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# Carbon Monoxide Oxidation on Platinum Studied by Local Current and emf in a Solid Electrolyte Concentration Cell

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Surface oxygen and CO concentrations ($N_O$ and $N_{CO}$) adsorbed on Pt during oxidation are determined as functions of $P_{O_2}$ and $P_{CO}$ by local current and emf measurements for a solid electrolyte concentration cell in the region where $P_{CO}$ is low compared to $P_{O_2}$. The temperature range is 570 to 680 K, $P_{O_2}$ is between $1 \times 10^2$ and $5 \times 10^4$ Pa, and $P_{CO}$ ranges from 2.5 to $1 \times 10^4$ Pa. The local current is measured potentiostatically using reference, counter, and working electrodes. As a result, $N_O$ is determined to be proportional to $P_{O_2}{}^{0.0} \cdot P_{CO}{}^{0.1}$ and $N_{CO}$ to $P_{CO}{}^{\delta}/P_{O_2}$ at about 640 K, where $\delta$ increases from 1 to about 1.6 as $P_{CO}$ increases. At lower temperatures, such as 580 K, $N_O$ is determined to be proportional to $P_{O_2}{}^{0.3} \cdot P_{CO}{}^{0.1}$, and $N_{CO}$ to the same formula as at 640 K. The dependence of $N_O$ is considered in terms of electronic effects of adsorbed CO on the Pt surface and that of $N_{CO}$ in terms of the residence time of mobile CO adsorbed on Pt. It is also considered that the initiation of oscillation in CO oxidation is related to the mobility of CO adsorbed on Pt. In the region where CO is more abundant, surface concentrations cannot be determined due to the predominance of resistance polarization in the local current.

## INTRODUCTION

It can be safely said that the mechanism for CO oxidation on Pt has been established in a whole range of gas compositions as a Langmuir–Hinshelwood one, or a process including a reaction between two adsorbed species (*1*) at very low pressures (between $10^{-6}$ and $10^{-3}$ Pa). This conclusion has been obtained by measuring adsorption during surface catalysis, the importance of which has been emphasized by Tamaru (*2*). Surface oxygen has been determined by AES (*3, 4*) and by transient CO pressure-jump (*5, 6*). Surface CO has not been determined continuously during the reaction owing to the cracking of the adsorbed CO by the electron beam (*4*), but has been determined destructively by flash heating (*6, 7*).

At high pressures, those in the order of 1 kPa, the mechanism for the oxidation, especially for the region where CO is scarce in respect to $O_2$, is as yet not well understood. This is because surface oxygen has not been measured, except for one case (*8*) in which surface potential was used as a measure. Also, surface CO has been measured exclusively by infrared spectroscopy (*8–12*), which, for the CO-scarce region, is inadequate for detecting surface CO, due to the small amount present. Thus, continuous and *in situ* measurements of both surface adsorption species have been rather difficult, especially at high pressures.

It has been established that the emf of a solid electrolyte concentration cell with Pt electrodes,

$$O_2(P_{O_2}) + CO(P_{CO}),\quad \text{Pt/stabilized } ZrO_2\text{/Pt},\ O_2(P'_{O_2}), \quad (1)$$

reflects both surface oxygen and CO concentrations on Pt at low temperatures, such as 600 K (*10, 13–17*). Therefore, emf measurement is suitable for continuous and *in situ* determination of such surface concentrations. Also, this measurement is, in principle, possible both under very low pressures and under high pressures, so it may be useful in connecting studies under these

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two conditions (*15*). Moreover, the emf measurement yields relative concentrations of the surface oxygen and CO during reaction as functions of $P_{O_2}$ and $P_{CO}$; this is very helpful when considering the relation between a reaction velocity and the concentrations of surface adsorbed species (*16*), though absolute values cannot be obtained.

However, since only the ratio of the concentrations of surface oxygen to that of surface CO is related to emf when experimental conditions provide a suitable electrode potential, these two concentrations cannot be determined separately without any assumption as to the surface adsorption states (*16*). Therefore, if, in addition to emf measurement, a local current near the three-phase boundary (the region of contact where the electrode, electrolyte, and gas phase meet) is carried out, these two concentrations can be determined separately.

This paper clarifies the applicability of local current and emf to the surface reaction, determines the concentrations of surface adsorption species as functions of $P_{O_2}$ and $P_{CO}$ through local current and emf measurements, and discusses the behavior of surface adsorption species in connection with the reaction kinetics.

