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PREFACE

An important area of recent research in electrochemical surface science has been the study of electrocatalysis in the anodic oxidation of various simple molecules such as H_2, HCOOH, CH_3OH, C_2H_4 and saturated hydrocarbons on noble metal electrodes in aqueous solution. In this work, the role of dissociative adsorption of the reactant, faradaic electrochemical oxidation of the adsorbed fragments and desorption of final products has been studied. The kinetics of these processes have been investigated at a number of noble metals and, in some cases, their alloys.

Use of alloys provides an interesting way of introducing variation in the properties of the metal electrode with regard to (a) electronic structure of the metal and (b) surface composition and structure at its interface.

In the present work, experiments are described in which the electrochemical oxidation of formic acid and methanol has been studied at a series of Au-Pt alloys in relation to the behaviour at pure Pt, Pd and Au electrodes. Interesting effects of alloy composition are found which are interpreted in terms of various surface reactions which are taking place at the electrode interface, including the surface oxidation of the electrode metal itself.

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SOME ABBREVIATIONS USED IN THE THESIS

"d.l." or "d.l. region" : double-layer or the region of a potential-sweep over which only double-layer charging currents arise, respectively.

i_p: the peak current, i, in a potential sweep current-potential profile.

"H-" or "H adsorption region" : the range of potentials in a potentiodynamic sweep over which H deposition or ionization desorption processes occur (viz. 0.0 to ca. + 0.35 V, E_H).

E_H : value of electrode potential on the scale of a reversible hydrogen electrode in the same solution.

FA_1, FA_3, MA_1, etc. peaks : anodic current peaks for formic acid (F) oxidation or methanol (M) oxidation over various regions of a potentiodynamic sweep in order of their appearance in the anodic - going direction. FC or MC, corresponding currents in the cathodic - going direction of a sweep.

C_i : concentration of species i at the electrode or in solution, as specified.

kT/h: contribution of well known universal constants and temperature (T) involved in the expression for a rate constant.

ABSTRACT

Studies on effects of changing metal electronic character in gold-platinum alloys and to a lesser extent in gold-palladium alloys on the electro-chemical kinetics of oxidation of formic acid and methanol are reported. Some previous work on these substances was done at the University of Ottawa and in other laboratories in relation to studies on mechanisms of electrocatalysis. The adsorption and reactivity of chemisorbed species arising from these molecules at the alloy electrodes were characterized and related to the atomic composition of the surface of the alloy electrocatalysts. The work has applications in fuel-cell technology.

CHAPTER I

INTRODUCTION AND REVIEW

1. Nature of Electrocatalytic Processes

The electrochemical oxidation of many organic molecules depends on the ability of the electrode first to dissociate the molecule catalytically into smaller adsorbed fragments which can then be electrochemically oxidized from the surface. The role of the electrode surface in providing sites where the intermediates resulting from this process can undergo electrochemical oxidation, has given rise to a new term, electrocatalysis. This term implies that there is a dependence of the rate of electrochemical reaction at a given potential on the condition and properties of the metal surface at which the process is occurring. Usually the term must be reserved for those electrochemical processes which involve the formation of adsorbed intermediates and desorption of the products resulting from chemical and/or electrochemical surface reactions involving those intermediates.

The main difference between electrocatalytic processes and ordinary catalysed reactions is the potential-dependent role of the electrode surface in the overall reaction mechanism and its rate.

In addition to factors such as chemisorption energy and coverage by intermediates, the question of two-dimensional diffusion of reacting species arises in catalysis, e.g. in recombination steps and in diffusion to active centres. The quantitative examination of surface mobility or diffusion of adsorbed intermediates is of prime interest when electrocatalysis occurs by a "bifunctional" mechanism. For this situation, a reaction intermediate must physically diffuse across an electrode surface to react at another site where, e.g., some other reacting species is adsorbed. Such an example is the electrocatalytic oxidation of formic acid; the details of this reaction will be considered later as it was the one in which further experimental studies were made in the present work.

2. Rates and Current Densities for Reactions at Electrodes

In an electrochemical reaction, the rate is measured directly in terms of the current density, i amp cm^{-2}. At equilibrium, i.e., at the reversible potential, V_r, for a process, no net current flows but the kinetics under equilibrium conditions are defined by the exchange current density, i_0, i.e., the equal current passing per cm^2 forward and backward (viz. anodically or cathodically, or vice versa) when the potential is at the reversible value, V_r. Normally, electrode-kinetic measurements are concerned with net currents for the reaction well displaced at some potential, V, from the reversible condition. Then the net current i is conveniently expressed in terms of the overpotential η defined as $\eta = V - V_r$ by the equation

$$i = i_0 \{ \exp \beta\eta F/RT - \exp[-(1-\beta)\eta F/RT] \}$$

which, for appreciable values of η, becomes simply

$$i = i_o \exp \beta\eta F/RT$$

where β is the barrier symmetry factor. The latter equation is the familiar Tafel relation in exponential form.

The quantity i_o is determined by the electrochemical rate constant of the process and the concentration c_i according to

$$i_o = zF\,(kT/h)c_i \exp \beta V_r F/RT.\exp[-\Delta G^{0\ddagger}/RT]$$

where c_i is the local concentration of reacting species at the electrode surface. If the process involves deposition of an adsorbed intermediate, e.g. H in the H_2 evolution, then the equation for i_o must include a free surface area factor, $1-\theta_H$, to allow for coverage θ_H by adsorbed H.

The properties of the electrode metal or its surface determine the rates of electrode processes through (a) the rate constant or $\Delta G^{0\ddagger}$; (b) the extent of adsorption of reaction intermediates and (c) the catalytic properties of the surface. The importance of the electrode material is well known in a number of reactions especially in the case of cathodic hydrogen evolution. The latter process normally occurs in two steps, a coupled proton discharge and hydrogen adsorption step onto the metal, namely, $M(e) + H_3O^+ \rightarrow MH + H_2O$, followed by an electrochemical desorption step, $MH + H_3O^+ + e \longrightarrow M + H_2 + H_2O$ or a chemical catalytic desorption step, $MH + HM \rightarrow H_2$. Considering the first step, the reaction rate is closely connected with the mechanism of this electronation reaction and the adsorption properties of M for H binding. The essential act of the reaction which leads to the adsorption of hydrogen as H on the electrocatalyst is the tunneling of an electron from the electrode to the hydrated proton in an activated state on the solution-side of the double-layer at the electrode interface.

The energetic conditions that determine the probability of electron transfer and proton deposition on to a metal in the first step of the hydrogen evolution reaction can be considered in the following terms defined by Butler[1] : for zero field at the interface, the condition for electron tunneling in the step $M(e) + H_3O^+ \longrightarrow MH + H_2O$ is

$$R + A < I + L - \Phi$$

where

R is the $H-H_2O$ repulsion energy,

A the M-H bond energy,

I the ionization potential of the hydrogen atom,

L the proton hydration energy

and

Φ the work function of the electrode.

Obviously, R, I, L do not depend on the nature of the electrode material while the hydration energy of the proton is not affected by a change of the electrode from, for example, nickel to platinum; however, the M-H interaction energy A and the work function Φ do depend in an important way on the nature of the electrocatalyst.

Hence we can now write

$$A + \Phi < \text{constant}$$

where the constant is characteristic of the particles involved in the reaction, H^+, H and H_2O. However, in an experiment where the electrode potential has to be measured against a reference electrode, the work function cancels out, so that there is no direct effect of the work function upon the rates of deposition reactions which arise from electron transfer (its effect cancels out in a two-electrode cell because of the unavoidable contact p.d. with, for example, the reference electrode elsewhere in the measuring circuit). Therefore, the observed dependence of the rate-determining step for the hydrogen evolution reaction, and even of the overall reaction pathway on the nature of the metal must originate from a dependence of the rate on the M-H bond strength and on coverage by H. The M-H bond energy, however, was shown by Conway and Bockris[2] to be linearly related to Φ for a series of metals, so that the rate of the hydrogen evolution reaction, measured e.g. in terms of the exchange current density, i_0, at the reversible potential, depends on Φ indirectly because of the dependence of energy of H adsorption on Φ. Also, it was shown by Conway and Bockris[2] that the electrochemical catalytic properties of a series of electrode materials for the hydrogen evolution reaction, as indicated by the exchange current densities for this process, could be correlated with %-d character in the d^2sp^3 hybrid bonding in the metal lattice and in the surface.

By considering how the coverage was related to the standard free energy of chemisorption of H at the reversible potential, Parsons[3] showed how i_0 would vary with the chemisorptive properties of the metal for various mechanisms of the cathodic H_2 evolution reaction.

3. Alloys in Catalysis and Electrocatalysis

In comparing an electrode reaction with a chemical reaction occurring on a surface, i.e. a heterogeneous reaction, it is useful first to look at how the rates of the two types of reactions are expressed. The rate of a heterogeneous chemical reaction is expressed in moles of substance transformed per second per square centimeter of the surface. The electrode reaction rate, however, is expressed in terms of current density, i.e., in amperes per square centimeter. However, this dissimilarity is only superficial since it readily follows, using Faraday's Laws, that the current density divided by the charge zF transferred per mole of reactant is the rate in mole cm^{-2} sec^{-1}. Thus, the number of moles of electron acceptor (or donor) electronated (or deelectronated) per second per square centimeter of the interface is obtained, that is i/zF has the same units (moles per second per square centimeter) as the rate of a surface chemical reaction. The expression for the rate of an heterogeneous reaction is identical in form with that for the zero-field rate of an electrode reaction, i.e.

$$v = (kT/h)\cdot \Pi c_i \exp -\Delta G^{0\ddagger}/RT$$

where Πc_i is the symbol used to indicate the product of the surface concentrations of the species involved in the reaction and $\Delta G^{0\ddagger}$ is the standard free energy of activation for the reaction in the absence of assistance from an interfacial field. Normally the surface concentrations required in the rate equation for an heterogeneous reaction must be related to the experimentally known bulk concentration through an adsorption isotherm for the reactant species.

A further comparison is that in the case of heterogeneous catalysis, the reactants must diffuse to the catalyst surface and become adsorbed there before the catalytic or electrochemical reaction takes place.

Correspondingly, the products must move away to provide surface sites for other molecules of reactants to adsorb. For example, in the case of the gas-phase hydrogenation of ethylene at a nickel surface, the ethylene and hydrogen molecules must first adsorb on the nickel surface; the reaction then occurs and then the ethane desorbs from the surface. In an electrode reaction, the ions have to reach the interface region, become adsorbed in the double-layer and undergo the charge-transfer reaction. The electronated particle in a one-step reaction, then moves off into the solution or is chemisorbed, e.g. in the case of deposited H or OH species from water.

The most important distinction between electrode reactions and chemical heterogeneous reactions is that the former involve a net transfer of charge. The rate of the electrode reaction is therefore potential-dependent according to a relation of the form

$$v(\text{electrodic}) = \frac{i}{zF} = \frac{i_o}{zF} e^{-\beta F\eta/RT}$$

which arises because the electrode potential modifies the free energy of activation through a change ηF of the Fermi level energy.

The catalytic aspects of electrode reactions arise in two ways:

(i) In a discharge step of the type considered above, e.g.

$$H_3O^+ + e + M \longrightarrow MH_{ads} \qquad (1)$$

in the hydrogen evolution reaction, the standard rate constant (i.e. at the reversible potential) of the electrochemisorption step (1) certainly depends on the properties of the metal M, being greater at metals that adsorb the H intermediate more strongly than at those where the H adsorption is weaker. However, the use of the term "catalytic" in this sense requires some reservations since, by the nature of electrode reactions, there can be no "uncatalysed" reaction pathway with which the rate of the "catalysed" reaction may be compared.

(ii) More direct examples of electrocatalysis arise in reactions where a chemical step, usually dissociative adsorption, occurs first on the surface and is followed by steps involving electrochemical oxidation or reduction of the chemisorbed species. The electrode metal then acts as a true catalyst for the dissociative step and as an electron source or sink for the following charge-transfer steps. Cases where this type of process arises are in the oxidation of formic acid or methanol where C-H bond dissociation and adsorption occur first, followed by coupled oxidation steps; also in reduction of oxygen or oxidation of hydrogen (H_2), dissociative steps arise through adsorption on the electrode catalyst surface. Examples of the initial dissociative chemisorption steps are:

$$HCOOH + 2M \rightarrow MH_{ads} + MCOOH_{ads} \qquad (2)$$

$$CH_3OH + 6M \rightarrow 3MC\text{-}OH_{ads} + 3MH_{ads} \qquad (3)$$

$$O_2 + 2M \rightarrow 2MO_{ads} \qquad (4)$$

$$H_2 + 2M \rightarrow 2MH_{ads} \qquad (5)$$

where M's are the adsorption sites on the metal electrode surface.

(iii) True catalytic processes also arise as post-electrochemical steps, e.g. in the gas evolution reactions (H_2, Cl_2, O_2) where discharged adsorbed intermediates are recombined on the electrode surface to form stable gas molecules. For example, following eqn (1), the catalysed recombination/desorption step

$$MH_{ads} + H_{ads}M \rightarrow H_2 + 2M \tag{6}$$

can occur. Similar steps are involved in reactions producing O_2 and Cl_2.

A general example of an electrocatalytic reaction is the electronation or reduction of oxygen molecules to give water: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$. This reaction is the basis of "electrochemical combustion" in fuel-cells which bears an interesting relation to chemical combustion. When a substance reacts chemically with oxygen, it is said to burn. Thus hydrogen burns in O_2 with explosive release of thermal energy to form water, but only at an elevated temperature:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{7}$$

In the corresponding electrochemical process, hydrogen is deelectronated at the electron-sink electrode (the anode) and oxygen is electronated at the electron-source electrode (cathode). The two charge-transfer reactions are:

$$2H_2 \rightarrow 4H^+ + 4e \tag{8}$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \tag{9}$$

giving the overall process:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{10}$$

which is equivalent to a catalysed oxidation of H_2 by O_2, since the electrochemical reaction between H_2 and O_2 occurs at low temperatures. Thus, hydrogen is said to undergo cold combustion.

An heterogeneous chemical reaction has a fixed reaction velocity at a given pressure and for given concentrations of reactants. The only way that the reaction velocity can be increased is to raise the temperature. The exponential factor in the expression for a chemical reaction rate constant is $e^{-\Delta G^{o\ddagger}/RT}$. For an analogous electrochemical reaction, the exponential factor is $e^{-(\Delta G^{o\ddagger} \pm \beta VF)/RT}$ where V is the metal/solution potential difference. Of course, as mentioned above, there is often no true "chemical" analogue to the electrochemical reaction so that even when $V = 0$ (no field effect on the electron charge-transfer rate), $\Delta G^{o\ddagger}$ does not have a purely "chemical" significance since it still applies to an electrochemical charge-transfer step. The opportunity, in electrochemical reactions, to modify the free energy of activation through the $\beta VF/RT$ term enables very large changes of rate to be controllably introduced. Thus, if a typical value of 10,000 calories/mole is assumed for $\Delta G^{o\ddagger}$, and taking $\beta=\frac{1}{2}$ and $T = 300^{o}K$, an increase of potential by only 0.5V, causes an anodic electrode reaction rate to increase by a factor of about 10^5. In order to cause a similar increase in the chemical rate by temperature alone, an impractical increase of temperature of approximately $1000^{o}K$ would be required.

The search for improved electrocatalysts for fuel cells has shown that, for organic reactions, enhanced activity over that attainable at pure platinum is difficult to achieve. Platinum is usually found to be the most active single metal for the complete electro-oxidation of many water-soluble organic compounds such as methanol, formaldehyde and formic acid to carbon dioxide in both acid and alkaline solutions. However, some improvements can be obtained for certain reactions by incorporation of other metals as alloy constituents such as rhenium,[4] tin,[5,6] ruthenium[7,8] or osmium[4] and, as in the present work, gold. The improvement in performance in the presence of these metals has been attributed to better oxidation of various adsorbed organic intermediates that arise in reactions of this type by adsorbed oxygen-containing species that are associated with the added metal and are more reactive than adsorbed OH species on platinum. Also, the chemisorption of the organic species itself depends on the surface composition of the alloy or the nature of the metal. For example, it has been observed by Shropshire[9] that the adsorption of molybdate ions increases the activity of platinum, the proposed mechanism for this system being oxidation of the organic fuel molecule with adsorbed molybdate as a mediator, followed by electro-oxidation of the reduced molybdate species. Also, improved electrocatalytic reduction of O_2 occurs on Au-Pd alloys in comparison with that on either pure metal. This is connected with the strength of binding of adsorbed O-species and coverage effects[10].

The activity of the transition metals, especially for the dissociative adsorption of molecular hydrogen and in hydrogenation reactions, has been correlated in the past with the existence of partially filled d-bands. Many alloy studies were prompted by the expectation that catalytic activity would change abruptly once these vacancies were filled by alloying with a group IB metal. An example of such behaviour is the Au-Pd system. Gold, which has no unpaired d-electrons, has a Tafel slope of -2RT/F for oxygen reduction while palladium, however, shows a Tafel slope of -RT/F owing to an intermediate oxygen coverage and a different rate-determining step. Alloys of gold and palladium exhibit Tafel slopes of either -RT/F or -2RT/F depending upon the alloy composition. The change from $\frac{-2RT}{F}$ to

-RT/F as palladium is added to gold has been related, by Damjanović[11], to the occurrence of sufficient palladium in the alloy to create d-orbital vacancies and consequently to a change of the oxygen coverage from a low to an intermediate value.

The oxidation of simple organic molecules such as ethylene, formic acid and methanol has been studied extensively and the special significance of platinum as an electrocatalyst material is now well known, although there is increased evidence that there are some noble metal alloys which do give reaction rates at certain potentials, which are appreciably larger than those on platinum alone as will be seen later in the present work. Other baser metals are not considered since they normally undergo anodic dissolution in the potential regions over which oxidations of organic substances usually take place at reasonable rates.

For example, a study of the mechanism of ethylene oxidation on a series of noble metals other than platinum, and on noble metal alloys[12], leads to the conclusion that the oxidation of ethylene often proceeds, at least at first, along the same path as that on platinum, i.e.,

$$H_2C = CH_2 \rightleftharpoons H_2C = CH_{2_{ads}}{}^{*} \qquad (11)$$

$$H_2O \rightleftharpoons OH_{ads} + H^+ + e \qquad \text{(r.d.s.)} \qquad (12)$$

$$H_2C = CH_{2_{ads}} + OH_{ads} \rightarrow \text{Adsorbed organic intermediate} \rightarrow CO_2 + zH^+ + ze \qquad (13)$$

but with a different rate-determining step (13) instead of (12). Since ethylene adsorbs from solution in competition with hydroxyl radicals

---

*The state of adsorption of an unsaturated molecule such as ethylene is complex since either associative or dissociative chemisorption (or both) occurs, depending on the metal and the coverage.

electrodeposited from water in step (12), then the more strongly adsorbed species, i.e. the one having the greater negative free energy of adsorption, tends to competitively desorb the more weakly adsorbed species from the surface. Experiments of Kuhn and al.[12] show the ratios of coverages θ^{eth}_{Au} : θ^{eth}_{Pt} : θ^{eth}_{Rh} to be about 0.2:1:0.02 and the coverage with oxygen or OH species tends to increase with increasing d-band vacancies and is hardly disturbed by competition from ethylene. However, the ethylene coverage, low for Group IB metals (copper, silver and gold), increases to a maximum on certain of the Group VIII metals (platinum, iridium, osmium, palladium, rhodium and ruthenium). Thus, $\theta^{eth}_{Au} \ll \theta^{eth}_{Pt}$. In Group VIII, the metal with the largest heat of adsorption of OH radicals, i.e. supposedly with the greatest number of d-band vacancies, will tend to reject ethylene, i.e. have the lowest coverage by ethylene: thus platinum has the lowest heat of adsorption of OH species and the smallest number of unpaired d-electrons per atom; therefore coverage of ethylene on platinum tends to be higher than at other metals. "Volcano" type relationships were obtained by Kuhn et al[12] when the reaction rate was plotted against heat of sublimation L of the electrocatalyst metal or as a function of the number of d-band vacancies (Figs.1a and 1b). In terms of the kinetics of reaction, the ethylene oxidation rate proceeds faster as the number of d-band vacancies increases from gold to platinum.

This type of plot is often encountered in heterogeneous catalysis when two principal factors (coverage and bond strength) affect the reaction rate in opposing directions.

In the ascending part of the curve, the dominating factor is the increase of coverage by the reactants. The relatively low bonding energy of radicals to the surface and therefore their faster oxidative desorption leading to a more rapid overall reaction, is less important than the fact that coverage with ethylene and OH is low. Consequently, as the coverage increases with increasing heat of sublimation, the reaction rate increases. On the descending side of the volcano relation, further increases in radical coverage are no longer dominant because the coverage is already relatively high; thus the increase in the radical-substrate bond energy will become dominant and the reaction rate will decrease. Optimum rates of the oxidation process controlled by reaction between chemisorbed OH and organic species will arise when the two species attain comparable coverages and product molecules can be desorbed easily.

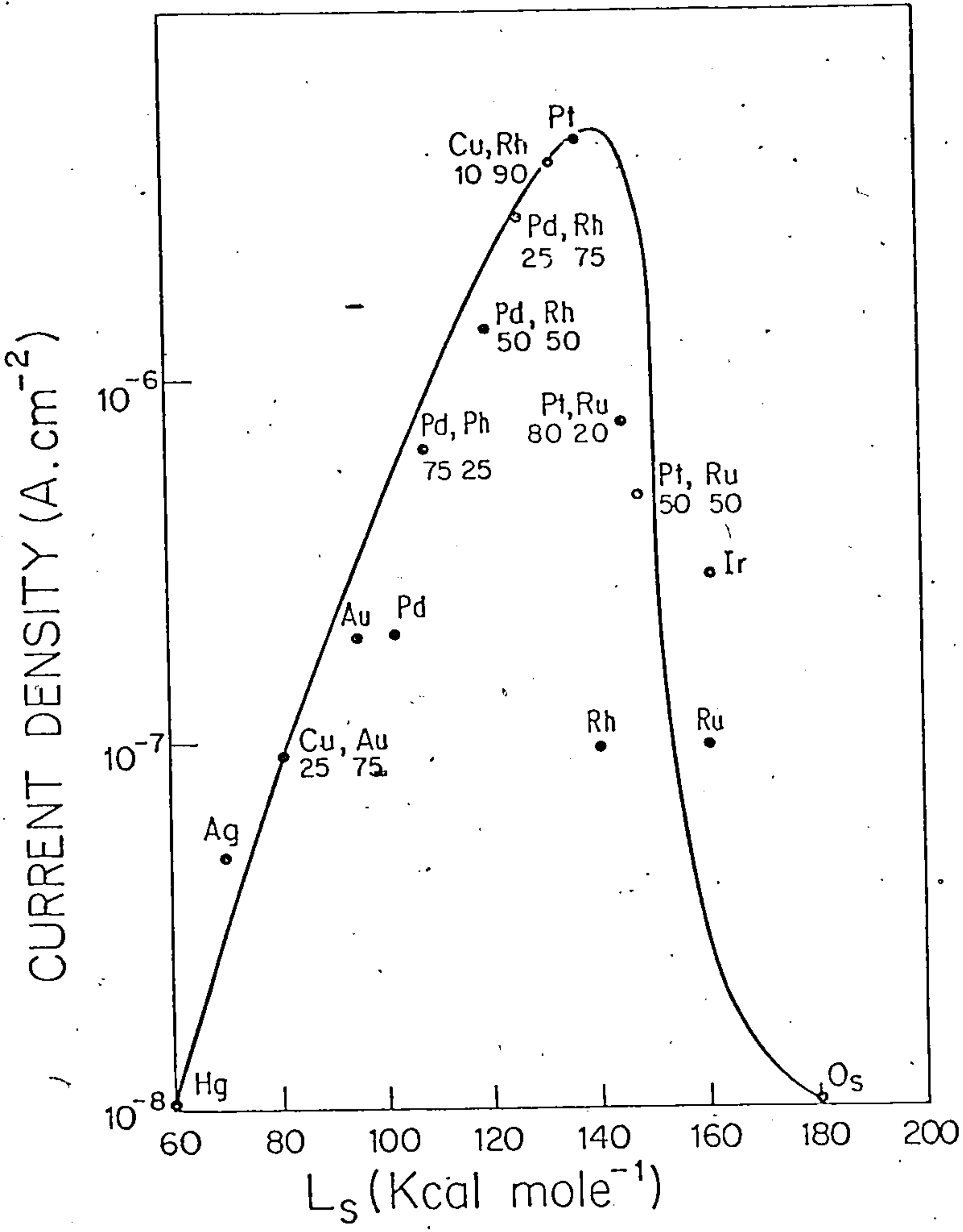

Fig. 1 (a) The volcano relationship for the oxidation of ethylene on various substrates, relating the reaction rate in amperes per square centimeter to the heat of sublimation of the substrate metal. (from Kuhn et al, ref. 12)

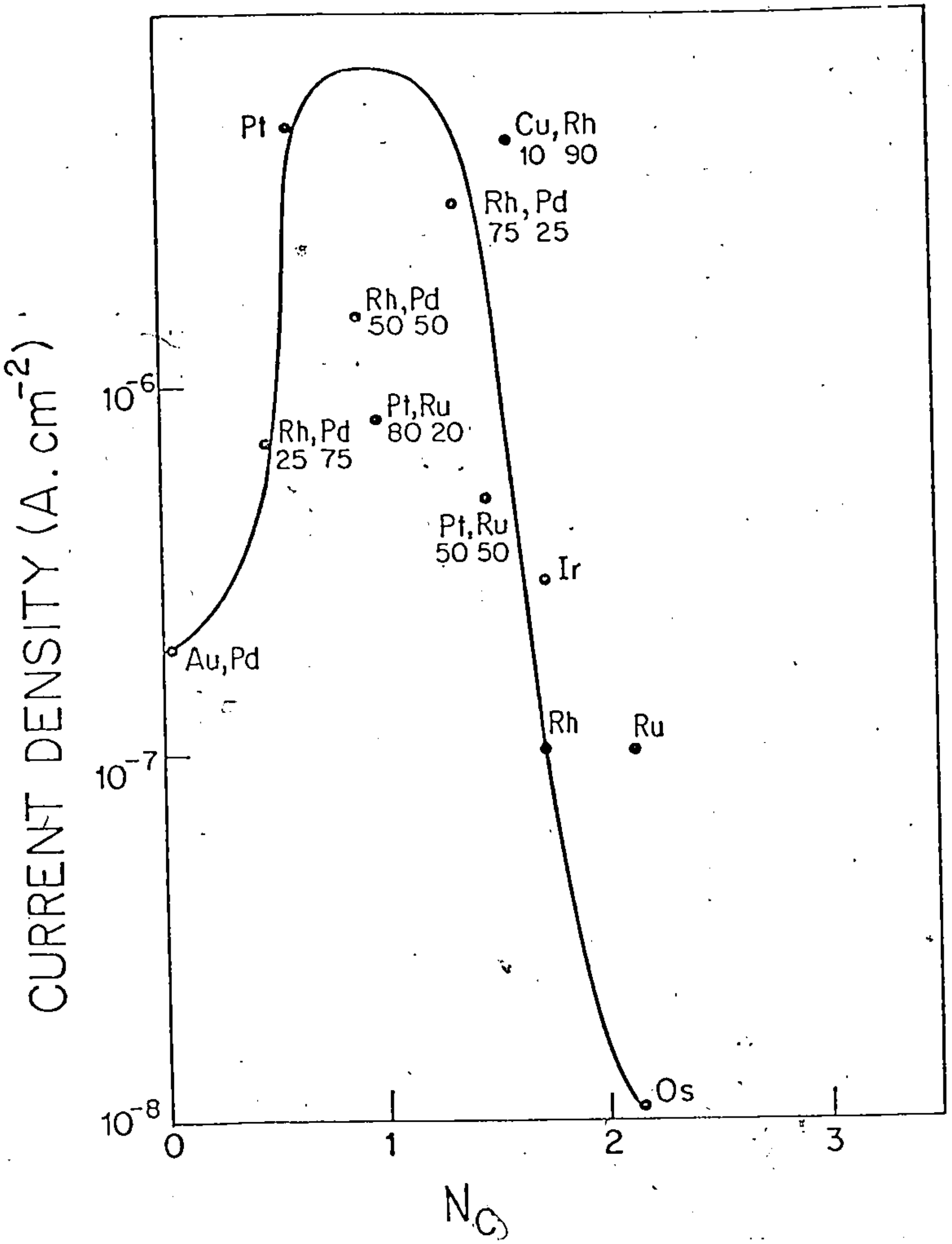

Fig. 1 (b) The volcano relationship for the oxidation of ethylene on various substrates, relating the reaction rate in amperes per square centimeter to the unpaired d-electrons. (from Kuhn et al, ref. 12)

4. Mechanisms of Formic Acid Oxidation at Platinum Electrodes

Electrochemical oxidation mechanisms involving organic molecules or H_2 may be divided in two groups according to the nature of the rate determining step:

(a) A chemical reaction without charge transfer, or

(b) an electrochemical reaction with charge transfer.

