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A Study of the Rate of Oxidation of Carbon Monoxide On Three Dispersed Electrode Systems

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The carbon monoxide oxidation reaction has been investigated on three compound electrodes: (a) platinum, platinum; (b) platinum, tantalum carbide; (c) gold, tantalum carbide. In each system the first material of the two named was a solid electrode and the second a powder electrode, dispersed in the electrolyte. The two reactants in the oxidation, carbon monoxide and water, were adsorbed separately on either the solid or the dispersed electrode, in order to regulate their relative concentrations. The steady state rates of oxidation were thereby increased.

INTRODUCTION

There are several inherent problems involved in measuring the kinetics of an electrocatalytic reaction between two different adsorbed species at a single electrode surface: The extent of adsorption of each must be measured in the presence of the other, and although this may not be a problem in a particular instance, the surface morphology of the patches of the two adsorbates is unknown (*1*). A second aspect of this problem occurs in a search for a catalyst for this type of reaction. If one of the species is strongly adsorbed, at the expense of the other, an electrode material may wrongly be rejected as inactive.

A compound electrode can overcome these problems. Two parts of the electrode, each carrying a separate adsorbed reactant, are brought together to allow the reaction to proceed. This is, of course, in many ways equivalent to a polyfunctional catalyst. Practically, a compound electrode consists of a solid electrode and of a powder electrode in suspension in the electrolyte. This system has been employed in a different context to measure the adsorbed material on dispersed powders, and to measure the rates of some oxidation reactions, such as that of methanol (*2, 3*).

In a compound electrode system the reactants are adsorbed separately. That is, one is adsorbed on the dispersed powder and the other on the solid electrode. Therefore the adsorption of each can be measured more easily than at a single electrode and the surface morphology of the reactants is known. When the two electrodes are brought together, each reactant molecule on the powder is brought into an adjacent position with one of the other kind of reactant on the solid. This facilitates reaction and the reaction rate can be higher than it is on a single electrode. When an electrode material adsorbs one of the reactants very strongly at the expense of the other, the compound electrode is particularly useful. In this instance, the strongly adsorbed reactant can be adsorbed on the dispersed powder (and perforce on the solid). Then the other reactant is dissolved in the electrolyte. As the strongly adsorbed reactant is (slowly) oxidized from the solid electrode, the weakly adsorbed reactant replaces it. When the strongly adsorbed reactant on the powder is brought up to the solid (say by stirring), a large area of the two adsorbed reactants can interact. The crucial point is that both reactants are present in favorably large concentrations

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in suitable juxtaposition. An example would be the oxidation of carbon monoxide on platinum. This proceeds by a "reaction pair" mechanism between adsorbed carbon monoxide and adsorbed water (*1*). Unfortunately the carbon monoxide is so strongly adsorbed on platinum, as almost to exclude the adsorption of water. However carbon monoxide can be adsorbed on a Pt dispersed electrode and the excess swept out of the system with nitrogen. The carbon monoxide adsorbed on the solid electrode is gradually oxidized, leaving space for adsorbed water. When the two electrodes are brought into contact by stirring, the two reactants are brought together in more favorable conditions than they would be on a single electrode surface, and the steady state rate of the reaction is increased. The rate constants, of course, should be the same in both cases.

There is another advantage of the compound electrode; the two parts of the electrode may be different materials and may be chosen as suitable adsorbents for the reaction and then both reactants may be supplied simultaneously to the system. The platinum, tantalum carbide system used in this investigation is an example. Platinum, which adsorbs carbon monoxide strongly, is made the solid electrode and the tantalum carbide is the dispersed electrode. Tantalum carbide was chosen because it does not adsorb carbon monoxide. Also it is very hard and has a high surface energy, and is probably therefore a strong adsorbent for water. Carbon monoxide is supplied continuously in this instance. Such a system is the obvious analog of the polyfunctional catalyst.

