

Stationary Voltammogram for Oxidation of Formic Acid on Polycrystalline Platinum

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The stationary voltammogram does not depend on the sweep rate and shows the same curves in the positive and negative sweep directions. We successfully obtain, strictly speaking, a quasi one, for the oxidation of formic acid in a sulfuric acid solution at 42 °C at a sweep rate of 0.1 mV s⁻¹. It takes a very long time to obtain one at lower temperatures. The voltammogram consists of a single current peak at 0.6 V in both the positive and negative sweep directions in the potential range between 0.05 and 1.4 V. It is quite different from the one measured at a normal sweep rate, e.g., 100 mV s⁻¹, in that the latter has four current peaks in the same potential region. The shape of the stationary voltammogram is hardly affected by the temperature and the concentration of formic acid. Both the shape and current are hardly affected by the concentration of sulfuric acid, by the adsorption of anions, and by the mass transfer in solution. We have obtained electrochemical evidence that at the current peak potential, the adsorbed CO, the one reaction intermediate, is oxidized to produce CO₂ in the positive sweep direction and is formed in the negative sweep direction.

Introduction

The oxidation of formic acid on Pt shows potential oscillation under galvanostatic conditions in acidic solution. We have been studying the oscillating system^{1–3} and a similar one with formaldehyde^{4–7} among various chemical or electrochemical oscillation systems, because we can utilize the accumulated information^{8–13} about the reaction to investigate oscillation behavior. Although the oxidation of formic acid shows both potential and current oscillations,⁵ we have been especially studying the potential oscillation because the potential oscillation system is simpler than the current one for the following two reasons: (1) in the current oscillation system, both the current and the electrode potential across the double layer (the true electrode potential) vary, whereas in the potential oscillation system, only the true electrode potential varies, and (2) the current oscillation is caused both by a surface process and by a solution and/or external resistance, whereas the potential oscillation is caused only by a surface process.

The potential or current oscillation occurs due to a Hopf bifurcation, a destabilization of a stationary state of an electrochemical reaction system. Koper¹⁴ has developed a method by which the saddle node and the Hopf bifurcations can be graphically identified from the impedance diagram.¹⁶ Naito et al.¹⁵ have derived a general relationship between the linear stability and complex impedance. The relationship also describes an analytical formula for the complex impedance related to the reaction kinetics. If we can observe a stationary state at each potential, namely, if we can measure the stationary voltammogram, we will be able to measure the impedance at each potential and then evaluate the parameters, such as the rate constants, under the assumption that the reaction kinetics is known. Although we are in principle able to do this only if the stationary voltammogram is obtained, it is more pertinent to do this when the reaction system undergoes a Hopf bifurcation, because the

impedance is then simplified and expressed by a dominating single term related to the instability.^{14,15} Thus, in addition to the voltammograms at various sweep rates, the stationary voltammogram is also important for obtaining further insight into the mechanism of formic acid oxidation and its oscillation.

Naito et al.² including one of the present authors (H.O.) have analyzed the instabilities found in the oxidation of formic acid on the basis of a mechanistic model³ for the galvanostatic potential oscillation. The stationary state used there was not the one determined by experiment but the one assumed by equalizing all the time-differential terms to be zero. It is well-known,^{9,10} however, that a repeating voltammogram obtained after many triangular potential sweeps for the formic acid oxidation shows different curves in the positive and negative sweep directions and their shape depends on the sweep rate. This means that such a voltammogram is not the true stationary voltammogram, because the stationary one should show the same curves independent of the sweep rate in the positive and negative sweep directions.

There is a probability that the stationary voltammogram may not exist, because a hysteresis effect may dominate the voltammogram during the measurement. Hence we need to clarify the existence of the stationary voltammogram to investigate the impedance. We can then evaluate parameters that have been partly determined by other experiments and partly estimated as optimum. Incidentally, Capon et al.⁹ and Llorca et al.¹⁷ have shown that the formic acid oxidation on adsorbed Pd provides a voltammogram that shows very similar curves with a single current peak in the positive and negative sweep directions. The latter researchers,¹⁷ however, also found that the peak current decreased with time on the order of 10 s, meaning that the voltammogram was not the stationary one for the formic acid oxidation on Pd.

Many researchers have studied the oxidation of formic acid using voltammograms for a long time and have provided quite a few chemical concepts such as a surface poison, electrons per site (eps), electrons per molecule (epm), and a dual path

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mechanism. The dual path mechanism^{8,9} is a widely accepted mechanism for the oxidation of formic acid and formaldehyde. It consists of two paths, one through a reactive intermediate and the other through a strongly bound intermediate, which is a surface poison at a potential lower than about 0.5 V vs NHE and a reactant at a potential around 0.8 V. Recently, Miki et al.¹⁸ have clarified by surface-enhanced infrared absorption spectroscopy (SEIRAS) that the reactive intermediate is a formate adsorbed on two platinum atoms via two oxygen atoms of the formate. Beden et al.¹⁹ and Kunimatsu²⁰ have established by infrared reflection-absorption spectroscopy (IR-RAS) coupled to electrochemical modulation technique (EMIRS) and IR-RAS only, respectively, that the strongly bound intermediate is a linearly adsorbed CO on Pt.