Group (a) includes dehydrogenation reactions, reactions between adsorbed carbonaceous species and $OH_{(ads)}$ or $O_{(ads)}$, pre-electrochemical steps, and desorption processes as rate-determining steps. Examples are

$$CH_3OH \rightarrow CH_3O_{ads} + H_{ads} \qquad (14)$$

$$HCO_{ads} + OH_{ads} \rightarrow CO_2 + 2H_{ads} \qquad (15)$$

$$HCOOH \rightarrow HCOO^- + H^+ \qquad (16)$$

$$2H_{ads} \rightarrow H_2 \qquad (17)$$

and

$$H_2 \rightarrow 2H_{ads} \text{ in } H_2 \text{ oxidation} \qquad (18)$$

Mechanisms with rate-determining discharge steps involving adsorbed carbonaceous species, or with a rate-determining water discharge, belong to group (b). Examples of this type of rate-determining step are:

$$CO_{ads} + H_2O_{ads} \rightarrow CO_2 + 2H^+ + 2e \qquad (19)$$

$$H_2O \rightarrow OH_{ads} + H^+ + e \qquad (20)$$

$$H_2O \rightarrow O_{ads} + 2H^+ + 2e \qquad (21)$$

The net reaction for the anodic oxidation of formic acid has been established in acid electrolytes as:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e \qquad (22)$$

Although the overall process here is very simple, the kinetics of this reaction are, in fact, unusual because the principal adsorbed species involved in this reaction is found not to be an intermediate in the main reaction sequence which proceeds through the steps proposed by Vasiliev and Bagotskii,[13,14] following physical adsorption in the double-layer (dl)

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{HCOOH}_{ads,dl}$$

$$\mathrm{HCOOH}_{ads,dl} + 2\mathrm{Pt} \rightarrow \mathrm{PtH} + \mathrm{PtCOOH} \tag{23}$$

$$\mathrm{PtCOOH} \rightarrow \mathrm{Pt} + \mathrm{CO}_2 + \mathrm{H}^+ + e \tag{24}$$

$$\mathrm{PtH} \rightarrow \mathrm{Pt} + \mathrm{H}^+ + e \tag{25}$$

The coverage θ of the principal species adsorbed decreases as the potential is made more positive, according to Brummer and Makrides,[15] from an initial value near the reversible H_2 potential of 0.95 to 0 at higher potentials. However, the rate of the main reaction falls off with time at constant potential and the current is linearly proportional to the fraction of the surface $1-\theta$ that is free from adsorbed species. Thus, the important result is found that the coverage which is measured in transients is principally that of an inhibitor and not that of the main reacting intermediates, H and COOH. This situation is quite different from that with methanol where the oxidation of the main chemisorbed particle, $\geqslant$COH, is the rate-limiting step of the overall process. An increase in θ is associated, in this case, with an increase in current. The adsorbed particle is chemisorbed $\geqslant$COH as indicated from the results of Vasiliev and Bagotskii[13] who observed the anodic adsorption transients that arise with methanol and also measured the extent of blocking of adsorbed H by this intermediate. In HCOOH oxidation, after initial adsorption of HCOOH, the current at constant potential falls with time, over an extended period of time, due to build-up of the blocking intermediate. In methanol electrosorption, a similar situation arises. In both cases, a self-poisoning effect on the Faradic oxidation reaction occurs but the poisoning intermediates are probably not the same. However, the poisoning effect with CH_3OH is much less than that with HCOOH at Pt.

The mechanisms of oxidation of formic acid and methanol are not only different because of quite different rates of reaction at a given potential but the stoichiometry of the primary intermediate is different: - COOH in the case of formic acid and $\geqslant$COH in the case of methanol. The rate of oxidation of the main adsorbed species (the poison) in the case of the formic acid reaction is about 10^3 times slower than the overall rate of Faradaic oxidation of HCOOH itself. The rate of the Faradaic reaction of oxidation of HCOOH is limited beyond ca. + 0.5 V by the dissociative adsorption of the reactant, since a non-diffusion-controlled current plateau (or peak in potentiodynamic measurements) arises so that the rate of this step can be easily measured. However, the magnitude of the rate of this chemically-limited current depends on the extent of co-adsorption of the poison species. On a fresh surface, it is much larger than on one which has been held at potentials in the range 0.0 - 0.2 V for some time. On the other hand, co-adsorption of additives such as S, observed by Binder, Köhling and Sanstede,[16] of Pb observed by Schwartzer and Vielstich[17] and, more recently, of Hg and CH_3CN by Kozlowska, MacDougall and Conway,[18] blocks the formation of the competing poison and then allows the main reaction to proceed up to six times faster. Thus, it was shown by MacDougall[18] in his work that the current for formic acid oxidation in the "double-layer" range of potentials at Pt (0.35 - 0.75 V, E_H) is substantially increased in the presence of acetonitrile, adsorbed impurities, or Hg atoms. This arises from an indirect effect associated with prevention of formation of the inhibitor for formic acid oxidation which is otherwise spontaneously formed, particularly in the potential range 0.05 to 0.6 V,E_H. The additives which chemisorb and block inhibitor formation appear to do so by a "third body" effect in which the rate of inhibitor production by a supposed dimerization reaction involving -COOH groups is diminished by blocking sites for nearest neighbour -COOH adsorption. It was suggested by MacDougall[18] that the inhibitor could be adsorbed formic anhydride*. It will be shown in the present thesis that similar behaviour is observed with gold-platinum alloys, this time not by blocking with catalyst poisons but by diminution of available neighbouring platinum sites by gold atoms. These results will be discussed more extensively later.

The oxidation of formic acid occurs by a mechanism materially different from that for the oxidation of methanol. In particular, the oxidation of formic acid is retarded by the adsorbed poisoning intermediate "P" formed in the side reaction, as was suggested by Brummer and Makrides,[15] while the oxidation of methanol is a process of oxidation of an adsorbed layer of the primary intermediate $\equiv$COH formed in the initial chemisorption step, as we have mentioned earlier. The oxidation of formic acid would normally proceed by an essentially similar step, but involving -COOH, were it not for the fact that the coverage of this species is much diminished

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* This species is not a known stable chemical compound but could exist in a stabilized state when chemisorbed at a surface.

by the poison P. If the adsorbed poisoning particle is actually "reduced CO_2", as Giner suggested[19], and if actually this same poisoning particle also becomes formed during the adsorption of saturated hydrocarbons as he has already reported, then the mechanism for the electro-oxidation of saturated hydrocarbons could be basically similar to the mechanism for the oxidation of methanol or HCOOH.

Therefore it appears generally that for the oxidation of various organic molecules on platinum, two qualitatively different types of mechanisms operate as illustrated in Fig. 2.

The mechanism for formic acid is described by the pathways I and II, where the intermediate P formed in II reduces the rate of the main pathway I, III + IV. In the case of methanol, the pathway of type I, followed by III + IV, characterizes the kinetics but long-time inhibition of this pathway does occur in this case as well, presumably by formation of some other intermediate of uncertain constitution.

5. Oxidation Behaviour of HCOOH and CH_3OH at Platinum

Since various chemisorbed species may arise from the dissociative adsorption of organic molecules such as HCOOH or CH_3OH at Pt, depending on electrode potential and coverage, it is desirable to have some way of characterizing them. Direct optical studies such as are applicable at gas/solid interfaces cannot be used in the presence of bulk aqueous solutions so an in situ electrochemical procedure is used. This consists of measuring the so-called electron number for desorptive oxidation of the chemisorbed species.

In an anodic-going potential sweep, formic acid gives rise to distinct oxidation current peaks over three potential ranges : (i) The H adsorption and double-layer regions, 0.25 - 0.75 V, E_H (FA_1) (The symbol FA_1 will be used to refer to the formic acid oxidation currents on the anodic

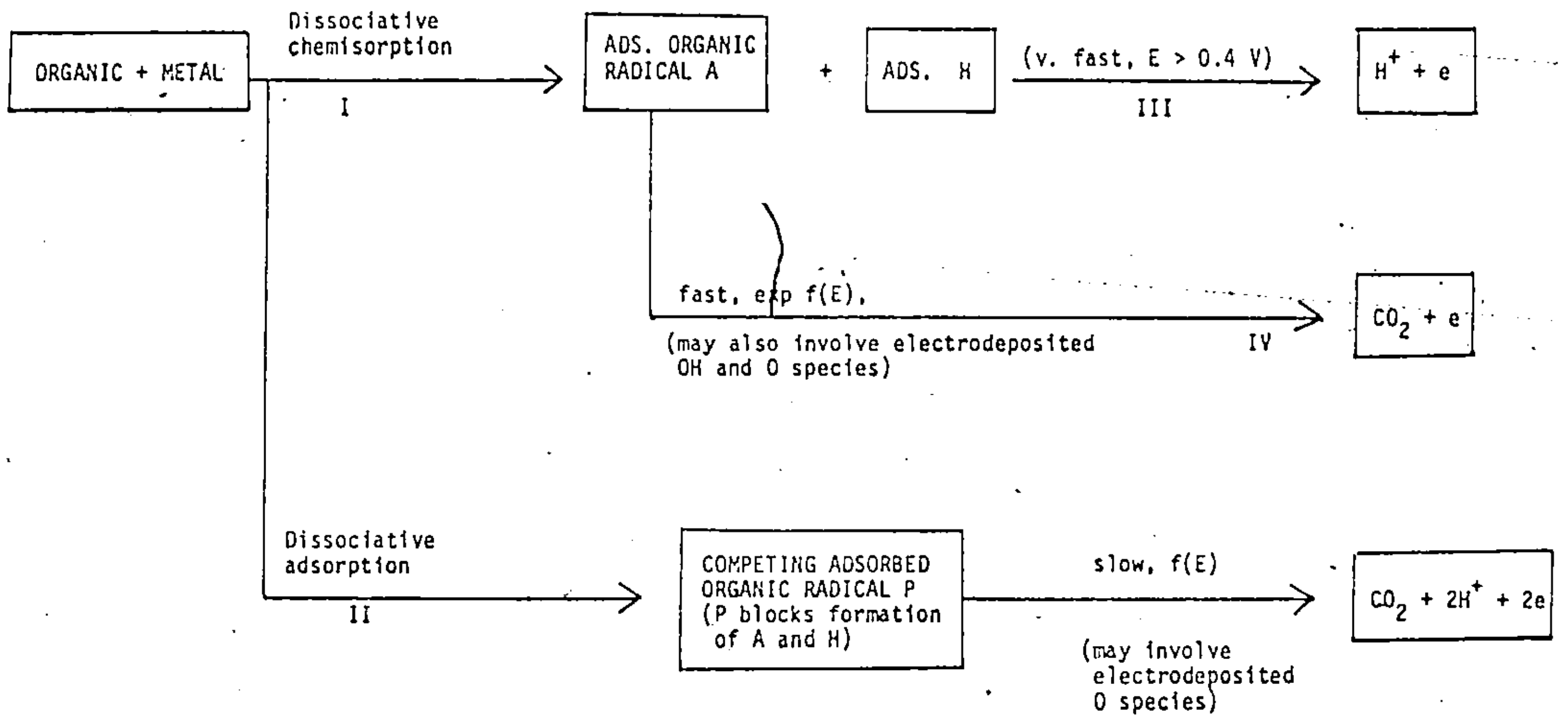

Fig. 2 Diagram representing qualitatively the two different types of mechanisms that operate in the oxidation of various organic molecules on platinum.

sweep at platinum; in an anodic-going sweep, it is the "first" [1] process to be distinguished); (ii) the region where surface oxidation of platinum begins, i.e., +0.85 to +0.95 V,E_H(FA_3)* and (iii) a region of higher anodic potentials, i.e., + 1.225 to +1.525 V,E_H (FA_4). In the cathodic-going potential sweep, a large <u>anodic</u> current peak, FC, arises in the potential region where surface oxide reduction is nearing completion so that free platinum surface sites, which have not had the opportunity to become poisoned by P, are made available. Similar electro-oxidation behaviour at platinum is observed with methanol although, in this case, there is no current peak in the anodic-going potential sweep in the d.l. region. In the case of methanol, the oxidation process occurs at the initial stage of platinum surface oxidation which provides a mechanism for oxidation of the $>$COH intermediate to CO_2 (Fig. 3).

In the case of formic acid oxidation, the FA_1 process is inhibited by its own poison as was mentioned before. The formation of P is slow, the maximum rate occurring at <u>ca</u>. 0.2 V,E_H where coverage with "formic acid" species (as-COOH) is a maximum. Various possible inhibiting species such as CO, "reduced CO_2", $>$COH, Cl^-**, $HCOO^-$ anions, and CHO·COOH [$\begin{matrix}\mathrm{CHO}\\\mathrm{COOH}\end{matrix}$: glyoxalic acid] formed by dehydration of two HCOOH molecules or by reductive coupling of CO, have been discussed by Brummer and Makrides.[15,20] In some respects, the behaviour of adsorbed CO is similar to that of the HCOOH poison, but the charge required to oxidatively desorb it is quite different and the oxidation kinetics are not the same. The first three species have been discounted as the inhibitor by Brummer[20] and adsorbed HCOOH itself (Breiter) cannot be responsible for the observed behaviour: CHO·COOH requires 3e for its oxidation to CO_2 + H^+, and it is difficult to see that it can occupy less than 3 or 4 sites; that is, its electron oxidation number per site will be <1. [For the species adsorbed from HCOOH solutions, 2e are

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* A process designated on FA_2 is observed under some conditions but its special resolution is not referred to here.

** Cl^- impurities were considered by Brummer[22].

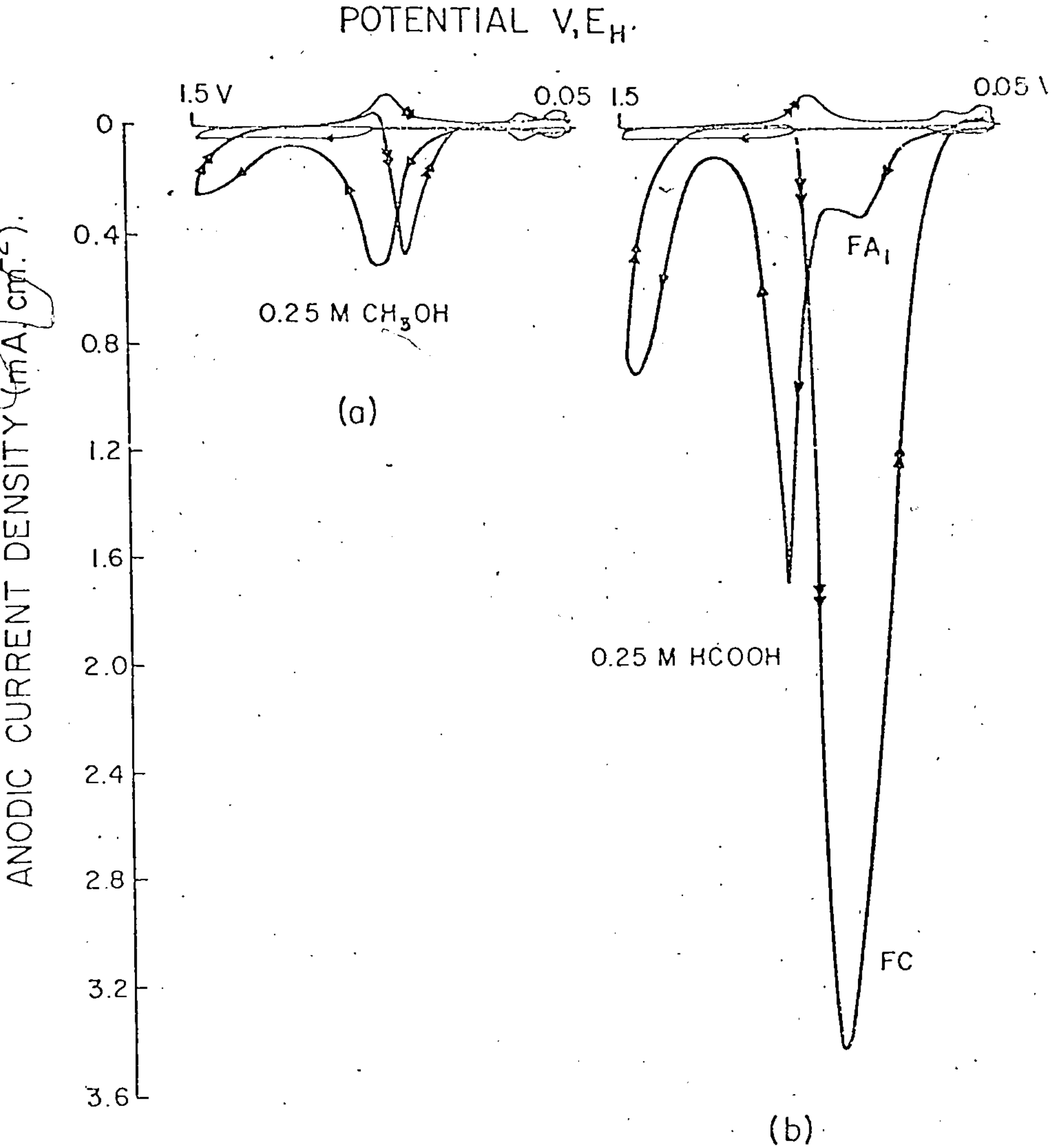


Fig. 3 (a) Potentiodynamic i-V profile for Pt in 0.25M CH_3OH at dV/dt = 50 mV sec^{-1}; potential range 0.05 to 1.5 V, E_H.

(b) Potentiodynamic i-V profile for Pt in 0.25M HCOOH at dV/dt = 50 mV sec^{-1}; potential range 0.05 to 1.5 V, E_H. (from B. MacDougall et al, ref. 18) required in an anodic transient in order to expose each free Pt atom.

The term "electrons per site" defines the average number of electrons released in the complete oxidation of the adsorbed species to CO_2, calculated per surface platinum atom which it covers. This number is obtained from the slope of the plot of Q_{ads}, the charge required to oxidize the adsorbed species, versus Θ_{org}, the coverage of that adsorbed organic species. The number of "electrons per site" is obviously important in defining the oxidation state of adsorbed carbonaceous residues and in helping to establish their relationship to one another and the overall reaction. Changes in the "electron per site" number [e] with coverage in oxidative desorption experiments is evidence for the presence of different adsorbed species or at least for different modes of bonding of the adsorbate. An example of the above is the relation found by Brummer[21] for the charge for oxidative desorption of species at 0.70V from C_3H_8 by adsorption at Pt as a function of its coverage arising from adsorption at 0.30V (Fig. 4). The desorption charge relation seems to have two linear regions, the slopes of which correspond to 1.35 electrons and ca. 7 electrons per covered Pt atom for the oxidation of the adsorbate to CO_2. The easiest material to desorb, i.e., the first material oxidized, is the species for which [e] = 1.35. The most difficult to desorb, i.e., the most difficult to oxidize to CO_2, is the material for which [e] $\doteq$ 7 electrons in the case of the C_3H_8 example.

It seems chemically more plausible that the species P which poisons the formic acid oxidation reaction is an anhydride of formic acid stabilised by adsorption. The work done by MacDougall[18] on the behaviour of co-adsorbed competitive poisons in term of a "third body"

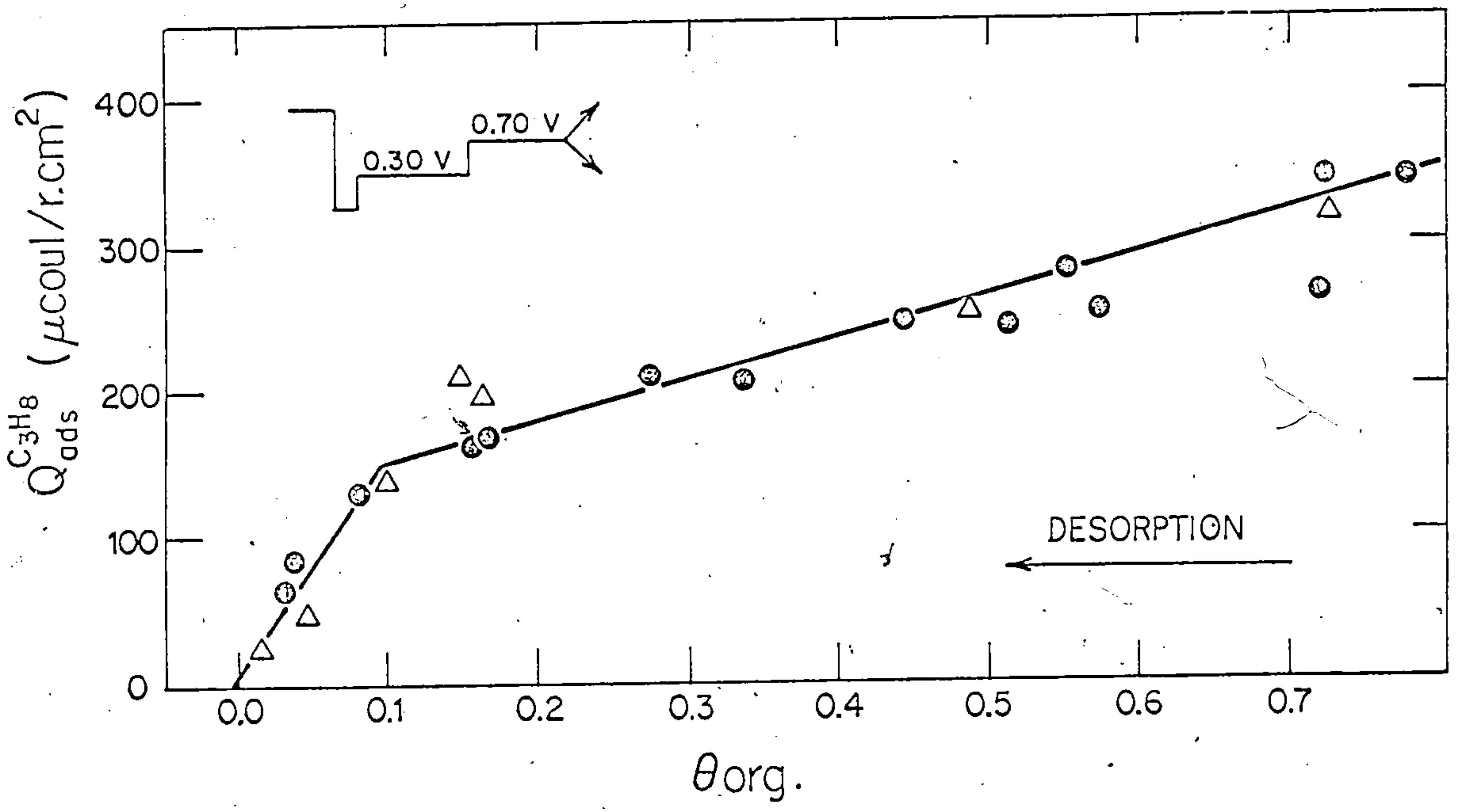
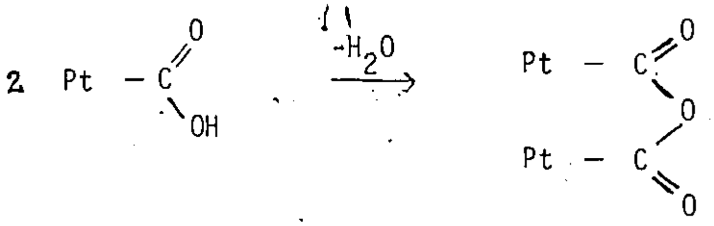


Fig. 4 Desorption at 0.70 V, E_H of species derived from propane chemisorbed at Pt for various times at 0.30 V and 130°C: ●, 100 sec.; △, 30 sec. (from Brummer et al, ref. 21)

effect led to the view that these "catalyst poisons" operate by dimerization as a route to poison production.