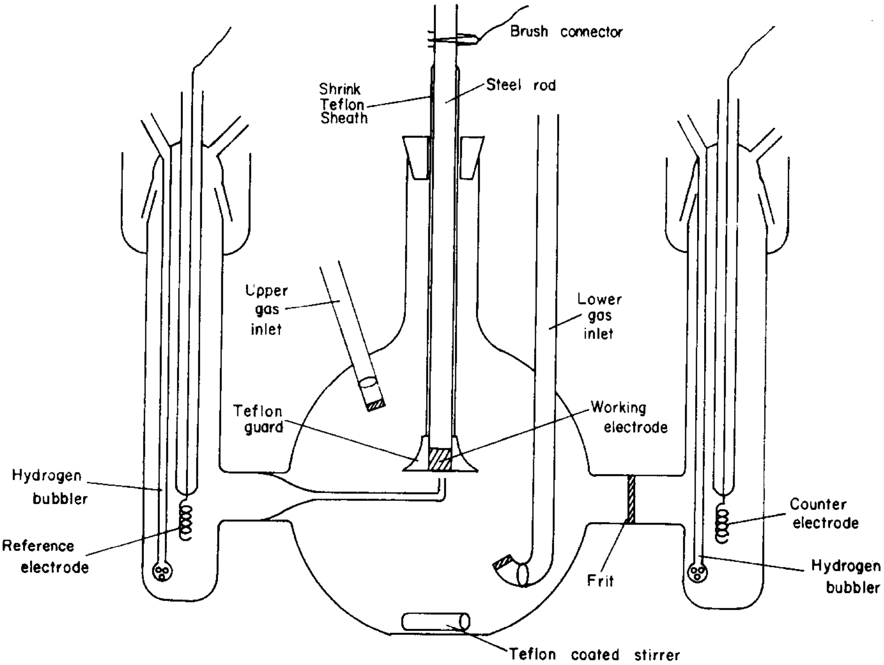

FIG. 1. The cell.

That a catalyst may be overlooked if one of the reactants is very strongly adsorbed, to the exclusion of the other, is illustrated in the gold system. Carbon monoxide is strongly adsorbed on gold and in acid solution the rate of oxidation is very small (*4*). However the rate of the reaction may be increased by several orders of magnitude by the addition of a dispersed powder of tantalum carbide. The rate constant is unchanged, except insofar as it is affected by the adsorption of one of the reactants on tantalum carbide instead of gold, and the method of bringing the reactants together (see below). The large increase in rate is attributed to the advantageous distribution of the two reactants.

EXPERIMENTAL PROCEDURE

The cell. The electrochemical cell was a conventional three-electrode design, Fig. 1. The center compartment contained the rotating disk, which was the working electrode, and the powder suspension, which was the dispersed electrode. The latter was stirred with a Teflon-coated magnetic stirrer. The working electrode, a cylinder of radius 4 mm, was cold-pressed into a steel rod and everything but the flat end of the electrode was sealed from the solution with "shrink" Teflon and Kel-F wax. The steel rod was connected to the shaft of a small motor through a flexible rubber connector and the current from the electrode was led from the steel rod through a wire brush. The lower end of the steel rod passed through a Kel-F-coated steel tube into the electrolyte and a Teflon seal at the bottom of this tube excluded the atmosphere from the electrolyte to some extent. As this seal was not perfect, nitrogen was blown over the top of the electrolyte and out of the seal to prevent any leakage of oxygen into the cell. The upper gas inlet, Fig. 1, was for nitrogen and the lower one for carbon monoxide or nitrogen.

The electrolyte was 1 N perchloric acid and the temperature ambient. All the potentials recorded were measured against the reversible hydrogen electrode.

Materials. The platinum and gold used for the electrodes were each 99.99% pure and were obtained from Englehard. The tantalum carbide powder was obtained from Alfa Inorganics (Beverly, Massachusetts), and was 325 mesh, purity 90%+. Hydrogen and nitrogen were Matheson "pre-purified" gases, 99.95% and 99.97% pure, respectively, and carbon monoxide was Matheson "chemically pure" grade, 99.5% pure. The water was distilled four times, the second distillation was from alkaline permanganate.

