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Adsorption and Anodic Oxidation of Formic Acid on Platinum Plated Tungsten Electrodes

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The adsorption of formic acid molecules and oxygen atoms on bright platinum and platinum plated tungsten as-plated and heat-treated at 750, 1000, and 1250°C has been measured as a function of the electrode potential and of the concentration of formic acid in 1 M H₂SO₄ solution. Anodic and cathodic charging curves measured from a finite potential in the constant potential electrolysis or during the anodic and cathodic potential sweeps were analyzed in detail. The characteristics of the current-potential curves were interpreted with the aid of adsorption measurements. The adsorption behaviors of formic acid on the platinum plated tungsten electrodes were found to be almost the same with those on bright platinum electrode. The coverage at 0.1 V vs. SCE increases with the concentration of formic acid. A nearly constant coverage is maintained from 0 V to 0.4 V vs. SCE during the anodic sweep. The formation of the oxygen layer on each electrode begins at the different potentials and is hardly influenced by the presence of formic acid. The characteristic shape of the current-potential curves is due to the change in the electrode surface. The experimental results on platinum plated tungsten electrodes lead to a conclusion of the same type of the reaction mechanism proposed by Gileadi.

1. Introduction

Platinum plated tungsten electrodes developed in our previous work¹⁾ gave various anode characteristics for the electrolytic formation of persulphate depending on the condition of heat-treatment applied after the platinum plating. It was suggested that the change in the surface area resulted from the heating condition may contribute to the variation of anode characteristics of the electrode for the anodic oxidation at the potential higher than oxygen evolution.

The anodic oxidation of formic acid provides an example for the anodic reaction at low potential. It is well known that, at low potentials, formic acid molecules^{2) 3)} or discharged radicals⁴⁾ are adsorbed on platinum electrode.

Müller and co-worker carried out an extensive study of the anodic oxidation of formic acid on several platinum group metals in aqueous electrolytes.^{5) 6) 7)} They interpreted the anodic oxidation of formic acid on the basis of a dehydration mechanism. This mechanism is represented by the following scheme :



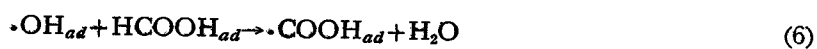
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Schwabe²⁾ presented an experimental evidence that formic acid molecules are the initial reaction species for anodic oxidation on platinum electrode. He explained that the dissociation of formic acid molecules on the platinum surface was a rate determining step.

Since, however, the value of maximum charge required for the oxidation of adsorbed species was too large to account for the adsorbed HCOOH itself, Brummer⁹⁾ concluded that the adsorbed species was hardly to be HCOOH itself, but likely to be CO or "reduced CO₂".

At the higher potentials, a mechanism involving water discharge should be considered,⁹⁾ as in the following scheme :



This scheme may be applied only to the oxidation reaction at high anodic potentials.

Mechanism of the anodic oxidation of formic acid may be elucidated by the determination of adsorbed species. The identification and the measurement of the amount of adsorbed species are very important in the study of anodic oxidation at low potentials under which the disturbance of the adsorption by oxygen layer is to be neglected.

In this study, anodic oxidation and especially adsorption of formic acid on platinum plated tungsten electrode has been investigated. Some of the characteristics of the current-voltage curves also discussed with the aid of the adsorption data.

2. Experiment

2.1. Electrode and electrolyte

The electrodes used in this study were as-plated, and heat-treated platinum plated tungsten electrodes. Platinum plating onto the tungsten substrate was carried out by using a diamminonitrite platinum plating bath in a manner described in the previous paper.¹⁾ The heat-treatments of the electrodes were carried out at 750, 1000, and 1250°C in the reducing atmosphere. The platinum plated tungsten electrodes consisted of a length of 7.5 mm platinum plated tungsten wire (2 mm ϕ) sealed in a polyethylene tube and so exposing 0.5 cm² as a working electrode. Bright platinum wire (0.5 mm ϕ × 6.4 mm) was also used as a test electrode.