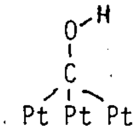
MacDougall's results suggest that formation of P must arise by a "dimerization" type of reaction on the electrode surface between adsorbed formic acid or some derived intermediate species leading to a lowering of coverage by the main electrochemically reactive species, -COOH. It cannot be a poison arising independently of the adsorbed formic acid species, e.g. from traces of chloride ion since, according to Brummer,[22] there is no reason why displacement of one such poison by another, e.g. Cl^- or acetonitrile in MacDougall's work, should increase the peak current for the FA_1 process. The most probable reaction between two adsorbed formic acid (-COOH) residues adjacent to each other on the electrode surface is dehydration leading to adsorbed formic anhydride.



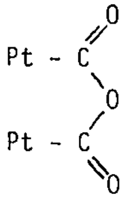
(26)

The identity of the P species as formic anhydride was supported by the observed potential dependence of the rate of formation of P. Significant P formation occurs only in the less positive potential regions, i.e., when the electrode acts relatively as a source of electrons. This is consistent with the following mechanism, since increase of electron donating tendency by the platinum will tend (i) to increase the protonation of adsorbed-COOH groups, leading to stabilization of the resulting protonated species and (ii) to increase the nucleophilicity of those adsorbed species which are not protonated, i.e., the attacking species. At more positive potentials, the rate of reaction (26) should decrease since the platinum then acts as an electron withdrawing agent and the surface coverage by -COOH is also diminished as potential becomes more positive. Eventually, reaction (26) will become reversed which is consistent with the change of direction of time effects with potential.

An alternative basis for the identity of the poison species P which could also be generated at low potentials i.e., 0.2 V,E_H, is



which is also generated in CH_3OH oxidation. This poison requires 3 "free Pt sites" as compared to the two "free Pt sites" required by



The $\geqslant$COH species was discussed by Parsons and Capon.[23]

6. Aims and Methods of Approach Used in the Present Work

The aims of the present work were to investigate and explore the effects of changing metal electronic character in alloys on electrochemical kinetics of oxidation of formic acid, not by competitive blocking with other poisons, e.g. Hg as had been done in other work,[18] but by using alloys where the platinum content in the surface is progressively diminished by the presence of gold. At the same time, it would be possible to relate the kinetic effects observed to the surface composition of the alloys which can be determined by the relative charges associated with the current peaks for reduction of the oxidized alloy surface (in Au-Pt alloys, the peaks for reduction of oxidized Pt and oxidized Au can be easily resolved so that the surface composition can be determined rather accurately).

This is a very important feature of studies of surface processes in electrochemistry, as the surface composition of the electrode can be determined exactly in each experiment without removal of the metal from the solution.

CHAPTER II

EXPERIMENTAL

1. Methods

There are two principal methods of measurement of the current-potential curve characteristic of an electrode reaction. One is called the galvanostatic method, that is where the current is the independently controlled variable and the potential established is measured on a potentiometer or a recorder according to the kinetics of the reaction.

The other method is known as the potentiostatic procedure in which the potential is the independently varied quantity and resulting currents, determined by the kinetics of the reaction, are measured on an ammeter or recorded on an X-Y recorder by means of the potential V generated by passage of this current through a standard resistance; V is equal to the current (i) passing, times whatever setting of the resistance (R) is made. If this resistance is R and the current is i, the potential established is iR which is then measured on the recorder.

A very important development of "potentiostatic" studies involves the dynamical examination of a current-potential curve in which the potential instead of being adjusted point-by-point manually, is increased in one direction or the other in a linear fashion with time. This is achieved by feeding into the potentiostat a linearly varying programme signal from a function generator, equivalent to adjusting the instrument potential dial at a rate which is constant with time. Thus, one "injects" a linear voltage-time signal from a function generator which generates a repetitive triangular or ramp type signal with controlled upper and lower limiting values.

For ordinary electrochemical reactions that have a linear logarithmic current-potential curve, the results measured by means of a potentiostat and by means of controlled current (galvanostatic) procedures should be identical, and indeed they always are, provided the instruments are functioning satisfactorily. The potentiostatic method, however, is somewhat more complicated as it is always necessary to avoid spurious results from instrumental malfunctions which can sometimes arise. However, many reactions are known, particularly anodic ones, which initially give a linear logarithmic curve but at higher potentials the rate decreases, instead of increasing with potential, so that there is a maximum in the current-potential curve. Under these circumstances, beyond the maximum, the current decreases with increasing potential. This is usually due to the formation of an inhibitor on the surface generated by the reaction itself. Later on, the reaction may, after exhibiting another bend in the current-potential curve, go on again in the normal direction with increasing potential. Under these circumstances, the range of potentials where the current is diminishing with increasing potential cannot normally be followed by the galvanostatic method since this region is unstable. It can only be satisfactorily measured by means of a potentiostat and it is therefore for this reason that this type of instrument was used in the present work as reactions showing current maxima due to inhibition commonly arise in the anodic oxidation of organic and other substances.

2. Preparation of Electrodes; Sealing Technique, etc.

The platinum electrodes used in the present work were prepared from spectroscopically pure platinum wire degreased for 24 hours in refluxed acetone in a Soxhlet extractor. The platinum wire was then sealed into a cleaned glass electrode holder.

The gold-platinum and gold-palladium wires, supplied by Engelhard Industries Inc., were prepared in a similar fashion with the exception that care was taken not to use a flame higher in temperature than ca. 1000°C (the m.p. of gold being 1063°C).

For "manual" point-by-point experiments which were also conducted, platinum electrodes were prepared by sealing Johnson-Matthey "spec-pure" platinum wires into glass bulbs in hydrogen. The bulbs were broken beneath the solution in an all-glass cell when required.

3. Cell, Temperature, Cleaning Procedures

The cell was a three compartment all-glass vessel. The centre compartment, in which as many as seven different working electrodes could be used without opening the working electrode compartment to the atmosphere, held the test electrodes. The three compartments were separated from one another by water-sealed stopcocks; the hydrogen reference electrode was connected to the centre compartment by means of a Luggin capillary. Purified nitrogen could be bubbled in the working and the counter-electrode compartments in a continuous slow stream. The bubbled nitrogen was allowed to pass out of the cell through bubble traps to prevent back-diffusion of oxygen and any atmospheric pollutants. Prepurified hydrogen was used for the reference electrode.

Prior to use, and before each complete experiment, both cell and the working electrodes were washed with concentrated sulphuric acid and left to stand in the acid overnight. The next day, they were thoroughly washed (approximately ten to fifteen washings of every part of the cell) with pyrodistilled water and then once or twice with the test solution. The use of pyrodistilled water in surface electrochemical work was found to be necessary in recent years due to the presence of steam-volatile, not easily oxidizable, impurities in tap and regular distilled water. The apparatus for preparation of pyrodistilled water was developed by Sharp in this laboratory and described in a thesis and a published paper.[24]

All experiments were performed at 26°C with thermostatic control employed when necessary.

4. Reference Electrode

Hydrogen reference electrodes were prepared by platinizing platinum-gauze electrodes in an acidic solution of platinic chloride. After extensive washing, they were used for many months in various runs. Pairs of hydrogen electrodes were used so that their potentials could be compared from time to time against one another and periodically checked against a standard calomel electrode. When not in use in an experiment, the platinized electrodes were kept in very pure dilute aq. sulphuric acid in closed vessels.

5. Nature of Gold-Platinum Alloys and Phases

The wires were 0.015" in diameter supplied by Engelhard Industries Inc. An X-ray crystallographic analysis on the wires was made at Bell-Northern Research laboratories (Project GR3261) and a spectral analysis was made to check bulk compositions at the National Research Council.

The following conclusions were drawn: Alloys nominally with 20%, 40%, 60% in gold are composed of two immiscible solid solutions, α_1 and α_2, with lattice parameters of 4.013 Kx and 3.920Kx (1 Kx unit = 1.0020 $\overset{\circ}{A}$). The 80% Au alloy is basically a single α solid solution with a lattice parameter of 4.018 Kx. The three phases, α_1, α_2, α, are face-centred cubic. X-ray film analysis indicated both microstrains and deformation textures in all specimens, i.e. distortion orientation of the bulk structures. Both these conditions are normal but interfere with precise lattice parameter determinations. Confirming evidence was also afforded metallographically, the alloys with 20%, 40%, 60%, gold being composed of two immiscible solid solutions and the alloy with 80% gold, a single-phase solution. The grain structures of all alloys were severely deformed and elongated as a result of cold drawing. Alloys with 20%, 40%, 60% gold showed structural striations indicating alloy segregation (coring) in the ingots.

It was suggested that these alloys could be quenched from the above the two-phase region thereby achieving a single α_2 solid solution. This is possible, but the resulting alloys would be hard and brittle as a result of retention of quenching stresses and would in all likelihood exhibit stress cracking. This would probably be most pronounced in the alloys containing between 20% and 60% gold. Problems would, however, arise in thermally sealing such quenched alloys as regeneration of a 2-phase system would probably then occur.

6. Special Problems with Gold-Platinum Alloys and Characterization of their Surfaces

In experiments on alloy electrodes, a major problem is that the surface composition is not necessarily, or indeed normally identical with the bulk composition. This arises for two types of reason: (a) A Gibbs adsorption effect: there will tend to be a surface excess of one component or the other of the alloy in the surface layer; and (b) on account of differential etching, e.g. in anodization of an electrode, one component may tend to be preferentially dissolved from the surface. While the latter effect can lead to surface compositions very different from bulk values, it can, however, provide a useful method for producing controlled changes in surface composition of an alloy electrode of otherwise definite composition.

Because of the relative difficulty in sealing of the gold-platinum wires (m.p. of gold being 1063°C) the surface composition was not the same as the apparent or analytical bulk composition. For example, as was found in the present work, a given 60% Au-Pt wire could have as little as 10% gold in its surface after treatment in the sealing flame.

Another problem was the impossibility of obtaining surface gold compositions between 20% and 45%. These were finally obtained after etching the alloys in aqua regia. For example, by varying the time held in aqua regia, an original 60% Au-Pt electrode could be made to take up various surface compositions, e.g. 50%, 40%, 30%, 20%, 10% Au-Pt. Au-Pt, which could be accurately determined (see p. 28).

7. Circuitry

The circuit for potentiostatic steady-state polarization measurements is shown in Fig.5 . The potential between the working and reference electrodes was controlled with a Wenking potentiostat and the potential readings were taken on a Radiometer model PHM-4 potentiometer.

The current was read from a multirange ammeter in series with the counter electrode.

The circuit used in obtaining potentiodynamic current-potential relations is shown in Fig. 6. In this case, the Wenking potentiostat is driven by a Servomex LF 141 wave-form generator capable of giving single and multiple triangular potential-time functions. The constantly varying potential between the working and the reference electrodes results in a current which usually also varies in response to the potential. The resulting current-potential profile was recorded on a Hewlett-Packard X-Y recorder. The current-potential profile was precisely recorded by exact conversion of the time-dependent currents to corresponding potentials by passage of the current through a calibrated decade resistance box in series with the cell. A cathode follower was employed to communicate the electrode potential to the X-Y recorder without drawing significant ($>10^{-8}$ A) currents from the electrode system.

8. Water, Solutions and Formic Acid Preparations

The aqueous solutions were prepared from water that had been doubly distilled, the last stage of distillation being from an alkaline permanganate solution. It was finally pyrodistilled through a silica

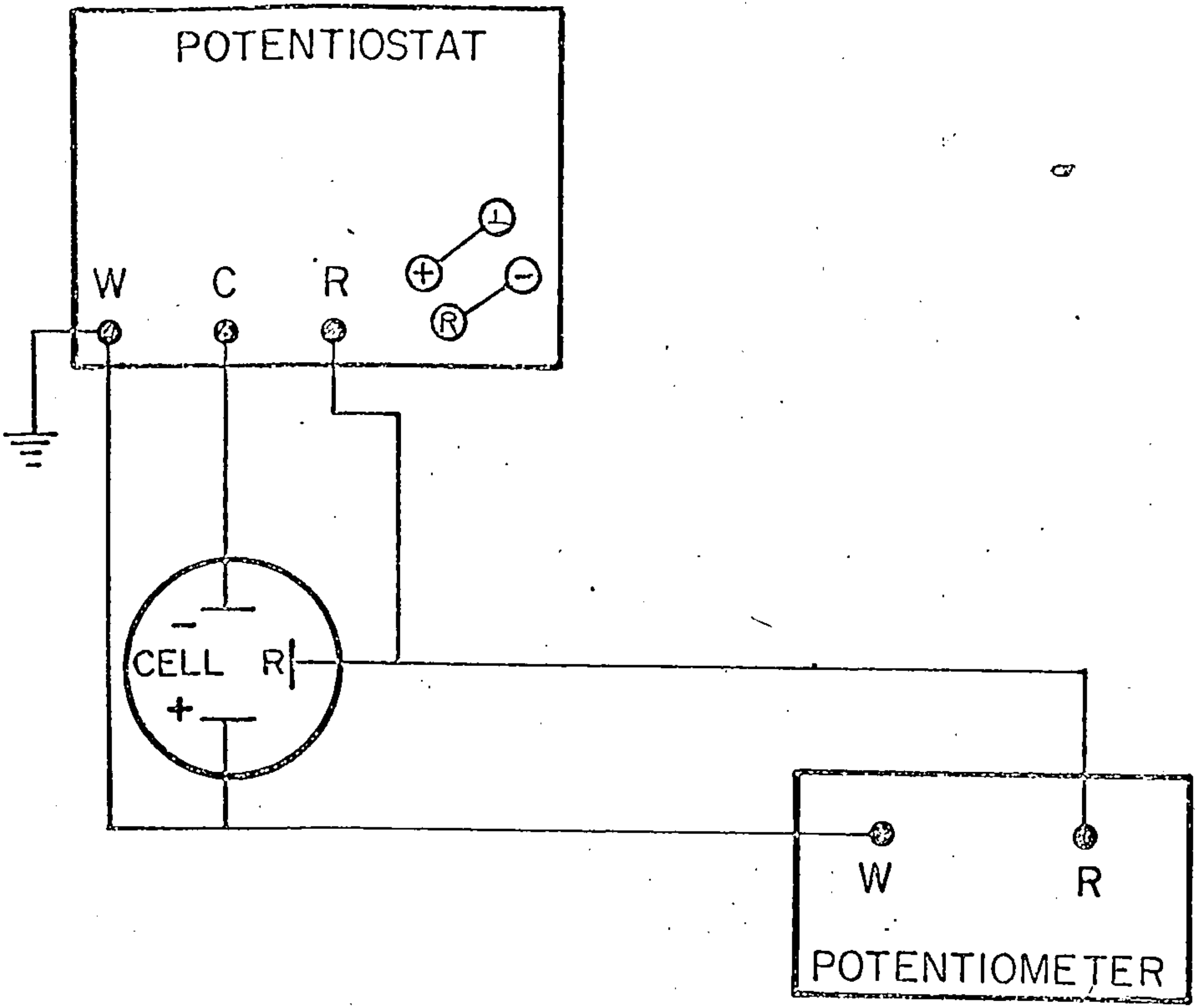


Fig. 5 Electrical circuit for potentiostatic steady - state polarization. (from B. MacDougall's Phd Thesis)

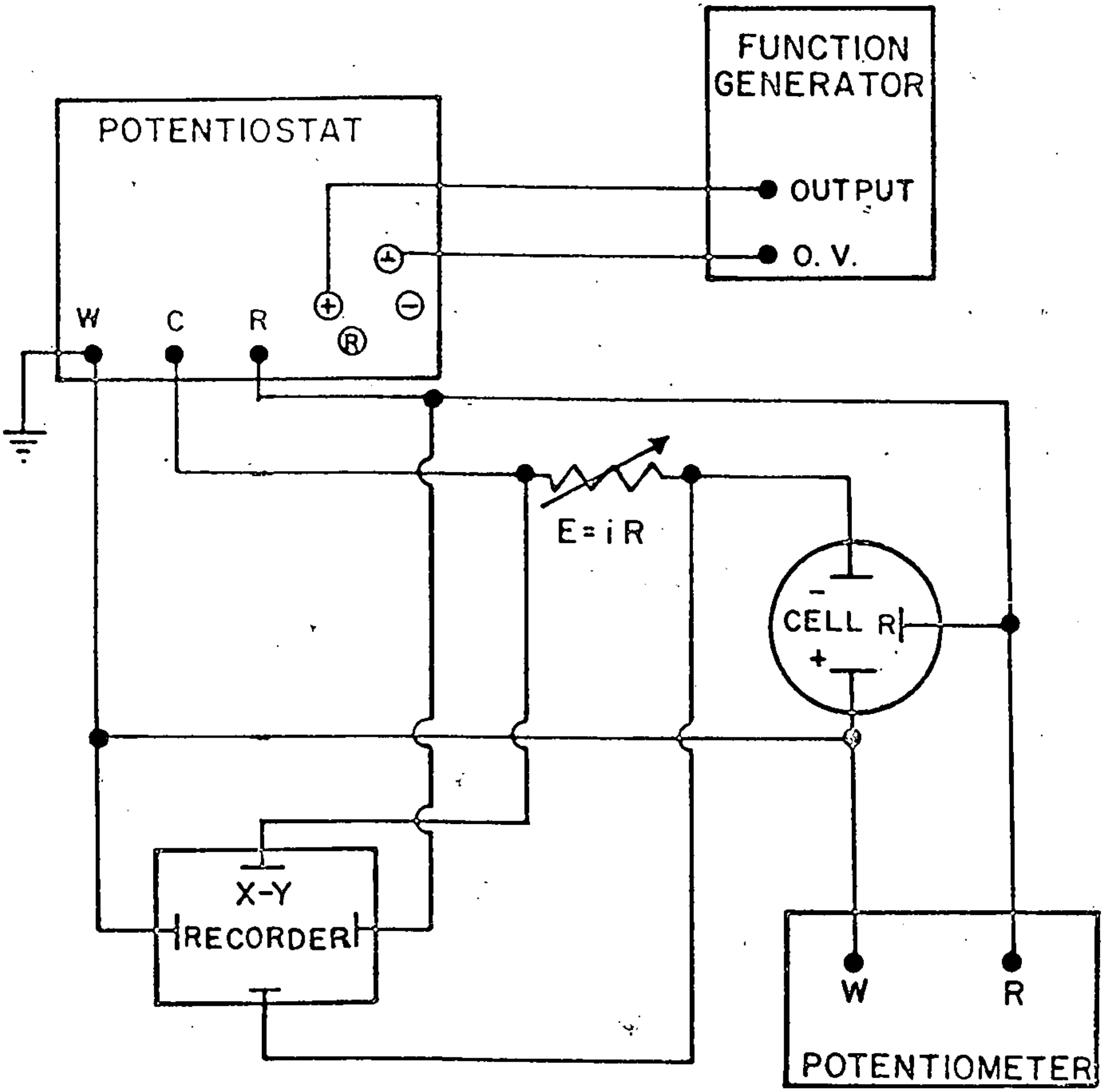


Fig. 6 Electrical circuit for potentiodynamic current-potential measurements. (from B. MacDougall's Phd Thesis)

column in oxygen over a Pt-Rh catalyst gauze at 800°C according to the procedure developed earlier in this laboratory and described elsewhere[24].

Acidic solutions were prepared from B.D.H. micro-analytical grade sulphuric acid without any further purification being necessary. Pre-electrolysis treatment of the solutions was employed where required, i.e. when the criteria for solution purity listed below were not initially satisfied.

Some criteria for high solution purity were as follows(cf. ref.24):

(i) Resolution of the two cathodic and three anodic atomic hydrogen electrosorption peaks in the potential range 0.05 to 0.35 V,E_H.

(ii) Resolution of the three anodic peaks for platinum surface oxidation in the potential range 0.8 to 1.2 V,E_H.

(iii) Independence of the charges and the peak current/potential coordinates for the oxide and hydrogen peaks on solution stirring.

(iv) Absence of any spurious peaks in the cathodic or anodic "double-layer" regions of the sweep.

When the above requirements are met, it can be safely concluded that a high degree of purity of the electrolyte solution and also a very clean platinum electrode surface has been achieved. This was the case for all the experiments from which the results discussed in this work were obtained.

Formic acid solutions were prepared from the "AnalaR" analytical reagent and the methanol solutions from Baker "Spectroanalyzed" reagent which was once distilled.

CHAPTER III

RESULTS AND DISCUSSION

1. Point-by-Point and Cyclic-Voltammetry Current-Potential Curves

The manual, point-by-point method for obtaining current-potential curves was employed at first for Pt but was found to be unsatisfactory when applied to the alloy electrodes. For these, cyclic voltammetry was used. The origin of the difficulties was soon discovered: in a lengthy manual run the surface composition changes sufficiently quickly that, before the run is terminated, the surface has changed, making the results irreproducible. A point-by-point run takes up to one hour to make (including time effects at every 25mV increment of potential) compared with a duration of only a few minutes in a potentiodynamic run at a moderate sweep-rate. For the pure metals, however, point-by-point runs are satisfactory and the results for Pt and Pd are shown in Figs. 7a and b where the lines drawn are based on points taken at 25mV intervals at 30 seconds per point.

2. Surface Composition of the Alloys and its Characterization by means of Cyclic Voltammetry

At alloy catalyst or electrode surfaces, it is the local surface composition of the material that is of significance and must be related experimentally to catalytic activity.

Analysis of mechanisms of electrochemical organic oxidation reactions at binary platinum alloy catalysts suggests that enhanced activity over that of platinum alone can be expected for both heterogeneous and homogeneous alloy systems because a "bifunctional" type of mechanism involving chemisorbed organic intermediates and electrodeposited O or OH species are involved. In the heterogeneous alloy case, the activity could be limited by the supply of adsorbed oxygen species to the organic species adsorbed on the platinum-rich phase, since transport would have to take place across a phase boundary,

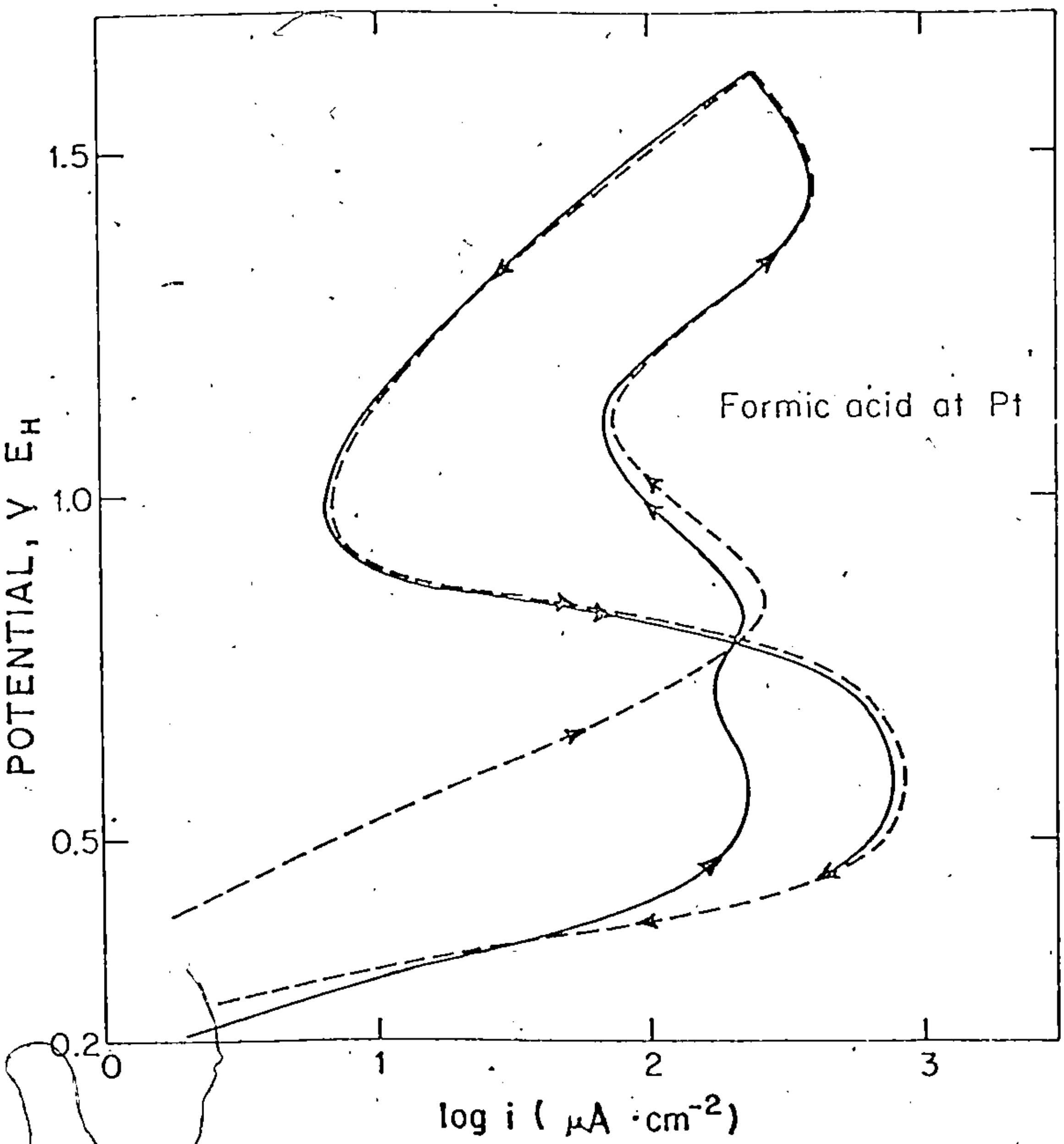


Fig. 7 (a) Steady-state point-by-point i-V curves for (1N) formic acid oxidation at platinum (——); after 5 min. at open-circuit (----).