The platinum black was cleaned before use by boiling for several hours with concentrated hydrochloric acid and then refluxing with hot water in a Soxhlet apparatus for at least a week. After the first experiment with a particular sample of platinum black, it was reused after the hot water cleaning only.

Potentiostatic measurements were made with a Wenking potentiosat, and the current was recorded continuously through a Varian recorder. The surface area of the platinum working electrode was measured by means of a cathodic pulse during which H atoms were deposited on the electrode's surface. During this pulse, the potential was followed on the screen of an oscilloscope. The brush which carried the current from the rotating working electrode, caused some "noise" on the oscilloscope trace. Although this connection was well lubricated with phosphoric acid, it limited the electrode area measurements considerably; the areas were only reproducible to about ±5%. The working electrode was rotated at speeds between 2000 and 15 000 rpm and the speed was measured with a stroboscope.

The cell was pre-electrolyzed overnight, with the working electrode at +0.1 V to remove oxygen. Both the working electrode and the magnetic stirrer were rotated during this time, to minimize diffusional problems, and nitrogen was bubbled from both the upper and the lower gas inlets. It was found that the cell could only be used for about 1 to 2 days, as the system became contaminated and could not be recleaned even by prolonged pre-electrolysis with the working electrode at +0.8 V.

RESULTS AND DISCUSSION

System I—Platinized Platinum Working Electrode and Platinum Powder Dispersed Electrode

It was necessary to eliminate diffusional problems in bringing the dispersed platinum to the working electrode. However, the rate of oxidation of carbon monoxide depended in a complex manner on the rate of stirring and it was necessary to elucidate this first (see below). Subsequently it was recorded that the minimum concentration of platinum powder was 0.1 g per 100 ml of electrolyte and the minimum speed of rotation of the working electrode was 2000 rpm with the magnetic stirrer stationary. Any stirring rate higher than this or any higher concentration of platinum black was sufficient to avoid diffusional control, but an excess of each was employed, e.g., ~1 g of platinum black, per 100 ml a speed of rotation of 4000–6000 rpm for the working electrode and the magnetic stirrer at the highest speed of the motor. The necessity for this was to counter the effects of flocculation by the platinum black. After prolonged oxidation of the carbon monoxide, adsorbed on the powder, the adsorbate became depleted and the powder agglomerated. Subsequent adsorption of carbon monoxide reversed this process and the powder redispersed.

