DIGITAL CARBON MONOXIDE DETECTOR /11/

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The switch off concentration phenomena in carbon monoxide oxidation on platinum and the parallel steep variation of resistance or surface potential of thin platinum films are used to develop a carbon detector. Coating the platinum film with an increasing thickness of polytetrafluorethylene (PTFE) makes this switch off point move to increasing CO concentrations. Therefore, a series of electrical elements, platinum thin film resistances, platinum M.O.S. diodes or platinum gate M.O.S. transistors covered by calibrated thicknesses of PTFE will switch off at well determined CO concentrations and can continue the basis of a digital detector.

1. INTRODUCTION

It was shown earlier that carbon monoxide oxidation on platinum has a typical kinetic behaviour.^{1,2} The reaction rate rises linearly with the ratio CO/O_2 in the gas phase and stops abruptly for a critical ratio at a given temperature (Figure 1). An interpretation of this behaviour was given by Dagonnier and al.³ Due to the Langmuir-Hinshelwood mechanism, mixed adsorbates cannot exist beyond a critical CO concentration at constant temperature or under a critical temperature at constant CO concentration. On the other hand, at constant temperature, under the critical CO concentration, the oxygen coverage variation is low. Therefore any property such as electrical resistivity (for thin films), or surface potential depending on the oxygen coverage, will only vary significantly and abruptly at the inhibition point.

Provided that care is taken to reproduce exactly the method of preparing the samples, good reproducibility of this critical point is obtained. After calibration, it can be a measure of the CO concentration.

By placing on the surface a membrane permeable to the gases (PTFE) this forms a mass transfer resistance for both CO and O_2 , so that it is possible to determine the value of the CO concentration that can be detected.

FIGURE 1 Reaction rate as a function of $[\text{CO}]/[\text{O}_2]$ ratio at 135°C .

2. SAMPLES PREPARATION

2.1 Circuits. In order to simplify the preparation, the samples used here are thin film resistances of platinum (thickness $\approx 100 \text{ \AA}$). A variation of electrical resistance of 5 to 10% is observed when the surface of the film is passed from CO to O₂ coverage. Any other element sensitive to adsorbate composition such as MOS tunnel diode⁴ or platinum gated MOS transistor⁵ can be employed to give larger signals but they are less easy to prepare.

The circuits utilized in Figure 2 are obtained by classical photolithography with lift off technique for resistances sizing. The smallness of the resistances in comparison with the substrate avoids excessive heating of the catalyst surface by the reaction itself. The sample to be tested is pasted with silver lacquer on a thermostabilized gold plated copper block in an infrared absorption cell.

2.2 Films. The films are obtained as PtO₂ by DC reactive sputtering of platinum in an Argon-Oxygen mixture⁶ and stocked in this form. On this PtO₂ the wanted thickness of PTFE is deposited by R.F. sputtering of a cooled massive PTFE cathode in an argon-CF₄ mixture.⁷ The thickness of the membrane is measured after deposition by the Tolansky method.⁸

2.3 Measurement system. The electrical resistance of each sample is followed as a function of the CO concentration measured by Infrared absorption. The sample is put in the cell and the CO concentration is slowly increased (quasistatic system) by a needle valve progressively opened until the inhibition point is obtained (Figure 3).

3. MODEL AND MEASUREMENTS

The system Gas/PTFE/Platinum as pictured in Figures 4.1 and 2 has two interfaces:

1 is the interface Pt/PTFE and 2 the interface PTFE/gas. The two reacting gases will dissolve in the PTFE at the interface 2, diffuse to the interface 1, be adsorbed on the Pt and react on the Pt surface. The CO₂ formed during the reaction could be retained near the surface because of the membrane but its adsorption energy is so small that it does not influence the reaction rate.

It can be assumed the gas flow is large enough so that no gradient exists in the gas phase. Therefore the oxygen and carbon monoxide gradient are only in the PTFE. On the other hand, in the region where the reaction occurs the CO partial pressure is low compared to oxygen. Thus small oxygen partial pressure variations in the gas phase will have a negligible effect at the interface 1 and we need only take account of CO dissolu-

FIGURE 2 Thin film resistances. 1. Platinum. 2. Gold contacts.

FIGURE 3 Experimental set-up for measurement of the inhibition point.

tion and diffusion unless very strong differences of these parameters exist between oxygen and carbon monoxide. That does not seem to be the case for PTFE.