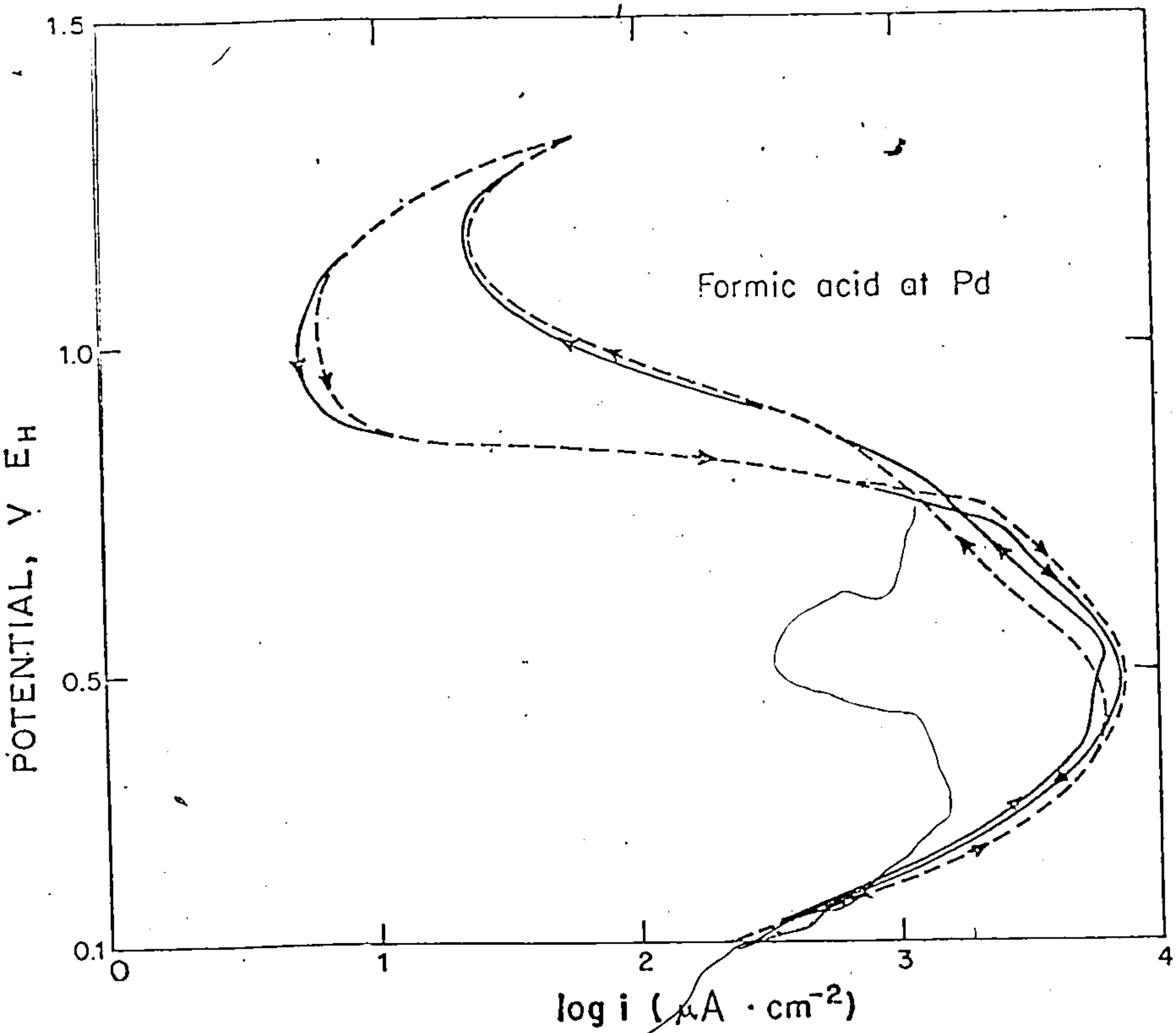


Fig. 7 (b) Steady-state point-by-point i-V curves for formic acid (1N) oxidation at palladium (——); after 5 min. at open-circuit (----).

but the theoretical maximum velocity per unit area will normally be determined by the rate of dissociative adsorption of the organic species on platinum at "zero" coverage. The activity of homogeneous alloys would not necessarily reach this limit because the rate of adsorption of the organic species will be expected to decrease with addition of the less catalytic alloying metal. In most of the present work, heterogeneous Au-Pt alloys were used. Homogeneous Au-Pd alloys were also examined but problems of time-dependent H-absorption into these systems prevented reliable and reproducible results being obtained.[32]

Platinum and gold form a homogeneous alloy phase, α, at temperatures just below the solidus (Fig. 8). At lower temperatures, separation into two phases can occur: an α_1-phase rich in platinum and the α_2-phase rich in gold. As the temperature is decreased, the composition boundary of the α_1-phase approaches the pure platinum limit.

Breiter[25] suggested that the surface composition of heterogeneous gold-platinum alloys could be characterized by utilizing the differences in the hydrogen and oxygen electrosorption properties of the two component metals. Voltammetry at platinum, gold and their alloys in the potential region 0.5 - 1.5V, E_H where oxygen is adsorbed, yielded current-potential curves in which the currents were equivalent to the sum of the current components for pure platinum and pure gold surfaces, weighted in proportion to the relative exposed areas or surface atom fractions. Voltammetry in the potential range for hydrogen adsorption on platinum, over which negligible H adsorption occurs in the case of gold, gave an equivalent platinum surface area which could be correlated well with that derived from electrochemical oxygen adsorption. Breiter[25] concluded that the Pt and Au in the surface of the α_1 and α_2-phases have the same hydrogen and oxygen electrosorption properties as those of pure platinum and gold, respectively (Fig.9).

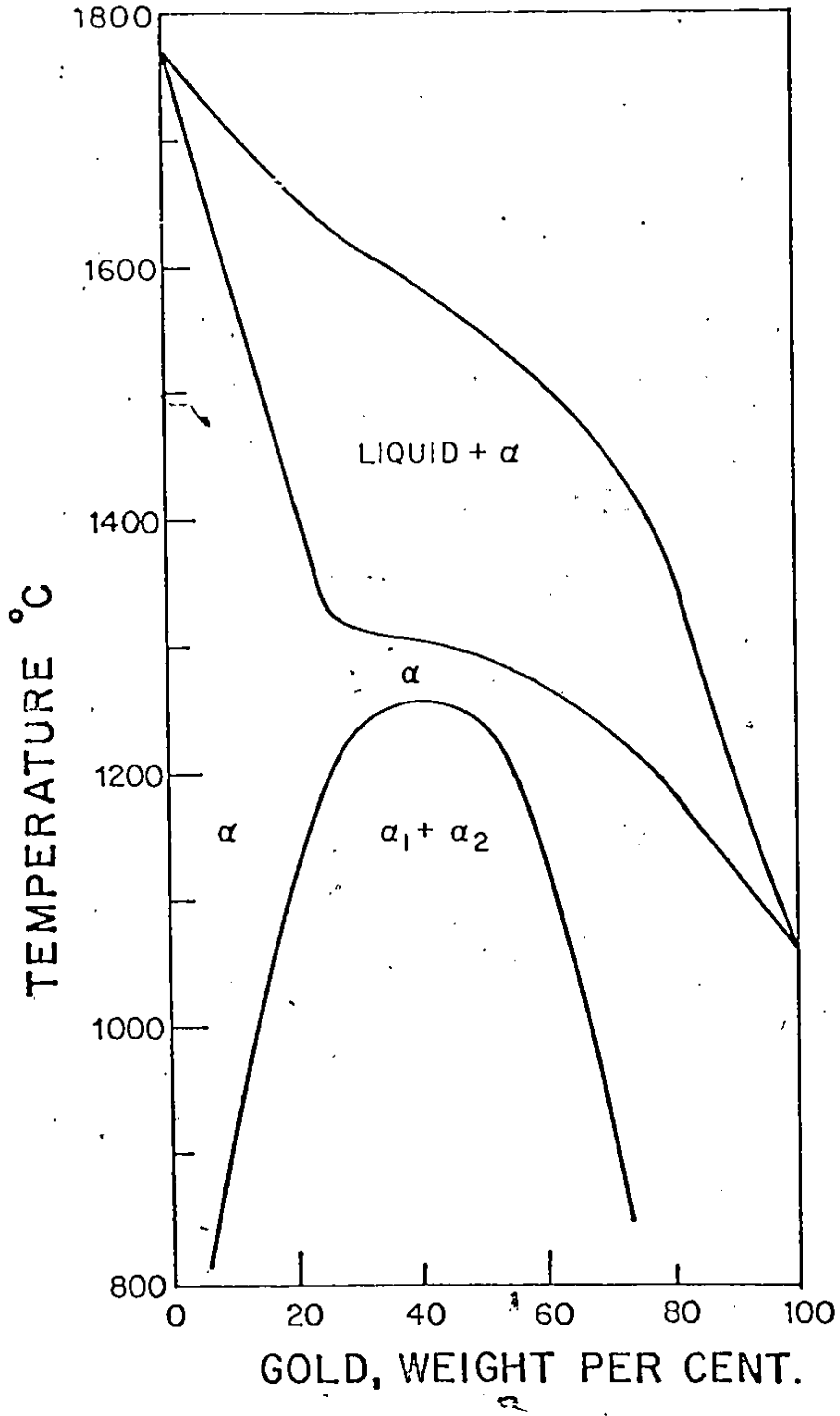


Fig. 8 Phase diagram for the gold-platinum system, (from Hansen et al, ref. 36)

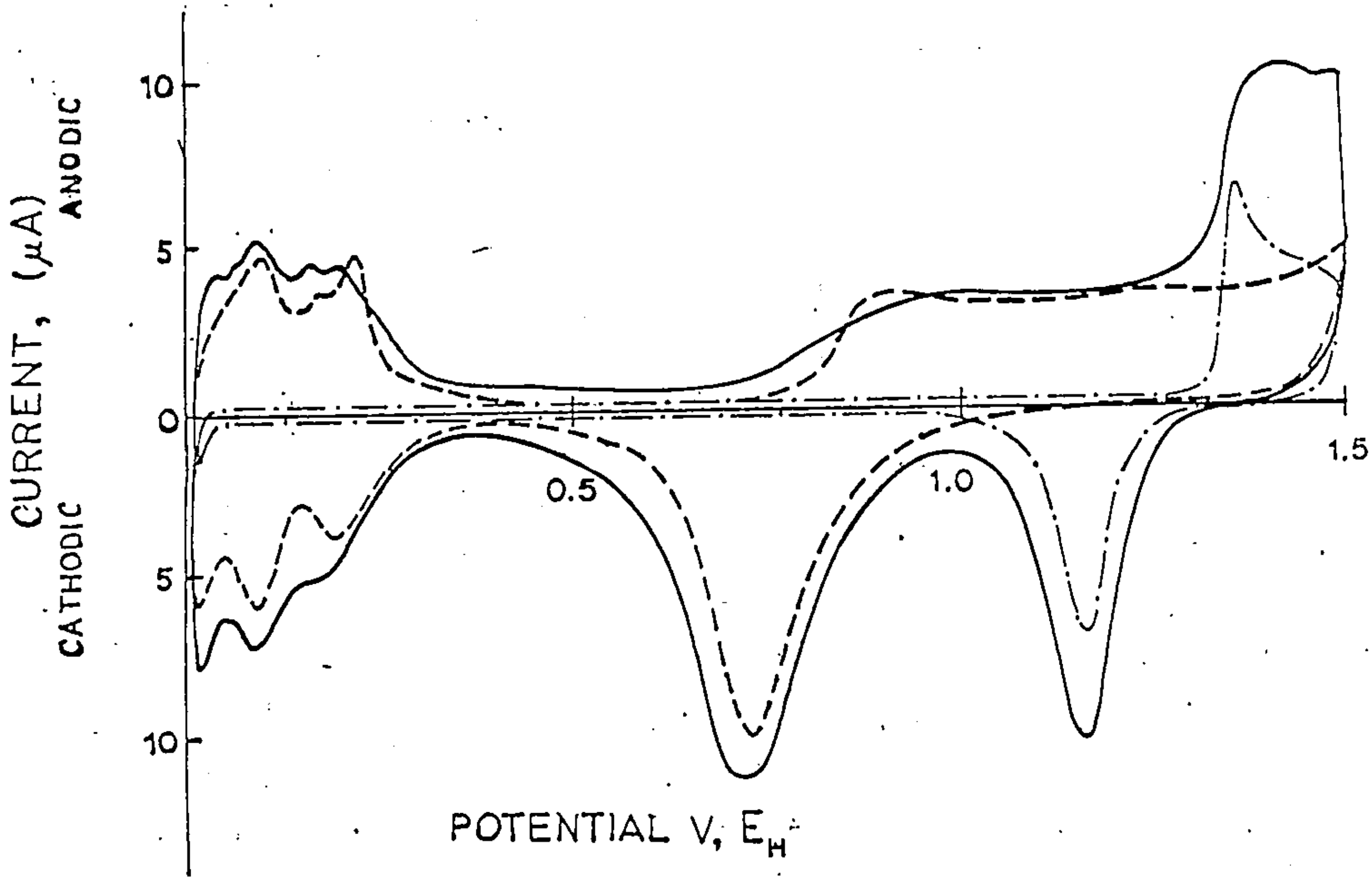


Fig. 9 Current-potential curves showing hydrogen and oxygen adsorption at Pt in 1N sulphuric acid for a linear potential sweep of 40 mV. sec^{-1} ---Pt; -·-·-Au; —— 35% Au-Pt alloy. (from R. Woods, ref. 37)

The real surface area of a platinum electrode can be measured by determining the amount of charge transferred during the adsorption of a monolayer of hydrogen in the process $Pt + H^+ + e \rightarrow Pt(H)_{ads}$. From knowledge of the surface area occupied by each Pt atom in a particular crystal plane, it is possible to calculate the number of hydrogen atoms per cm^2 which corresponds to an H coverage of one adsorbed atom per Pt site. Since there is a transfer of charge of one electron for each hydrogen atom deposited in the above reaction, the theoretical charge per cm^2 for H monolayer formation is readily determined. A review of earlier hydrogen adsorption studies on Pt was presented by Gilman[26] who concluded that "if an equal proportion of low index planes on an annealed polycrystalline wire is assumed, then $210 \mu C\ cm^{-2}$ would correspond to a simple (Pt: H = 1:1) monolayer for a roughness factor of one." The value of $210 \mu C\ cm^{-2}$ is thus generally accepted for the charge per cm^2 for hydrogen adsorption on an "ideal" plane surface of Pt. The technique of cyclic voltammetry provides the most sensitive method for measuring this charge, since the area under the "hydrogen region" in the i-V profiles at a known sweep-rate can be found accurately and without difficulty, thus providing a direct integration of the current with respect to time.

For example, in order to calculate the real surface area of a platinum electrode having a geometrical area of $0.42\ cm^2$ the following equation is used:

$$A_{Pt} = \frac{q_H\ (\mu C\ )}{210\ \mu C\ cm^{-2}}$$

Therefore, if the charge for the hydrogen adsorption region, q_H, was measured, for example, as 154.1μC, then the real surface area of the platinum electrode would be 154.1μC/210μC cm^{-2} = 0.73 cm^2.

It is not possible to evaluate the real area of gold electrodes from the charge for H adsorption since no significant under-potential deposition of H occurs on Au. However, it is possible to calculate the real surface area of a gold electrode employing Burshtein's [27] assumption that the amount of oxygen chemisorbed up to the potential of the current minimum observed just prior to the onset of significant O_2 evolution corresponds to the adsorption of one oxygen atom per surface gold atom and requires a charge of 400μC.cm^{-2}. Therefore, if the charge for the oxide reduction peak on gold is measured as 190.8μC, for example, the real surface area for the gold electrode would be 190.8μC/400μC.cm^{-2} = 0.48 cm^2.

Another procedure for calculation of the real surface area of gold which gave similar results within an accuracy of 2%, to those obtained with Burshtein's method was the so-called "double-layer capacity method". In this approach, a gold electrode was subjected to a potential sweep at various sweep rates ranging from 0.015 $V.sec^{-1}$ to 0.24 $V.sec.^{-1}$ only over the double-layer potential region and the resulting currents ($i_{d.l.}$) were recorded. The same experiment was conducted on a platinum electrode for which the real area was known from an H-charge determination as described above. The ratio of the double-layer capacities $C_{d.l.}$ to q_H for a monolayer at the Pt electrode could hence be evaluated, so that $C_{d.l.}$ per real cm^2 of Pt could be evaluated. Assuming that $C_{d.l.}$ per real cm^2 at Au is the same as $C_{d.l.}$ per real cm^2 at Pt, i.e. over the region where neither

H nor O-species are adsorbed, enables the real area of a gold electrode for which $C_{d.l.}$ has been determined, as above, to be evaluated (Fig.10). A value for the real surface area of the gold electrode used was found to be 0.474 cm^2. This is in excellent agreement with the value (0.48 cm^2) obtained by the Burshtein method described above.

The voltammetric current-potential curves for platinum and gold differ appreciably. At platinum, atomic H becomes electrodeposited at potentials more negative than 0.4 V, E_H and oxygen species (OH and O) at potentials more positive than 0.8 V, E_H : gold, on the other hand, does not adsorb hydrogen to any significant extent but oxygen species become electrodeposited at potentials more positive than 1.35 V, E_H in 1N H_2SO_4. For potential sweeps between ~ 0.5 and 1.5 V, E_H at 0.05 V $sec.^{-1}$, the current peaks for surface oxide reduction at Pt and Au are well separated, occurring at ~ 1.2 V, E_H for gold and ~ 0.75 V, E_H for platinum. The alloy electrodes gave current-potential curves which were equivalent to the sum of currents for a pure Pt and a pure Au surface weighted in proportion to the relative exposed areas of Pt and Au in the alloy electrode surface (Figs. 9, 11, 12, 13, 14, 15).

In contrast to the behaviour of pure metal electrodes, alloy electrodes are much affected by thermal, chemical or electrochemical pretreatment. According to Damjanović and Brusić[11], chemically or thermally treated Au-Pt alloy electrodes give log i vs V relationships for oxygen reduction which depend on the alloy composition. A Pt-rich (95% Pt) alloy electrode gives a Tafel slope close to that for pure Pt (ca. -RT/F) but is less active than Pt. Electrodes rich in gold (80-90% Au) give the same slope as that for pure Au (ca. -2RT/F) and an activity somewhat higher than that of pure Au itself.

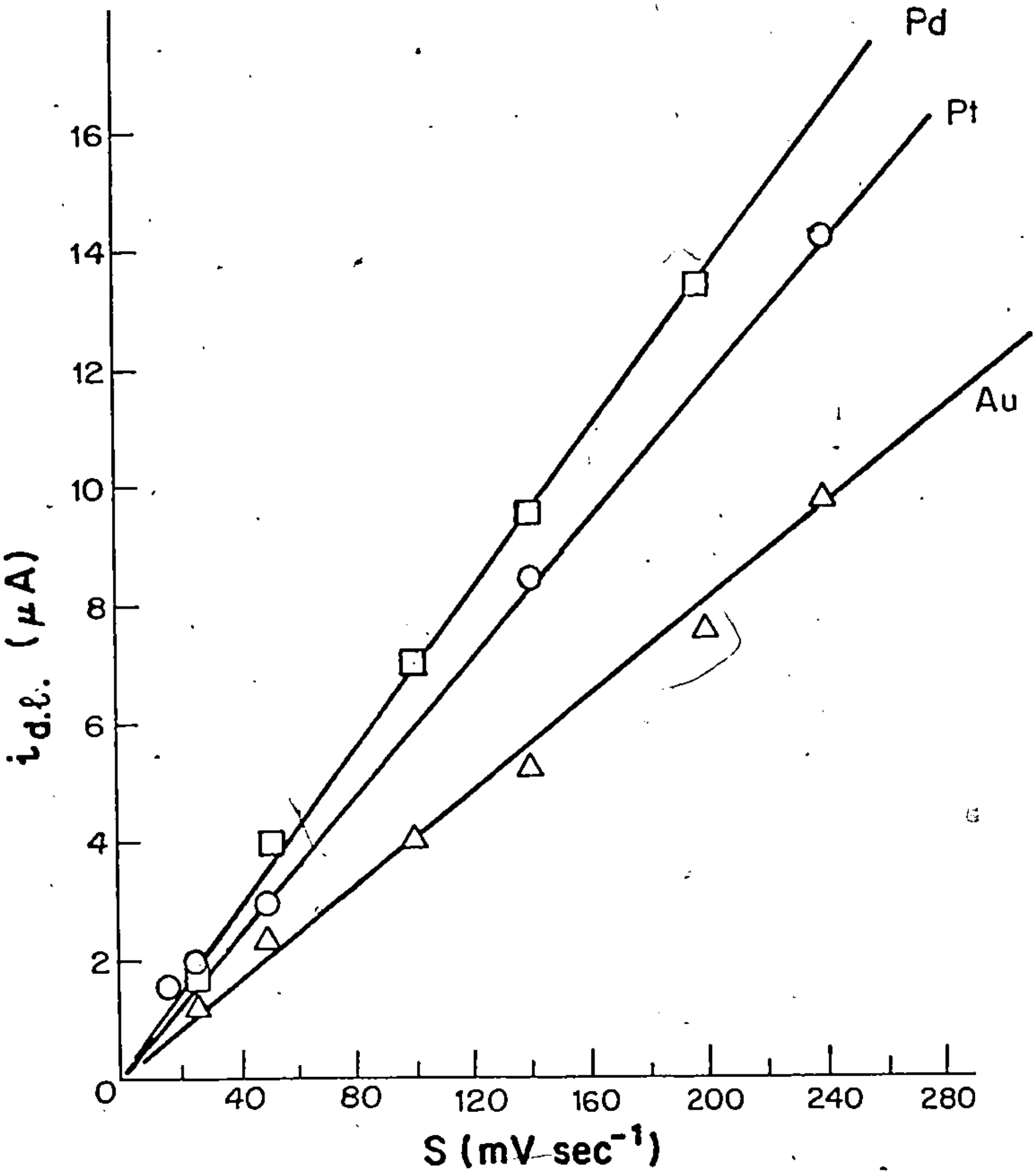


Fig. 10 Plots of changing current vs sweep-rate in the "double-layer capacity method" for the calculation of the real surface area of a gold electrode (△) in relation to that for Pt (○) and Pd (□) electrodes.
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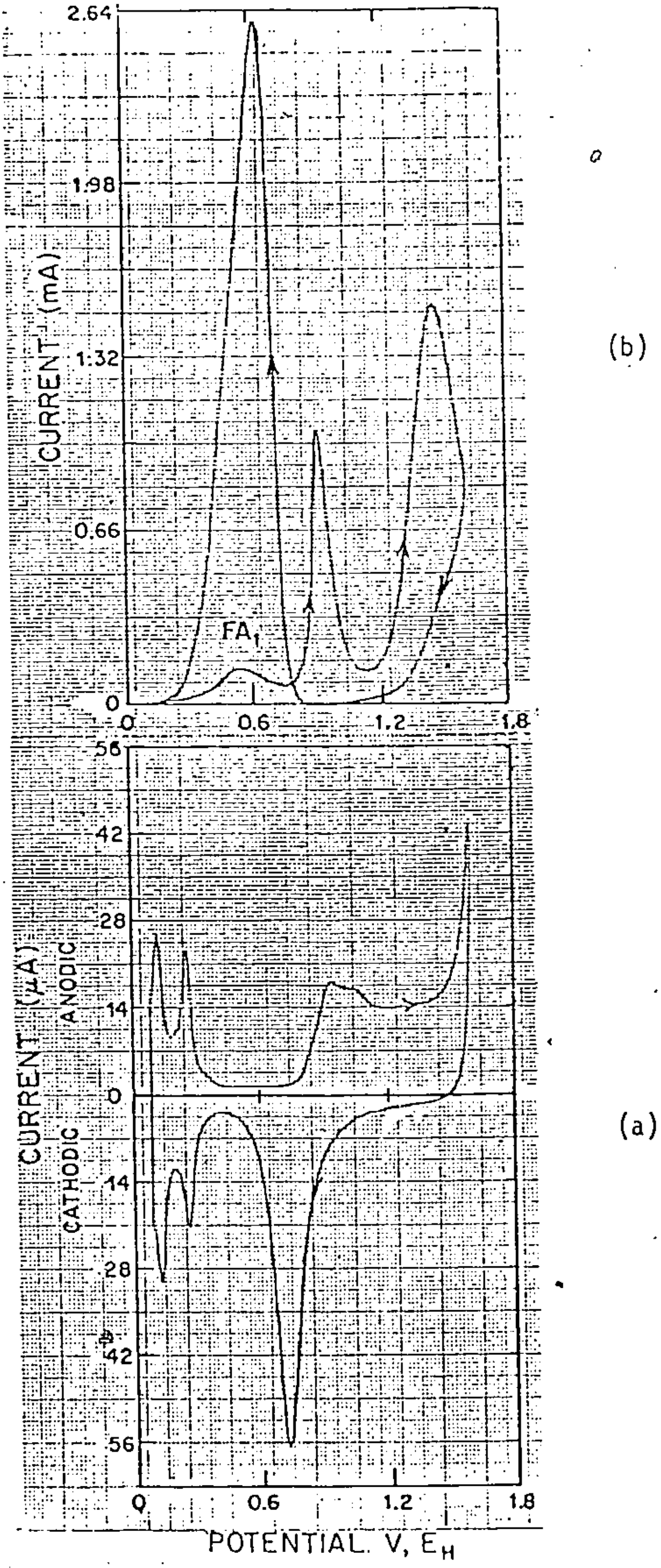