Surface area of the heat treated electrode was found to change on the temperature of heating. By comparing the amount of adsorbed hydrogen estimated by the potential sweep method in 1 M H₂SO₄ solution, the surface roughness of the bright platinum, as-plated platinum plated tungsten, and platinum plated tungsten

heated at 750, 1000, and 1250°C used in this experiment was determined as 1.68, 2.25, 2.25, 2.55, and 51.0, respectively. Before the measurement, electrode was cathodically treated, followed by anodic electrolysis at 3 mA/cm² in 1 M H₂SO₄ for 3 min.. And then the electrode was rinsed in concentrated HNO₃ for 30 min. and electrolyzed at 0V vs. SCE for 10 min..

Conventional H-type cell separating anode and cathode compartments by sintered glass filter was used as an experimental cell. Reference electrode used in the present experiment was SCE and a counter electrode was platinum foil of 10 cm². Measurement was carried out at 25°C throughout this experiment. All the potentials in this study are referred to a SCE.

HCOOH and H₂SO₄ used were analytical reagents. The solutions were prepared by using a redistilled water. The experiments were carried out in the solution saturated with purified nitrogen.

2.2. Measurement

The adsorption of formic acid, oxygen, and hydrogen was measured at the different potential and the bulk concentration of formic acid by means of anodic or cathodic charging curves obtained from a finite potential in the potentiostatic electrolysis or during the anodic and cathodic potential sweeps.

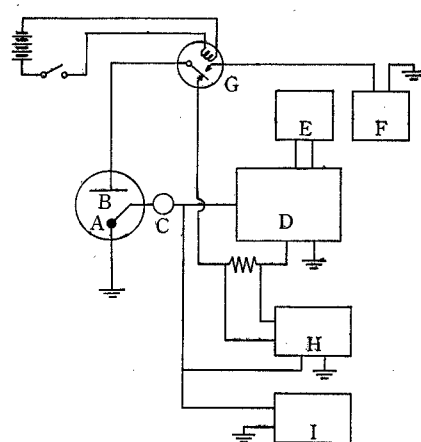


Fig. 1. Circuit diagram.
 A: Working electrode
 B: Counter electrode
 C: Reference electrode
 D: Potentiostat
 E: Voltage generator
 F: Current generator
 G: Relay
 H: X-Y recorder
 I: Oscilloscope

The electric circuit employed in this study was shown in Fig. 1. Voltage-generator is a low frequency oscillator generating a cyclic triangular voltage signal of the sweep rate $v=0.025$ V/sec. Current-generator is a current supplier generating a constant current of short square wave form. The switching from the potentiostatic circuit to the galvanostatic circuit was accomplished by means of a mercury wetted relay whose operation was started manually by a micro-switch when the potential reached a finite value during the low-speed sweep or when the time reached a desired value in the electrolysis of a constant potential. The potential sequence thus applied to the electrode was shown in Fig. 2.

The potential of +0.1 V was chosen for the measurement of the adsorption of

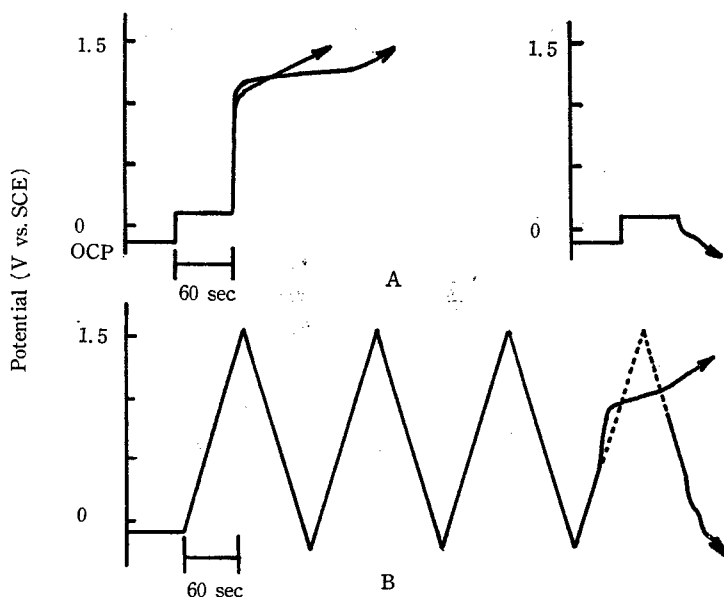


Fig. 2. Potential sequence applied to the electrode.
 A: Adsorption at constant potential
 B: Adsorption during a slow triangular sweep