In these conditions the rate of CO_2 production by the surface unit of the catalyst for a membrane thickness L is:

$$J_{\text{CO}_2}^L = \frac{D_{\text{CO}}}{L} (S_{\text{CO}} C_{\text{CO}}^g - C_{\text{CO}}^1)$$

where D is the CO diffusion coefficient, L the membrane thickness, C_{CO}^g the CO concentration in gas phase, C_{CO}^1 the CO concentration at the interface 1 and S the CO solubility in PTFE.

The critical CO concentration $(C_{\text{CO}}^1)^*$ where the reaction inhibits and the corresponding value $J_{\text{CO}_2}^*$ are constants of the reaction and of the catalyst PTFE interface. They will be identical for any thickness X .

Then we can write:

$$(J_{\text{CO}_2}^X)^* = \frac{D_{\text{CO}}}{X} (S_{\text{CO}} (C_{\text{CO}}^g)^* - (C_{\text{CO}}^1)^*) = \frac{D_{\text{CO}}}{L} (S_{\text{CO}} (C_{\text{CO}}^g)^* - (C_{\text{CO}}^1)^*)$$

FIGURE 4 Scheme of the gas/PTFE/platinum-system.

where the started values are taken at the inhibition point. So we obtain

$$(C_{CO}^g)_x^* = \frac{(C_{CO}^1)^*}{S} + (C_{CO}^g)_L^* - \frac{(C_{CO}^1)^*}{S} \frac{x}{L}$$

In Figure 5 we have plotted at 135 C°, $(C_{CO}^g)^*$ determined by IR absorption for different membrane thicknesses as a function of the ratio x/L , L being the thickness of reference. Examples of resistance variation are given in Figure 6. As was noted above the resistance ratio R_{O_2}/R_{CO} is high for low CO concentrations and decreases rapidly when the percentage of CO to O₂ is between 0.5 and 1.0. Above 1% the resistance ratio remains constant.

It is seen that a series of resistances covered with different thicknesses will be a series of switches which will be on or off depending on the CO concentration. They constitute a digital detector.

4. DETERMINATION OF THE SOLUBILITY AND DIFFUSION COEFFICIENT OF CO IN PTFE

In order to verify the correctness of our model we calculated from our measures the solubility and the diffusion coefficient of CO in PTFE.

The ordinate at $x/L = 0$ gives us the ratio $(C_{CO}^1)^*/S$ where $(C_{CO}^1)^*$ is the inhibition concentration without PTFE. Taking its value at 135 C° and putting it in the relation we have

$$S = \frac{0.21 \cdot 10^{-7}}{1.68 \cdot 10^{-7}} = 0.13$$

FIGURE 5 Plot of $(C_{CO}^g)^*$ as a function of membrane thickness ($L = 1800 \text{ \AA}$).

FIGURE 6 Relative resistance variation recorded versus the $[CO]/[O_2]$ ratio for different membrane thicknesses.

Knowing this value and the CO_2 production at C_{CO}^* we have verified the expression to be correct with and without PTFE. One obtains the diffusion coefficient from the diffusion equation

$$D_{CO} = \frac{J_{CO_2} L}{(S(C_{CO}^g)_L^* - (C_{CO}^1)^*)} = \frac{4.4 \cdot 10^{-7} \times 1800 \cdot 10^{-8}}{(0.13 \times 5.2 - 0.21) \cdot 10^{-7}} = 1.7 \cdot 10^{-4} \text{ cm}^2/\text{sec}.$$

Taking as activation for diffusion 40 kJoules which is a mean value for gases in polymers⁹ we obtain,

$$D_{CO}^{25C^\circ} = 2.24 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$$

which is a good order of magnitude.⁹

5. AGEING OF THE SAMPLES, PRECISION AND REPRODUCIBILITY

Two samples were tested during a week at $135^\circ C$ the C_{CO}^* being measured twice a day. We observed an evolution to lower concentrations during the first 48 hours. After this period it stabilized at a value about 10% lower than at the beginning of the experiment. At this time the variation becomes lower than the sensitivity of the infrared detector ($< 1\%$). The structure of the PTFE can influence the measure. An ESCA study of the PTFE films¹⁰ shows double bonds formation and cross linking but provided the discharge conditions of the sputtering are reproduced, the same type of PTFE is obtained.

The mean square deviation in our results is 7.1%. It is obvious that if a standardisation of each element which will form the sensor is made, a precision at least ten times greater can be obtained (see the ageing test).

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