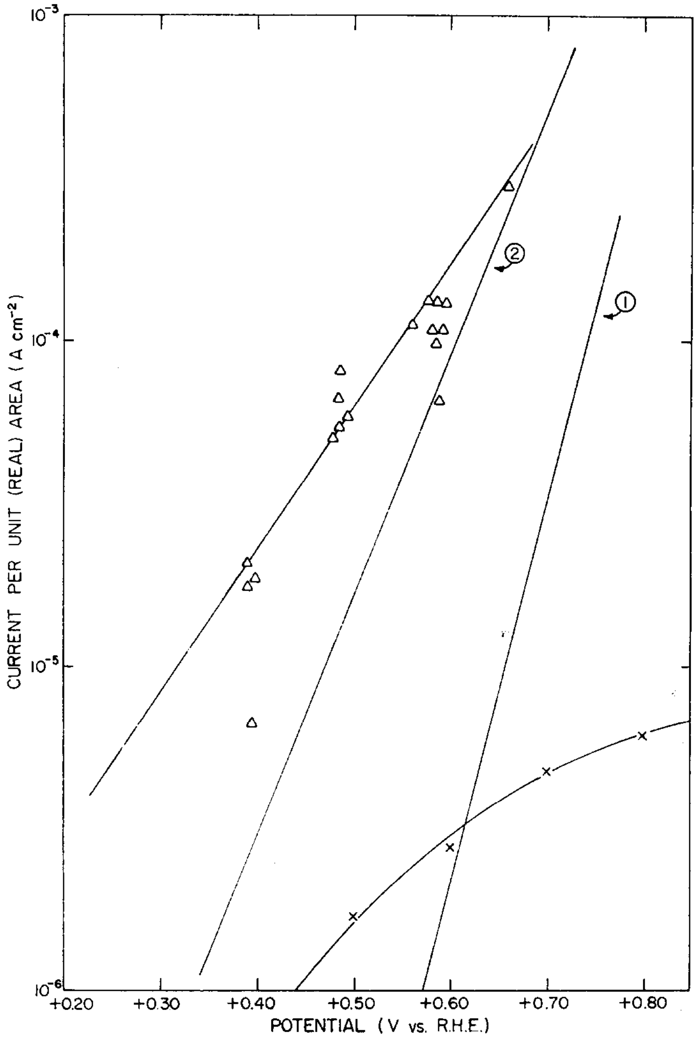

FIG. 2. The rate of oxidation of carbon monoxide at a compound platinum electrode, with carbon monoxide bubbling through the cell (×). The rate constant for carbon monoxide oxidation at a compound platinum electrode, with nitrogen bubbling through the cell (△). The rate constants for the oxidation of linear and bridged carbon monoxide, at a simple platinum electrode, (*6*) lines 1 and 2.

The procedure for making measurements was to pre-electrolyze the cell with nitrogen bubbling through it to remove oxygen, as described in the experimental section, then to saturate the powder with adsorbed carbon monoxide by bubbling the gas through the cell for a few minutes. The currents observed at potentials between +0.3 and +0.8 V were as shown in Fig. 2, where the currents are given as amps per unit total surface area, regardless of the coverage with carbon monoxide. The total surface area of the platinized Pt electrode was 94 "real" cm^2. This was estimated by applying a cathodic current pulse in the absence of CO. This plates H atoms onto the surface and it was assumed that 210 microcoulombs of charge is equivalent to 1 real cm^2 (*5*). The coverage of the electrode with CO was high under the conditions of Fig. 2 and could not be measured with a cathodic pulse. The carbon monoxide gas stream was then replaced by nitrogen and the current was measured at constant potential during the replacement of carbon monoxide dissolved in the electrolyte by nitrogen. As the gas streams were changed the current decreased and stayed at a low value for up to 20 min (this time depended inversely on the rate of nitrogen bubbling) until most of the dissolved carbon monoxide was removed. Then the current began to increase slowly for 2 to about 12 min to a value about twenty times higher than that obtained with carbon monoxide bubbling through the cell. The current then stayed at this new value but from time to time it decreased sharply for only 1 to 2 sec and then climbed slowly back to its original high value. This high value of the current depended on the rates of stirring; it was lower with very high stirring rates.

This behavior was inexplicable in terms of simple diffusion rates of material to the surface. It appears that

(a) after the carbon monoxide gas stream was replaced by nitrogen the current decreased and later increased and that the time during which the current was at a low value was inversely proportional to the rate of nitrogen bubbling;

(b) the magnitude of the current, after this increase, was lower as the stirring rate increased;

(c) the sharp decreases in current from this high value occurred at random, but were more frequent with higher rates of stirring.

It was thought that these variations of the current would be understandable in terms of the variation of the carbon monoxide coverage on the working electrode, rather than in terms of the diffusion of material to its surface per se. Of course it is the rate of diffusion relative to oxidation, etc, which ultimately determines the coverage. To determine CO coverage, its oxidation was interrupted from time to time and cathodic current pulses were applied to the electrode. A 1:1 coverage of platinum atoms with hydrogen was assumed and in estimating CO_{ads} it was assumed that $\theta_{CO} + \theta_H = 1$ (*1*). By comparing the current passing before this pulse was applied with the coverage, a specific rate of carbon monoxide oxidation was obtained. The results at three potentials are given in Fig. 3.