HCOOH at the constant potential. Electrolytes used were 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} M HCOOH—1 M H_2SO_4 solution. Pre-treated electrode as described above was inserted in the electrolysis cell filled with an electrolyte, and electrolyzed at +0.1 V for 60 sec. . And then, the circuit was switched to the galvanostatic one. In the galvanostatic electrolysis, current density used was $0.1A/cm^2$ for the bright platinum (Pt), and platinum plated tungsten (Pt-W) as-plated and heat-treated at 750 and $1000^\circ C$, and was $0.4 A/cm^2$ for the heat-treated Pt-W at $1250^\circ C$. Charging curves for the anodic and cathodic electrolysis were recorded with a cathode ray oscilloscope.

The current-potential curve measured from -0.26 V to 1.55 V at 0.025 V/sec by means of the triangular voltage scanning device gave reproducible results after a few cycles. Then, the anodic or cathodic charging curve was measured from a finite potential during the anodic and cathodic potential sweeps.

Surface oxygen layer could also be determined by means of the cathodic charging curve during anodic and cathodic potential sweeps. Electrolyte used was 10^{-2} M HCOOH—1 M H_2SO_4 solution. The arrest of a cathodic charging curve corresponding to the reduction of oxygen layer could be distinguished in these measurements, and the quantity of electricity required for the reduction of oxygen layer may be estimated from the length of the arrest. The conditions of the electrolysis were the same as above.

The measurement of the current-potential curve by means of the potential sweep method was carried out in the same manner described above in 10^{-2} , 10^{-1} , 3×10^{-1} , 5×10^{-1} , and 1 M HCOOH—1 M H_2SO_4 solution. Steady-state poten-

tiostatic current-potential curves were also measured in a usual manner in 10^{-2} , 10^{-1} , and 1 M HCOOH—1 M H₂SO₄.

3. Results and discussion

3.1. Cathodic and anodic charging curves

As has been demonstrated by Breiter^(9,10), the coverage of the adsorbed HCOOH molecules can be computed from the decrease of the length of the hydrogen branch of cathodic charging curves. Fig. 3 shows a series of cathodic charging curves which were obtained from the different potential during the anodic sweep with a current density of 0.1 A/cm² in 10^{-2} M HCOOH—1 M H₂SO₄ or 1 M H₂SO₄ solution. The two steps in which the hydrogen monolayer is formed were observed in the curve measured with 1 M H₂SO₄ solution. The addition of HCOOH and also the decrease of the potential from which the cathodic charging curve was obtained lead to a decrease of the length of hydrogen branch. The first step decreases more rapidly than the second one. The appearance of these two steps has been explained on the concept that hydrogen evolution on platinum involves two adsorption sites with small or large heat of adsorption.

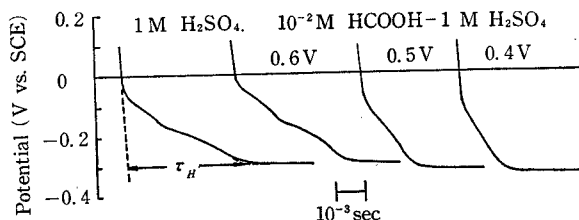


Fig. 3. Cathodic charging curves obtained from different potentials during the anodic sweep with 0.1 A/cm² in H₂SO₄ and in 10^{-2} M HCOOH—H₂SO₄.

The degree of coverage θ of the electrode can be estimated by the following expression:

$$\theta = (sQ_H - Q_H) / sQ_H$$

where sQ_H and Q_H correspond to the electricity required for the formation of monolayer of hydrogen atom in 1 M H₂SO₄, and in the solution containing HCOOH, respectively.