## METHODS

First, basic equations as to the relations between local current ($i_0$), emf, and surface concentrations of adsorbed species will be drawn, as will those between $i_0$, emf, and partial pressures for reactant gases. Then, the experimental method will be described.

*Assumptions.* The emf of a galvanic cell (1) deviates significantly at low temperatures from that calculated on the basis of thermodynamics, or the Nernst equation:

$$\text{emf} = |(RT/4F)\ln(P'_{O_2}/P''_{O_2})|. \qquad (2)$$

Here, $R$ is the molar gas constant, $T$ the absolute temperature, $F$ the Faraday constant, and $P''_{O_2}$ the oxygen partial pressure at the anode in equilibrium. It has been established (*10, 13–17*) that this emf deviation is caused by a mixed electrode potential, which will be described below. As the system is not in equilibrium, we will consider it in a stationary state.

The following assumptions are made to relate $i_0$ and emf to the surface concentrations of oxygen and CO on Pt during steady-state reaction, or to partial pressures. These assumptions are essentially the same as previously described (*16*).

(1) During CO oxidation, surface oxygen is dissociative and surface CO is associative.

(2) Surface oxygen and CO concentrations, $N_O$ and $N_{CO}$, respectively, adsorbed near the three-phase boundary, are the same as those elsewhere on Pt.

(3) $N_O$ and $N_{CO}$ are proportional to power expressions of partial pressures:

$$N_O \propto P_{O_2}{}^a \cdot P_{CO}{}^b, \qquad (3)$$

$$N_{CO} \propto P_{O_2}{}^c \cdot P_{CO}{}^d. \qquad (4)$$

Here, $a$, $b$, $c$, and $d$ are parameters which may vary with $P_{O_2}$ or $P_{CO}$.

(4) Both CO chemical oxidation on the whole Pt surface and electrochemical reactions near the three-phase boundary take place simultaneously. The latter do not disturb the former.

(5) These electrochemical reactions are

$$O_\sigma + 2e^- = O^{2-} + \sigma, \qquad (5)$$

$$CO_\sigma + O^{2-} = CO_2 + \sigma + 2e^-. \qquad (6)$$

Here, $O_\sigma$ and $CO_\sigma$ are oxygen and CO adsorbed on Pt respectively, $e^-$ an electron in Pt, $O^{2-}$ an oxide ion in stabilized $ZrO_2$, and $\sigma$ a vacant site on Pt. These reactions determine the mixed electrode potential. Charge transfer coefficients are assumed to be 0.5.

Assumption (1) relates to oxygen and CO adsorption states during reaction on Pt. Although these adsorption states have been studied individually by many investigators (*1, 6, 18, 19*), they are assumed during reaction to be dissociative for oxygen and associative for CO at very low pressures (*1, 3–7*). The latter has been evidenced by infrared spectroscopy both at very low pressures (*11, 20*) and at high pressures with sufficient CO (*8–12, 15*). As for the oxygen adsorption state, a discrepancy still exists between that at very low pressures, where dissociative adsorption is assumed, and that at high pressures with sufficient CO, where associative adsorption is assumed to explain the rate equations (*9*). This paper primarily follows assumption (1).

Assumption (2), which is related to assumption (4), is indirectly supported by three facts. One is that the temperature increase due to the heat of the reaction was the same for deposited Pt both over stabilized $ZrO_2$ and over $SiO_2$ where hardly any electrochemical reactions are considered to take place (*15*). The second is that the dependence of local current on partial pressures differed from that for a chemical reaction rate, as will be described in the next section. And the last is that the current, which was higher than the local current, observed by polarizing the electrode potential did not show any saturation. Such saturation would be expected if electrochemical reactions proceed very fast and their velocities are diffusion limited, yielding different surface concentrations near the three-phase boundary and elsewhere on Pt. From these two assumptions, local current and emf measurement can be applied to determine the surface concentrations during oxidation, regardless of the progress of electrochemical reactions.

As for assumption (5), Eq. (5) has been established by Okamoto *et al.* (*21*). However, Eq. (6) is assumed to be operative in this paper, though other electrochemical reactions may be possible.