There are two interesting features of these results. The first is the range of coverage, θ, obtained at each potential. At the lower potentials only high values of θ were obtained; that is, the rate of oxidation of material on the surface was low and was insufficient to remove the carbon monoxide arriving at the surface. At +0.6 V the largest range of θ was obtained. At a higher potential than this only a very small range of θ was obtained and θ was small (about 0.3). For example, with a bare surface area of 60 cm^2, the oxidation current was 3.8×10^{-2} amps at +0.7 V. A higher rate of stirring at this potential produced only a marginal increase in θ. The time available for an experiment before the powder flocculated was much reduced at +0.7 and +0.8 V, because of the high rates of consumption of adsorbed carbon monoxide. The measurements at +0.8 V were not recorded as they may have been diffusion-limited.

The second interesting feature of Fig. 3 is the first order dependence of the rate of oxidation on $(1 - \theta)$ over a wide range of θ between 0 and 1. This result will explain most of the above mentioned peculiarities in the current–time behavior. Item (c) above would mean that some powder particles transfer CO to the solid electrode.

In general, though, a different mechanism must be operating and the $i-(1-\theta)$ relation indicates its character. This result is not necessarily in disagreement with the results showing the dependence of the rate on both θ and $(1-\theta)$ obtained by Gilman (*6*). The two sets of data are in close agreement and may be explained in a similar manner. The mechanism for carbon monoxide oxidation, suggested by Gilman, is through a "reaction pair" of adjacent adsorbed carbon monoxide and adsorbed water molecules. In the present system the same explanation may be employed; however, now the adsorbed water molecule of the reaction pair is situated on the working electrode surface and the CO molecule of the reaction pair is situated on the dispersed electrode surface. Therefore, the highest rate of oxidation would be expected at the lowest values of θ on the working electrode, as is observed experimentally, rather than at values of θ close to 0.5, as was observed by Gilman. The two experiments are comparable if, in this investigation, we consider the total electrode to be both the surface of the working electrode and the surface of the dispersed electrode adjacent to it. The assumption is made that there is a one-to-one correlation between these two surfaces. That is, in the conditions where the rate is not limited by diffusion, there is a carbon monoxide molecule on the dispersed electrode available for each water molecule on the working electrode. We may write the rate equation as