This method in measuring HCOOH adsorption is based on the assumption that the hydrogen atoms can not be adsorbed on the sites which are already covered with HCOOH molecules.

Fig. 4 shows two anodic charging curves on Pt electrode obtained from 0.1 V at 0.1 A/cm² in 1 M H₂SO₄ (curve a) and in 10^{-2} M HCOOH—1 M H₂SO₄ (curve b). τ_O in curve a indicates the transition time for the establishment of oxygen layer on Pt in pure H₂SO₄ solution. Curve b indicates the increase in the transition time owing to the oxidation of adsorbed HCOOH on Pt electrode.

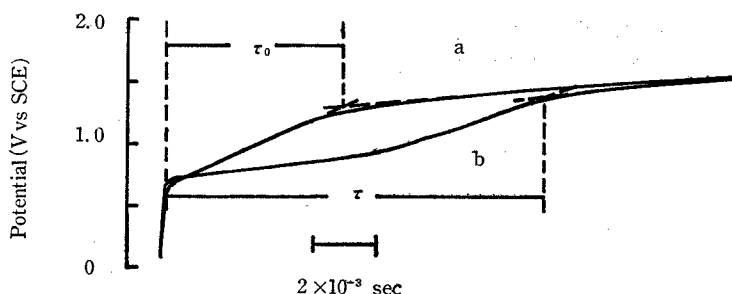


Fig. 4. Anodic charging curves obtained from 0.1 V at 0.1 A/cm² in 1 M H₂SO₄ (curve a) and in 10⁻²M HCOOH-1 M H₂SO₄ (curve b).

Therefore, τ represents the time required for the simultaneous oxidation of adsorbed HCOOH molecules and surface layer of Pt electrode. The time required for the oxidation of adsorbed HCOOH molecules, τ_F is indicated as $\tau_F = \tau - \tau_0$. The coverage of HCOOH is also represented as $\theta' = \tau_F / s\tau_F = Q_F / sQ_F$ where $s\tau_F$ is the transition time required for the oxidation of a monolayer of HCOOH on the electrode, and sQ_F is the quantity of electricity required for the oxidation of a monolayer HCOOH on the electrode. The applied current density should be large enough so as to neglect the oxidation of additional HCOOH molecules diffusing to the electrode surface from the bulk of the solution. In this study, sQ_F is computed with the assumption that one HCOOH molecule occupies one Pt atom and is oxidized by two electron discharge per one molecule.

3.2. Adsorption of formic acid at 0.1 V vs. SCE

The coverage of the Pt electrode with HCOOH molecules at 0.1 V is plotted against the bulk concentration (c_F) of HCOOH in Fig. 5. Coverage, θ (Fig. 5a)

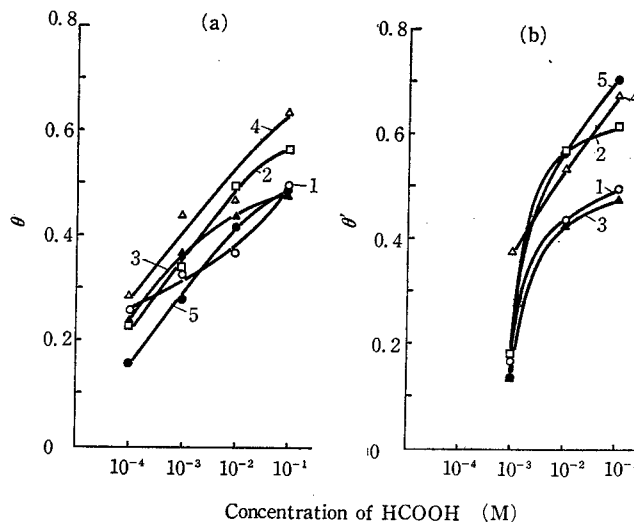


Fig. 5. Coverage, θ of formic acid molecules on each electrode obtained by the cathodic (a) and anodic (b) charging curves after the electrolysis at 0.1 V as a function of the concentration of formic acid. 1: as-plated Pt-W, 2-4: Pt-W heat-treated at 750°C; 2, at 1000°C; 3, at 1250°C; 4, 5: bright Pt