*Relation between $i_0$, emf, and partial pressures.* If resistance polarization can be ignored, the current, $i$, taken from the cell system under steady states is directly derived from Eqs. (5) and (6) and with assumption (5):

$$\begin{aligned} i = k_5 N_O \exp(FE/-RT) \\ - k_{-5} N_\sigma \exp(FE/RT) \\ - k_6 N_{CO} \exp(FE/RT) \\ + k_{-6} N_\sigma P_{CO_2} \exp(FE/-RT). \quad (7) \end{aligned}$$

Here, $k_i$ represents constants and $E$ is the electrode potential relative to the reference electrode potential. If $i = 0$, $E$ is a mixed electrode potential, that is, a rest electrode potential, $E_m$. When $P_{CO}$ is increased, $E_m$ decreases.

Since the standard reversible potential for reaction (6) is about −1.2 V, and the observed $E_m$ is between 0.0 and −0.8 V with $E$ close to $E_m$, the backward reaction can be ignored. Under the experimental conditions where $\Delta E_m$($E_m$ difference from that in the absence of CO) is less than $-RT/F(|\Delta E_m| > RT/F)$ and $E$ is close to $E_m$, the backward reaction for reaction (5) can also be ignored. Therefore, Eq. (7) is approximately reduced to

$$\begin{aligned} i = k_5 N_O \exp(FE/-RT) \\ - k_6 N_{CO} \exp(FE/RT). \quad (8) \end{aligned}$$

When $i = 0$, Eq. (8) leads to

$$E_m = (RT/2F)\ln(k_5 N_O / k_6 N_{CO}). \quad (9)$$

Since $E_m$ was defined as the electrode potential relative to the reference electrode potential,

$$\mathrm{emf} = |E_m| = |(RT/2F)\ln(k_5 N_O / k_6 N_{CO})|. \quad (10)$$

This is the same expression as previously derived (*16*).

If $E$ is changed from $E_m$ by a small amount $dE$, then the observed $i$ or $di$ can be expressed approximately by a Taylor expansion as

$$di = i_0(-2F/RT)dE, \quad (11)$$

$$i_0 = k_5 N_O \exp(FE_m/-RT) \quad (12)$$

$$= k_6 N_{CO} \exp(FE_m/RT). \quad (13)$$

Here, $i_0$ is local current flowing near the three-phase boundary at $E = E_m$. Equation (11) presents an experimental method for obtaining $i_0$. Using Eqs. (3) and (4), Eqs. (12) and (13) yield

$$i_0 \propto P_{O_2}{}^a \cdot P_{CO}{}^b \exp(FE_m/-RT), \quad (14)$$

$$\propto P_{O_2}{}^c \cdot P_{CO}{}^d \exp(FE_m/RT). \quad (15)$$

Therefore, parameters $a$, $b$, $c$, and $d$ are

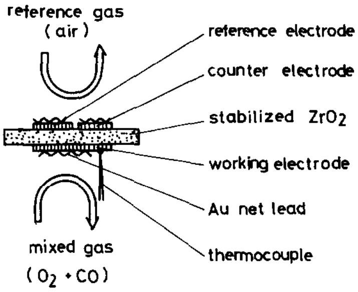

FIG. 1. Schematic representation of the apparatus for local current and emf measurements.

determined by experiments using the following set of equations

$$a = \partial(\ln i_0 + (FE_m/RT))/\partial \ln P_{O_2}|_{P_{CO}}, \quad (16)$$

$$b = \partial(\ln i_0 + (FE_m/RT))/\partial \ln P_{CO}|_{P_{O_2}}, \quad (17)$$

$$c = \partial(\ln i_0 - (FE_m/RT))/\partial \ln P_{O_2}|_{P_{CO}}, \quad (18)$$

$$d = \partial(\ln i_0 - (FE_m/RT))/\partial \ln P_{CO}|_{P_{O_2}}. \quad (19)$$

With the experimentally obtained parameters, $N_O$ and $N_{CO}$ are determined as functions of $P_{O_2}$ and $P_{CO}$.

The biggest advantage of this method over mere emf measurement is that it is not necessary to make any assumptions as to the surface adsorption states. For example, in order to determine $N_{CO}$ as a function of partial pressures from mere emf measurement, some assumption, such as that $N_O$ is independent of gaseous compositions, is necessary (*16*).

