

ELECTROCHEMICAL OXIDATION OF FORMIC ACID AND ITS SALTS ON A ROTATING PLATINUM ELECTRODE

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The electrochemical oxidation of formic acid and its salts has been the subject of a great number of papers [1], in which it is demonstrated that CO_2 and CO are the main reaction products. E. Müller [2] measured polarization curves on stationary solid electrodes by the compensation method and found that in all cases the curve showed maximum current at potentials of about 0.5 V overvoltage. Both in the region of the maximum and at more positive potentials, formic acid is oxidized with liberation of CO_2 . The author supposed that the reaction mechanism at a more positive potential differs from that at a more negative potential.

We studied the anodic reaction in the electrolysis of formic acid and its salts on a rotating smooth platinum electrode. The investigations included the taking of polarization curves by the compensation method with PE-312 and PO polarographs of the 01 TsLA type [3]. Good reproducibility of the results was achieved by previous alternate cathodic polarization of the electrode and by thorough purification of the solutions.

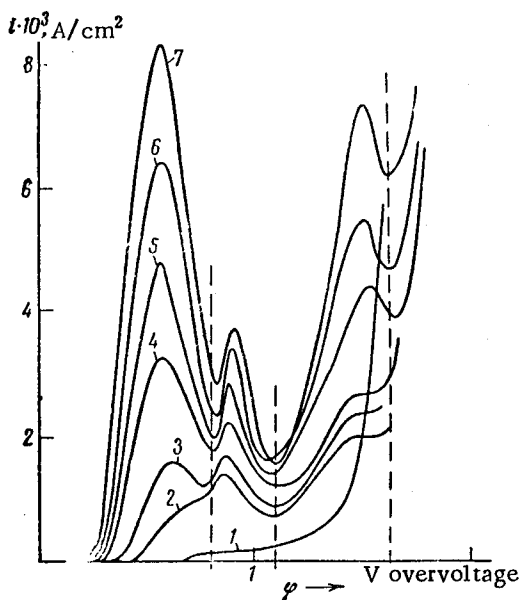


Fig. 1. Polarization curves of formic acid oxidation on a rotating platinum disc electrode. $m = 2500$ rotations/min, $t = 25^\circ$. The potential was raised at a rate of 10 mV/sec. 1) 1N H_2SO_4 background; 2) background + 0.062 M HCOOH ; 3) background + 0.106 M HCOOH ; 4) background + 0.194 M HCOOH ; 5) background + 0.370 M HCOOH ; 6) background + 0.59 M HCOOH ; 7) background + 0.103 M HCOOH .

Measurements in solutions containing H_2SO_4 have revealed the existence of three maxima in the polarograms of formic acid (Fig. 1). Falling regions in the polarograms and kinetic retardation of the oxidation are mentioned in several papers [4-7]. This retardation of the oxidation of a platinum electrode can be explained chiefly by a change in the electrode state due to adsorption of oxygen and to formation of oxidic surface layers or to adsorption of an intermediary oxidation product [7]. It is difficult to ascribe the falling curve sections to adsorption of the only stable product CO_2 in the electrochemical oxidation of formic acid. Regardless of the formic acid concentration in the solution, minima in the polarograms are also found at strictly defined potentials: 0.8; 1.1; 1.64 V overvoltage (in 1 N H_2SO_4) and -0.050; +0.28; 0.66 V overvoltage (in 1 N KOH). Since retardation has been observed three times at different potentials, this phenomenon may be ascribed to the action of different forms of adsorbed oxygen. In fact, various states of oxygen on a platinum surface had already been observed at potentials of 0.7 - 0.8 V [8, 9] and of 1.1 - 1.5 V [6-10] when the surface of a platinum electrode was examined during anodic polarization.

At potentials below 0.4 V, i.e., in the region where oxygen is not adsorbed, the experimentally found dependence of the rate of oxidation on the potential, and on the concentrations of formic acid and hydroxyl ions, satisfies the empirical relation:

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

Upon a tenfold rise of the formic acid concentration, the potential at a fixed constant current is displaced over 60 mV, and upon a rise of the pH to unity this shift is 120 mV (Fig. 3) in the negative direction (Fig. 2).

At potentials near 0.5 V, the curve of $\lg i$ versus φ is found to deviate slightly from a straight line; this is probably due to adsorption of the SO_4^{2-} anion on platinum, which affects the rate of formic acid oxidation. At higher potentials, the rate of oxidation is found to drop exponentially with the potential, i.e., the falling branch of the $\lg i$ versus φ curve also obeys a linear relation, but has a negative slope (Figs. 2 and 3) similar to that in the curves reported by Kolotyrkin and co-workers [11] for passivation of various metals.

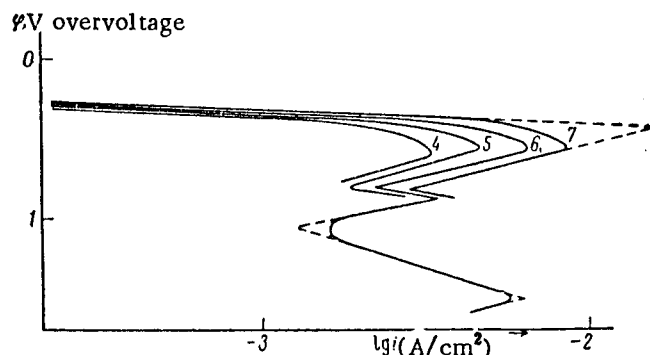


Fig. 2. Plot of φ versus $\lg i$. The designations are equal to those in Fig. 1.

