 atm). It was several times higher than the pressure of carbon dioxide formed as a result of thermal dissociation of carbonates. It should be noted that washing the electrode with a mixture of only oxygen and nitrogen, without any admixture of carbon dioxide, led to continuous thermal decomposition of the carbonates. This was manifested in the non-reproducibility of the measurement results.

Fig. 1. Dependence of the potential of a platinum electrode, washed by a mixture of oxygen and carbon dioxide, on the partial pressure of CO_2 (1) and O_2 (2)

Since carbon dioxide is not inert with respect to the carbonate melt by virtue of equilibrium (1), in order to clarify the influence of its partial pressure on the electrode potential, the second type of gas concentration cell was studied. The partial pressure of oxygen at the electrodes of this cell was the same and was kept constant, while the partial pressure of carbon dioxide was varied from 0.05 to 0.8 atm.

In the third gas cell, the pressure of carbon dioxide in the mixture washing one of the electrodes was twice the oxygen pressure, as follows from equation (2). At the second electrode, the partial pressure of oxygen was varied, while the pressure of carbon dioxide brought the total pressure up to 1 atm.

Fig. 2. Dependence of the potential of a platinum electrode on the simultaneous change in the partial pressure of CO_2 and O_2

Assuming, in accordance with the literature data ([9,11,12]), that at an indifferent platinum electrode washed by a mixture of oxygen and carbon dioxide the equilibrium

$$CO_3^{2-} \rightleftarrows CO_2 + \tfrac{1}{2}O_2 + 2e, \tag{2}$$

is established, the electrode potential can be written by means of the equation

$$\varphi = \varphi_0 + \frac{2.3RT}{2F} \lg \frac{p_{CO2} \cdot p_{O2}^{1/2}}{[CO_3^{2-}]}. \tag{3}$$

Then the emf of the gaseous concentration cells indicated above can, in general form, be expressed by the following equation:

$$E = \frac{2.3RT}{2F} \lg \frac{p_{CO2} \cdot p_{O2}^{1/2}}{'p_{CO2} \cdot 'p_{O2}^{1/2}}, \tag{4}$$

if it is assumed that the concentrations of carbonate ions $[CO_3^{2-}]$ near both electrodes are approximately the same.

Since the partial pressures p_{O2} and p_{CO2} were maintained constant during one series of experiments, the electrode washed by a gas mixture with these partial pressures may be regarded as the reference electrode. Then the emf measured in the experiment will be expressed by the equation:

$$E = A - \frac{2.3RT}{2F} \lg {'p_{CO2}} \cdot {'p_{O2}^{1/2}}, \tag{5}$$

where

Figure 3. Temperature dependence of the emf of gaseous cells. 1—cell (IV), 2—cell (V)

Figure 1: Figure 3. Temperature dependence of the emf of gaseous cells. 1—cell (IV), 2—cell (V)

$$A = \frac{2.3RT}{2F} \lg p_{\mathrm{CO2}} \cdot p_{\mathrm{O2}}^{1/2}.$$

Fig. 3. Temperature dependence of the emf of gaseous cells. 1—cell (IV), 2—cell (V)

This same emf will be the potential of the electrode under investigation relative to the reference electrode, since the potential of the reference electrode may be taken as zero.

In Fig. 1 the theoretical straight lines calculated from equation (5) are plotted for the dependence of the potential on the composition of the gases washing the electrodes. Straight line 2 represents the linear dependence of the potential on $\lg {}' p_{\mathrm{O2}}$ for cell (I), and straight line 1 the dependence of the potential on $\lg {}' p_{\mathrm{CO2}}$ for cell (II). The experimental data obtained for cell I are marked in Fig. 1 by circles, and for cell II by crosses. It should be noted that in the experiments the reversal of electrode polarity expected according to equation (5) was observed.

In Fig. 2 the theoretical curve for cell III, obtained according to equation (5), is given. The experimental data are marked in this figure by crosses. As is seen from the graph, in this case no reversal of electrode polarity occurs, since the decrease in the partial pressure of oxygen is compensated by the corresponding increase in the partial pressure of carbon dioxide.

As can be seen from Figs. 1 and 2, the experimental data for measuring the emf of gaseous concentration cells agree quite satisfactorily with those calculated from equation (5). Along with the agreement of the experimental and theoretical data for the dependence of the emf on gas composition and pressure, an important proof in favor of the establishment of equilibrium (2) is the agreement of the temperature-dependence coefficients of the emf with the calculated values.

For this purpose the dependence of the emf on temperature was studied for the following two cells:

$$\mathrm{Pt}\ (p_{\mathrm{CO2}} = 0.104;\ p_{\mathrm{O2}} = 0.234)\,|\,\mathrm{CO}_3^{2-}\,|\,({}'p_{\mathrm{CO2}} = 0.81;\ {}'p_{\mathrm{O2}} = 0.19)\ \mathrm{Pt}, \quad \mathrm{(IV)}$$

$$\mathrm{Pt}\ (p_{\mathrm{CO2}} = 0.182;\ p_{\mathrm{O2}} = 0.148)\,|\,\mathrm{CO}_3^{2-}\,|\,({}'p_{\mathrm{CO2}} = 0.215;\ {}'p_{\mathrm{O2}} = 0.785)\ \mathrm{Pt}. \quad \mathrm{(V)}$$

The experimental data obtained for these cells are presented in Fig. 3. The data joined by straight line 1 correspond to cell (IV), and those joined by straight line 2 to cell (V). As is seen from Fig. 3, the emf of both cells depends linearly on temperature. The temperature coefficient $\Delta E/\Delta T$, obtained from

graphical data, for element (IV) is equal to 0.0875 mV/deg, and for element (V) is equal to 0.053 mV/deg, which agrees well with the values theoretically calculated from equation (5): 0.0838 mV/deg and 0.046 mV/deg, respectively.

The good agreement between the experimental and theoretical data in the study of the dependence of the emf of gas cells on temperature, composition, and gas pressure indicates that, on a platinum electrode washed by a mixture of oxygen and carbon dioxide in molten carbonates, the following equilibrium is established:

$$CO_3^{2-} \rightleftarrows CO_2 + \tfrac{1}{2}O_2 + 2e.$$

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Note: Figure translations are in progress. See original paper for figures.