*Experimental method.* Preparation of the galvanic cell (1) and experimental apparatus were the same as previously described (*17, 21*). A $Y_2O_3$ (8 mol%) stabilized $ZrO_2$ sintered pellet 20 mm in diameter and about 1 mm thick, with electron beam deposited Pt electrodes 12 mm in diameter and about 0.1 $\mu$m thick on both sides, was used as the sample. The air electrode (air was used as a reference gas, $P'_{O_2}$ = 20 kPa) was divided into two parts, the reference electrode and the counter electrode, as shown in Fig. 1. The Pt surface temperature of the working electrode was monitored by a chromel-alumel thermocouple in contact with the electrode.

Local current, $i_0$, was obtained potentiostatically using Eq. (11), with $dE = \pm 5$ mV, which was monitored by a digital voltmeter with an accuracy of ±0.5%, in addition to the reading of the potentiostat. The value of $dE$ is so much less than $RT/F$ that the approximate equation (11) is operative. A Hokuto Denko HA-501 potentiostat was used.

All gases were commercially available types. Their purity levels were more than 99.9%. These gases were appropriately mixed with the aid of a thermal mass flow control system with an accuracy of ±0.25%. The furnace temperature was PID (proportionally, integrally, and differentially) controlled to within ±0.02 K.

## RESULTS

### *Influence of Resistance Polarization on $i_0$*

The local current $i_0$ and the rest electrode potential $E_m$ with reference to the air electrode potential over a wide range of $P_{CO}$ with $P_{O_2}$ = 1 kPa at 630 K are shown in Fig. 2. Here, $i_0$ may include influence from resistance polarization because of formal application of Eq. (11) to $i_0$. As previously described (*13–15*), $E_m$ oscillates over a certain $P_{CO}$ range. This region is called region II, and those for lower and higher $P_{CO}$, regions I and III, respectively. The local current $i_0$ increased with $P_{CO}$ in region I, but

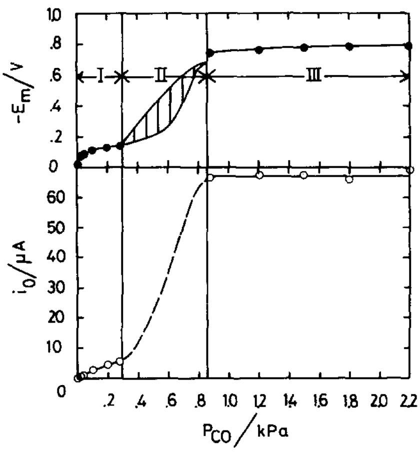

FIG. 2. Dependences of local current, $i_0$, and electrode potential, $E_m$, relative to air electrode potential on $P_{CO}$ with $P_{O_2}$ = 1 kPa, at 630 K.

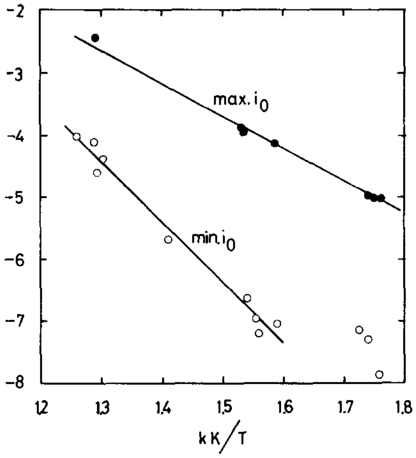

FIG. 3. Dependences of maximum $i_0$ and minimum $i_0$ values on temperature. Minimum $i_0$: $i_0$ in absence of CO with $P_{O_2}$ = 1 kPa.

in region III it reached a maximum and kept almost constant. It was impossible to obtain $i_0$ in region II due to $E_m$ oscillation. The maximum $i_0$ seemed to be close to the calculated value with the assumption that resistance polarization prevailed over $i_0$ rather than activation polarization.

In order to ascertain this finding, the maximum $i_0$ was measured as a function of temperature. Figure 3 shows the result as well as the minimum $i_0^0$, $i_0$ in the absence of CO. The activation energy for maximum $i_0$ was about 109 kJ mol$^{-1}$, which is near the activation energy for resistance polarization between 670 and 780 K, which is 112 kJ mol$^{-1}$ (*22*).