A research group of Schell has shown interesting cyclic voltammogram behaviors of formic acid and other organic molecules by considering cyclic voltammetry as a measurement of behavior of a periodically forced nonlinear system. In the voltammograms, they found bistability for the oxidation of formic acid etc.²¹ and period doubling and chaos for the oxidation of methanol etc.²² They also showed the possible use of chemical instabilities found in the voltammogram to deduce the dominant elementary reactions during the oxidation of ethylene glycol.²³ Such intriguing studies have not been carried out without a nonlinear dynamical viewpoint. They have shown the possibility that familiar voltammograms provide new features if we study them with nonlinear dynamics in mind, because voltammograms themselves essentially show dynamic characteristics of the surface catalytic reactions. This is another reason for investigating the stationary voltammogram for the oxidation of formic acid.

This paper describes the existence, shape, and some characterization of the stationary voltammogram for the oxidation of formic acid.

Experimental Section

The current and potential were measured and controlled with a conventional three-electrode cell mainly at 42 °C. The working electrode was a polycrystalline platinum net with a purity of 4 N (99.99%) or a polycrystalline platinum rotating disk with a purity of 3 N, the reference electrode was a normal hydrogen electrode (NHE), and the counter electrode was a platinum wire. The true surface area was 2.5 cm² for the net and 0.60 cm² for the disk, determined with the generally accepted value of charge, 0.21 mC cm⁻². The Pt net working electrode was pretreated by heating it in a hydrogen flame for several seconds, immediately immersing it in an electrolytic solution, and then cleaning it by repeatedly applying a triangular potential sweep between 0.05 and 1.4 V at a sweep rate of 0.1 V s⁻¹. The Pt disk working electrode was pretreated by immersing it in hot nitric acid (ca. 3 mol dm⁻³) solution for 20 min, rinsing it with Millipore "Milli Q" water, and then cleaning it by repeatedly applying a triangular potential sweep in the same way as for the Pt net electrode.

We carried out the experiments very carefully to avoid contamination with impurities because some experimental runs took hours to finish. The supporting electrolytic solution was sulfuric acid (Kanto "Ultrapur" or Wako "Super Special Grade") or perchloric acid (Cica-MERCK "Ultrapur") diluted with Millipore "Milli Q" water. The formic acid solution was prepared by adding formic acid (Aldrich, ACS reagent) to the supporting electrolytic solution. To deoxygenate the electrolytic solution, nitrogen gas (Nippon Sanso, over 6 N) was bubbled through the solution before the measurement, and to keep the

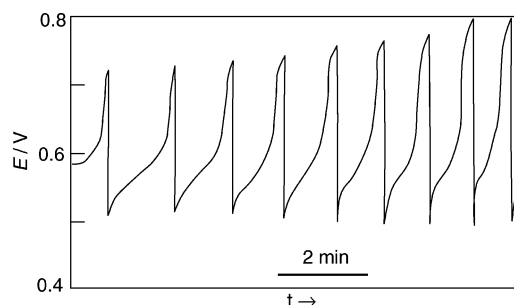


Figure 1. Typical potential oscillation observed during the oxidation of formic acid. Conditions: 0.1 M formic acid, 0.5 M H₂SO₄, 2.5 mA, 42 °C. Potential oscillation appears spontaneously under constant current conditions.

solution deoxygenated, nitrogen was flowed over the solution during the measurement.

We used a function generator (Hokuto Denko, HB-105) and a potentiostat/galvanostat (Hokuto Denko, HA-501G) for the static cell, or a dual potentiostat/galvanostat (Hokuto Denko, HR-101B) for the rotating disk cell in which the disk revolution speed was controlled by a motor speed controller (Nikko Keisoku, SC-5). The time sequence of the potential or current values was acquired through an AD converter (National Instruments, PCI-6034E) and saved in a personal computer after averaging 100 values acquired at a sampling rate of 100 kHz or slower on a program (National Instruments, LabVIEW). At the same time, the time sequence was recorded with an X-T or X-Y recorder.

Results and Discussion

Potential Oscillation and Voltammograms. When a 2.5 mA current was applied to the platinum electrode in a solution containing 0.1 mol dm⁻³ (M) formic acid and 0.5 M sulfuric acid at 42 °C, a potential oscillation spontaneously occurred, as shown in Figure 1. As time passed, the oscillation period decreased from ca. 1.5 to 0.5 min and the oscillation potential range widened from approximately 0.50–0.72 to 0.49–0.8 V, and then the potential jumped to a value higher than 1.2 V and the oscillation ceased (the latter part is not shown in the figure). Such an oscillation pattern change under constant experimental conditions is probably due to the slow diffusion of formic acid compared to surface reactions.

