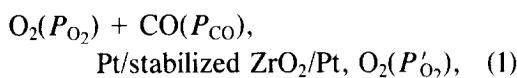# Relation between Surface Adsorption States and emf in a Solid Electrolyte Concentration Cell during Carbon Monoxide Oxidation on Platinum Studied by Local Current Measurement

The emf of solid electrolyte concentration cells with Pt electrodes of the type

$$O_2(P_{O_2}) + CO(P_{CO}),$$
$$Pt/\text{stabilized ZrO}_2/Pt, O_2(P'_{O_2}), \quad (1)$$

deviates significantly from that calculated using the oxygen concentration cell equation or the Nernst equation at low temperatures of about 600 K(*1–6*). This emf deviation is brought about by imperfect catalytic activity of the Pt electrode. Therefore, surface adsorption states during the reaction under steady states can be learned from emf measurement with appropriate assumptions. The importance of measuring adsorption during surface catalysis has been emphasized by Tamaru (*7*).

Two mechanisms for emf generation have been proposed. One is that only oxygen activity on Pt during the reaction determines emf, i.e., only oxygen is involved in an electrochemical reaction (*8–12*). The other is that both the oxygen and CO adsorbed on Pt during the reaction generate emf, i.e., both the surface oxygen and surface CO are directly involved in electrochemical reactions (*2–6*). These two mechanisms lead to different interpretations of the surface adsorption states. Therefore, in order to determine the surface adsorption states through emf measurement, the mechanism for emf generation must be established.

This note establishes the mechanism for emf generation from local current (i_0) measurement under the condition that P_{CO} is very small with reference to P_{O_2}. The local current is analogous to the corrosion current in a solution system. If P_{CO} is zero, this current is called the exchange current. It is a local current anodically or cathodically flowing near the three-phase-boundary (the region of contact where the electrode, electrolyte, and gas phase meet) on the anode, namely the working electrode, at a rest electrode potential.

The air electrode (air was used as a reference gas, i.e., $P'_{O_2} = 20$ kPa) was divided into two parts, the reference electrode and the counter electrode (*13*). The local current was obtained potentiostatically using the equation

$$i_0 = -(RT/2F) \cdot di/dE. \quad (2)$$

Here, di is the current observed when the electrode potential is changed from the rest electrode potential by a small amount dE, e.g., ± 5 mV, which is much less than RT/F. Equation (2) is established for a single two-electron reaction. If the reaction involves other than 2 electrons, only the coefficient in Eq. (2) changes. Since only relative i_0 is important in this note, this is not significant. It can also be shown that Eq. (2) is valid for a system where several electrochemical reactions take place, if these reactions involve the same electron numbers and their charge transfer coefficients are 0.5 (*14*). Resistance polarization can be ignored (*14*).

To determine the P_{CO} effect on i_0, i_0 was measured as a function of P_{CO} with $P_{O_2} = 10$ kPa, at 636 K. The temperature change was less than 0.2 K. The result was plotted against the rest electrode potential, E_m, relative to the reference electrode potential. This, together with the result obtained with varied P_{O_2} in the absence of CO, is shown
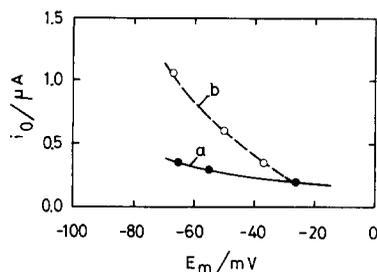
FIG. 1. Local current (i_0) in the presence and absence of CO. E_m: electrode potential relative to the reference electrode potential, (a) i_0 in the absence of CO, (b) i_0 in the presence of a small amount of CO with constant P_{O_2}, temperature: 636 K.

in Fig. 1. With decreasing E_m, the difference between i_0 values in the presence and absence of CO at the same electrode potential increased and the ratio of the former to the latter reached 2 or 3.

On the basis of this result, the mechanism for emf generation will be discussed for a CO + O_2 nonequilibrium gas mixture. First, we assume that the emf is determined only by oxygen activity on the Pt electrode. Since Wagner (8) has proposed application of a solid electrolyte concentration cell to the study of heterogeneous catalysis on the basis of this assumption, several studies of SO_2 oxidation on Pt (9), ethylene oxide oxidation on Ag (10), and others (11, 12) have been conducted.

In this case, as the electrochemical reaction near the three-phase-boundary does not include adsorbed CO explicitly, the following reaction takes place (13)

$$O_\sigma + 2e^- = O^{2-} + \sigma. \tag{3}$$
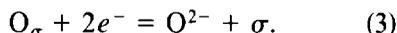
Here, O_σ denotes oxygen dissociatively adsorbed on Pt, and σ a vacant site on Pt. Based on reaction (3), E_m and i_0 can be derived in the same way as described previously (13) with the assumption that charge transfer coefficients are 0.5:

$$E_m = (RT/2F) \cdot \ln(k_3N_O/k_{-3}N_\sigma), \tag{4}$$

$$i_0 = (k_3N_O \cdot k_{-3}N_\sigma)^{0.5}. \tag{5}$$

Here, k_3 and k_{-3} are forward and backward rate constants for reaction (3), and N_O and

N_σ are surface oxygen and vacant site concentrations during CO oxidation.