Therefore, it is concluded that the observed $i_0$ in region III was not local current due to activation polarization, or reactions (5) and (6), while $i_0$ in region I appeared to be the true local current, because $i_0$ in region I was much less than that in region III. Hence, the relation of $i_0$ and $E_m$ to partial pressures will be dealt with only in region I.

### *Relation of $i_0$ and $E_m$ to Partial Pressures in Region I*

The results for $i_0$, $E_m$, and parameters $b$ and $d$ with $P_{O_2}$ = 1 kPa at 642 K are shown in Fig. 4. Error bars are standard deviations for several runs. They were about ±0.2 for the parameters. These data are isothermal because the surface temperature change was less than 0.5 K. As each $\Delta E_m$ was less than $-RT/F$, Eqs. (17) and (19) were applicable to every plot. It was found that $b$ was constant and about 0.1, while $d$ was $P_{CO}$ dependent and increased from 1 to about 1.6 as $P_{CO}$ increased.

The changes in $i_0$, $E_m$, and parameters $a$ and $c$ with $P_{CO}$ = 40 Pa, at 638 K are shown in Fig. 5. These data are also isothermal

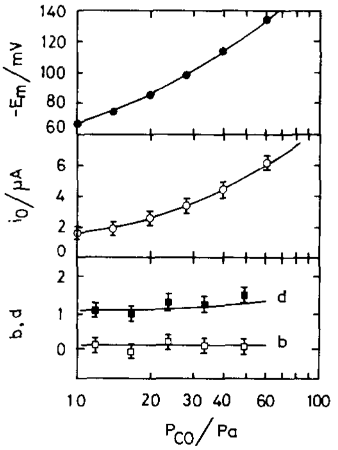

FIG. 4. Dependences of $i_0$, $E_m$, and parameters $b$ and $d$ on $P_{CO}$ in region I with $P_{O_2}$ = 1 kPa, at 642 K. $b$, $d$: $N_O \propto P_{O_2}{}^a \cdot P_{CO}{}^b$, $N_{CO} \propto P_{O_2}{}^c \cdot P_{CO}{}^d$, $N_O(N_{CO})$: surface oxygen (CO) concentration on Pt during oxidation.

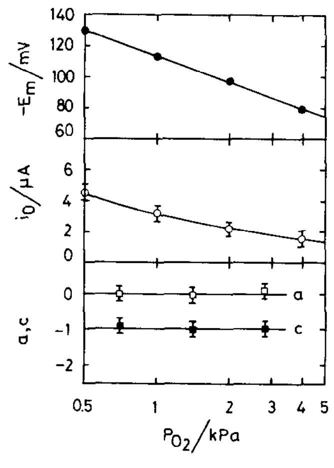

FIG. 5. Dependences of $i_0$, $E_m$, and parameters $a$ and $c$ on $P_{O_2}$ in region I with $P_{CO}$ = 40 Pa, at 638 K. $a$, $c$: see legend to Fig. 4.

because surface temperature change was essentially zero. Since all $\Delta E_m$ values were less than $-RT/F$, Eqs. (16) and (18) were operative for all plots. It can be seen that $a$ remained zero and $c$ was about $-1.0$. Therefore, the dependences of $N_O$ and $N_{CO}$ on the partial pressures in region I around 640 K were expressed as

$$N_O \propto P_{O_2}{}^0 \cdot P_{CO}{}^{0.1}, \qquad (20)$$

$$N_{CO} \propto P_{CO}{}^{\delta}/P_{O_2}, \qquad (21)$$

where $\delta$ increased from 1 to about 1.6 as the reaction system approached region II.

Here again, the relation between $i_0$ and $P_{O_2}$ shown in Fig. 5 will be looked at. In region I, the reaction velocity of $CO_2$ production is independent of $P_{O_2}$ (*15*), while $i_0$ depends on $P_{O_2}$. This fact indirectly supports assumptions (2) and (4).

At lower temperatures, such as 580 K, it was found that only parameter $a$ increased a little and the other parameters were similar to those around 640 K, as shown in Table 1. This table shows that, at any rate, the partial pressure dependence of $N_O$ was weak and that for $N_{CO}$ was strong at temperatures between 580 and 640 K.