Dynamic behavior like a potential oscillation is closely related to a voltammogram, as mentioned in the Introduction. It is well-known that the voltammogram for the formic acid oxidation shows different curves in the positive and negative sweep directions, as shown in Figure 2a. The oscillation potential range is indicated there, which includes a region of a negative differential resistance (NDR). The NDR qualitatively explains the mechanism of the potential oscillation. Because the voltammogram shown in Figure 2a changed according to the sweep rate, it is not the stationary one. The stationary voltammogram is also important to investigate the instability of the reaction system, as mentioned in the Introduction. We therefore tried to obtain the stationary voltammogram.

Here, for the convenience of explanation, current peaks at ca. 0.6, 0.85, and 1.45 V in the positive sweep direction are called, respectively, peak I, peak II, and peak III, the last one being shown in Figure 2b, and a current peak in the negative sweep direction at ca. 0.71 V in Figure 2a and at ca. 0.6 V in Figure 2b is called peak IV, according to the literature^{9,10} and our previous paper.⁴ Additionally, we name the familiar slight shoulder⁹ at ca. 0.47 V in the negative sweep direction peak V,

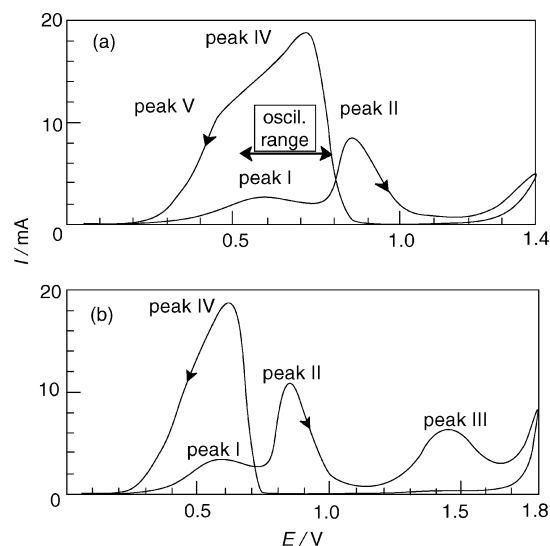


Figure 2. Voltammograms for the oxidation of formic acid. Potential sweep range : 0.05–1.4 V (a) and 0.05–1.8 V (b) vs NHE. Conditions: 0.1 M formic acid, 0.5 M H_2SO_4 , 100 mV s^{-1} , 42 $^\circ\text{C}$. The oscillation potential range is shown by the thick arrow bar. There are four current peaks, peaks I, II, III, and IV, and one shoulder, which we name peak V, at ca. 0.47 V in the negative sweep direction.

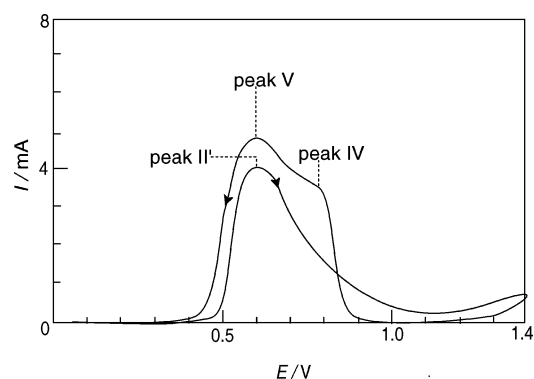


Figure 3. Quasi-stationary voltammogram measured at a sweep rate of 0.1 mV s^{-1} . Conditions: 0.1 M formic acid, 0.5 M H_2SO_4 , 42 $^\circ\text{C}$. Only one current peak is observed both in the positive and in the negative sweep directions. The current peak in the positive sweep direction corresponds to a new peak, named peak II', which is formed by merging peaks I and II. The current peak in the negative sweep direction corresponds to peak V. We expect the shoulder corresponding to peak IV at ca. 0.8 V during the negative-going sweep disappears in the stationary voltammogram.

which will prove to be the one and only current peak in the stationary voltammogram.

Stationary Voltammogram. In principle, the stationary voltammogram should be obtained at a very slow sweep rate. We then measured the voltammogram at a very slow sweep rate like 0.1 mV s^{-1} and successfully obtained a quasi-stationary voltammogram, as shown in Figure 3. Although there are some differences between the curves in the positive and negative sweep directions, the two curves are substantially the same or very similar. The results shown in Figures 3 and 4(c1–c4) obtained by systematically decreasing the sweep rate promise to give the stationary voltammogram at a slower sweep rate. Because a shoulder at ca. 0.8 V in the negative sweep direction is expected to disappear, as shown below, the features of the stationary voltammogram are the presence of a single current peak at 0.6 V in both the positive and negative sweep directions. A systematic change in the voltammograms shown in Figures 3 and 4(c1–c4) shows that the single current peak corresponds

to peak V or a new peak, named peak II', which is formed by merging peaks I and II, and the shoulder at ca. 0.8 V in the negative sweep direction corresponds to peak IV.