$$i = k\,A\,(1-\theta) \qquad (1)$$

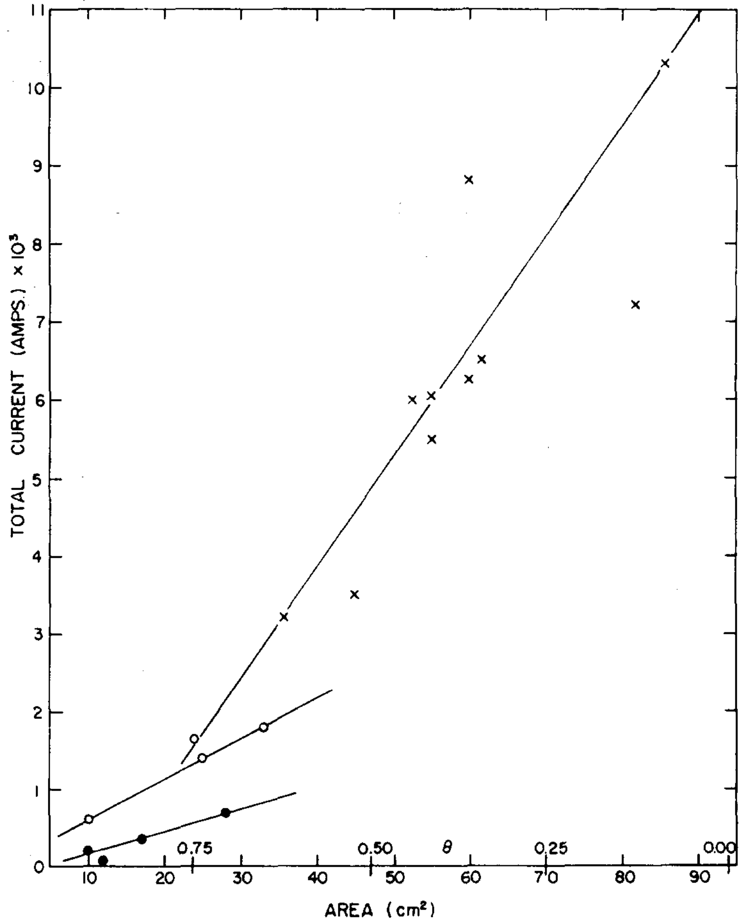

FIG. 3. The rates of oxidation of carbon monoxide at a compound platinum electrode versus the coverage of the working electrode: at +0.60 V, ×; at +0.50 V, ○; and at +0.40 V, ●.

where i is the rate of CO oxidation, k is the rate constant, A is the real area of the working electrode, and θ is the coverage of CO on the working electrode; or we may write

$$i = k\,2A\ (1-\theta)\theta' \qquad (2)$$

where $2A$ is the area of the working electrode plus the area of the dispersed electrode adjacent to it (this will be referred to as the compound electrode) and θ' is the fraction of the dispersed electrode adjacent to that part of the working electrode which is bare of carbon monoxide, i.e.,

$$\theta' = 1 - \theta$$

Equation (2) is therefore formally analogous to the rate equation of Gilman (*6*), with the following difference. In this investigation it is reasonable to suppose that every adsorbed molecule on the compound electrode is in a position to react and we do not have to make allowance, as does Gilman, for the molecules of a particular species adsorbed in the middle of a patch of adsorbed molecules of the same species, which are sterically hindered from reacting with a molecule of the other species. The rate constants are compared in Fig. 2. It was necessary to make allowance for the oxidation of carbon monoxide adsorbed on the working electrode, by combination with an adjacent water molecule, also adsorbed on the working electrode. This rate was found to be negligible compared with the rate of the reaction on the compound electrode. The reason for this is that only a small percentage of the adsorbed material on the working electrode is at the edge of the adsorption patch, and therefore in a position to react. No distinction could be made in this investigation between the rates of oxidation of linear and bridged carbon monoxide. Considering the differences in the experimental methods involved in these two investigations the agreement between the results is good. However the difference in slope between the two sets of data is unexpected.

It was at first thought that the high slope of 250 mV resulted from the carbon monoxide, adsorbed on the dispersed electrode, being at a lower potential than the working electrode. The dispersed electrode is at open circuit potential, which when measured registered a potential of 0.36 to 0.40 V. The following experiments were conducted to test the importance of this problem. A working electrode was made out of a concentric ring and disk of platinized platinum. The two were separated by a Teflon sleeve and the sides of the electrode were sealed from the solution as before with "shrink" Teflon and Kel-F wax. Electrical contact was made to each one separately through a wire brush and the ring electrode was connected to the potentiostat. The potential of the disk was maintained through a separate nongrounded potentiometer circuit.

First, the disk was set at a series of different potentials and the ring was kept at open circuit. The potential of the ring followed that of the disk although it remained about 50 mV lower. It was concluded that the platinum particles arrived at the ring electrode at a higher potential than +0.40 V when the disk was at a higher potential than +0.40 V. Therefore, if a low rate were obtained because the carbon monoxide was only at a potential of +0.40 V, a higher rate of oxidation should be obtained at the ring electrode, if the disk electrode were at the same potential as the ring. This was not so. The current which was measured at the ring electrode was independent of whether the disk was at the same potential or at open circuit, and the high Tafel slope of the results shown in Fig. 2 could not be explained in this way.

A high Tafel slope could be obtained in the presence of adsorbed oxygen on either the working or the dispersed electrode, but this was shown to be absent by the open circuit potentials of these electrodes which were a little less than +0.4 V, when covered by adsorbed carbon monoxide (*7*).

System II—Platinized Platinum Working Electrode and Tantalum Carbide Dispersed Electrode

The object of this system was to reverse the positions of the two adsorbed species, that is, to react carbon monoxide adsorbed on the working electrode with water adsorbed on the dispersed electrode. The reasons for choosing tantalum carbide as the dispersed electrode were as follows: (a) it is conducting and (b) corrosion-resistant, and (c) it was thought to be a good substitute for tungsten oxide, which is used in conjunction with platinum, to oxidize carbon monoxide (*8*).