is obtained from the cathodic charging curve and θ' (Fig. 5b) from the anodic charging curve, respectively, after the electrolysis at 0.1 V for 60 sec.. The coverage of the electrode, θ and θ' are not identical in the solution containing less than 10^{-3} M HCOOH. It was pointed out by Gilman¹⁰⁾ in the study of CO adsorption of Pt whether one or two Pt atoms could be occupied by the adsorbed molecules depending on the concentration of the solution. It is well known from the study of catalytic reaction in the gas phase that both one and two adsorption sites exist in Pt surface. Since the amount of hydrogen adsorbed on the electrode refers to the surface area available for the further adsorption, and oxidation of the electrode refers to the amount of adsorbed molecules directly, the coverage obtained by cathodic charging method differs from that obtained by anodic charging method when one site or two site adsorptions exist. For the solution containing less than 10^{-3} M HCOOH, adsorption of HCOOH molecules involves two site adsorption appreciably. On the other hand, for the solution $c_F > 10^{-3}$ M, one site adsorption occurs exclusively.

In general, all the electrodes studied in this experiment develop nearly the same degree of the capacity for adsorption of HCOOH molecules.

3.3. Adsorption of formic acid at various potentials

Fig. 6 shows the change of the coverage of HCOOH molecules with potential

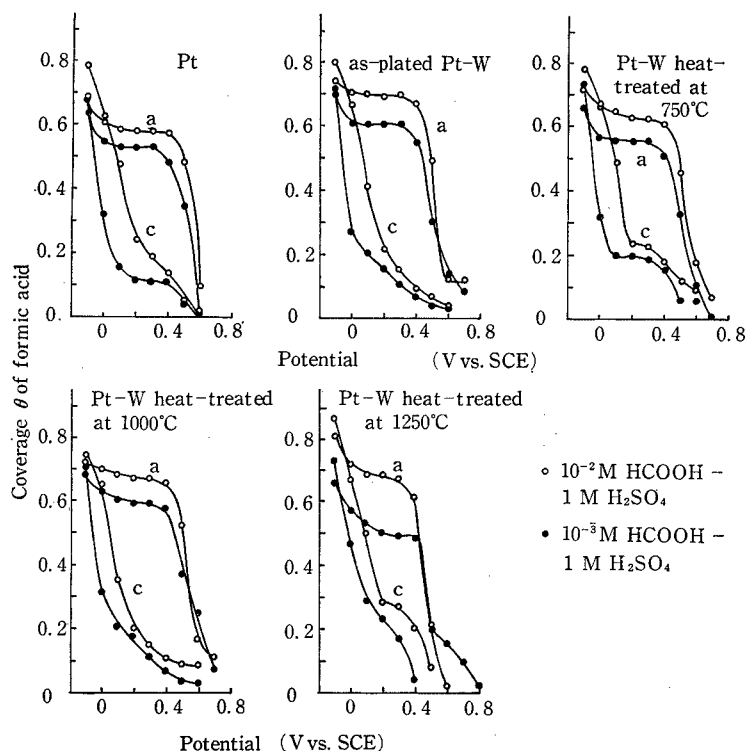


Fig. 6. Coverage, θ of formic acid molecules on each electrode during the anodic a) and cathodic c) low-speed potential sweeps as a function of potential.

in the solution of different bulk concentrations. These results were obtained by means of the cathodic charging curves during the anodic (a), and the cathodic (c) potential sweeps. The adsorption does not seem to occur to an appreciable extent in all the solutions studied and on each electrode before the potential becomes 0.2 V during the cathodic sweep. A nearly constant coverage is maintained from 0 to 0.4 V during the anodic sweep.

The potential dependence of the adsorption of HCOOH molecules is almost the same at all the electrodes studied as far as the adsorption is measured from real surface area. The amount of adsorbed HCOOH on Pt-W heat-treated at 1250°C decreases in somewhat less noble potential. It is interesting to note that the capacity for the adsorption of HCOOH molecules is about the same order of magnitude on the electrodes studied, although they are appreciably different from the real surface.