We can expect that peak IV disappears in the stationary voltammogram because the peak height reduces comparatively fast with the decreasing sweep rate, as observed in Figures 3 and 4(c1–c4). It is well-known that peak IV appears due to the reduction of Pt oxides and/or hydroxides and the activation of the surface sites. To confirm the disappearance of peak IV, we then measured the voltammograms with a decreasing upper potential limit from 1.4 to 1.1, 1.0, or 0.9 V to suppress the formation of Pt oxides and/or hydroxides. In this experiment, the sweep rate was set to 0.3 mV s^{-1} for the experimental convenience. This resulted in the disappearance of peak IV as expected, as shown in Figure 5.

We were able to comparatively easily obtain a quasi-stationary voltammogram. This is mainly because the solution temperature happened to be high compared to that adopted in usual measurements, as shown in Figure 4. Figure 4 shows voltammograms measured at systematically changed temperatures and sweep rates. We can see that at each temperature the curves in the positive and negative sweep directions tend to become similar and get closer to each other with a lower sweep rate and that the higher the temperature, the faster the curves get closer. At 62 $^\circ\text{C}$, the two curves were almost the same at the high sweep rate of 1 mV s^{-1} , whereas at 22 $^\circ\text{C}$, the sweep rate probably should be slower than 0.01 mV s^{-1} to obtain a quasi-stationary voltammogram, meaning it takes longer than 3 days.

Stationary Voltammogram under Various Conditions. As shown above, the stationary voltammogram consisted of a single current peak and the peak originated from the often-neglected subtle shoulder peak V. We suspected that such an unexpected shape of the voltammogram happened to be found under the specially adopted conditions. We then investigated the quasi-stationary voltammograms under various conditions. Incidentally, such a voltammogram shape has been observed by several researchers. Capon et al.⁹ and Llorca et al.¹⁷ obtained a similar voltammogram with a single current peak in both the positive and negative sweep directions for the oxidation of formic acid on Pd, though it was not the stationary one, as mentioned in the Introduction. Capon et al.²⁴ observed a voltammogram with a single current peak at ca. 0.7 V in the first positive-going sweep for the formic acid oxidation on Pt after boiling the electrode in distilled water, though it was not observed in the second sweep and thereafter. Lu et al.¹³ obtained a voltammogram with a single current peak at 0.57 V as the voltammogram in the absence of the adsorbed CO. Our voltammogram obtained here is influenced by adsorbed CO, because it is the stationary one.

We first changed the concentration of formic acid from 0.01 to 3 M with the sulfuric acid concentration fixed at 0.5 M and obtained voltammograms as shown in Figure 6. Figure 6 demonstrates a tendency that at each concentration of formic acid, peaks I and II merge to form peak II', peak IV diminishes comparatively fast, and the inconspicuous shoulder peak V remains comparatively unchanged with the lower sweep rates, though such a tendency is not so easy to see at 0.01 M. Thus we can confirm that the shape of the stationary voltammogram does not depend on the concentration of formic acid. Incidentally, we can see a trend that the voltammogram for a lower concentration of formic acid becomes the stationary one at the higher sweep rate. This is probably because it becomes more

