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RECENT ADVANCES IN THE SCIENCES OF ELECTROCATALYSIS.(U)
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OFFICE OF NAVAL RESEARCH

CONTRACT N00014-75-C-0953

PROJECT NR 359-451

Technical Report No. 52

RECENT ADVANCES IN THE SCIENCE OF ELECTROCATALYSIS

by

Ernest Yeager

Prepared for Publication

in the

Journal of the Electrochemical Society

Acheson Medal Award Lecture

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Case Laboratories for Electrochemical Studies
and the Chemistry Department
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1 November 1980

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 52	2. GOVT ACCESSION NO. AD-A095095	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Recent Advances in the Science of Electrocatalysis,		5. TYPE OF REPORT & PERIOD COVERED Technical Report #52
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Ernest Yedger		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0953
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Chemistry and Case Laboratories for Electrochemical Studies, Case Western Reserve University, Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-451
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		12. REPORT DATE 1 November 1980
		13. NUMBER OF PAGES 54
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrocatalysis, optical techniques in electrochemistry, hydrogen electrode reactions, oxygen electrode reactions

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper was presented as the Acheson Award lecture at the national meeting of the Electrochemicla Society in October 1980 and surveys recent developments in the field of electrocatalysis, including work in the author's laboratory, most of which was carried out with the support of ONR. The first part surveys techniques for obtaining information concerning electrode surfaces and particularly species adsorbed on such surfaces. Special attention is focused on in-situ optical techniques (ultraviolet, visible, infrared, Raman) and

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S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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the use of ex-situ surface physics techniques, the latter in conjunction with electrochemical studies of single crystal electrode surfaces. The second part of the paper summarizes the present state of understanding of hydrogen and oxygen electrocatalysis.

Recent work at Case on electrosorbed hydrogen on platinum single crystal surfaces and macrocyclic catalysts for oxygen reduction is presented.

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RECENT ADVANCES IN THE SCIENCE OF ELECTROCATALYSIS

by

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I. INTRODUCTION

Electrochemistry is experiencing a renaissance. The meetings of The Electrochemical Society and its Journal provide ample evidence of this renaissance, which has been stimulated by the energy problem and the importance of electrochemistry conversion, and conservation. Equally important are indications that electrochemistry has reached a critical stage where especially rapid development of the science is likely to occur over the next decade.

Already early in this century, much of the thermodynamics of electrochemistry was reasonably well in place but electrochemical kinetics and electrocatalysis remained more an art than a science. Reproducibility in kinetic studies has been a particular problem but in recent years electrochemists have gained sufficient control over the various experimental factors, including impurity effects, to achieve reproducible results even with surface demanding reactions. Substantial theoretical developments have also occurred over the last two decades in the areas of electron and proton charge transfer at electrochemical interfaces. Further, the impact of various surface chemical physics techniques, both in-situ and ex-situ to the electrochemical environment, is starting to be felt in electrocatalysis studies.

Adsorption on the electrode surface plays a key role in electrocatalysis. Little information is available, however, concerning the chemical nature of the interactions of adsorbed species with the electrode and the adsorption

sites. This situation has been detrimental to the development of electrocatalysis as a science. There has been a general lack of good molecular level techniques for examining the chemical structure of electrochemical interfaces, analogous to the various spectroscopic techniques which have had such an impact on the physics and chemistry of bulk phases. In most instances electrochemical techniques provide a sensitive tool for the detection of electrosorption but lack the needed molecular level specificity. Even the charge on electrosorbed species cannot be determined electrochemically in most instances because of the difficulty of resolving what fraction of the externally provided charge is transferred to the adsorbed species rather than just residing on the metal surface and compensating the charge of the electrosorbed species and the remainder of the ionic double layer.

In this lecture I shall first assess some of the more promising in-situ and ex-situ techniques of a more or less non-traditional type for obtaining such information and then consider the state of our understanding of some important electrocatalytic systems.