One gram of tantalum carbide was suspended in 200 ml of electrolyte and before the measurements were made adsorbed oxygen was removed from the system, as described in the experimental section, and the corrosion current of the tantalum carbide was measured. This was of the order of 10^{-7} A cm^{-2} and was therefore negligible.

The working electrode, platinized platinum of area 50 cm^2, was fully covered with adsorbed carbon monoxide, by bubbling the gas through the lower inlet of the center compartment of the cell. The reason for assuming that carbon monoxide was not adsorbed on tantalum carbide was that, as nitrogen displaced dissolved carbon monox-

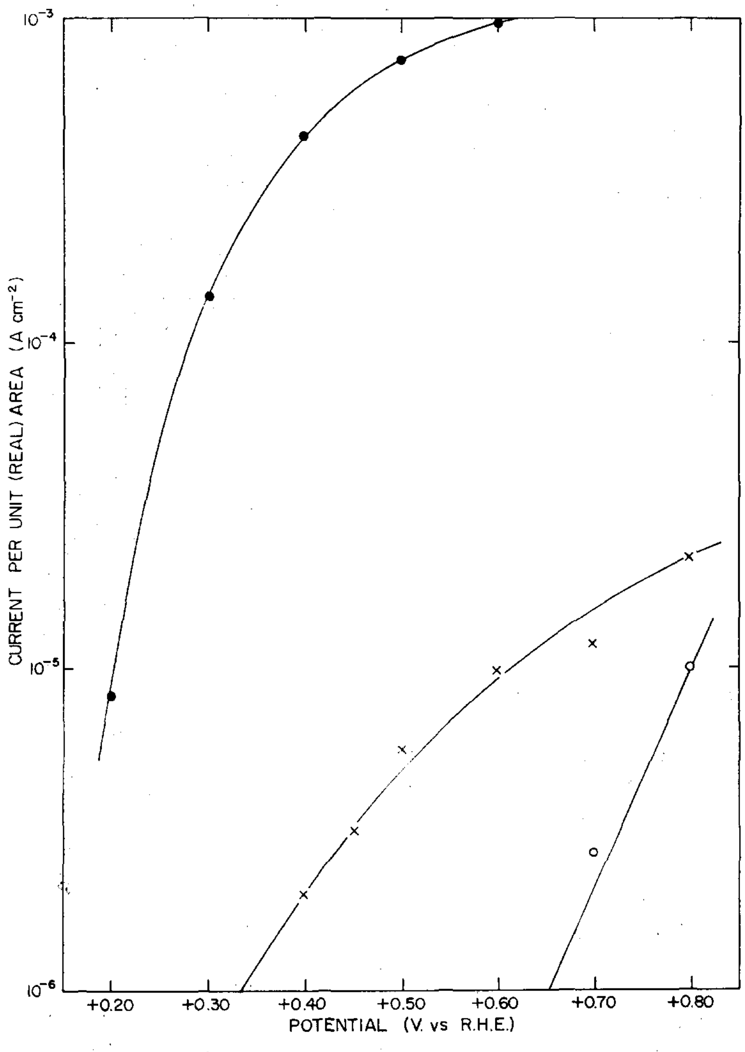

FIG. 4. The rates of oxidation of carbon monoxide at a platinum–tantalum carbide compound electrode (×), a simple gold electrode (○), and a gold-tantalum carbide compound electrode (●). Carbon monoxide is bubbling through the cell in each instance.

ide in solution, the rate of oxidation became vanishingly small, unlike the result in System I. That is the supply of carbon monoxide disappeared.