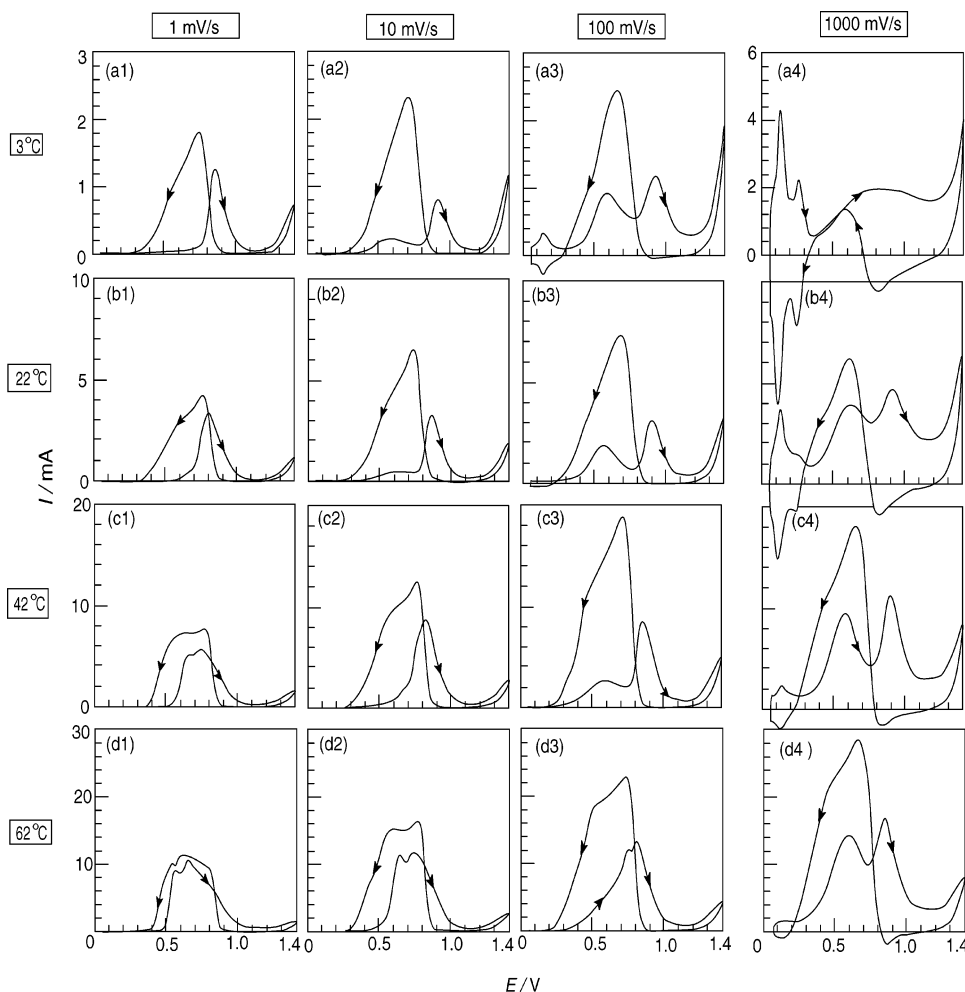


Figure 4. Voltammograms measured at systematically changed temperatures and sweep rates. Conditions: 0.1 M formic acid, 0.5 M H₂SO₄. At each temperature, the curves in the positive and negative sweep directions tend to become similar and get closer to each other with the lower sweep rates, and above all, the higher the temperature, the faster the curves get closer.

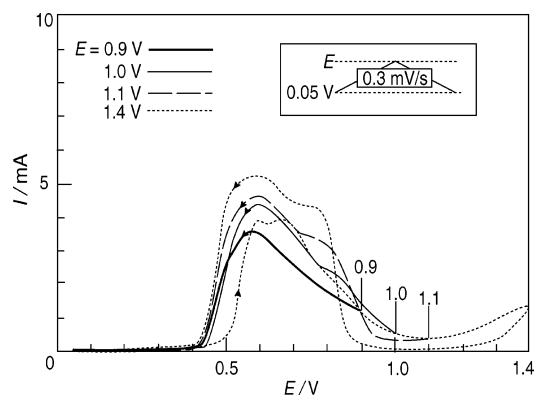


Figure 5. Quasi-stationary voltammograms measured by lowering the upper potential limit. Conditions: 0.1 M formic acid, 0.5 M H₂SO₄, 0.3 mV s⁻¹, 42 °C. On lowering the upper potential limit from 1.4 to 0.9 V, the height of peak IV decreases and then disappears.

difficult to form adsorbed CO in a solution with a lower concentration of formic acid.

We then changed the concentration of sulfuric acid from 0.05 to 1.5 M with the formic acid concentration kept at 0.1 M and measured the voltammograms at a sweep rate of 1 mV s⁻¹ for the experimental convenience. As shown in Figure 7, the resultant voltammograms were similar to that of 0.5 M sulfuric acid, although that of 0.05 M showed a sharp peak IV. The latter result may be due to a low concentration of H⁺ ions rather than to a low concentration of sulfate ions. This is because, as

shown below, the voltammogram for 0.5 M perchloric acid used as a nonadsorbing supporting electrolyte was more similar to that of the same concentration of sulfuric acid rather than that of 0.05 M sulfuric acid, although the adsorption of perchlorate ion on Pt is open to argument.²⁵ Thus we can say that voltammograms similar to that shown in Figure 3 are obtained at least when the sulfuric acid concentration is greater than 0.15 M.

We then measured voltammograms for the solution with perchloric acid as a nonadsorbing supporting electrolyte instead of sulfuric acid at sweep rates of 100 and 1 mV s⁻¹. As shown in Figure 8a,b, the resultant voltammograms were similar to those of sulfuric acid shown in Figure 4(c1,c3) in that a single peak became conspicuous in both the positive and negative sweep directions with a decrease in the sweep rate, although some small differences can be seen due to the adsorption of anions such as a sulfate ion and/or a bisulfate ion. Thus we can conclude that the shape of the stationary voltammogram is not influenced by the adsorption of anions.