Fig. 11 (a) Potentiodynamic current potential profile for Pt in 1N H_2SO_4 with

(b) the corresponding profile in 1N HCOOH + 1N H_2SO_4

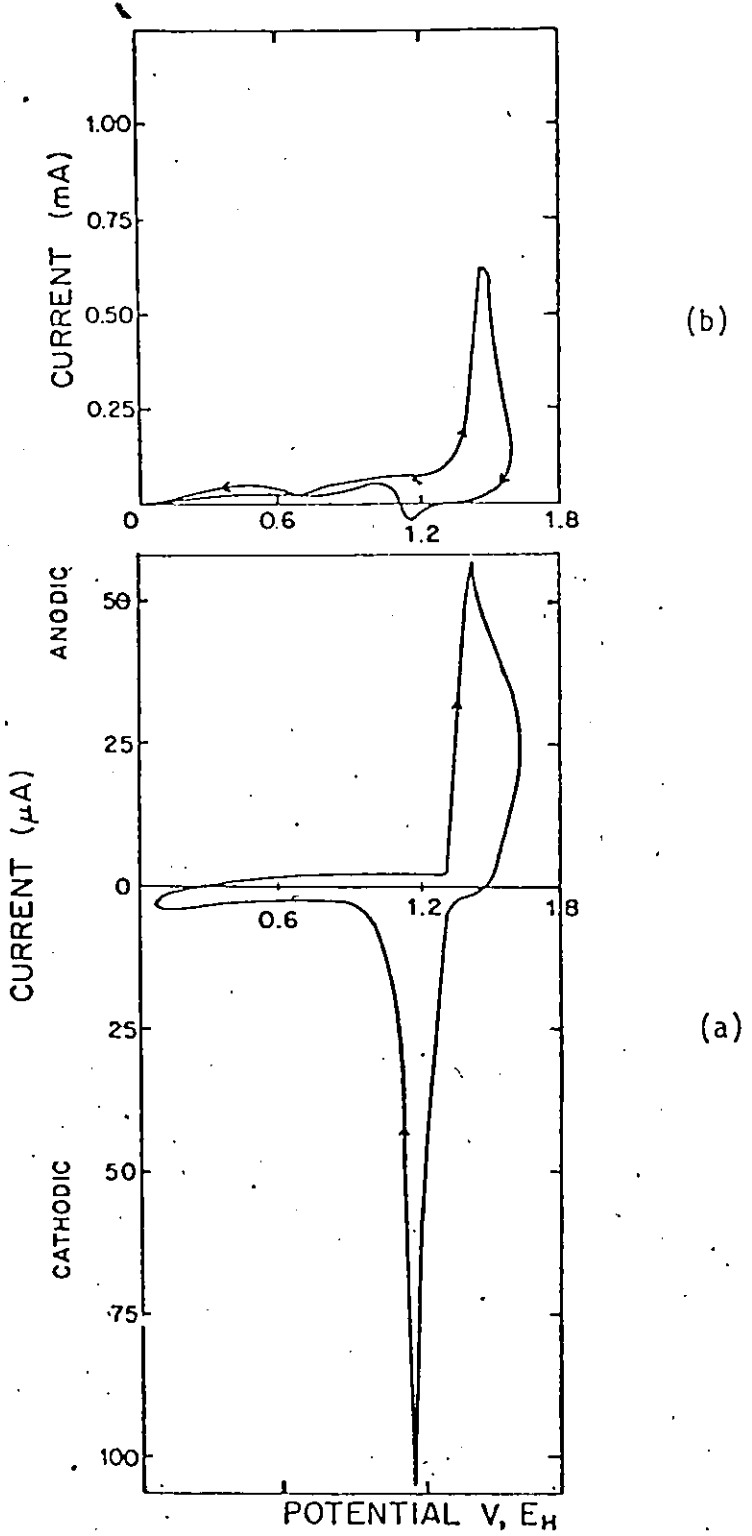

Fig. 12 (a) Potentiodynamic current potential profile for Au in 1N H_2SO_4 with

(b) the corresponding profile in 1N HCOOH + 1N H_2SO_4

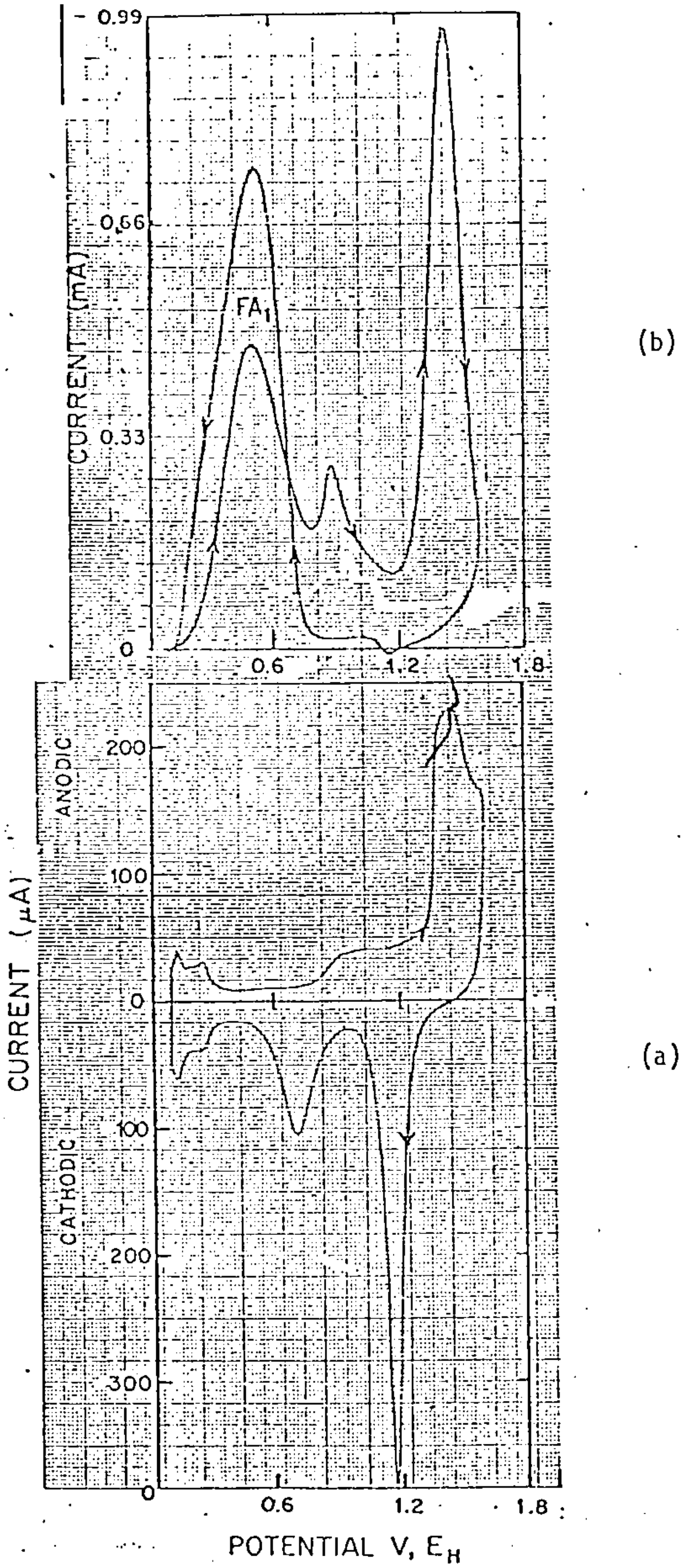

Fig. 13 (a) Potentiodynamic current potential profile for 80% Au-Pt alloy in 1N H_2SO_4 with

(b) the corresponding profile in 1N HCOOH + 1N H_2SO_4

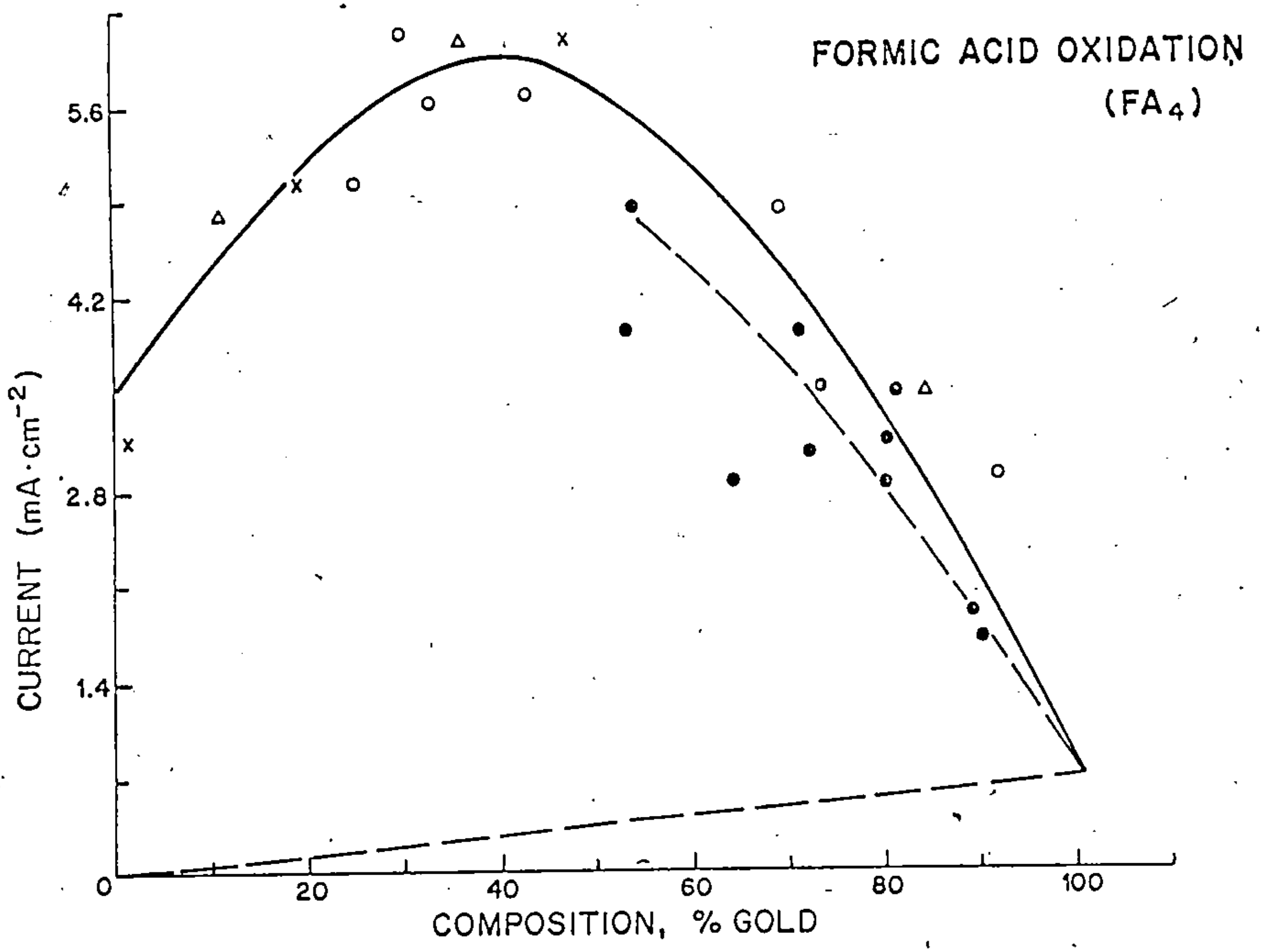

Fig. 18 Effects of surface composition on electrode activity for Au-Pt alloys. Currents for the FA_4 formic acid process are plotted against % gold-content in gold-platinum alloys, where ●, represents the homogeneous 80% Au-Pt electrodes (----) and ○, ×, △, the heterogeneous 60, 40, 20% Au-Pt electrodes respectively (——).

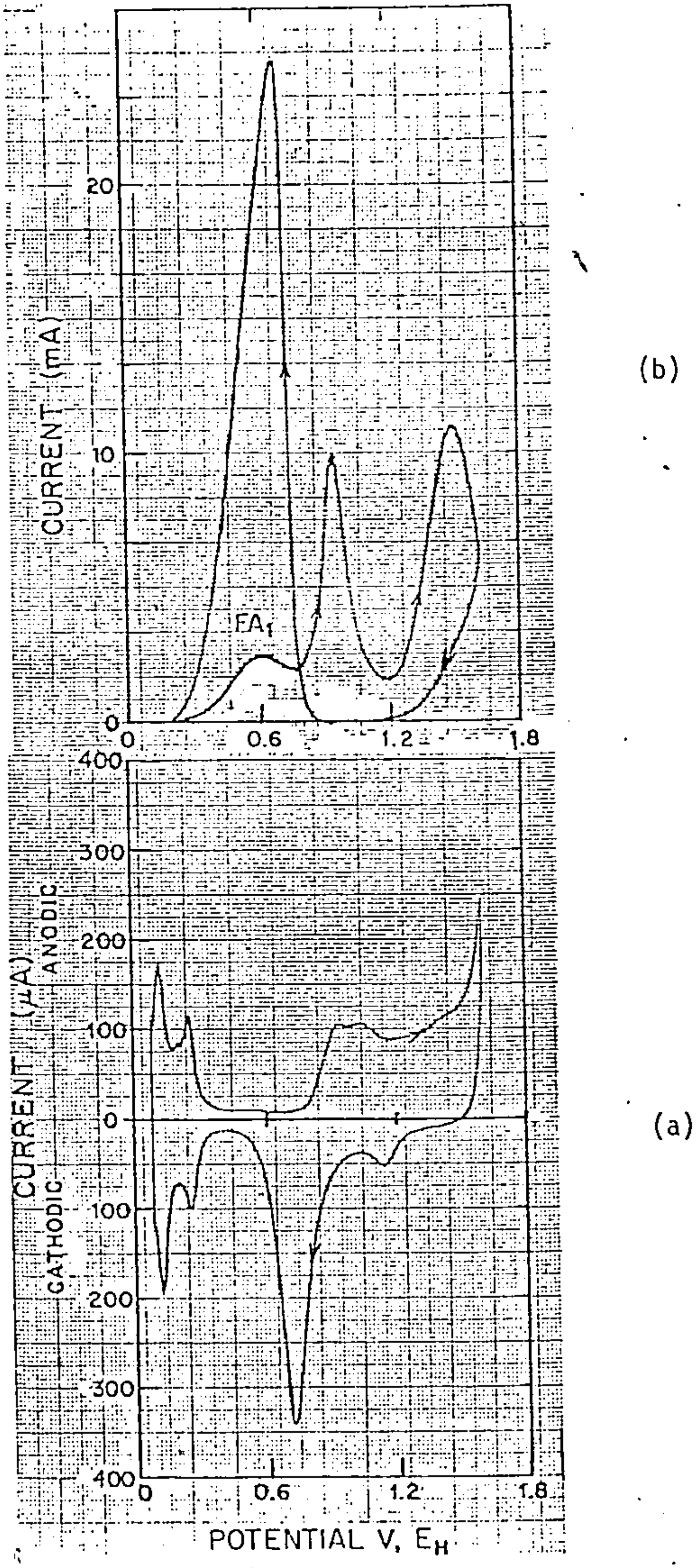

Fig. 15 (a) Potentiodynamic current potential profile for 20% Au-Pt alloy in 1N H_2SO_4 with

(b) the corresponding profile in 1N HCOOH + 1N H_2SO_4

In the present work, it was often observed that the nature of the surface of the alloys significantly changed when anodic and cathodic pulses were applied to them, so that careful examination of the relative proportions of exposed Pt and Au atoms in the surface had to be made in each experiment. These effects arise on account of preferential anodic dissolution of Au atoms.

In order to characterize the surface of the gold-platinum electrodes, the area of exposed Pt sites on the α_1-phase (the platinum-rich phase) was first obtained from the measured hydrogen electrosorption assuming monolayer coverage of 210 $\mu C.cm^{-2}$ on Pt regions. Then, the area of exposed Au on the α_2-phase (the gold-rich phase) was obtained following Burshtein's method described earlier. Therefore, the actual area, A_{Pt}, of exposed Pt on a Au-Pt alloy surface can be obtained as:

$$A_{Pt} \text{ in alloy} = \frac{q_H\ (\mu C)}{210\ \mu C.cm^{-2}}$$

and the actual area of exposed Au as:

$$A_{Au} \text{ in alloy} = \frac{q_{ox\ Au}\ (\mu C)}{400\ \mu C.cm^{-2}}$$

where q_H is the charge for the hydrogen adsorption region and $q_{ox\ Au}$ is the charge for the oxide reduction peak on gold. The total actual area for the Au-Pt alloy electrodes is, therefore, the sum of both these areas: A_{Pt} in alloy + A_{Au} in alloy. Some data obtained by this procedure for the electrodes used are shown in Table I.

Table I

Apparent and Real Surface Composition of Au-Pt Alloys used

App. %Au in Au-Pt alloys	q_H (μC)	A_{Pt} (cm^2)	$q_{ox\ Au}$ (μC)	A_{Au} (cm^2)	A_{total} (cm^2)	Real %Au in Au-Pt alloys
0	73.50	0.35	------	-----	0.35	0.00
20	443.10	2.11	98.49	0.25	2.36	10.59
40	468.30	2.23	10.08	0.03	2.26	1.33
60	102.90	0.49	415.15	1.04	1.53	67.97
80	39.90	0.19	193.05	0.48	0.67	71.64
100	------	-----	199.22	0.50	0.50	100.00

3. Identification of Peaks in the i-V Profiles for Formic Acid Oxidation

The activities of the metals Pt, Au, Pd and of Au-Pt, Au-Pd alloys toward the oxidation of formic acid were compared under conditions of constant potential cycling. In this way, the oxidation reaction was made to take place on an electrode surface that was undergoing continuous re-activation by sweeping between the potential regions of hydrogen deposition and surface oxide formation, viz. 0.05 V to 1.4 V, E_H.

A typical voltammogram for platinum in 1N H_2SO_4 containing HCOOH was shown in Fig. 11b. In an anodic potential sweep, as was seen earlier in Chapter I, Section 4, formic acid exhibits appreciable oxidation currents in three distinct potential regions:

(i) The region of double-layer charging which arises over the range 0.4 V - 0.75 V, E_H, (FA_1)

(ii) The region where surface oxidation begins, i.e., over the range 0.85 V - 0.95 V, E_H, (FA_3)

(iii) A region of higher anodic potentials, i.e., 1.225 V - 1.525 V, E_H, (FA_4)

In the cathodic potential sweep, a large anodic current peak always arises in the potential region where surface oxide reduction occurs; it is observed over approximately the same potential range as the first anodic peak FA_1 but the potential range for its appearance is more

P

determined by the range over which surface oxide reduction occurs at Pt, leading to new free area on the electrode.

The voltammogram for Au in 1N HCOOH was displayed in Fig. 12b. Little oxidation of HCOOH occurs outside the oxide region except for a very gradual increase in current just before the surface oxide formation potential is reached. On the cathodic sweep, a small oxidation current can be detected when the oxide reduction peak has just been passed.

In the formic acid oxidation reaction at Au-Pt alloy electrodes, the major feature of interest is the activating effect (see Fig.16 a) which gold in the gold-platinum alloys has on the FA_1 process. This effect is even larger if the increase in activity is calculated per Pt atom in the alloy surface (Fig. 16b). It is evident that the increase in the current for the FA_1 reaction in this experiment is associated with diminution of the effect of the self-poisoning reaction which normally occurs at pure Pt in the hydrogen region as described earlier. The content of gold in the alloy surface appears to allow the peak current for the FA_1 process to attain a value which is closer to that which would arise in the absence of self-poisoning effects, i.e. gold atoms in the surface diminish the extent of formation of the poison species.

These results are similar to the ones obtained in a different way with added competing poisons, e.g. Hg and acetonitrile, by MacDougall in this Laboratory[18]. He proposed that acetonitrile increased the FA_1 peak current by blocking sites on the surface where a side process in the formic acid oxidation reaction, producing an inhibiting species P, otherwise occurs.

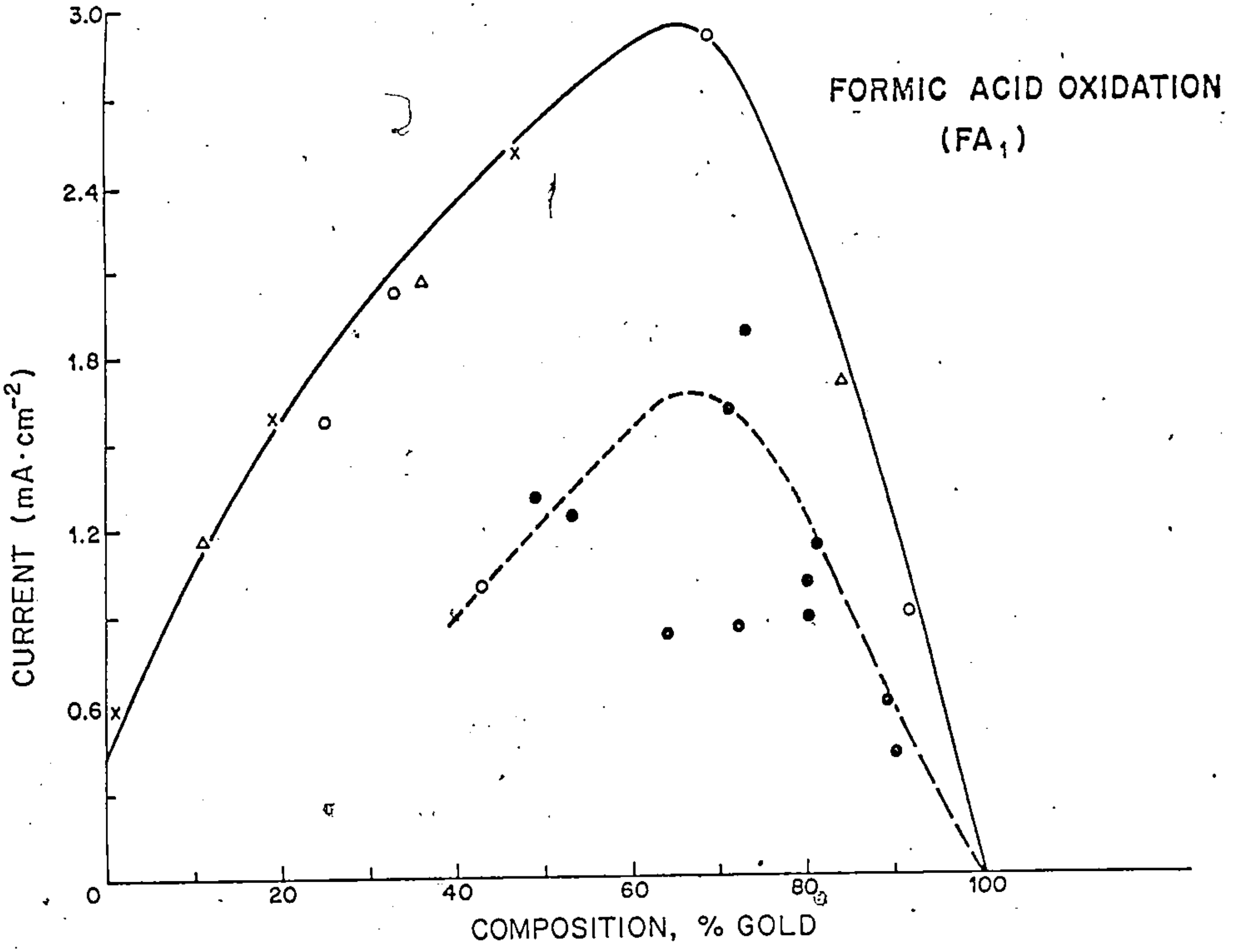

Fig. 16 (a) Effects of surface composition on electrode activity for Au-Pt alloys. Currents for the FA$_1$ formic acid process are plotted against % gold-content in gold-platinum alloys, where ●, represents the homogeneous 80% Au-Pt electrodes (----) and ○, X, Δ, the heterogeneous 60, 40, 20% Au-Pt electrodes respectively (——)