TABLE 1

Parameters $a$, $b$, $c$, and $d$ at Different Temperatures

| Temperature (K) | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|
| 580 | 0.3 | 0.1 | −1.0 | 1 → 1.6 |
| 640 | 0.0 | 0.1 | −1.0 | 1 → 1.6 |

## DISCUSSION

The study of surface adsorption states on Pt during CO oxidation in region I leads to several points for discussion. However, before treating them, the error in the parameters should be addressed. The error of about ±0.2 that was mentioned in the previous section can be thought of as produced by both the scatter of $i_0$ and $E_m$ and the method of differentiation according to Eqs. (16)–(19). However, the assumption that charge transfer coefficients are 0.5 also causes some error. For example, if a charge coefficient varies by 0.1, the parameters can be changed by from 0.1 to 0.15.

We now discuss the important points.

### $N_O$ *and Reaction Mechanism*

As was described in the preceding section, $N_O$ depended weakly on partial pressures. This result is very consistent with that obtained by Matsushima *et al.* (*4*), Hopster *et al.* (*3*), and others at very low pressures. It is also in agreement with the previously obtained result (*21*) that under the experimental conditions similar to those adopted here except for a lack of CO, $N_O$ was almost independent of $P_{O_2}$. This result provides a base which enables $N_O$ to be almost constant in the analysis of mere emf measurement (*16*).

Nevertheless, especially at lower temperatures, such as 580 K, $N_O$ was slightly dependent on $P_{O_2}$. This may be explained by considering that the surface electronic state of Pt is changed by the adsorption of a small amount of CO. This causes $N_O$ to become dependent on $P_{O_2}$ (*17*). This effect will generally appear to be more significant at low temperatures rather than at high temperatures due to the Boltzmann distribution, which is in keeping with our results. However, since this effect is small, it will be ignored in the following discussion.

The dependence of $N_{CO}$ on the partial pressures, on the other hand, did not change, at least between 580 and 640 K. The oxidation velocity in region I, $v$(I), was determined (*15*) to be

$$v(\mathrm{I}) \propto P_{CO}, \qquad (22)$$

but $N_O \cdot N_{CO}$ does not satisfy this rate equation. That is, the reaction between surface species as a rate-determining step is not operative. On the other hand, emf measurements (*15, 16*) have strongly supported the view that the Langmuir–Hinshelwood mechanism does function. Therefore, a Langmuir–Hinshelwood mechanism with a rate-determining step for CO supply must operate to unify the rate equation (22). This requires many vacant sites, though $N_O$ is nearly independent of $P_{O_2}$, as described above. This has been ascertained by Gland (*18*), Hopster *et al.* (*3*), and Norton *et al.* (*23*) and will be referred to later in this section.

### *Dependence of $N_{CO}$ on $P_{O_2}$*

Now, let us discuss a major problem, the dependence of $N_{CO}$ on $P_{O_2}$ (Eq. (21)). If the oxygen dissociatively adsorbed on Pt is in equilibrium with gaseous $O_2$, $N_{CO}$ will be proportional to $P_{O_2}{}^{\gamma}$, where $\gamma$ is between $-0.5$ and 0. This is because, in region I, the concentration of surface CO is so low that the main surface species must be oxygen. This dependence does not agree with the experimental result.

Three models can be used to interpret the dependence of $N_{CO}$ on $P_{O_2}$. One is that oxygen adsorbs associatively even in region I. However, this model is difficult to accept, because, in the absence of CO, oxygen dissociatively adsorbs over the temperature range under consideration both at very low pressures (*18, 19*) and at high pressures (*21*). Therefore, in the presence of a very small amount of CO, oxygen should still adsorb dissociatively even if the very scarce CO changes the surface electronic state of Pt.

The second model is that two vacant sites are needed for adsorption of CO. Since it is established by infrared spectroscopy that the reaction intermediate on Pt is a linear type CO (*8–12, 15*), only for a very short time after adsorption could the CO on Pt be a bridged type or a linear type with one adjacent vacant site. However, if the Pt surface is free from oxygen, the sticking coefficient for CO, $s(N_{CO})$, has been expressed (*24*) as

$$s(N_{CO}) = s_0(1 - (N_{CO}/N_t))/(1 - (zN_{CO}/N_t)). \quad (23)$$

Here, $s_0$ is the initial sticking coefficient, $N_{CO}/N_t$ the fractional coverage by CO, and $z$ a constant, e.g., 0.85 for Pt(111) and 0.88 for Pt(110). This goes against the present model. The remaining possibility to support this model is that, in the presence of surface oxygen, the kinetics of CO adsorption change into a form suitable for this model. However, such a drastic change in adsorption kinetics is difficult to accept.