Last, we investigated the effect of mass transfer in the solution on the shape of the stationary voltammogram. We measured the voltammograms using a rotating Pt disk at a rotating speed of 4000 revolutions per min (rpm) instead of a static Pt net at sweep rates of 100 and 1 mV s⁻¹. As shown in Figure 8c,d, the resultant voltammograms showed a change basically similar to those at 0 rpm in that a single peak became conspicuous in both the positive and negative sweep directions with a decrease

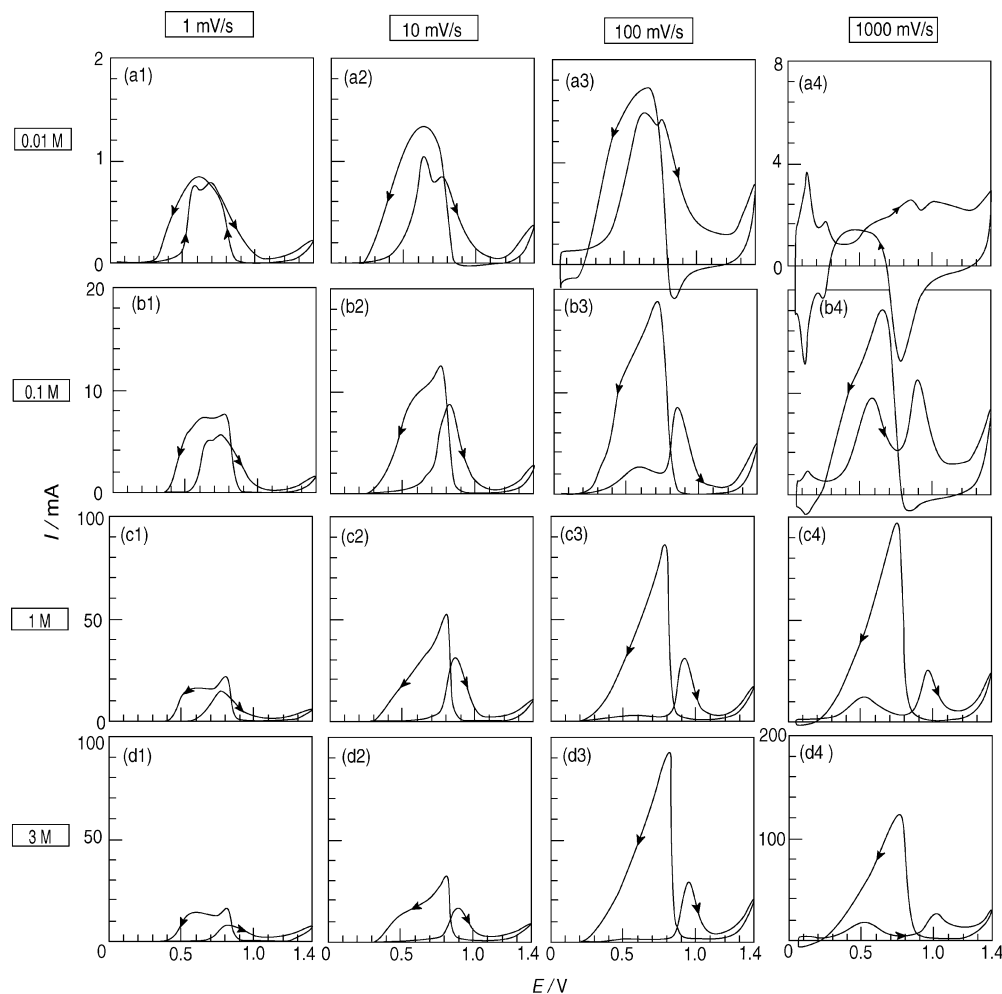


Figure 6. Voltammograms measured at systematically changed concentrations of formic acid and sweep rates. Conditions: 0.5 M H_2SO_4 , 42 °C. At each concentration of formic acid, the voltammograms tend to become the one shown in Figure 3 by lowering the sweep rate, and the tendency is stronger with the lower concentration of formic acid.