If the electrode potential without CO is the same as that with CO, the following relation can be obtained from Eq. (4),
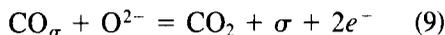
$$N'_O/N'_\sigma = N_O/N_\sigma, \tag{6}$$

where the symbols with and without a prime are those in the absence and presence of CO, respectively. From the fact that i_0 is larger than i'_0, Eqs. (5) and (6) give

$$N_O > N'_O, \tag{7}$$

$$N_\sigma > N'_\sigma. \tag{8}$$

It is almost physically impossible to consider that these two inequalities are compatible with each other.

On the other hand, if the reaction

$$CO_\sigma + O^{2-} = CO_2 + \sigma + 2e^- \tag{9}$$

is taken into account as well as reaction (3), E_m and i_0 are derived by a similar method to that described previously (13) with the following assumptions, as

$$E_m = (RT/2F) \cdot \ln(k_3N_O/(k_{-3}N_\sigma + k_9N_{CO})) \tag{10}$$

$$i_0 = (k_3N_O \cdot (k_{-3}N_\sigma + k_9N_{CO}))^{0.5}. \tag{11}$$

Here, k_9 is a forward rate constant for reaction (9) and it is assumed that charge transfer coefficients are 0.5 and the backward reaction for reaction (9) is ignored, because the standard reversible potential for reaction (9) is much less than the potential under consideration.

Using the same procedure as described above, inequalities

$$N_O > N'_O, \tag{12}$$

$$N_\sigma + (k_9/k_{-3}) \cdot N_{CO} > N'_\sigma, \tag{13}$$

are obtained from the fact that i_0 is larger than i'_0. It is physically possible for these two inequalities to be compatible with each other, provided k_9 is larger than k_{-3}. Therefore, it is concluded that the emf during CO oxidation on Pt is generated by a mixed
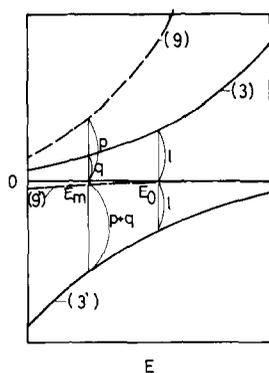
FIG. 2. Schematic illustration for the mechanism of emf determination. E: electrode potential, i: current, (3): $O^{2-} + \sigma \rightarrow O_\sigma + 2e^-$, (3'): $O_\sigma + 2e^- \rightarrow O^{2-} + \sigma$, (9): $CO_\sigma + O^{2-} \rightarrow CO_2 + \sigma + 2e^-$, (9'): $CO_2 + \sigma + 2e^- \rightarrow CO_\sigma + O^{2-}$, E_0: the electrode potential determined by reactions (3) and (3'), E_m: the electrode potential determined by reactions (3), (3'), and (9).

electrode potential brought about by two electrochemical reactions, e.g. (3) and (9).

The above discussion is illustrated in Fig. 2. If the emf is determined only by oxygen activity on the Pt electrode, the anodic and cathodic currents due to reaction (3) are the same except for sign, thus generating an electrode potential at E_0 in the figure. Therefore, i_0 is uniquely determined by the electrode potential whether CO is present or not, because i_0 is determined by N_O and N_σ, which do not increase or decrease simultaneously. On the other hand, two electrochemical reactions (3) and (9) give a mixed electrode potential at E_m in the figure, at which potential the sum of anodic currents due to reactions (3) and (9) equals the cathodic current owing to reaction (3), since the backward reaction for reaction (9) can be ignored under the experimental conditions. In this case, i_0 may change with a given E_m according to the presence or absence of CO. This mechanism is consistent with the results.

From the fact that i_0 in the presence of CO was 2 or 3 times that in the absence of CO, it is thought that N_O increased during CO oxidation, since i_0 is proportional to N_O at a fixed electrode potential. This seems to be inconsistent with the previously ob-

served result (13) that under the experimental conditions N_O was almost independent of P_{O_2}. Moreover, this phenomenon has not been explicitly described in the literature. However, Primet et al. (15) have reported that when many cycles (O_2, CO, O_2, . . .) or (CO, O_2, CO, . . .) were performed on supported Pt at room temperature, the intensity of the infrared absorption band attributable to PtO(CO) greatly increased. This phenomenon suggests that the amount of oxygen adsorption was aided by CO.

It is thus concluded that the emf of a solid electrolyte concentration cell (1) is generated by a mixed electrode potential brought about by two electrochemical reactions, e.g. (3) and (9). It is also considered that the amount of oxygen adsorbed on Pt increases in the presence of CO. From the viewpoint of this mechanism for emf generation, the emf provides direct information as to both the surface oxygen and CO concentrations on Pt. However, these two concentrations cannot be separated only by emf measurement alone without any assumption about the surface adsorption states (6). If local current, as well as emf, are measured, these two concentrations can be determined separately. A quantitative treatment is presented elsewhere in this journal (14).

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HIROSHI OKAMOTO
GO KAWAMURA
TETSUICHI KUDO

Central Research Laboratory
Hitachi Ltd.
1-280 Higashi-Koigakubo
Kokubunji, Tokyo 185, Japan