The last model is that the adsorbed CO diffuses over the surface, reacting with oxygen adsorbed long beforehand or just adsorbed oxygen and $N_{CO}$ is determined by CO residence time. This model was described earlier (*16*), so only a brief description will be presented here. If CO is adsorbed near long-before adsorbed oxygen, then it reacts readily, giving a residence time of about zero. On the other hand, if CO is adsorbed in the midst of vacant sites, it must diffuse over the surface before reacting with adsorbed oxygen. In this case, the residence time for CO has some positive value. If diffusion length is great, the probability of reaction with just adsorbed oxygen adjacent to the adsorbed CO is significant. The adsorption rate for oxygen near the adsorbed CO in the midst of vacant sites is presumed to be proportional to $P_{O_2}$. Therefore, the residence time will decrease in proportion to the reciprocal of $P_{O_2}$. In this way, $N_{CO}$ will be approximately proportional to $P_{O_2}{}^{-1}$. Surface diffusion for CO is often referred to in the study of CO oxidation on Pt (*1, 3*), and its path length is estimated to be about 1000 lattice constants within the adsorption time around 550 K (*3*). The surface oxygen concentration is about a quarter that of surface Pt atoms at room temperature (*3, 18, 23*). If the surface oxygen is distributed in islands (*25*) and the temperature is higher than room temperature, the distance between surface oxygen islands will be long. Thus, this model is rather persuasive.

### *$N_{CO}$ Near the Boundary between Regions I and II*

The pressure dependence of $N_{CO}$ near the boundary between regions I and II, labeled

$B_{12}$, was

$$N_{CO} \propto P_{CO}^{1.6}/P_{O_2}. \quad (21)$$

At $B_{12}$, there was a relation to gas composition (*15*) of

$$P_{CO}/P_{O_2}^{0.62} = \text{const.}, \quad (24)$$

which can be rewritten as

$$P_{CO}^{1.6}/P_{O_2} = \text{const.} \quad (25)$$

By comparing Eq. (21) with Eq. (25), it can be presumed that the initiation of oscillation in CO oxidation requires $N_{CO}$ to be greater than a constant determined by Eq. (25) at a given temperature. The activation energy for the constant in Eq. (24) was previously obtained (*15*) as 54 kJ $mol^{-1}$, which was thought to be about half that of the desorption energy of CO, viz. 126 kJ $mol^{-1}$ (*24, 26–28*). Hence, the occurrence of oscillation was considered to be caused by the surface state when adsorbed CO became mobile. This discussion may also hold roughly for Eq. (25). To illustrate the surface adsorption states on this basis, in region I, CO diffuses over only a small area because it is restricted by the islands of surface oxygen, while in region II, CO can diffuse widely through several surface oxygen islands.

Unfortunately, the surface adsorption states in region III cannot be discussed in this paper because resistance polarization prevails in $i_0$ there. Therefore, to study the adsorption states in region III through $i_0$ and emf measurement, low-resistant solid electrolytes, such as doped $CeO_2$ systems (*29, 30*) or doped $Bi_2O_3$ systems (*30, 31*), or acid solutions must be used. However, these electrolytes present some disadvantages: the first two solid electrolytes are less resistive to a reducing atmosphere and the third has low solubilities for $O_2$ and CO, since dissolved $O_2$ and CO are reactants.

## SUMMARY

Surface concentrations of oxygen and CO ($N_O$ and $N_{CO}$, respectively) during oxidation on Pt has been studied with the aid of local current and emf in a solid electrolyte concentration cell. They were determined as functions of partial pressures without any assumptions as to surface adsorption states, which were necessary for study by emf measurement only, and discussed with reference to reaction kinetics. Due to resistance polarization, however, it was possible to obtain information on $N_O$ and $N_{CO}$ only in the region where CO is scarce in relation to oxygen. There, it was found that $N_O$ was weakly dependent on partial pressures, while $N_{CO}$ was strongly dependent. Also, the occurrence of oscillation in CO oxidation was connected with the mobility of adsorbed CO. It was concluded that surface diffusion for CO was important in explaining surface concentrations. The present method of determining surface adsorption states through local current and emf measurement is applicable to various other catalytic reactions on electron-conductive materials with suitable electrolytes.

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