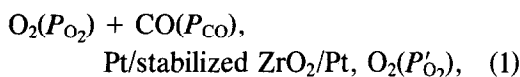# Electromotive Forces and CO Oxidation on Platinum:
Reply to Vayenas

We appreciate an opportunity to respond to the comment of Vayenas (1) and to clarify our position on the interpretation of the electromotive force (emf) of solid electrolyte concentration cells with Pt electrodes of the type

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

during oxidation on the Pt electrode (anode).

We reply to the remarks (1) in order. First, in the experimental results obtained by us (2, 3), the percentage conversion from CO to CO_2 was not described. This was because the content of CO_2 in the effluent was near the detection limit of the infrared gas cell and was thus not quantitatively determined under the most usually employed conditions. However, the conversion could be estimated to be less than 10%.

Such a low conversion can be thought to be due to several factors. Platinum electrodes were deposited by electron-beam evaporation. The surface area of such electrodes was about 1 cm² and their thickness was typically 0.1 μm (2), both dimensions being smaller than those used by Vayenas et al. (4). Moreover, the reactor was not of CSTR type, but of the type where reactant gases were blown against the Pt electrode with a high linear velocity (1.7 m s⁻¹) (2) in an attempt to avoid mass-transfer limitations.

Therefore, the composition of the gas mixture near the Pt electrode could be considered to be almost the same as that of the inlet gas mixture. However, when the reaction velocity is so high that the gas supply is a rate-determining step as in region I where P_{CO} is low compared to P_{O_2}, the actual composition of the gas mixture exposed to the Pt electrode may differ from that of the bulk gas phase. In this case, it is almost impossible to determine the former by any measurements. On the other hand, in region III where there are sufficient oxygen and CO with low oxidation rates (2), the conversion is negligibly small.

The differential reactor in Ref. (2) contained a pellet of about 20 mg of 3 wt% Pt/stabilized ZrO_2 powder with a diameter of 2 cm (2). Its conversion was less than 20% determined using an infrared gas cell. This reactor was used only to correlate the surface temperature (ΔT) and CO_2 content in the effluent (C_{CO_2}).

We agree with Vayenas that we should not have used the terms activation energy and Arrhenius plots for the data including thermodynamic factors. However, we believe that readers would not misunderstand the meaning here.

We refer next to the comment on the mechanism of emf generation in cell (1) above during CO oxidation on a Pt electrode. We assumed in our papers (2, 3) that the activity of oxygen adsorbed on Pt was very similar to its surface concentration. However, this assumption might not be correct under some conditions, as Vayenas has pointed out.

It can be shown from a general discussion that the emf of cell (1) during CO oxidation does not exhibit the activity of the adsorbd oxygen. Under steady-state conditions with P_{O_2} much greater than P_{CO} (region I), the oxygen activity on the surface, a_0, should be

$$P_{O_2} \geq a_0^2 \geq P_{O_2} \text{ (eq.)} = P_{O_2} - \tfrac{1}{2}P_{CO}, \quad (2)$$

374

where P_{O_2} (eq.) is the equilibrium oxygen partial pressure. Therefore, the emf change, $|\Delta E_m|$, when a very small amount of CO is added to the gas containing sufficient oxygen, can be calculated as

$$|\Delta E_m| = \frac{RT}{4F} \ln \frac{P_{O_2}}{a_0^2}$$

$$\leq \frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2} - \frac{1}{2}P_{CO}}. \quad (3)$$

The right-hand term is very small, being of the order of 0.1 mV (2). Therefore this does not explain the experimental result that $|\Delta E_m| \cong 100$ mV (2). Thus it can be concluded that the emf during the reaction is not brought about by the activity of the surface oxygen.

On the other hand, as Hetrick and Logothetis (5) suggested, the electrochemical reaction

$$CO_\sigma + O^{2-} \rightarrow CO_2 + \sigma + 2e^- \quad (4)$$
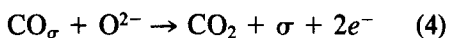
was taken into account to explain the emf behavior as well as the electrochemical reaction

$$O_\sigma + 2e^- \rightleftharpoons O^{2-} + \sigma. \quad (5)$$
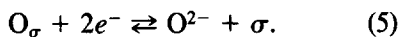
Here, CO_σ and O_σ represent oxygen and CO adsorbed on Pt during the reaction, and σ is a vacant site on Pt. Reaction (5) was implicitly used in the previous paragraph. It was assumed that two electrons were involved in reaction (4) (3, 6).