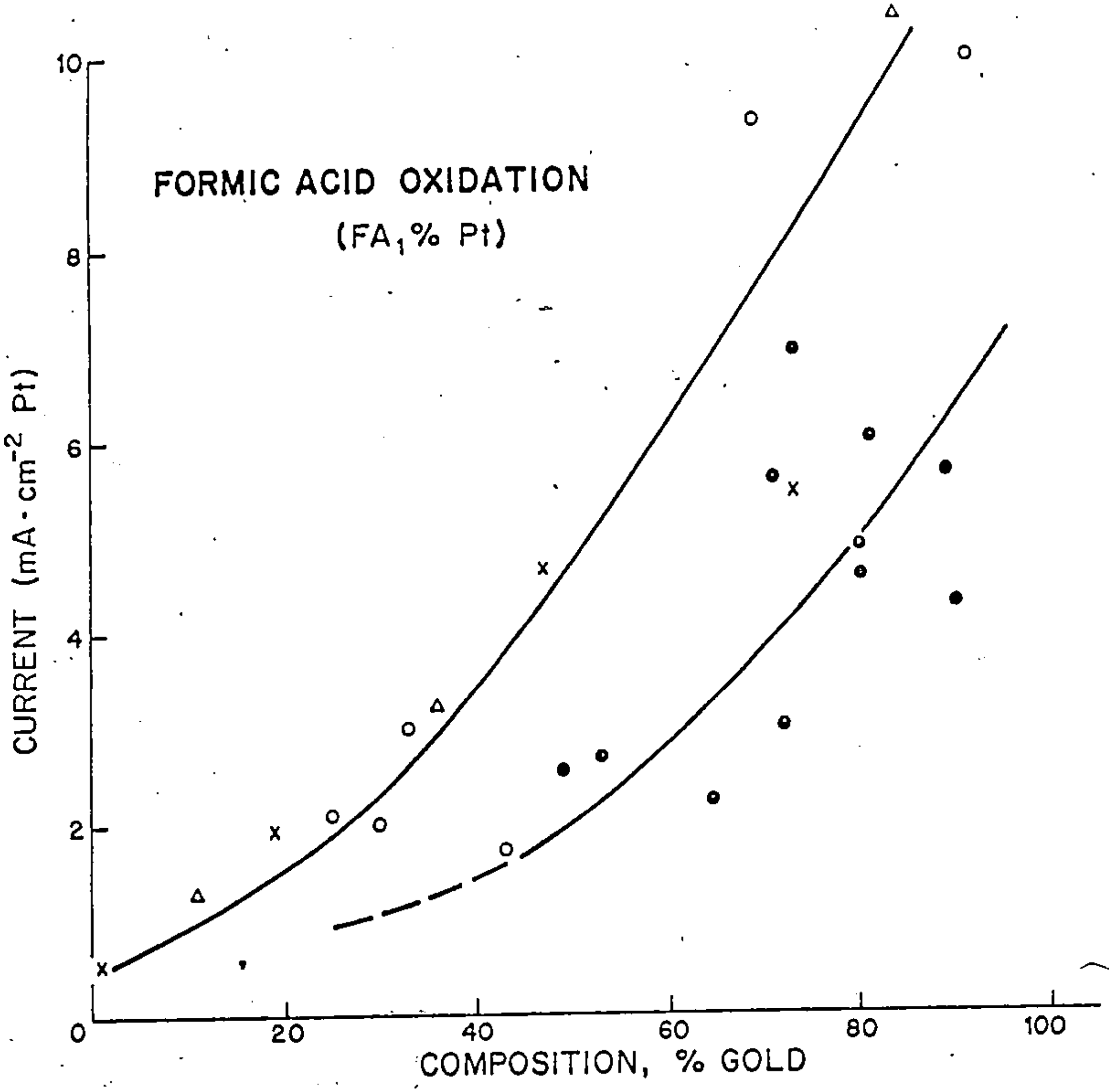

Fig. 16 (b) Calculated per Pt atom in the alloy surface, where ⊙, represents the homogeneous 80% Au-Pt electrodes (----) and ○ , X , △ , the heterogeneous 60, 40 20% Au-Pt electrodes respectively (——)

The current for the FA_1 process when plotted against % gold-content in gold-platinum alloys displays two volcano-type relationships as shown in Fig.16a; one predominantly involving the two-phase heterogeneous alloys (20,40,60% Au) and the other predominantly the homogeneous 80% Au-Pt alloy which gave a range of surface compositions depending on cycling pre-history.

The plot for the FA_3 process demonstrates (Fig.17) a linear relationship between the observed currents and the alloy composition. The peak currents for the FA_3 process decrease with increasing gold-content.

The FA_4 process and the cathodic process, FC also show a volcano-type relationship (Figs. 18, 19).

If the currents for the FA_1 process are calculated in terms of the actual concentration of Pt atoms per cm^2 of the surface, the FA_1 peak follows two parabolic-type relationships (Fig. 16b), one for the homogeneous alloys and the other for the heterogeneous alloys.

The clear distinction between the behaviour of the two types of alloys (homogeneous and heterogeneous) which is seen in most of the above results (Figs. 16a,16b,18, 19) confirms the conclusions from the X-ray diffraction data obtained for us by S.D. Entwistle of Bell-Northern Research (Ottawa) that the alloys with 20, 40, 60% Au are composed of two immiscible solid solutions and the alloy with 80% Au is composed of a single-phase solid solution.

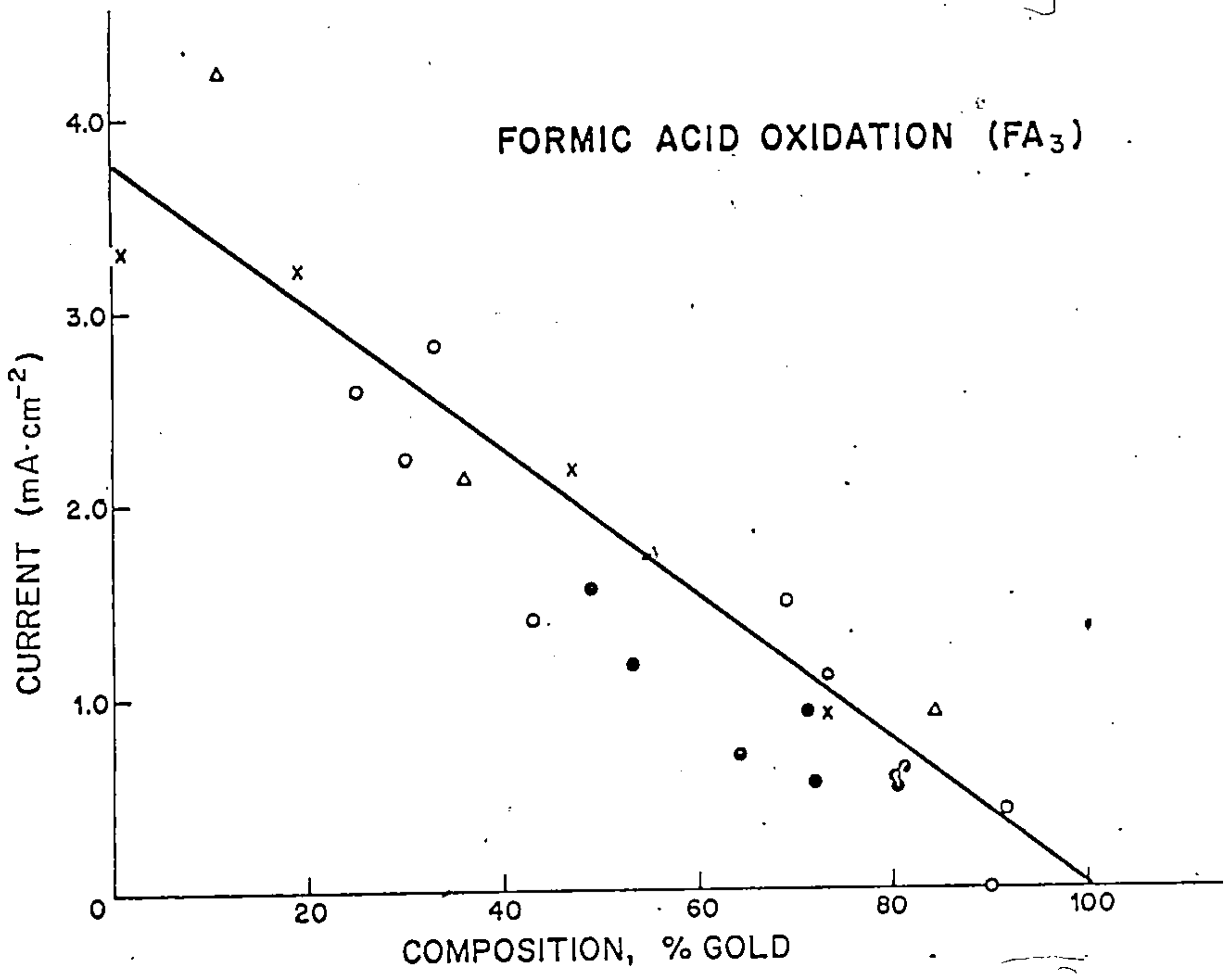

Fig. 17 Effects of surface composition on electrode activity for Au-Pt alloys. Currents for the FA_3 formic acid process are plotted against % of gold-content in gold-platinum alloys, where ●, represents the homogeneous 80% Au-Pt electrodes and ○, ×, △, the heterogeneous 60, 40, 20% Au-Pt electrodes respectively.

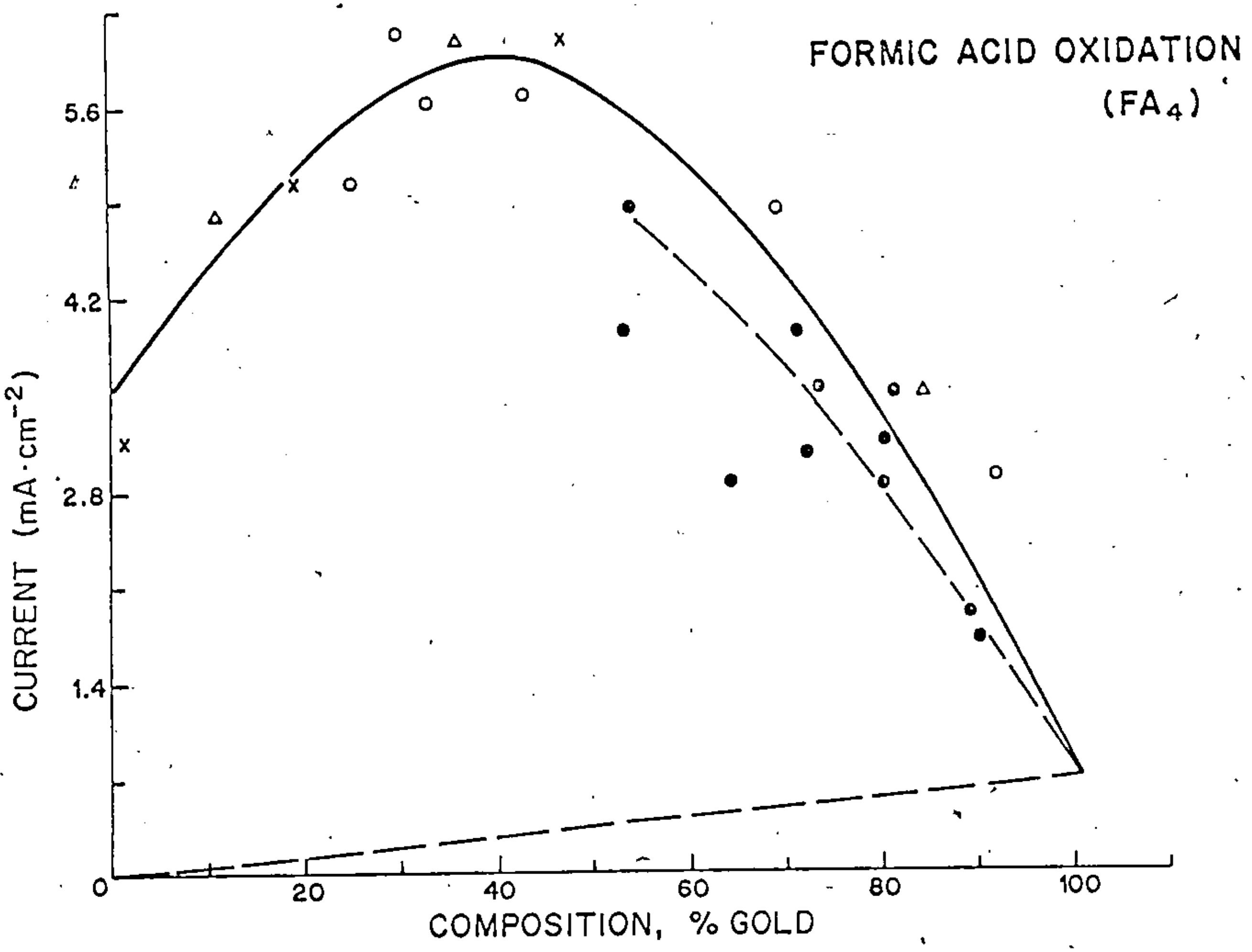

Fig. 18 Effects of surface composition on electrode activity for Au-Pt alloys. Currents for the FA_4 formic acid process are plotted against % gold-content in gold-platinum alloys, where ●, represents the homogeneous 80% Au-Pt electrodes (----) and ○, ×, △, the heterogeneous 60, 40, 20% Au-Pt electrodes respectively (——).

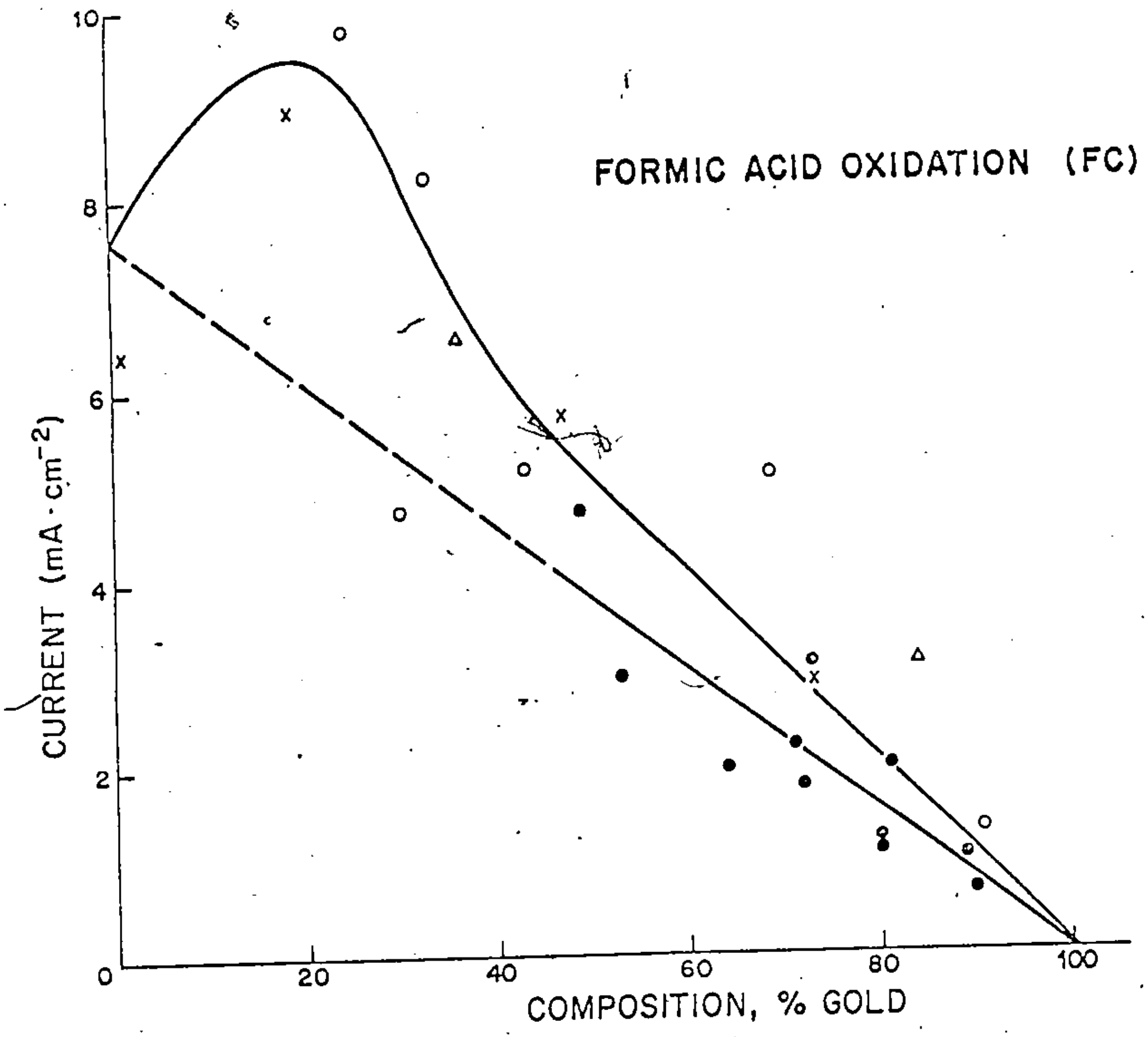

Fig. 19 Effects of surface composition on electrode activity for Au-Pt alloys. Currents for the FC formic acid process are plotted against % gold-content in gold-platinum alloys, where ●, represents the homogeneous 80% Au-Pt electrodes (----) and ○, ×, △, the heterogeneous 60, 40, 20% Au-Pt electrodes respectively (——).

4. Rates of Diminution of FA_1 Currents on Holding the Potential Constant at Selected Values

If the platinum or alloy electrode is held at 0.0V, E_H in HCOOH solution for several minutes, then the next anodic sweep displays no current, or only a diminished current, until the threshold of the second anodic peak is reached. Identical results are obtained when the electrodes are held on open-circuit in HCOOH for the same length of time. The lack, or diminution, of current in the region of the first anodic peak (FA_1) suggests that the electrode surface is totally blocked (in the case of platinum) by organic residues generated from HCOOH until they are oxidized at the threshold of the second anodic peak (Fig. 20).

From the time effects studied in 1N HCOOH at 0.5 V, E_H on Pt, Pd and the 80% Au-Pt alloy (Fig. 21), it can be seen that the Au-Pt electrode shows a smaller rate of current decay, i.e., an increased activity compared with that at pure platinum. The reason is, of course, that the presence of gold in the surface inhibits the formation of P; therefore the alloy surface does not become ~~almost~~ totally blocked by the organic residues as in the case with pure platinum electrode surfaces.

At Pd (Fig. 22), the rate of decrease of activity is substantially less than at either Pt or the 80% Au-Pt alloy. This is consistent with Parsons' observation[28] that the FA_1 peak is larger on Pd than on Pt.

5. Comparison with Methanol Oxidation Behaviour at Au-Pt Alloys

On the anodic fast potential-sweep curve made on platinized platinum in acid solutions containing CH_3OH and HCOOH, an "adsorption" peak appears

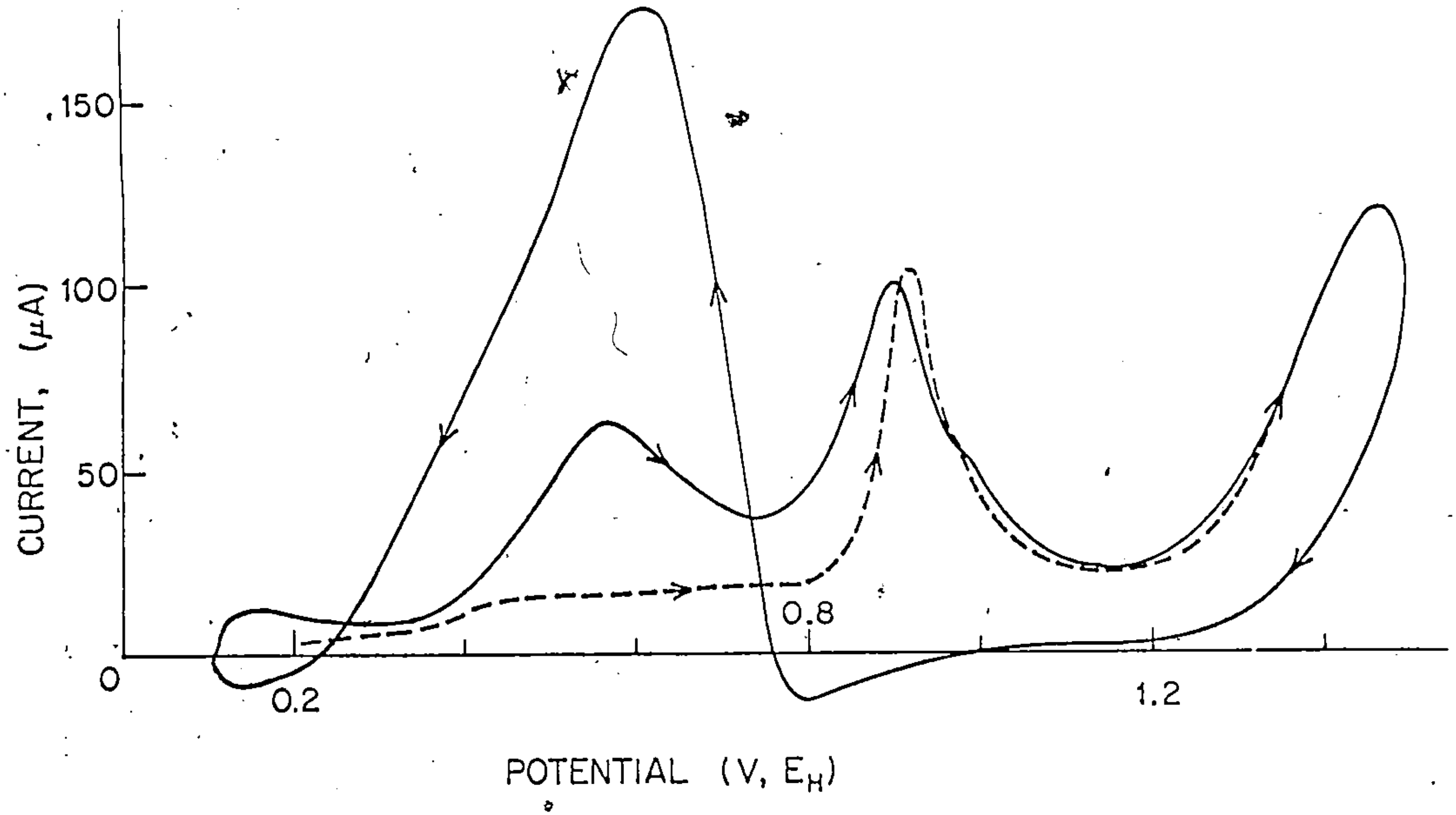

Fig. 20 Cyclic voltammogram for a smooth Pt electrode at 25°C in 1N HCOOH + 1N H_2SO_4 (——) continuous recording; (----) after 5 min. at open-circuit.

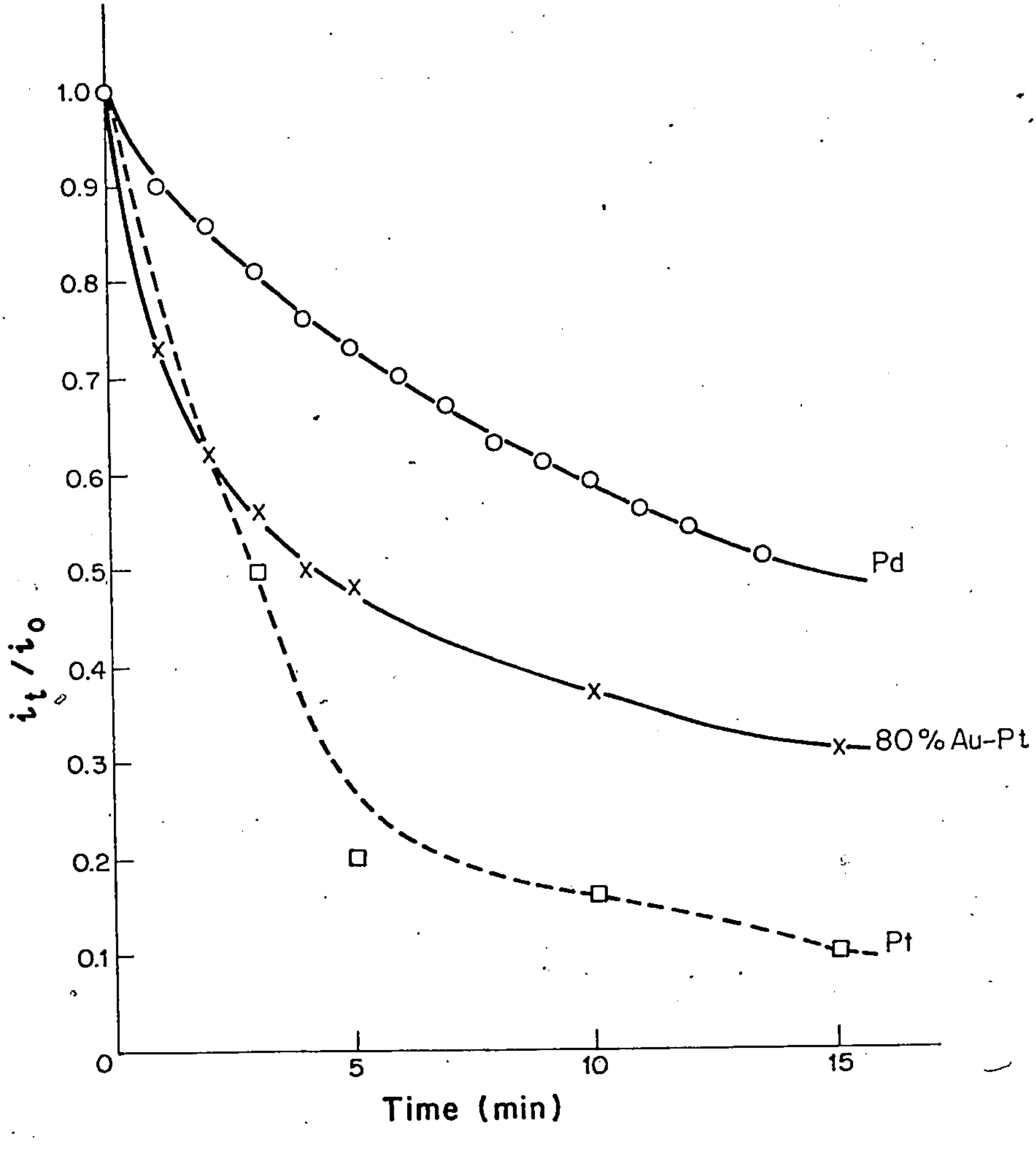

Fig. 21 Time dependence of currents measured in 1N HCOOH + 1N H_2SO_4 at 0.5 V, E_H on Pt Pd and the 80% Au-Pt alloy electrodes.