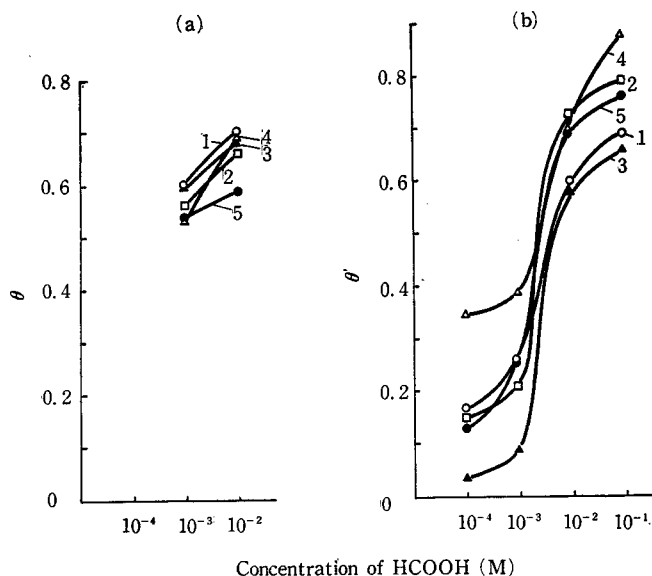


Fig. 7. Coverage, θ of formic acid molecules on each electrode at 0.1 V by means of the cathodic (a) and anodic (b) charging curves during the anodic low-speed potential sweep as a function of the concentration of formic acid.

1: as-plated Pt-W, 2: Pt-W heat-treated at 750°C,
3: at 1000°C, 4: at 1250°C, 5: bright Pt

Fig. 7 shows the change of the coverage of HCOOH molecules on the electrode with a bulk concentration by means of the cathodic (curve a) and the anodic (curve b) charging curves, respectively, obtained at 0.1 V during the anodic potential sweep. The difference between the coverage at 0.1 V obtained from the cathodic charging curves and that obtained from the anodic charging curves is again regarded as a measure of the difference of one site adsorption and two site adsorption of HCOOH molecules.

3.4. Oxygen coverage

In Fig. 8, the quantity of electricity required for the reduction of oxygen layer, Q_0 on each electrode which was determined from the length of oxygen branch appeared in the cathodic charging curves at 0.1 A/cm^2 is plotted against the potential during the anodic and cathodic sweeps in $10^{-2} \text{ M HCOOH}-1 \text{ M H}_2\text{SO}_4$ solution. On each electrode, the formation of oxygen layer during the anodic potential sweep begins at appreciably different potential. During the anodic sweep, the formation of oxygen layer seems to begin at about 0.6 V on bright Pt and Pt-W heat-treated at 750°C , and 0.5 V on Pt-W as-plated and heat-treated at 1000°C and 0.4 V on Pt-W electrode heat-treated at 1250°C . The potentials thus obtained coincide well to those obtained in pure H_2SO_4 solution. The formation of oxygen layer and the adsorption of HCOOH are competitive reactions. The more anodic potential being required to form oxygen layer means that the more anodic potential is necessary to free the surface from adsorbed HCOOH. On the Pt-W electrode heat-treated at 1250°C , therefore, the desorption of HCOOH molecules should occur at the most negative potential. These situations can be observed in Fig. 6. During the cathodic sweep, oxygen layer on each electrode disappears at the potential less than 0.4 V .

