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Fig. 1. Polarization curves of the oxidation of formic acid on a rotating disk platinum electrode. $m = 2500$ rpm, $t = 25°$. Potential sweep rate 10 mV/sec. 1—background 1 N H_2SO_4; 2—background + 0.062 M HCOOH; 3—background + 0.106 M HCOOH; 4—background + 0.194 M HCOOH; 5—background + 0.370 M HCOOH; 6—background + 0.59 M HCOOH; 7—background + 0.103 M HCOOH.

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Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. B. VASIL' EV, V. S. BAGOTSKII

ELECTROOXIDATION OF FORMIC ACID AND ITS SALTS ON A ROTATING PLATINUM ELECTRODE

(Presented by Academician A. N. Frumkin, July 18, 1962)

A large number of works have been devoted in the literature to the question of the electrooxidation of formic acid and its salts (1), in which it was shown that the principal reaction products are CO_2 and O_2. E. Müller (2) recorded polarization curves by the compensation method on stationary solid electrodes and found that, in all cases, the curve exhibits a current maximum at potentials of about 0.5 V relative to the normal hydrogen electrode. Both in the region of the maximum and at more positive potentials, the oxidation reaction of formic acid and the evolution of CO_2 take place. The author believed that the mechanism of the process at the more negative potential differs from the mechanism at the more positive potential.

Fig. 1. Polarization curves of the oxidation of formic acid on a rotating disk platinum electrode. $m = 2500$ rpm, $t = 25°$. Potential sweep rate 10 mV/sec. 1—background 1 N H_2SO_4; 2—background + 0.062 M HCOOH; 3—background + 0.106 M HCOOH; 4—background + 0.194 M HCOOH; 5—background + 0.370 M HCOOH; 6—background + 0.59 M HCOOH; 7—background + 0.103 M HCOOH.

Fig. 2

Figure 2: Fig. 2

We studied the anodic process during the electrolysis of formic acid and its salts on a rotating smooth platinum electrode. The investigations were carried out by recording polarization curves by the compensation method and on PE-312 and PO polarographs, model 01 TsLA (^{3}). As a result of preliminary alternating cathodic-anodic polarization of the electrode and high purification of the solutions, good reproducibility of the results was achieved.

Studies in solutions with an H_2SO_4 background showed that three maxima are observed on the polarogram of formic acid oxidation (Fig. 1). The formation of dips on the polarograms and kinetic inhibition of the oxidation reaction were observed in a number of works ($^{4-7}$). In general, in studies of oxidation reactions on a platinum electrode, inhibition of the oxidation reaction is explained as the result of a change in the state of the electrode owing to adsorption of oxygen and formation of surface oxide layers or adsorption of an intermediate oxidation product (^{7}). In the electrooxidation of formic acid, one stable product, CO_2, is formed; it is difficult to attribute the formation of dips to adsorption of this product. Regardless of the concentration of formic acid in the solution, the minima on the polarograms are always observed at strictly definite potentials: 0.8; 1.1; 1.64 V relative to the normal hydrogen electrode (in $1\,N\,H_2SO_4$).

and −0.050; +0.28; +0.66 V relative to the normal hydrogen electrode (in $1N$ KOH). Since the inhibition is observed three times at different potentials, it is probably associated with the presence of several forms of adsorbed oxygen. Indeed, in studying the state of the surface of a platinum electrode under anodic polarization, various states of oxygen on the platinum surface had previously been found at a potential of 0.7–0.8 V (^{8,9}), and also at potentials of 1.1–1.5 V ($^{6-10}$).

Fig. 2. Dependence of φ on $\lg i$. The designations are the same as in Fig. 1

At potentials more negative than 0.4 V, i.e., in the region where adsorbed oxygen is absent, the experimentally observed dependence of the rate of the oxidation reaction on the potential and on the concentration of formic acid and hydroxyl ions is expressed by the empirical equation:

$$i = k[\mathrm{HCOOH}]^{0.5}[\mathrm{OH}^-]\exp\left\{\frac{F}{2RT}\varphi\right\}. \qquad (1)$$

With an increase in the concentration of formic acid by one order of magnitude, the potential at constant current shifts by 60 mV, and with an increase in pH by one unit—by 120 mV (Fig. 3) in the negative direction (Fig. 2).

Fig. 3. Dependence of φ on $\lg i$ for the oxidation of formic acid at different pH values in a solution of $H_3PO_4 + KOH$ of total concentration $0.5N$.