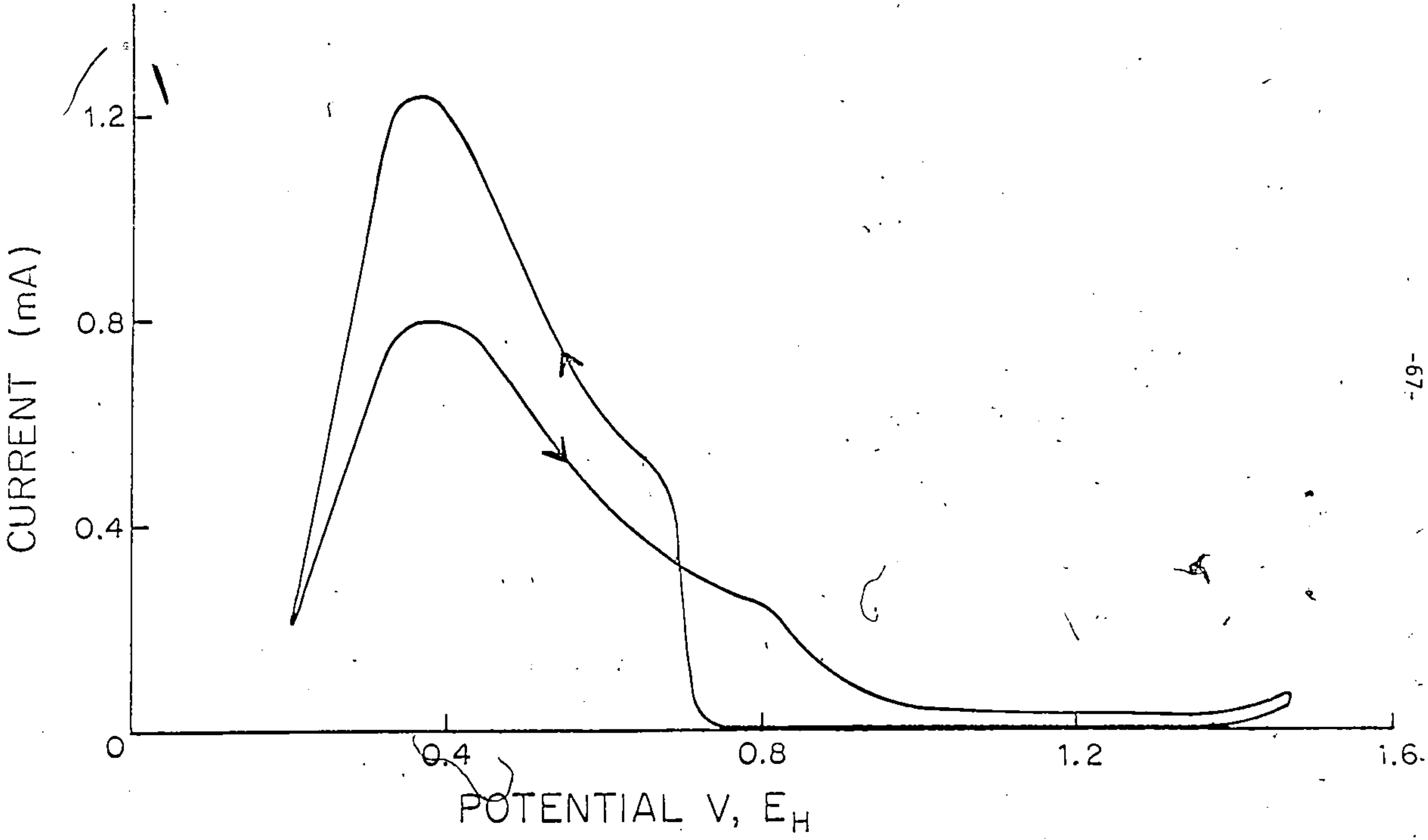

Fig. 22 Cyclic voltammogram for palladium electrode in 1N HCOOH + 1N H_2SO_4.

at approximately 0.6 V, E_H. This adsorption peak has been ascribed to the oxidation of a chemisorbed intermediate, which can possibly be formed by reduction of CO_2, and which was called by Giner[19] "reduced CO_2" (possibly CO or COOH). It has been suggested that this species is formed by partial oxidation of methanol or formic acid and, to some extent, by catalytic decomposition of these reactants on open-circuit. Below the potential of the peak, this species accumulates on the electrode and blocks further oxidation of the reactants; above the potential of the peak, the species is oxidized to CO_2 faster than it is produced, thus freeing the surface for continuous oxidation of the substrate in solution.

In cyclic-voltammetry studies of HCOOH oxidation, it is found that in the anodic sweep a small wave arises at 0.5 V, E_H. It is assumed that during the course of this pre-wave, an additional amount of chemisorbed poison species is formed from the HCOOH reagent in addition to that formed during the previous cathodic sweep.

Both methanol and formic acid (especially the latter), when anodically oxidized on platinum electrodes in acid solutions, form the chemisorbed side-product P in addition to a reactive intermediate in the main reaction sequence ($\geq$COH in the case of methanol, -COOH in the case of formic acid).

The formation of the poisoning intermediate, P, it has been proposed[18,29] explains the rapid decay of current (e.g. see Figs. 20 and 21) during the anodic oxidation of methanol and formic acid at low polarization (viz. 0.2 - 0.4 V; E_H). The current decay is accompanied by a progressive increase of coverage of the electrode by organic residues. As soon as the electrode is brought to potentials at which the poison, P, can be readily oxidized (> 0.75 V), the activity of the electrode is regained. It is with regard to oxidation of the organic residue that the methanol and formic acid reactions are believed to differ, the adsorption mechanism which gives rise to the reactive species being, however, similar, viz, a dehydrogenation for both molecules on platinum.

In the case of methanol, the anodic current resulting from oxidation of the adsorbed intermediate species at a fixed potential increases with increasing coverage by species derived from methanol. For formic acid, on the other hand, an increase in coverage by the adsorbed species which is measurable in electrochemical experiments at a fixed potential, results in a decrease in the anodic current. These results indicate that the species giving rise to most of the coverage of the electrochemically detectable adsorbed species derived from methanol at platinum is involved in the main sequence of steps in the oxidation reaction. With HCOOH, on the other hand, a large proportion of the electrochemically detectable species resulting from formic acid adsorption is not the main reactive species, viz. -COOH, involved in the reaction $2Pt + HCOOH \rightarrow PtH + Pt\text{-}COOH \rightarrow 2Pt + 2H^+ + 2e + CO_2$; it is rather an inhibitor resulting from a parallel side reaction as discussed by a number of workers[13,15,18,23]. As the coverage by this inhibiting species increases, the currents for formic acid oxidation decrease.

Similar experiments to the ones made in formic acid were made with gold-platinum alloys, in methanol in acidic media. The results are shown in Figs. 23, 24, 25. It seems that the peak currents for the MA_3, MA_4 and MC processes decrease with increasing gold-content indicating that the gold atoms on the surface decrease the rate of surface oxidation at a given potential.

However, work done by Watanabe and Motoo[7], shows an interesting enchancement of activity of platinum by ruthenium ad-atoms for the oxidation of methanol: in order for the reaction to proceed continuously, it is necessary* that the $\geqslant$ COH species be removed by adsorbed oxygen-containing species on the electrode which are normally deposited at higher potentials (on platinum at 0.75 V, E_H and on gold /acid media/ at 1.35 V, E_H.) Therefore, if it were possible for the oxygen-containing species to be electrodeposited at appreciably lower potentials, the methanol oxidation reaction would proceed much faster.

Because the surface of Ru itself already becomes oxidized at relatively low potentials (0.15 - 0.2 V, E_H), so that the surface remains covered with increasing potential, this metal is not itself a good methanol oxidation electrocatalyst. Thus, there would be no free area on which the initial dissociative adsorption can occur. However, if Ru is used as ad-atoms on Pt at low coverage, oxygen-containing sites at Ru atoms can co-exist with bare-platinum sites on which the dissociation can occur. Thus, a "bifunctional" electrocatalyst surface is generated. The Ru must be used in very small quantities because otherwise it would prevent the initial formation of the primary intermediate, $\geqslant$ COH.

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*This is because it is usually found that C to Pt bonds are not dissociated in a direct electron-transfer step but require reaction with electrodeposited O species

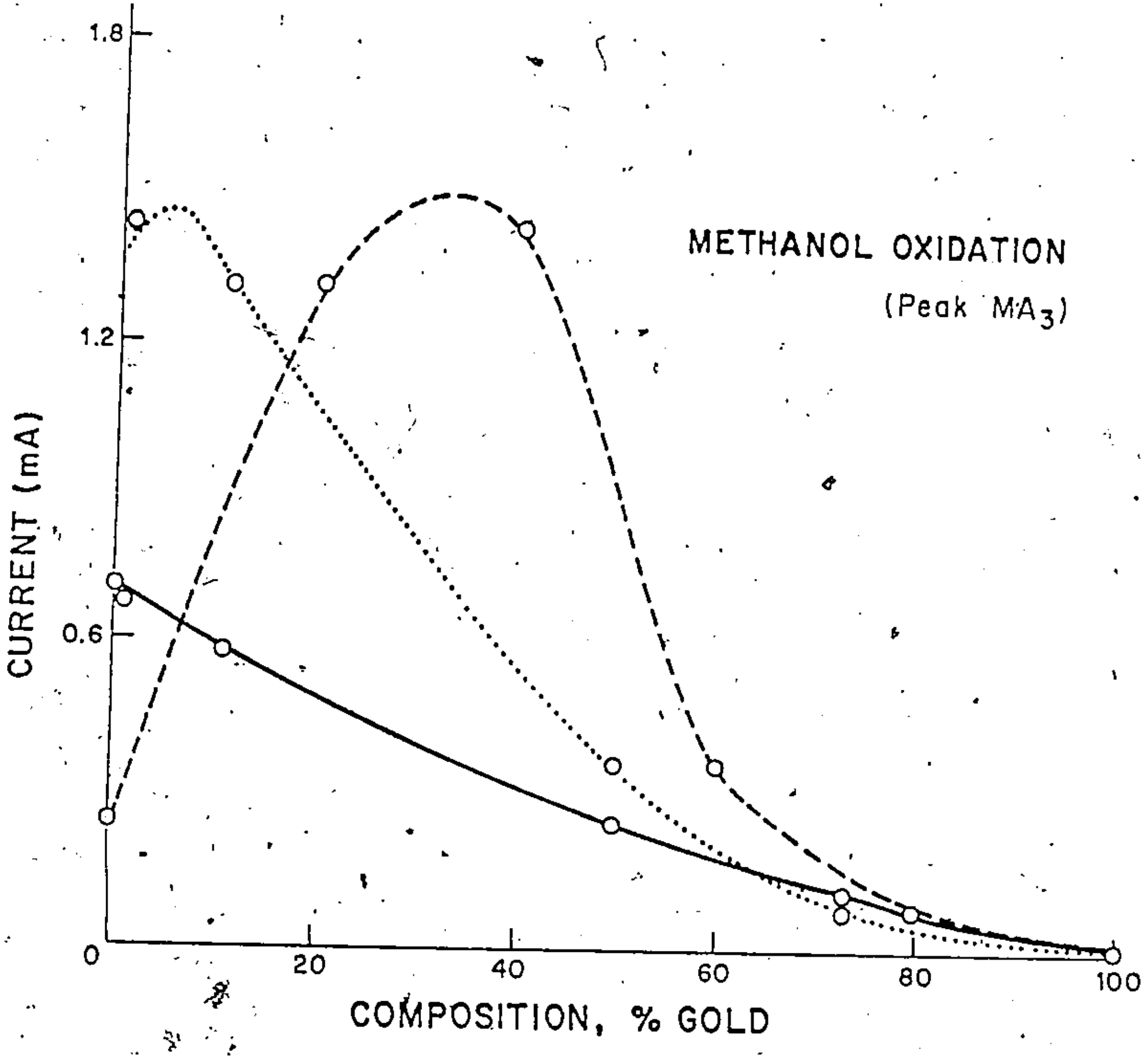

Fig. 23

Currents for the MA_3 methanol oxidation process plotted against % gold-content in gold-platinum alloys, where (----) is the curve for the bulk composition vs. apparent currents; (....) tge curve for the corrected surface composition vs. apparent currents; and (——) the curve for the corrected surface composition vs. corrected currents (area factor)

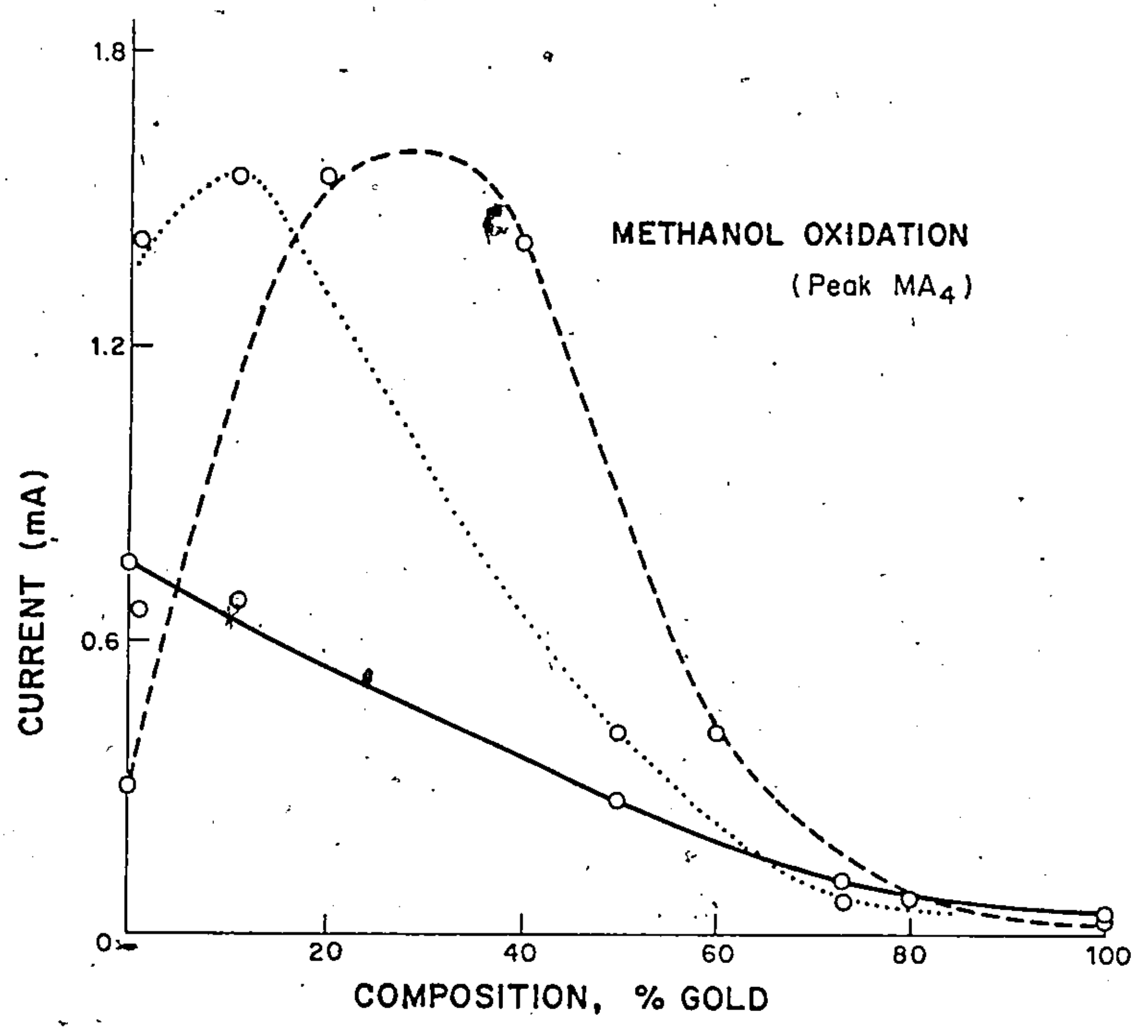

Fig. 24

Currents for the MA_4 methanol oxidation process plotted against % gold-content in gold-platinum alloys, where (----) is the curve for the bulk composition vs. apparent currents; (····) the curve for the corrected surface composition vs. apparent currents; and (——) the curve for the corrected surface composition vs. corrected currents (area factor)

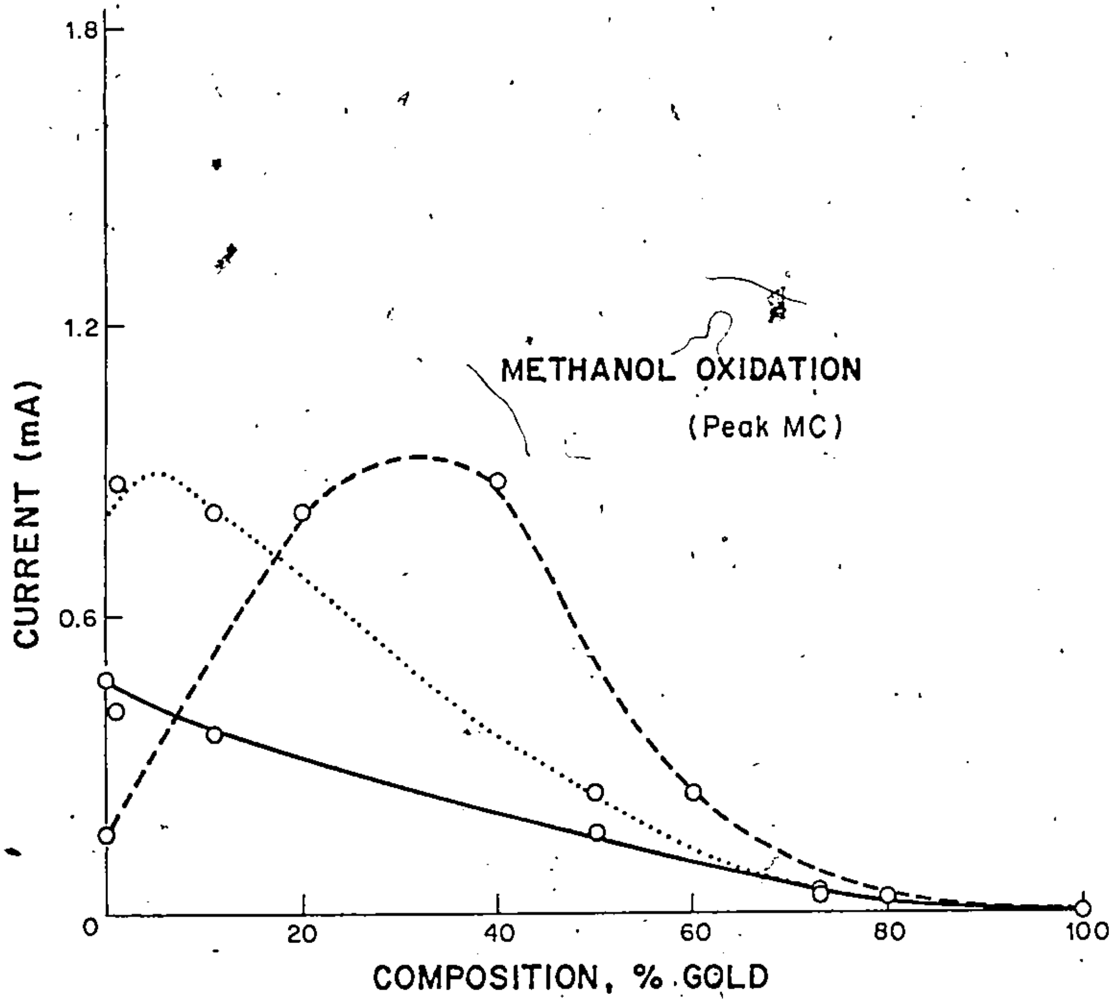

Fig. 25 Currents for the cathodic-sweep methanol oxidation process, MC, plotted against % gold-content in gold-platinum alloys, where (----) is the curve for the bulk composition vs. apparent currents; (....) the curve for the corrected surface composition vs. apparent currents; and (——) the curve for the corrected surface composition vs. corrected currents (area factor)

Gold[10] may also enhance the activity of Pt for methanol oxidation by a similar mechanism but must be used in alkaline solution, otherwise the required oxygen-containing species are not generated until too high ($\geqslant 1.35$ V, E_H) potentials are reached.

More recently, finely divided Pt-Ru[7] catalysts have been found useful for methanol electro-oxidation. The importance of surface composition of these catalysts in relation to the conditions of their activation was stressed in this work.

Recent work by Janssen and Moolhuysen[30] on methanol oxidation shows that the catalytic activity of platinum can be increased by addition of tin and that the active tin species are best produced at a Pt surface initially fully covered with hydrogen. It is found that the ad-atom modified surface exhibits enhanced activity over Pt atoms but must be obtained by the "immersion" method described by these authors.

6. Behaviour of Formic Acid at Pd Electrodes and Problems with Au-Pd Alloys

The voltammograms for the oxidation of HCOOH at Pd are different from those made at Pt. The most striking difference is the fact that there are no current peaks (except a shoulder at FA_3) equivalent to the second and third anodic peaks observed at Pt. Also, the single anodic peak which does arise at Pd (Fig.22) is very large compared with that at Pt. It is practically of equal height and of similar shape to that observed on the cathodic sweep (FC). This implies that almost the same proportion of the surface is available for reaction on both the anodic and cathodic sweeps; thus, there is less blocking of active sites by the strongly adsorbed intermediate produced in the side reaction, than that occurring at Pt. There is, however, a small current component at ca. 0.8 V, E_H at a potential similar to that at Pt where the FA_3 process of reaction of chemisorbed HCOOH residues with the initially deposited oxygen species arises. The smaller FA_3 current at Pd is consistent with the larger FA_1 current at this metal. The fact that there is no FA_4 peak means that the surface oxide formed on Pd is not active for oxidation of HCOOH, as is the oxide on Pt (see Fig. 22).

The observations of Poliak et al.[31] suggest that little or no strongly adsorbed intermediates of the type found on Pt are present on Pd in the course of oxidation of HCOOH. The lack of an oxidation current peak in the oxide region is also evidence that HCOOH is unable to react with any type of electrodeposited OH or O species at Pd (Pt has two regions of "active oxide" giving the FA_3 and FA_4 currents). The relative lack of self-inhibition behaviour in the oxidation of HCOOH at Pd may be attributed to the relative absence of chemisorbed H, since H diffuses into the Pd electrode. Thus, with Pt, it is always found that the P species is formed from HCOOH in the H chemisorbed region.

7. Gold-Palladium Alloys

Homogeneous gold-palladium alloys display composite hydrogen and oxygen electrosorption properties as compared with the behaviour of gold-platinum alloys which exhibit the electrosorption characteristics of each of the individual pure metals.