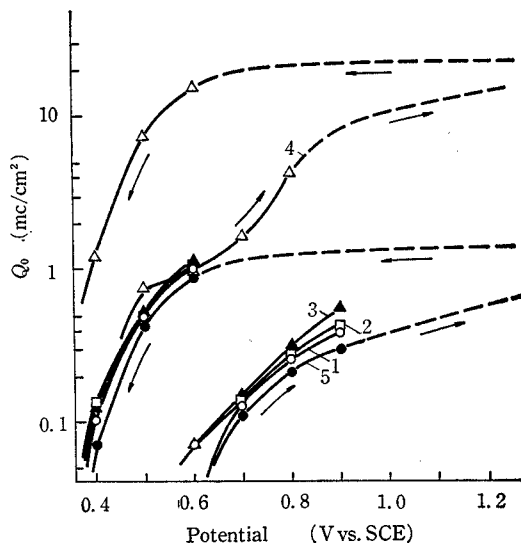


Fig. 8. Quantity of electricity required for the reduction of oxygen layer, Q_0 , on each electrode, as determined by cathodic charging curves with 0.1 A/cm^2 , against potential in $10^{-2} \text{ M HCOOH}-1 \text{ M H}_2\text{SO}_4$.
 1: as plated Pt-W, 2: Pt-W heat-treated at 750°C ,
 3: at 1000°C , 4: at 1250°C , 5: bright Pt

3.5. Current-potential curves

Fig. 9 shows the current-potential curves in $1 \text{ M HCOOH}-1 \text{ M H}_2\text{SO}_4$ obtained by potential sweep method in which the sweep rate is 0.2 V/sec . The shape of the curves vary during the first few cycles. After about 5 cycles, however, a steady

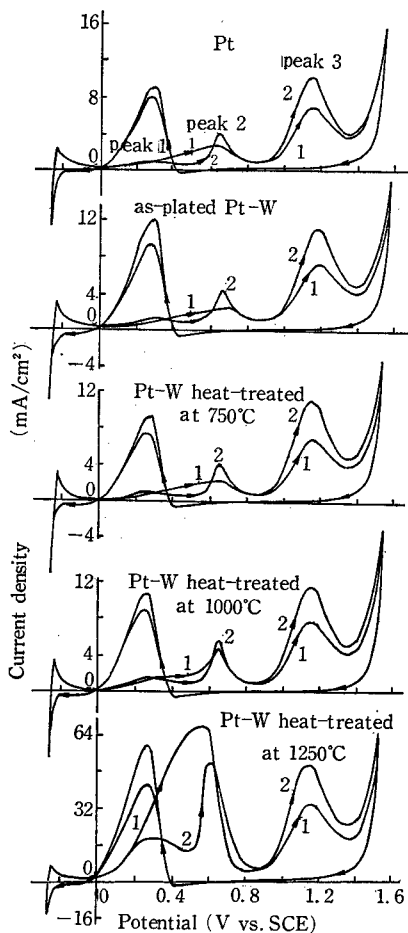


Fig. 9. Current-potential curves in 1 M HCOOH-1 M H_2SO_4 at 0.2 V/sec. 1: first cycle, 2: fifth cycle

current-potential curve can be obtained. When the electrode potential increased from the rest potential to the higher value in the initial anodic sweep, two oxidation peaks can be observed. The cathodic reduction wave of the oxygen layer almost disappears because of the scale order used for the current plot. After the small reduction wave of oxygen layer, pronounced oxidation wave was observed in the curve of cathodic sweep at about 0.3 V. During the second and the further anodic sweeps, three oxidation peaks appeared at about 0.25 V (peak 1), 0.65 V (peak 2), and 1.2 V (peak 3), respectively.

The comparison of these results with the data shown in Fig. 8 implies that the potential of the current rise in the second oxidation peak coincides with the potential of the formation of oxygen layer. The current increase below 0.4 V during the cathodic sweep is related to the decrease of oxygen layer. Oxygen-free surface, therefore, becomes active for the oxidation of HCOOH.

At the potential of the second oxidation peak, the electrode partly covered with oxygen layer seemed to take part in the oxidation reaction of HCOOH as already suggested by Kutschker and Vielstich¹³⁾. The appearance of the peak 3

can not be related to the same mechanism. The other mechanism such as direct oxidation of HCOOH has also been assumed by Müller⁷⁾ for the explanation of the third peak.