Fig. 3

Figure 3: Fig. 3

1 –pH 1.99, 2 –pH 2.16, 3 –pH 2.67, 4 –pH 3.08

At potentials close to 0.5 V, a certain deviation of the dependence $\lg i - \varphi$ from linearity is observed, probably associated with the influence on the rate of formic-acid oxidation of the adsorption of the anion SO_4^{2-} on platinum, or with the onset of oxygen adsorption. At higher potentials an exponential decrease in the rate of the oxidation process with potential is observed, i.e., the dependence $\lg i - \varphi$ for the decay also represents a straight line, but with a slope of the opposite sign (Figs. 2 and 3), which is analogous to the curves given by Kolotyrkin and co-workers ([11]) for the passivation of various metals.

Thus, beginning at a certain potential of about 0.5 V, along with the oxidation of formic acid, a layer of adsorbed oxygen is formed on the electrode surface, which hinders the oxidation of formic acid; as a result, the current falls with increasing amount of adsorbed oxygen according to an exponential law ([12]). Current-decay curves at constant potential ($i - t$ curves) show that the amount of adsorbed oxygen and the state of the electrode surface are functions not only of potential but also of time. At decay potentials, an exponential decrease in the oxidation rate with polarization time is observed according to the law $i_t = i_\infty + Ae^{-kt}$ at $a = \text{const}$.

Thus, the electrooxidation of formic acid on a platinum electrode can be described by the kinetic equation of the theory of delayed

discharge, if one takes into account the influence of the simultaneously occurring process of change in the state of the surface on the rate of discharge. The kinetic equation for the oxidation reaction of formic acid can be represented in the form:

$$i = k[\mathrm{HCOOH}]^{0.5}[\mathrm{OH}^-] \exp\left\{\frac{F}{2RT}\varphi\right\} \exp\{-k'[\mathrm{O}]_{\mathrm{ads}}\}, \quad (2)$$

where the function $\exp\{-k'[\mathrm{O}]_{\mathrm{ads}}\}$ reflects the influence of the surface state ([5]). As our investigations show, this function depends on the pH of the solution, the potential, the time, and the preliminary preparation of the electrode. The amount of adsorbed oxygen, as is known from charging curves ([8], [9]), increases linearly with increasing potential, which leads to an exponential decrease in the rate of oxidation of formic acid with increasing potential in the region where oxygen adsorption occurs. With increasing polarization time, the amount of adsorbed oxygen also increases, which leads to a decrease in the rate of oxidation.

Fig. 4. Influence of the rate of application of potential on the polarization curve of 0.37 M HCOOH in 1N H_2SO_4.
1 –rate of application of potential 0.005, 2 –0.01, 3 –0.125, 4 –0.250, 5 –0.5, 6 –1, 7 –2, 8 –4, 9 –8, 10 –16 V/sec; 11 –curve corresponding to the

Fig. 4. Influence of the rate of application of potential on the polarization curve of 0.37 M HCOOH in 1 N H2SO4.

Figure 4: Fig. 4. Influence of the rate of application of potential on the polarization curve of 0.37 M HCOOH in 1 N H2SO4.

kinetic equation of slow discharge without taking into account the influence of the surface state.

At potentials more negative than 0.5 V, i.e., in the region where adsorbed oxygen is absent, equation (2) passes into (1). If the time t is decreased by increasing the rate of application of the potential, then, as is seen from Fig. 4, the polarization curve approaches the curve described by the usual kinetic equation (1) of the theory of slow discharge.

The potentials of the maxima do not depend on the concentration of formic acid in the solution, and the nature of the drops does not change: with increasing concentration the drops in the coordinates φ–$\lg i$ merely shift parallel to one another (Fig. 1, b). The pH of the solution affects the inhibition process through a change in the amount of adsorbed oxygen.

A new rise of current after a drop need not necessarily be associated with a new electrochemical process, but may be the result of the fact that a potential has been reached at which the same electrochemical reaction becomes possible on a layer of adsorbed oxygen. The new rise of current will continue until a potential is reached at which, probably, additional adsorption of oxygen becomes possible, which will lead to a new change in the state of the electrode surface, to inhibition of the process, and to the appearance of a new maximum, etc.

In acidic solutions, as we see, three such maxima are observed. In neutral and alkaline solutions of formic acid salts, the first maximum degenerates into a small delay; two maxima are observed and, in addition, at a potential of 1.77 V a wave is observed, the height of which increases linearly with increasing activity of the formate ion. The kinetic equation for the process occurring in this case has the form

$$i = k''[\mathrm{HCOO}^-] \exp\left\{\frac{F}{2RT}\varphi\right\}. \tag{3}$$

It is interesting to note that discharge of the formate ion occurs before oxygen evolution, whereas the anions of other carboxylic acids discharge

at potentials more positive than the potential of oxygen evolution (^{13}).

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