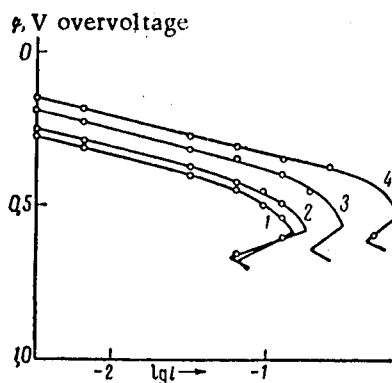


Fig. 3. Plots of φ versus $\lg i$ for the oxidation of formic acid at various pH values in a solution of $\text{H}_3\text{PO}_4 + \text{KOH}$ of 0.5 N total concentration. 1) pH 1.99; 2) pH 2.16; 3) pH 2.67; 4) pH 3.08.

Hence, starting at a defined potential of about 0.5 V, oxidation of formic acid is accompanied by formation of an adsorbed oxygen layer on the electrode surface, which hampers the oxidation of formic acid, so that as the amount of adsorbed oxygen increases the current falls according to an exponential law [12]. Curves showing a fall in current at constant potential (i versus t curves) indicate that the amount of adsorbed oxygen and the surface state of the electrode are functions not only of the potential but also of time. At the potentials of the falling branches, the rate of oxidation is found to decrease with the time of polarization according to the law $i_t = i_\infty + Ae^{-kt}$ at $\varphi = \text{const}$.

Hence, electrochemical oxidation of formic acid on a platinum electrode may be described by the kinetic equation of the theory of retarded discharge, if the effect of the simultaneous change in the surface state on the rate of discharging is taken into account. The kinetic equation of formic acid oxidation may be expressed as:

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

where the function $\exp \{ -k' [\text{O}]_{\text{ads}} \}$ reflects the effect of the surface state [5]. As our investigations show, this function depends on the pH of the solution, the potential, the time, and the pretreatment of the electrode. As is known from discharge curves [8, 9], the amount of adsorbed oxygen increases linearly with the potential, which results in an exponential lowering of the rate of formic acid oxidation with rising potential in the region where oxygen adsorption takes place. The amount of adsorbed oxygen also increases with the duration of the polarization, which leads to a lowered rate of oxidation.

At potentials below 0.5 V, i.e., in the region where oxygen is not adsorbed, equation (2) changes into (1). If the time t is reduced by slowing down the rate of raising the applied potential, then, as can be seen in Fig. 4, the polarization curve approaches the curve predicted by the usual kinetic equation (1) of the theory of retarded discharge.

The potentials of the maxima do not depend on the concentration of formic acid, and the shape of the falling branches remains unaltered; with increasing concentration the falling branches of the φ versus $\lg i$ curves show only parallel displacement (Fig. 1b). The pH of the solution affects the retardation only indirectly by changing the amount of adsorbed oxygen.

The new rise of the current beyond the drop need not necessarily be due to a new electrochemical process; it may also be ascribed to the fact that the voltage has increased up to a potential permitting the same electrochemical reaction to proceed on the layer of adsorbed oxygen. The new rise of the current will continue up to a potential at

which additional adsorption of oxygen becomes possible, which leads to a new change in the state of the electrode surface, to retardation of the reaction and to appearance of a new maximum, etc.

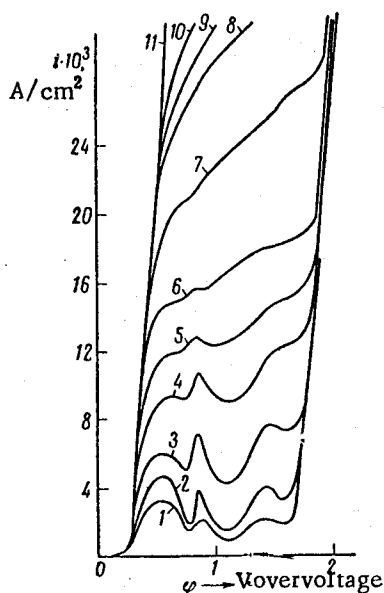


Fig. 4. Effect of the rate of raising the applied potential on the polarization curve of 0.37 M HCOOH in 1 N H₂SO₄. 1) Potential raised at a rate of 0.005; 2) 0.01; 3) 0.125; 4) 0.250; 5) 0.5; 6) 1; 7) 2; 8) 4; 9) 8; 10) 16 V/sec; 11) curve corresponding to the kinetic equation of retarded discharging, the effect of the surface state being left out of consideration.

In acid solutions, three such maxima are observed. In neutral and alkaline solutions of formic acid, the first maximum degenerates into a small shoulder; two maxima are observed and, in addition, a wave at the potential of 1.77 V, the height of which increases linearly with the activity of the formate ion. The kinetic equation of the reaction responsible for the latter wave has the form

$$i = k'' [\text{HCOO}^-] \exp \left\{ \frac{F}{2RT} \Phi \right\}. \quad (3)$$

It is interesting to note that discharge of the formate ion results in liberation of oxygen, whereas anions of other carboxylic acids are discharged at potentials more positive than that at which oxygen is liberated [13].

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