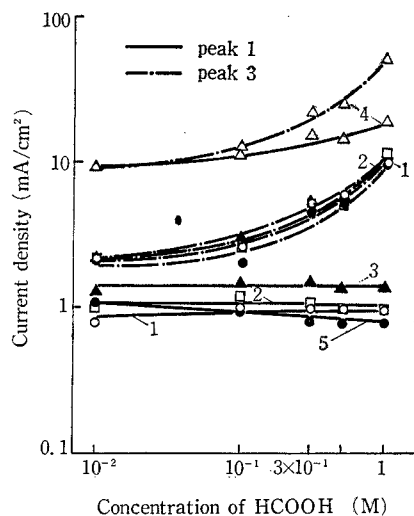


Fig. 10. Dependence of the peak current at peak 1 and peak 3 on the bulk concentration of HCOOH. 1: as-plated Pt-W, 2: Pt-W heat-treated at 750°C, 3: at 1000°C, 4: at 1250°C, 5: bright Pt

The anodic oxidation of HCOOH at the peak 1 is most interesting as a model reaction for organic anode material in fuel cells. Fig. 10 shows the dependence of the peak current at peak 1 and peak 3 on the bulk concentration of HCOOH. Peak current at peak 1 was maintained at almost constant value with the change of a bulk concentration of HCOOH. As shown in Figs. 3 and 6, the amount of adsorbed HCOOH does not seem to change in the concentration range used for studying the current-potential curves. Although the electrodes used in this study have various surface area, and consequently should have different activity in catalyzing organic substances, the current at peak 1 on each electrode was found to be independent on the bulk concentration of HCOOH, and is almost proportional to the real surface area of the electrode. These results suggest that the adsorbed

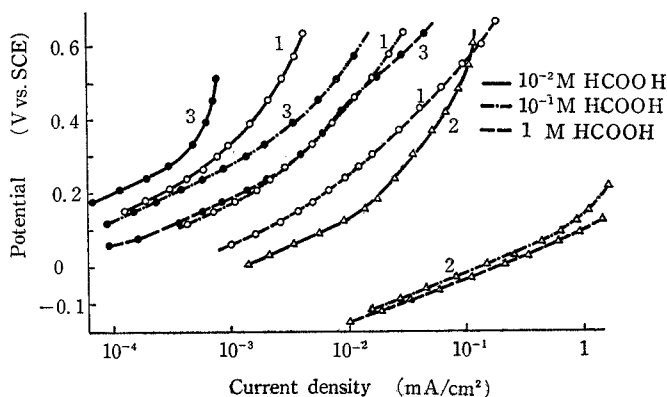


Fig. 11. Steady-state potentiostatic current-potential curves on each electrode in 1 M H₂SO₄ with an addition of different amounts of HCOOH. 1: as plated Pt-W, 2: Pt-W heat-treated at 1250°C, 3: bright Pt

species must be HCOOH molecule itself.

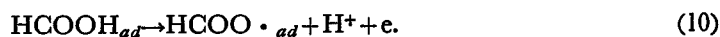
Fig. 11 shows the steady-state potentiostatic current-potential curves obtained with bright Pt and Pt-W electrodes, as-plated and heat-treated at 1250°C, in 10⁻², 10⁻¹, and 1 M HCOOH-1 M H₂SO₄. The curves for bright Pt and as-plated Pt-W exhibited a Tafel region in the potential range 0.1-0.25 V. The Pt-W electrode, heat-treated at 1250°C gave a Tafel line in the potential range -0.15-+0.1 V. The dependence of oxidation rate on HCOOH concentration obtained from Fig. 11 is 0.6 for bright Pt and 0.7 for as-plated Pt-W. The Tafel slope of 2RT/F and (∂ log *i*/∂ log *c_F*)_V of about 0.5 were obtained by Bagotsky and Vasilyev¹²⁾ for the same reaction at a Pt electrode.

The following reaction schemes have been presented:



According to Bagotsky, reaction (9) should give a linear Tafel relationship by which the overall rate is determined.

The reaction sequences in steps (9) and (4) as a single step as described in equation (10) has also been proposed by Gileadi.¹³⁾



When this step is rate-determining in the reaction sequence a Tafel slope of 2RT/F is predictable. Under Langmuir or Freundlich-type condition, a reaction order of the fractional value is also obtainable.

The adsorption characteristics and the polarization behavior of the platinum plated tungsten electrode imply that the mechanism of the anodic oxidation of HCOOH on the Pt-W electrode can be explained by Gileadi's theory.

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