# EFFECT OF IMPURITIES IN SOLUTION ON EQUILIBRIUM POTENTIAL OF OXYGEN ELECTRODE IN ACIDIC ELECTROLYTE

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As a rule the currentless potential at electrodes of noble metals in electrolytes saturated with oxygen lies between 1.0 and 1.1 V (here and henceforth the potentials are referred to an equilibrium hydrogen reference electrode in the same solution), which is 0.2-0.25 V more negative than the thermodynamic potential of the oxygen electrode ($\varphi_{equi}$ =1.227 V) corresponding to the reaction:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O.$$

Only with careful preliminary oxidation of the electrode and in work under very clean conditions is it possible to realize an oxygen electrode potential near the thermodynamic value. The reasons for the displacement of the oxygen electrode potential from the thermodynamic value have been the subject of numerous investigations. In some of these it was attributed to the fact that, owing to irreversibility, processes of individual surface oxide formation become potential-determining [1]. In other papers the equilibrium potential is regarded as a compromise, due to the fact that the cathodic reduction of oxygen is compensated either by anodic oxidation of microimpurities in the solution [2] or by anodic oxidation of the electrode material itself (most frequently platinum) [1]. In addition, some papers draw attention to the possible role of hydrogen peroxide, which is formed in some cases during cathodic polarization of the electrode in an atmosphere of oxygen.

In order to investigate the validity of these proposals in more detail we carried out an investigation into the behavior of a platinum electrode in 1 N sulfuric acid solution at potentials near the equilibrium potential by recording anodic and cathodic polarization curves with the addition of small quantities of hydrogen peroxide or methanol to the electrolyte solution. Methanol is readily oxidized at a platinum electrode and can serve as a material for imitating the behavior of various other organic microimpurities which may be present in the electrolyte.

The investigation was carried out on a platinized platinum electrode with a surface area of 6 $cm^2$. The electrode was platinized in a 2% solution of $H_2PtCl_6$ with a current density of i=1 $mA/cm^2$ for 15-20 min. The true surface area of each freshly prepared electrode was determined from the hydrogen region of the charging curve. The roughness factor of such an electrode amounted to about 100. The electrolyte was 1 N sulfuric acid solution prepared from twice-distilled sulfuric acid and twice-distilled water. Before the experiment the solution was thoroughly purified by cathodic polarization at a platinum electrode for 24 h in an atmosphere of hydrogen followed by prolonged treatment on a large platinized gauze, with agitation by a magnetic stirrer, to remove possible traces of hydrogen peroxide. Analysis of the solution by means of a spectrophotometer (with a sensitivity of $10^{-7}$ mole/liter hydrogen peroxide) showed the absence of hydrogen peroxide.

The behavior of the platinized platinum electrode was investigated at potentials between 0.85 and 1.5 V and at room temperature. Polarization curves were recorded on electrodes which had been treated in various ways. In one case the electrode was activated over for 3 min by alternating anodic–cathodic polarization for 15 sec each at the oxygen and hydrogen evolution potentials in a working solution, saturated

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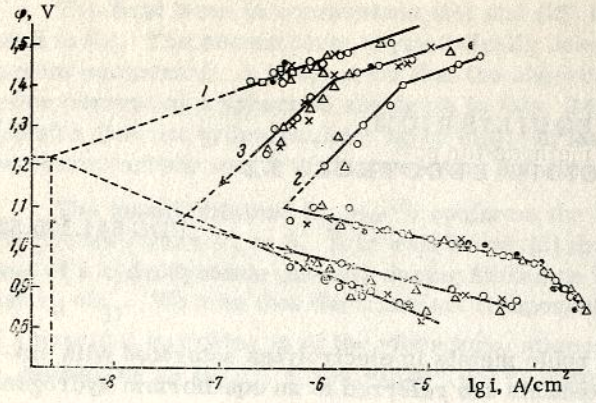



Fig. 1. Tafel curves recorded on oxidized (at $\varphi$ = 1.6 V) (1) and activated (2 and 3; direction in which curves were recorded is shown by arrow) platinum–platinum electrode in 1 N sulfuric acid.