These two reactions (4) and (5) provide a mixed electrode potential. A proof for this is given in Ref. (7). There it was found that a local current flowing near the three-phase boundary (the region of contact where the electrode, electrolyte, and gas phase meet) in region I, increased more with increasing P_{CO} at a given P_{O_2} than with decreasing P_{O_2} in the absence of CO. This observation indicates that the two reactions (4) and (5) are operative.

On the basis of these considerations, the comments by Vayenas (1) will be examined. Even in region I, it was found from emf measurement that surface CO was

present but its amount was very small since it was not detected by infrared spectroscopy (2, 3). Therefore, in Fig. 10 of Ref. (3), N_{CO} (surface CO concentration) was shown to be small but not zero.

Etsell and Flengas (6) showed that the intrinsic exchange current density of reaction (4) was negligible compared with that of reaction (5). However, their observation should not be applied directly to ours, because the temperatures used in their studies (700 to 1000°C) were much higher than ours (250 to 410°C). In addition to that, in the same reference, reaction (4) was suggested and Bauerle (8) suggested the possibility of a slow electron transfer in reaction (5) at 400–800°C with a high activation energy of 2–2.5 eV, this value being consistent with our measured activation energy of 2.1 eV (Fig. 3 of Ref. (9)). Therefore, it is not in conflict with the results obtained by Etsell and Flengas (6) that both reactions (4) and (5) take place on a Pt electrode and produce a mixed electrode potential.

The net reaction on the anode, the sum of reactions (4) and (5), is

$$CO_\sigma + O_\sigma \rightarrow CO_2 + 2\sigma. \quad (6)$$
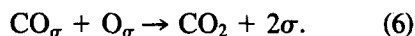
Although this is not an explicit charge transfer reaction and not a half-cell reaction, it is a mixed electrode cell reaction (like a corrosion) and a charge-transfer-controlled reaction. Therefore, the electrode potential during the reaction, i.e., the mixed electrode potential, can be determined as described earlier. It should be recalled that two kinds of reaction take place simultaneously on the Pt electrode. One is a simple chemical oxidation and the other is a set of electrochemical reactions (4) and (5). It is assumed with some indirect evidence (2, 9) that the latter does not disturb the former, that is, the latter can be a probe reaction to determine adsorption states during the former.

Finally, the mechanism of oscillations is now still under investigation. We proposed a mechanism in which the oscillations were caused by a surface state where the ad-

sorbed CO became mobile (3, 9). On the other hand, Vayenas et al. (4, 10) suggested that they were caused by the surface oxidation–reduction mechanism including surface oxide. However, we obtained several different results (2) from those obtained by Vayenas et al. (4, 10) with regard to the relation between P_{CO} and P_{O_2} at the oscillation boundaries, dependence of the oscillation frequencies on the temperature and gaseous composition, and temperature range of the oscillations. Therefore, the mechanism for oscillations proposed by Vayenas et al. does not seem to hold good for CO oxidation on Pt.

REFERENCES

1. Vayenas, C. G., J. Catal. **90**, 371 (1984).
2. Okamoto, H., Kawamura, G., and Kudo, T., J. Catal. **82**, 322 (1983).
3. Okamoto, H., Kawamura, G., and Kudo, T., J. Catal. **82**, 332 (1983).
4. Vayenas, C. G., Lee, B., and Michaels, J., J. Catal. **66**, 36 (1980).
5. Hetrick, R. E., and Logothetis, E. M., Appl. Phys. Lett. **34**, 117 (1979).
6. Etsell, T. H., and Flengas, S. N., J. Electrochem. Soc. **118**, 1890 (1971).
7. Okamoto, H., Kawamura, G., and Kudo, T., J. Catal. **86**, 437 (1984).
8. Bauerle, J. E., J. Phys. Chem. Solids **30**, 2657 (1969).
9. Okamoto, H., Kawamura, G., and Kudo, T., J. Catal. **87**, 1 (1984).
10. Vayenas, C. G., Georgakis C., Michaels, J., and Tormo, J., J. Catal. **67**, 348 (1981).

H. OKAMOTO
G. KAWAMURA
T. KUDO

Central Research Laboratory
Hitachi Ltd.
Kokubunji, Tokyo 185
Japan