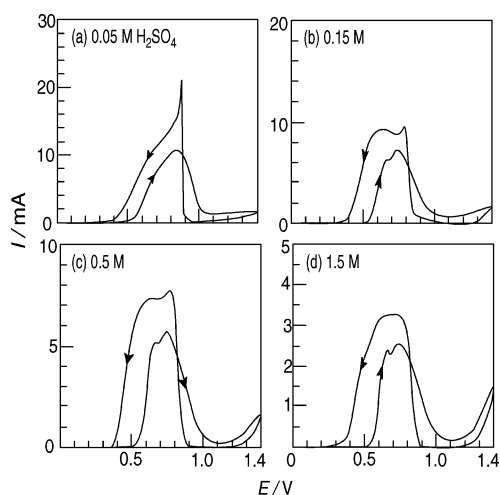


Figure 7. Voltammograms measured at systematically changed concentrations of sulfuric acid. Conditions: 0.1 M HCOOH , 1 mV s^{-1} , 42 °C. All the voltammograms except one, (a), are very similar in that a single current peak (with a slight shoulder) is observed both in the positive and in the negative sweep directions and they are comparatively closely positioned to each other. The reason for the sharp peak in the negative sweep direction observed in (a) is mentioned in the text.

in the sweep rate, although some small differences can be seen. Thus we can conclude that the shape of the stationary voltammogram is not influenced by the mass transfer in the solution.

Consequently, we can say that the stationary voltammogram like the one shown in Figure 3 is characteristic of the oxidation of formic acid.

Adsorbed CO in the Stationary Voltammogram. We next examined where on the single current peak in the stationary voltammogram the adsorbed CO was oxidized to produce CO_2 in the positive sweep direction and was formed in the negative sweep direction. To investigate this, we used the fact that peak II clearly appears during the positive-going sweep at a sweep rate of 100 mV s^{-1} if the adsorbed CO is present. For experimental convenience, we investigated a quasi-stationary voltammogram measured at a sweep rate of 0.3 mV s^{-1} as the stationary voltammogram. We swept the potential to a certain value, E , at 0.3 mV s^{-1} in the positive sweep direction and then swept at 100 mV s^{-1} in the positive sweep direction, as shown in Figure 9a, or swept the potential to a turning potential of 1.4 V in the positive sweep direction and then swept back to a certain value, E , at 0.3 mV s^{-1} in the negative sweep direction followed by a sweep at 100 mV s^{-1} in the positive sweep direction, as shown in Figure 9b.

The results are demonstrated in Figure 9c,d for the potential profiles shown in Figure 9a,b, respectively. Figure 9c shows that the adsorbed CO remains until about 0.6 V in the positive sweep direction. Figure 9d shows it forms at 0.5 V in the negative sweep direction. Because the peak potential is 0.6 V and the voltammogram is a quasi-stationary one, we conclude that in the stationary voltammogram, the adsorbed CO is present

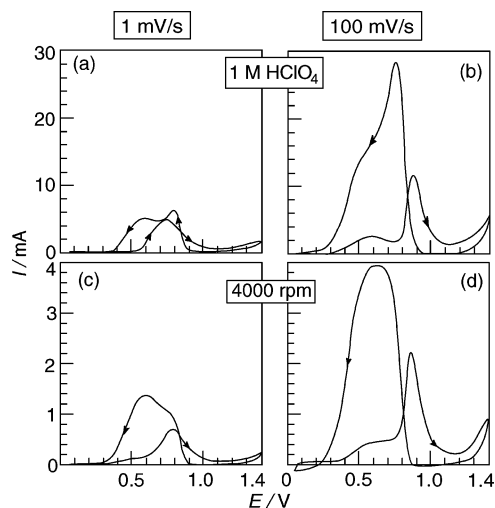


Figure 8. Effect of anion adsorption and mass transfer on the change in the voltammograms measured at sweep rates from 100 to 1 mV s⁻¹. Conditions: 0.1 M HCOOH, 42 °C. (a), (b) Voltammograms measured in a solution with perchloric acid instead of sulfuric acid. (c), (d) Voltammograms measured with a rotating disk at a rotating speed of 4000 rpm. The observed changes in the voltammograms are similar to those of sulfuric acid at 0 rpm in that a single peak becomes conspicuous both in the positive and in the negative sweep directions and they get closer to each other with a decrease in the sweep rate, although some small differences are seen.

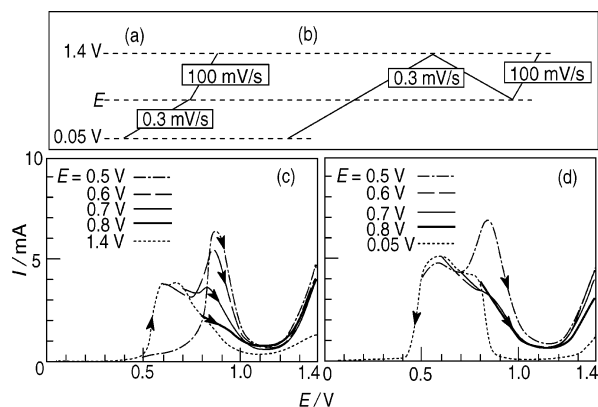


Figure 9. Oxidation and formation of adsorbed CO during measurement of a quasi-stationary voltammogram. Conditions: 0.1 M formic acid, 0.5 M H₂SO₄, 42 °C. (a), (b) Potential sweep profiles. (c), (d) Voltammograms at 100 mV s⁻¹ in the positive sweep direction following the potential profiles (a) and (b), respectively. Regarding the appearance of peak II as a sign of the presence of adsorbed CO, we can say that the adsorbed CO is present on the negative side of the current peak at 0.6 V and absent on the positive side.

on the negative side of the current peak and is absent on the positive side, and it is oxidized or formed around the peak potential.