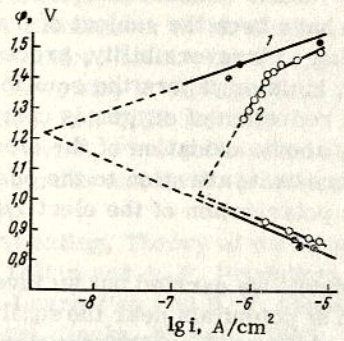



Fig. 2. Effect of hydrogen peroxide ($c_{H_2O_2} = 10^{-6}$ mole/liter) and methanol ($c_{CH_3OH} = 10^{-6}$ mole per liter) on behavior of platinum–platinum electrode at potentials between 0.85 and 1.50 V. The continuous line 1 corresponds to the curve in Fig. 1, and the points on this curve correspond to measurements in a solution containing additions of methanol; curve 2 corresponds to measurements in a solution containing additions of hydrogen peroxide.

with oxygen and free from hydrogen peroxide. The activation was concluded by a weak anodic polarization ($\varphi$ =1.2 V). The polarization curves were recorded 3 min after this treatment, and in this case the measurements were made either from $\varphi$ =0.85 V to $\varphi$ =1.5 V or in the opposite direction from $\varphi$ =1.5 V to $\varphi$ =0.85 V.

The second electrode treatment involved anodic oxidation at $\varphi$ =1.6 V for 3 h. With this treatment the polarization curve was recorded by measuring the current at each given potential, while the electrode was held at $\varphi$ =1.6 V for a further 3 min.

The experimental results are given in Fig. 1 against semilogarithmic coordinates. (The different notations on each curve refer to experiments carried out at different times; the currents are calculated for the apparent surface area.) As seen from this figure, the extrapolated Tafel anodic and cathodic polarization curves intersect at 1.23 V in the case of the oxidized electrode (curve 1) and at 1.06 and 1.0 V (depending on the direction in which the polarization curves are measured) in the case of the activated platinum electrode (curves 2 and 3). Intersection of the Tafel curves at $\varphi$ =1.23 V has been observed in a number of papers [1, 3, 4]. The exchange current, calculated at the point of intersection, for the oxidized electrode amounts to $2.1 \cdot 10^{-9}$ A/cm$^2$, and the gradient of both the anodic and cathodic curves is close to 100 mV, which is in agreement with the data obtained by Bockris [4] ($i = 10^{-9}$ A/cm$^2$).

Experimental data obtained in solutions of sulfuric acid with hydrogen peroxide additions showed that this additive has a different effect on the behavior of electrodes of the two types. Addition of hydrogen peroxide at a concentration of $10^{-5}$–$10^{-6}$ mole/liter has practically no effect on the behavior of the activated electrode, whereas with the anodically oxidized electrode addition of $10^{-7}$ mole/liter hydrogen peroxide leads to a slight and $10^{-6}$ mole/liter hydrogen peroxide to an appreciable change in the current values and to a change in the gradient of the anodic Tafel curve (Fig. 2). As a result the form of the Tafel curves becomes similar to the curves recorded at the activated electrode (Fig. 2, curve 2 and Fig. 1, curves 2 and 3). Such a result could be explained by the action of hydrogen peroxide either added from outside (oxidized electrode) or formed by cathodic polarization during activation of the electrode (activated electrode). The possible formation of hydrogen peroxide during activation of an electrode in an atmosphere of oxygen has been mentioned in a number of papers [5-6]. Special experiments were undertaken to examine this circumstance in greater detail, and for this purpose the electrode was activated in a solution saturated with argon. Under these conditions the possibility of hydrogen peroxide formation and anodic oxygen evolution was eliminated. After activation the argon atmosphere in the cell was replaced by oxygen, and the polarization curves were recorded without further activation. The results obtained with such an electrode were compared with those obtained with an electrode activated in an atmosphere of oxygen. This showed that the absence of hydrogen peroxide is a necessary but insufficient condition for the attainment of the equilibrium potential.

Investigation of the effect of methanol additions between $10^{-6}$ and $10^{-5}$ mole/liter on the rates of the cathodic and anodic processes showed no appreciable change in the current values for both activated and

oxidized electrode in at least the first 6 h of operation (Fig. 2, points on curve 1). Thus, even in the presence of $10^{-5}$ mole/liter methanol, the anodic and cathodic polarization curves on oxidized platinum do not change in form and, as before, intersect at the equilibrium potential of the oxygen electrode. This result does not confirm the suggestion that the shift of the equilibrium potential results from anodic oxidation of organic microimpurities in the solution [2]. With normal methods for purification of the solution the content of such impurities can readily be reduced to a concentration less than $10^{-6}$ mole/liter, at which (like methanol) they have practically no effect on the electrode potential.

The results show that neither formation of hydrogen peroxide near the electrode surface nor the presence of microimpurities can by themselves explain the shift of the currentless potential of the oxygen electrode.

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