The rate of oxidation, expressed as a current per unit real area of the working electrode, is shown in Fig. 4. The current at high potentials is beginning to be limited by the diffusion of tantalum carbide to the working electrode; the powder is heavy and could be kept in suspension only with difficulty. At lower potentials however, the Tafel slope is again very high, as it was in System I, and this may also be interpreted as the slow discharge of the adsorbed species between the particles of the dispersed electrode and the working electrode.

System III—Smooth Gold Working Electrode and Tantalum Carbide Dispersed Electrode

Carbon monoxide may be oxidized on a gold electrode in alkali, when the rate is first order with respect both to carbon monoxide and hydroxyl ion concentration (*4*). Carbon monoxide is adsorbed on the gold surface. The low rate of oxidation in 1 *N* acid, recorded in Fig. 4, is thought to reflect a very high surface coverage by carbon monoxide, leaving little room for the adsorption of another reactant, namely water, from the dispersed electrode. The oxidation current on a gold working electrode, with 1 to 2 g of tantalum carbide powder suspended in 200 ml of electrolyte, is shown in Fig. 4. The results are shown from two separate experiments. The current at high potentials is diffusion-limited and is different in the two experiments because of the different extent to which the tantalum carbide settled out of suspension. Only the results at the lower potentials are activation-controlled. The important differences between these measurements and those recorded at a platinum electrode are the difference in magnitude of the current and the difference in Tafel slope. In the gold–tantalum carbide system the slope is 60 to 80 mV, which suggests a mechanism where the rate-limiting step is the decomposition of an adsorbed electroactive intermediate, preceded by an equilibrium between carbon monoxide and another reactant, probably water. An attempt was made to measure the amount of such an intermediate adsorbed on the electrode by reducing it, but the results were inconclusive.

A Comparison of the Rates of Carbon Monoxide Oxidation

The relative rates of carbon monoxide oxidation on the various catalyst systems are shown in Figs. 2 and 4. There are three systems involving platinum only—first, the smooth electrode where both reactants are adsorbed on the same surface. This is the least efficient method of utilizing the catalyst for the reasons that the coverage is high and that not all the molecules of one species are accessible to the other species. The other two systems are compound electrodes, one with carbon monoxide bubbling and the other with nitrogen bubbling. Of these the first one is the least efficient. The coverages of both the collector and the dispersed electrodes are high and the current is quite low because the conditions for bringing the adsorbed reactants together are not optimum. When nitrogen is bubbling, however, the working electrode is cleared of adsorbed carbon monoxide, while the carbon monoxide coverage on the dispersed electrode remains high. The conditions for a high rate of oxidation are an optimum, because every water molecule adsorbed on the working electrode has carbon monoxide, adsorbed on the dispersed electrode, available to it. The same situation exists for the platinum, tantalum carbide system, where every carbon monoxide molecule adsorbed on the working electrode is near to water, adsorbed on the tantalum carbide.

An analogous description would be applicable to the two systems with a gold working electrode, where the higher rate of oxidation occurs when the carbon monoxide, adsorbed on the gold working electrode, has water, adsorbed on the dispersed electrode, available for reaction.

In comparing the different catalysts the comparison should be made under optimum conditions for each system. That is, for the platinum system the current obtained with nitrogen bubbling and a coverage of carbon monoxide of zero on the working electrode, should be considered. For the platinum, tantalum carbide system optimum conditions occur with carbon monoxide bubbling through the system, and similarly for the gold, tantalum carbide system. The order of efficiency of these catalysts is

$$\text{Au/TaC} > \text{Pt/Pt} > \text{Pt/TaC}$$

CONCLUSIONS

(1) A compound electrode may be used to increase the rate of reaction between two adsorbed species, by allowing the concentration of the more weakly adsorbed species to be increased.

(2) The rate constant may be measured directly, without the necessity for making a correction for the sizes of the patches of the adsorbates.

(3) The way in which two reactants may be adsorbed separately, one on the dispersed electrode and one on the working electrode, and may be brought together to react is demonstrated for the platinum system.

(4) Two reactants may be adsorbed separately on different electrode materials; this is shown for the platinum, tantalum carbide system and the gold, tantalum carbide system.

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