II. IN-SITU TECHNIQUES FOR THE STUDY OF ELECTROCHEMICAL INTERFACES

Table 1 lists the majority of the presently used in-situ spectroscopic techniques for the study of electrochemical interfaces. Various windows exist for electromagnetic radiation in solvents such as water; i.e., for X-ray, UV-visible and, for very short path lengths, certain parts of the infrared. Consequently optical spectroscopy lends itself to in-situ studies (1). The majority of the UV-visible and infrared studies make use of intensity changes upon reflectance from the electrochemical interface in the external or internal attenuated total reflectance modes, the latter with transparent electrodes. With the external mode, both specular and

diffuse reflectance techniques have been used. With transparent electrode, transmission techniques have also been used. The optical changes attending the change of electrode potential and the adsorption of various species at mono- and submonolayer levels are small but still easily measured with modern signal detection-processing techniques. Ellipsometric spectroscopy (2-4), using automatic instrumentation (3), is a particularly powerful technique for obtaining information concerning the collective dielectric properties of the interface and adsorbed layers as a function of wavelength and potential.

The various ultraviolet-visible optical measurements have yielded substantial information concerning surface charge, adsorption isotherms, structural information for adsorbed molecules, the state of water in the compact double layer, structural transitions in underpotential deposited layers, surface roughness and the electronic properties of anodic films and passivation layers on metals. For the most part, however, these optical techniques have not made as great a fundamental contribution to the understanding of electrochemical interfaces and adsorption at such interfaces as some of us expected at the start of such work in the mid 1960's. In part this is because of limitations on the type of information which can be gained with only ultraviolet-visible spectroscopy. The impact of these measurements, however, has been lessened by the lack of quantitative theoretical treatments of the collective optical properties of the metal-electrolyte interface and adsorbed species to provide a quantitative frame work within which to interpret such optical measurements. Only with layers much thicker than monolayer dimensions [e.g., passivation layers on active metals (5)] is a simple three-layer optical model involving two bulk phases with an intermediate thin layer

adequate.

Vibrational data for adsorbed species can be very useful. In-situ infrared studies using internal reflectance have been carried out with semi-conductor transparent electrodes. It has been possible to detect the C-H stretched frequency for adsorbed layers of higher molecular weight molecules (6) using D_2O as the solvent to minimize solvent interference. With semiconductor electrodes of sufficient transparency in the infrared, however, most of the potential drop is in the space charge region in the electrode phase and relatively little information is gained concerning the adsorption process. Further, solvent absorption in the infrared imposes very severe restrictions.

Recently Bewick and Pons (7) at the University of Southampton have used external infrared reflectance spectroscopy with very thin electrolyte layers combined with a.c. electromodulation techniques to study the water layer adjacent to the interface. This approach is very promising although much care must be exercised to guard against artifacts in the measurements.

Particularly exciting developments have occurred over the past few years in the application of in-situ Raman spectroscopy to the study of electrochemical interfaces. Since the observation of unusually strong Raman signals for pyridine adsorbed on silver by Fleischmann, Hindra and McQuillan at Southampton (8,9) in the early 1970's, great interest has developed in Raman studies of adsorbed species on electrode surfaces. A large number of publications (10,11) have appeared, mostly concerned with experimental and theoretical studies of possible mechanisms for the extraordinarily large surface enhanced Raman signals observed with most adsorbed molecules on silver and, to a lesser extent, copper.

Several explanations have been offered for the surface enhancement; it is likely that more than one mechanism is involved. Although the Raman signals may only be observable with certain electrode surfaces, this technique is expected to prove of great importance to electrochemistry in providing much needed in-situ vibrational data. With adsorbed molecules exhibiting strong intrinsic resonance Raman, strong Raman signals can be obtained on other electrodes besides silver and copper (13-15). For example, in our laboratory, we have studied such species as paranitrosodimethyl aniline (14) and the transition metal phthalocyanines (15) adsorbed on platinum as well as silver. Further, Raman spectroscopy has been used in our laboratory to examine the passivation films on iron (16) as well as silver (17).

Aside from the implications of various photoelectrochemical processes for solar energy conversion, they afford interesting information concerning band bending in semiconductor electrodes, surface states and other electronic features of the interface of importance to electrocatalysis (11). Photoemission from metals into electrolytes also has been studied by electrochemists (see e.g. ref 18,19) but so far has not proven very useful for studies of adsorption and electrocatalysis.

Mössbauer spectroscopy has been applied to in-situ studies of various layers on electrode surfaces containing appropriate elements to serve as either emitters or absorbers e.g., iron, cobalt. From the Mössbauer spectra, under favorable conditions it is possible to gain insight into spin states and nearest neighbor interactions. Particularly interesting results have been obtained for electrochemical passivation layers on iron (20) and iron transition metal macrocyclic catalyst layers on electrode surfaces such as carbon (21,22).