The above conclusion was supported by the following experiment. During the measurement of the voltammogram at 100 mV s⁻¹, we stopped sweeping the potential at various potentials, E , and then measured the current for 1000 s at E , as shown in Figure 10a,b.

The result for the potential sequence shown in Figure 10a with a potential stop during the positive-going sweep is shown in Figure 10c, and that of the sequence shown in Figure 10b with a potential stop during the negative-going sweep is shown in Figure 10d. The former result shows that at 0.5 V, the current change is very slight with a reduced maximum at about 450 s, whereas at potentials between 0.6 and 0.8 V, the current change shows a clear maximum, the time of which becomes shorter

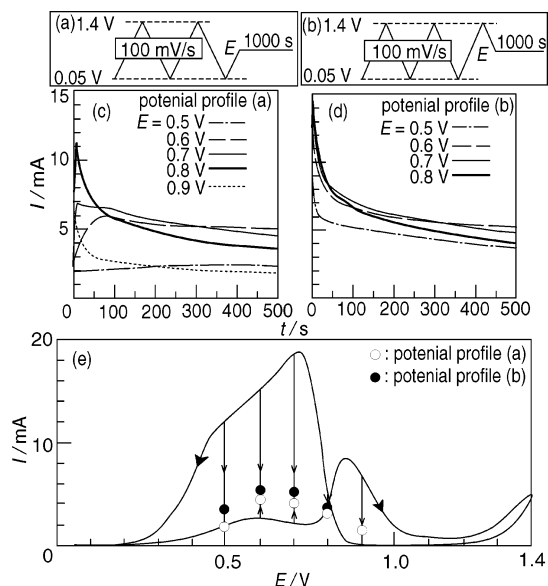


Figure 10. Current changes at potentials held during measurement of voltammograms. Conditions: 0.1 M formic acid, 0.5 M H₂SO₄, 42 °C. The current at a fixed potential following the potential profile (a) is shown in (c) and that of (b) in (d). The results agree well with that shown in Figure 9 (c, d). The current values after holding the potential at various values for 1000 s are plotted in (e). The discrete plot is in accordance with the values of the quasi-stationary voltammogram shown in Figure 3.

with a higher potential, and at 0.9 V, the current monotonically decreases. Similar results have been obtained by Kita et al.¹⁰ This result means that at 0.5 V, the amount of the adsorbed CO hardly changes, whereas at potentials between the peak potentials of peaks I and II, the adsorbed CO is oxidized faster at a higher potential, and at a potential higher than that of peak II, the adsorbed CO is absent.

The result shown in Figure 10d demonstrates that all the current curves monotonically decrease, and above all, at 0.5 V, the current very steeply decreases. This indicates that at a potential between 0.8 and 0.6 V, the surface is deactivated due to some change in the adsorption state or surface structure, whereas at 0.5 V, surface deactivation is due to formation of the adsorbed CO. Thus, the result shown in Figure 10c,d agrees well with that shown in Figure 9c,d.

The current values after holding the potential at various values for 1000 s were very close to those of the stationary voltammogram, as shown in Figure 10e. Therefore, this is another way to obtain the stationary voltammogram, though such a way only gives a discrete one.

Because the description above on the adsorbed CO is only a speculation based on the electrochemical measurement, direct evidence is needed such as spectroscopy. We also expect that spectroscopy would clarify the reason for the monotonic current decrease on the positive side of the current peak. We have now established the existence of the stationary voltammogram for the oxidation of formic acid. On the basis of the stationary voltammogram, we are measuring the impedance and evaluating parameter values.

Conclusions

The stationary voltammogram, or strictly speaking, a quasi-stationary voltammogram was obtained at 42 °C at a sweep rate of 0.1 mV s⁻¹ for the oxidation of 0.1 M formic acid in a 0.5 M sulfuric acid solution. The stationary voltammogram consisted of a single current peak at 0.6 V both in the positive and in the

negative sweep directions in the potential range between 0.05 and 1.4 V. Its overall current was low compared to that of the voltammogram measured at 100 mV s⁻¹. The shape of the stationary voltammogram was hardly affected by the temperature and the concentration of formic acid. Both the shape and current were hardly affected by the concentration of sulfuric acid, by the adsorption of anions, and by the mass transfer in solution. However, we found it difficult to obtain the stationary voltammogram at room temperature or lower. We also found that the adsorbed CO was present on the negative side of the current peak and absent on the positive side.

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