The first sweep for a 20% Au-Pd electrode cycled at 50 mV. sec^{-1} between 0.30 V, E_H and 1.55 V, E_H shows a single cathodic surface oxide reduction peak at 0.85 V, E_H. (The corresponding peak for pure gold occurs at 1.20 V, E_H and for pure palladium at 0.69 V, E_H). A second cathodic peak develops with continued cycling and the potential of this peak becomes close to that for gold after only a few cycles (Fig. 26). The change in surface oxidation/reduction behaviour is associated with preferential dissolution of palladium from the electrode surface. It seems, however, that the removal of palladium does not result in a continuous change in surface alloy composition, but rather in the replacement of the alloy surface with areas of high gold content

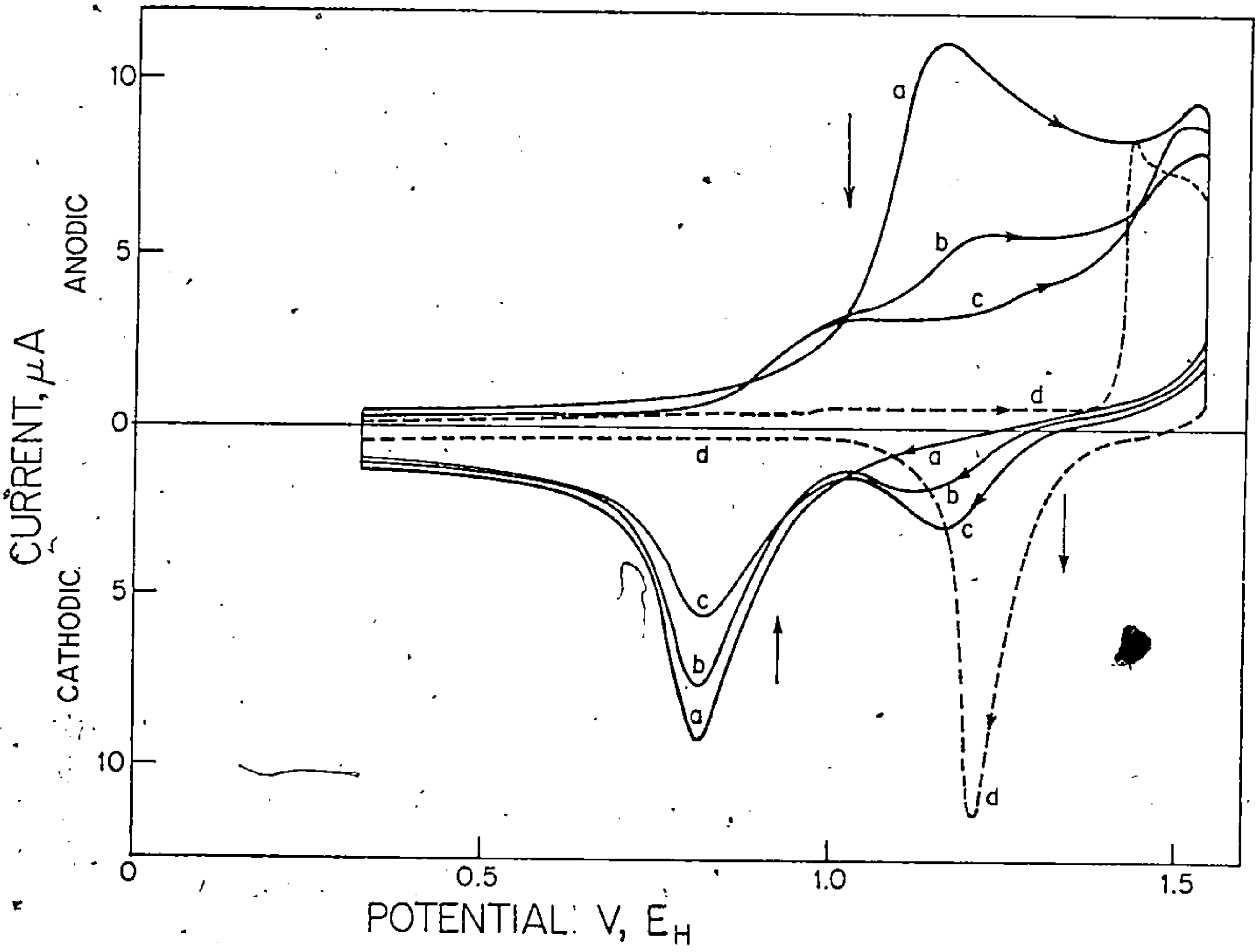

Fig. 26 Current vs. potential curves for a 24% Au-Pd electrode in 1M H_2SO_4 at 25°C. Sweep rate 40 mV. sec.$^{-1}$. Curves a, b, c are for cycles 1-4, 20 and 1000 respectively; curve d is for pure gold (from Rand and Woods, ref. 38).

Thus, instead of a gradual shift in surface oxide reduction peak potential expected if one component were progressively removed from the surface, the oxide reduction peak potential remains constant but a second peak appears at higher potentials.

One of the problems that arises with gold-palladium alloy series for compositions < 60% Au is that the alloys sorb hydrogen appreciably and this complicates the study of processes occurring on the electrode, hindering the determination of the value of the true active surface area [32]. With the 60% Au-Pd electrodes, therefore, no H absorption was observed at potentials positive to that where molecular hydrogen is evolved.

Another problem that arises with the gold-palladium alloy series of electrodes is that the surface composition changes so rapidly with successive anodic/cathodic sweeps that a meaningful i-V profile for formic acid oxidation is difficult to establish in a reproducible way; even a sweep rate of 50 V sec^{-1} did not improve the situation appreciably.

8. Behaviour of Zn-Pt Electrodes

Interest in the possible effects of adsorbed Zn^{++} ion arose from some preliminary work on cation effects on the H adsorption current profile and from the previously known effects of electrodeposited Pb and Hg atoms on the formic acid FA_1 oxidation current [4,18,33].

In this part of the work, the effects of adsorption of Zn^{2+} ions on the behaviour of the platinum electrode were studied. The platinum electrode was "zincified" in a solution of 10N KOH + $ZnSO_4 \cdot 2H_2O$ for 6 minutes with current passing at 0.6 mA; later the electrode was subjected to cyclic potential sweeps in sulphuric acid but there was no significant difference between the i-V behaviour then observed and that for pure platinum except for a small shift in the H adsorption peaks in the positive direction (Fig. 27).

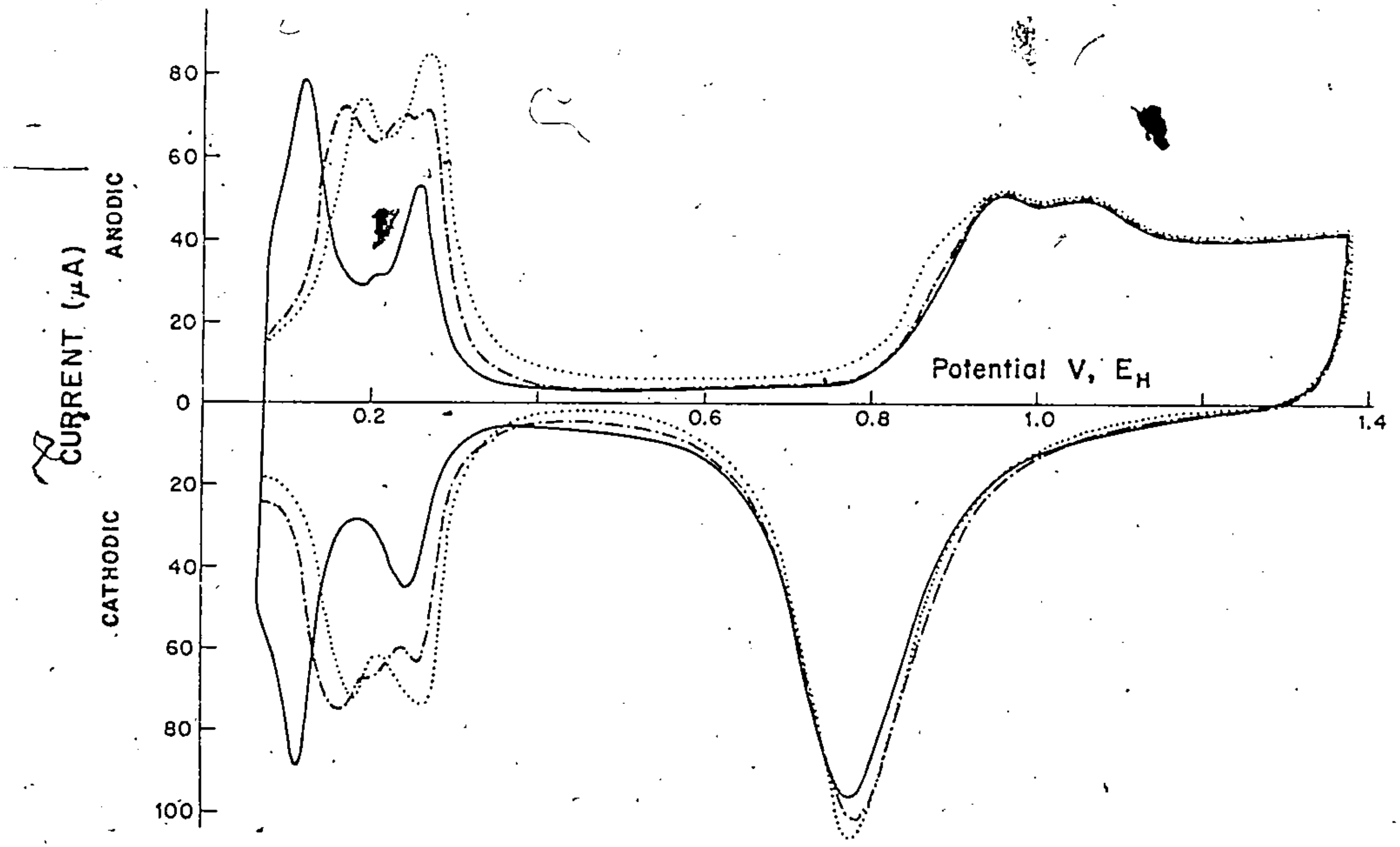

Fig. 27 (a) Potentiodynamic current potential profile for Pt in 1N H_2SO_4 at a sweep rate = 50 mV sec^{-1} over the potential range 0.05 V to 1.35 V E_H (——) with addition.

(b) of 3 x 10^{-3} M $ZnSO_4$ (·—·—·)

(c) of 3 x 10^{-2} M $ZnSO_4$ with a repetative sweep maintained for 24 h (····)

The same results were obtained when the concentration of $ZnSO_4$ was increased. The electrode was then again zincified for 15 minutes at i=0.6 mA and left to age for one hour. This time the potential sweep gave first a considerable increase in currents over the whole potential range [the electrode had apparently developed a porous surface] followed by a gradual decrease. This "roughening"[34] of the electrode can also be caused by repetitive voltage cycling. The mechanism of roughening has not yet been all well established. It seems that the roughening involves a soluble platinum species [Pt II or Pt IV] and occurs by a dissolution-redeposition mechanism. The only soluble species produced during potential cycling scans in 1N H_2SO_4 at platinum electrodes are H_2, O_2, Pt II and Pt IV. During these repeated cycling treatments, e.g. between 0.48 and 2.05 V, E_H, the surface would become hazy and dark, and later golden in appearance. The golden color slowly intensified as the electrode-potential cycling was continued and became permanent after removal of the electrode from solution. This yellow-orange deposit indicates that a phase platinum oxide may have been formed.

As for the adsorption of Zn^{2+} ions, in a regular potentiodynamic experiment, it seems that a new current maximum appears on the platinum i-V curves in $ZnSO_4$ solutions and is related to the Zn^{2+} ion-modified adsorption of hydrogen atoms on the platinum surface. The Zn^{2+} ions increase the amount of adsorbed H that can be measured in the sweep. Therefore it seems that specific adsorption of zinc ions on platinum causes a qualitative change in the state of the Pt surface with regard to adsorption of hydrogen in addition to changing the total amount which can be adsorbed; specifically, it shifts the current maximum which was previously at 0.12 V, E_H, while the peaks at 0.2 and 0.28 V, E_H, are substantially enhanced. This behaviour is evidently associated with a substantial redistribution of deposited H amongst the states available for H chemisorption at Pt. In particular, the Zn^{2+} ion seems to reverse the effect of adsorbed SO_4^{2-} ions and thus allows more H to be deposited at potentials more positive than those for H_2SO_4 solution alone. In fact, the total measurable charge for H desorption in Fig. 27 is 26% larger than in H_2SO_4 solution alone. This is not due to an area increase of the kind that occurs when metallic zinc is deposited on Pt (see above) since the surface oxidation charge remains almost constant with or without Zn^{2+} ion present.

Hence, it seems that H that is otherwise not measured, because it is deposited only at potentials more negative than the potential of H_2 evolution, /viz. +0.07 V, E_H / is enabled to be deposited at more positive potentials in the presence of Zn^{2+} ion. Thus, more of a full monolayer of deposited H can be measured at potentials positive to that for a significant rate of H_2 evolution to arise, when Zn^{2+} is specifically adsorbed in the "double-layer" at Pt.

This result with Zn^{2+} on Pt raises interesting and important questions regarding the correctness of the initial assumption (mentioned on p. 45; see ref. 26) that the 210 $\mu C.cm^{-2}$ charge for H deposition and ionization at Pt corresponds to a 1:1 monolayer of H atoms on Pt atoms. The behaviour corresponding to Fig. 27, with a 26% increase in charge over the H ionization region, suggests that the real charge for a monolayer of H on Pt might be approximatel 263 $\mu C.cm^{-2}$.

The "zincified" platinum electrodes were also used in aq. formic acid. The resulting electro-oxidation characteristics for HCOOH were no different than those observed for pure platinum.

9. Role of Adsorbed Species that Inhibit the Poison Formation for FA Currents

In the formic acid oxidation at platinum, where the overall reaction equation is $HCOOH + 2Pt \longrightarrow 2PtH + 2H^+ + 2e + CO_2$, a side reaction occurs which produces a poison P and inhibits the course of the main reaction, as mentioned in the Introduction. The formation of this poison P, occurs by a slow reaction which proceeds more readily at potentials near those for H deposition. The maximum rate is attained around 0.2 V, E_H, although significant amounts of P may still be formed at 0.45 V, E_H, with sufficiently long holding times.

Co-adsorbed addition agents, such as acetonitrile, mercury or others, increase the FA_1 current for the oxidation of formic acid at Pt in an indirect way by diminishing the extent of formation of P but not apparently altering the course of the main reaction. It is found that if the catalyst poison, e.g. acetonitrile, is added before the poison P has been formed, i.e. below a potential of 0.2 V, E_H, only then does it increase the FA_1 peak current by adsorbing and blocking sites on the surface where the reaction producing the inhibiting species would otherwise occur. However, if it is added later in the potential sweep beyond the potential 0.2 V, E_H, the poison has already become formed and adsorbed, so that acetonitrile cannot then displace it. It appears that added competitive poisons must act by a "third-body" effect,[18*] interfering in the production of P by preventing the approach on the surface of whatever intermediates are required for its formation. It was earlier seen that P, amongst other possibilities, could be formic anhydride, stabilized by two-site adsorption, that arose from dimerization of two adsorbed -COOH species. Other suggestions that it is the species $\geqslant$COH, also formed as a primary intermediate in methanol oxidation, were made by Parsons and Capon[23].

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[*] See p.20 where the nature of the "third-body" effect is described.

10. Relation to Behaviour at Au-Pt Alloys, vis-a-vis Surface Geometries

The FA_1 faradaic current peak for formic acid oxidation which (as was mentioned in the previous section) can be modified by additives which change the quantity of P adsorbed on the surface, may also be increased in a somewhat similar way by using gold-platinum alloys. In the surface of these alloys, the presence of gold diminishes the tendency for the poison, P, to be formed and remain adsorbed on the surface. The FA_1 currents exhibit a volcano-shaped relation to overall composition of the alloys (Fig. 16a). However, it is of interest to relate the kinetic behaviour to the actual composition in the surface of the alloys. Thus, in terms of the actual %Pt on the surface, determined as described in Section 3, the FA_{1b} currents increase (Fig.16b) as the gold content increases up to an accessible limit of ~ 90% Au in the surface. On gold itself, of course, there is virtually zero FA_1 current due to the inability of Au to dissociatively chemisorb HCOOH as H and —COOH.

It appears that so long as Pt atoms are separated on the average more and more in the Au-Pt alloy surface, the FA_1 current calculated on a "per Pt atom" basis tends to increase. This is presumably due to progressive diminution of the tendency for inhibition by the P species to arise and lower the rate of the FA_1 process.

11. Comparison of FA_1 and FA_3 Current Behaviour

It was previously seen in Section 3 that the current for the FA_1 process shows (Fig.16a) a volcano-type relationship with respect to alloy composition having a maximum [for $i_p(FA_1)$]at 65% gold content in the surface of the alloy. The corresponding plot for the FA_3 process (Fig.17) displays a linear, inverse relationship to gold content: thus, as the gold content on the surface of the electrode increases, the peak currents for the FA_3 process decrease. Similar results were found by MacDougall:[18] acetonitrile increases $i_p(FA_1)$ by an order of 600% for acetonitrile concentrations of up to 5×10^{-2} M. On the other hand, the peak current for formic acid oxidation at ~ 0.9 V, E_H, i.e., in the potential region corresponding to the initial stages of surface oxidation of platinum, decreases with increasing concentration of CH_3CN. Processes occurring around 0.9 V, E_H, where the initial stages of surface oxidation of Pt arise, are usually associated with a reaction between the oxygen species and previously chemisorbed organic residues. It is therefore reasonable to assume that at ~ 0.9 V, E_H, the FA_3 peak current arises from reaction of chemisorbed species derived from formic acid with the initially deposited surface oxide species, PtOH, formed on platinum: $PtOH + Pt\text{-}COOH \rightarrow 2Pt + CO_2 + H_2O$.

Breiter[39] proposed that the current for the first anodic peak was due to oxidation of HCOOH to CO_2 on the small fraction of the surface which was not blocked by the adsorbed poison P. Oxidation of such an intermediate, as more positive potentials are reached in a sweep, uncovers active Pt sites on which further oxidation of HCOOH from the bulk can take place, thus causing the rise in current leading to the third anodic peak. It seems that the reason for the almost linear decrease of $i_p(FA_3)$ (Fig. 17) with increasing actual gold content in the surfaces of the alloys is due to the fact that the gold atoms on the surface decrease the extent of surface oxidation per cm^2, at a given potential at the alloy. It is seen from Fig. 17 that the $i_p(FA_3)$ will actually be independent of Au atom content if this current is expressed per Pt atom since the relation is linear with zero $i_p(FA_3)$ at 100% Au. Hence, $i_p(FA_3)$ for the alloy series depends only on the Pt atom content per cm^2 of the surface.

12. Is the Electro-Catalytic Behaviour of Pt Retained Atomically in Alloy Surfaces?

The catalytic activity of an alloy can vary in a complex manner with composition and in some cases the activity can be greater than that of the individual pure metal components from which the alloy is formed. Platinum, in the case of homogeneous Pt-Rh alloys[36] (Fig. 28) does not, however, retain its individual electrosorption characteristics with changing surface composition. The reductive desorption of oxygen from noble metal electrodes during a linear cathodic potential sweep gives rise to a current peak at a potential that is characteristic of the metal under investigation. The potential of this peak, which is related to the kinetics of the surface oxide reduction reactions $OHPt + H^+ + e \rightarrow Pt + H_2O$ or $OPt + 2H^+ + 2e \rightarrow Pt + H_2O$ (depending on prior anodic sweep potential) provides a useful parameter for comparing the chemisorption behaviour of alloy electrodes. The appearance of a single surface oxide reduction peak for these alloys is in contrast to the behaviour of heterogeneous Au-Pt alloys where oxide reduction peaks characteristic of both pure metals, platinum as well as gold, are observed, showing that for this system the two components retain their individual electrosorption properties in the alloy surfaces. In the case of Pt-Rh alloys, the chemisorption at one surface atom is evidently affected by the nature of neighbouring metal atoms.

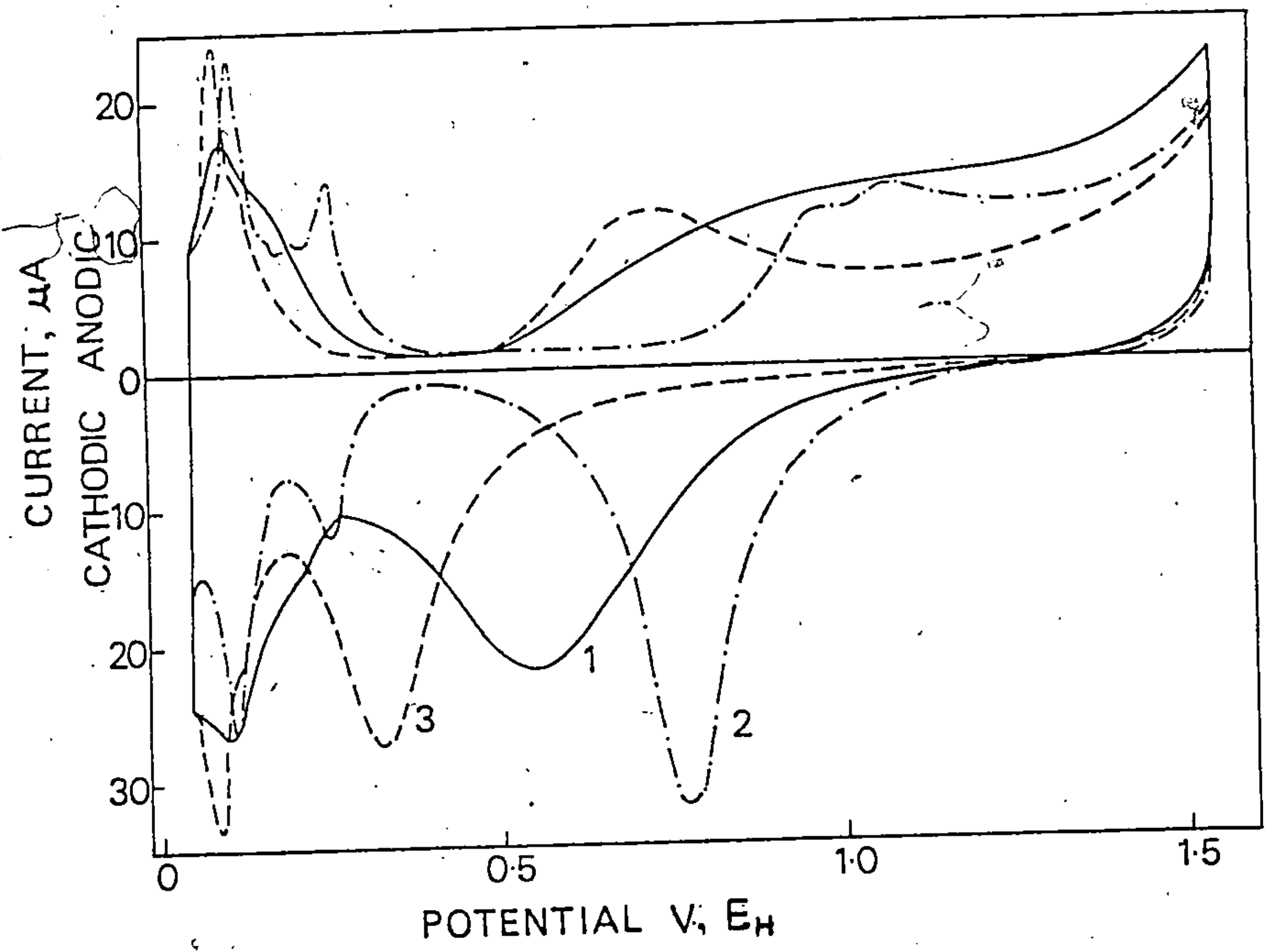

Fig. 28 Current potential curves for (1) Pt-Rh alloy with 1:1 surface composition; (2) Pt; (3) Rhodium electrodes in 1M H_2SO_4 at 25°C and sweep rate = 40 mV sec^{-1}. (from Rand and Woods, ref. 38)

This behaviour arises presumably because interaction between two neighbouring atoms is sufficient to cause the atoms of the two metals in the surface of a homogeneous noble metal alloy to exhibit similar adsorption characteristics. For the case of gold-platinum alloy electrodes, at which the electrosorption properties of the individual atomic components are evidently retained (at least for O-species), the constitutional diagram of the solid solutions formed exhibits a two-phase region of immiscibility, which is consistent with a weakness of interactions between the two metals.

For heterogeneous alloys, the surface atoms tend more to retain their individual chemical adsorption properties even when surrounded by different metal atoms according to the localized concept of Sachler et al.[35] on adsorption and catalysis.

CLAIMS TO ORIGINAL RESEARCH

The following claims are made to original research which has been described in this thesis:

(i) The presence of gold in a series of gold-platinum alloys was found to activate the first oxidation process in formic acid oxidation by diminishing the extent of formation of the "poison" species, P, which is known to be produced as a co-adsorbed reactant in formic acid oxidation.

(ii) A clear distinction was demonstrated between the behaviour of homogeneous and heterogeneous gold-platinum alloys as electrocatalysts for formic acid oxidation. The results show that the alloys with 20, 40, 60% Au are composed of two immiscible solid solutions and the alloy with 80% Au is composed of a single-phase solid solution.

(iii) A method was devised for calculation of the real surface areas of gold electrodes. This method is based on evaluation of the "double-layer capacity" and gave results similar, within an accuracy of 2%, to those obtained by a method due to Burshtein, based on evaluation of the extent of surface oxidation at 1.5 V, E_H.

(iv) Measurements have been made of the exact surface compositions of the gold-platinum alloy electrodes under the same conditions as those used in the electrochemical kinetic experiments. These results enable the composition - dependent currents for formic acid and methanol oxidation to be expressed per actual Pt atom of the electrode surface.

(v) Currents for formic acid oxidation, expressed in this way, are shown to increase in a linear way with Au content of the surface; otherwise the directly measured currents exhibit a volcano relation to bulk alloy composition. The variation of the currents per Pt atom with Au content of the alloys supports the "third-body" mechanism for activation in formic acid oxidation, originating from diminution of self-poisoning effects.

(vi) Time-effects in the oxidation of formic acid were studied in 1M HCOOH at 0.5 V, E_H. The results demonstrated that the gold-platinum alloy electrodes show a smaller rate of decline of current due to accumulation of auto-poisoning species than does Pt, and thus an increased activity in comparison with that of pure platinum surfaces.

(vii) The peak currents for the MA_3, MA_4, and MC processes in the methanol oxidation reaction at gold-platinum electrodes were all found to decrease with increasing gold content, indicating that gold atoms in the surface are not required for any enhancement of catalytic activity as they are for formic acid oxidation.

(viii) Results obtained with Zn^{2+} ion adsorbed at Pt suggest that these ions displace the underpotential deposition of H to more positive potentials. Then it is found that the real charge for deposition of a monolayer of H at Pt appears to be approximately 263μC cm^{-2} rather than the usually accepted value of 210μC cm^{-2}, the figure which has been used in various calculations in the present thesis and in much prior published work over the last 15 years.

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