When the potential across an electrochemical interface is a.c. modulated, both shear and compressional acoustical waves are generated. The shear waves result from the modulation of the a.c. interfacial tension and are detected in the solid electrode phase with a shear sensitive transducer attached to the back side of the electrode (23,24). The compressional waves are readily detected in the electrolyte phase with a hydrophone (25,26). With solid metal electrodes, these compressional waves are produced principally by the a.c. modulation of the volume of the ionic double layer -- particularly the compact double layer. With semiconductor electrodes, intrinsic and field induced piezoelectric properties may result in large compressional components in the electrolyte phase and both shear and compressional components in the solid electrode phase. Both the shear and compressional acousto-electrochemical effects are quite sensitive to adsorbed species at the electrode surface and can be used to follow the adsorption-desorption of such. Quantitative measurements of the compressional effect on metal electrodes should yield dV/dE (where V is the volume, E is the applied potential) and hence be of special interest in testing double layer models.

Electron spin resonance has been used to detect various free radicals in the electrolyte phase (27-29) and in principal can be used to examine radicals adsorbed on electrode surfaces by proper location and configuration of the electrode in the microwave cavity of the spectrometer.

Two techniques that appear promising for <u>in-situ</u> studies of electrochemical interfaces and particularly catalyst and passivation layers are extended X-ray absorption fine structure (EXAFS) and nuclear magnetic resonance. In both instances it will probably be necessary to use high

area electrodes such as dispersed ultra small metal particles on a high area carbon support or metal blacks. With the in-situ EXAFS, it is worthwhile to consider fluorescence yield as well as the more conventional absorption measurements. With the recent developments in NMR solids, using magic angle spinning and various spin decoupling techniques, it may be possible to obtain the fine line NMR spectra of adsorbed species even at the monolayer level using very high surface area dispersed electrocatalysts.

III. EX-SITU TECHNIQUES

The electron and ion spectroscopies listed in Table II can be used to characterize electrode surfaces including single crystal systems before and after electrochemical measurements. The critical question is whether the electrode surface can be transferred from the ultra high vacuum environment to the electrochemical environment and vice versa without substantial restructuring of the surface as well as chemical changes and contamination. Several research groups (30-35) have carried out electrochemical measurements such as hydrogen electrosorption and lead underpotential electrodeposition on noble metal single crystal surfaces which have been prepared and characterized with LEED or RHEAD in ultrahigh vacuum. Special precautions have been used to minimize the possibility of restructuring during the transfer into the electrolyte. The approach used in our laboratory for accomplishing such is as follows (30,31,36). Clean single crystal platinum or gold surface of known orientation are prepared by repeated sputtering with argon and high temperature annealing in an ultra high vacuum chamber on the right in Figure 1. The surfaces are examined with LEED and Auger spectroscopy in ultra high vacuum (10^{-10}-10^{-11} Torr) and then transferred into a second vacuum chamber on the left in Figure 1, also at $\sim 10^{-10}$ to 10^{-11} Torr without removal from the vacuum environment by means of a magnetically operated transfer wand. Ultrapure argon is then admitted to this vacuum container. A second parallel electrode surface with a drop of electrolyte on it is next brought close to the single crystal surface to form a thin layer electrochemical cell with a gap of $\sim 10^{-3}$cm. This second electrode is

chosen so as to serve as a combined counter and reference electrode. The use of the thin-layer cell technique results in a high area-to-volume of electrolyte ratio and hence much less sensitivity of the single crystal surface to impurities in the electrolyte (e.g., 10^{-6} M of a typical ionic impurity corresponds to 10^{-3} of a monolayer even if all adsorbed on the electrode surface). Following the electrochemical measurements, the electrodes are separated. With an electrolyte such as aqueous dilute HF, the electrolyte can be completely vaporized at room temperature as the argon is pumped out. The single crystal electrode is then re-transferred into the LEED-Auger chamber and the surface is re-examined.

This system has been used at Case with some success for studies of underpotential electrodeposition, hydrogen electrosorption, and anodic film formation on platinum and gold single crystal surfaces. The electrochemical behavior is highly dependent on the particular surface crystal plane. Such information is of critical importance to the understanding of electrocatalysis on a microscopic level.

IV. COMPLEMENTARY EX-SITU EXPERIMENTS

The electrochemical interface cannot be simulated even approximately with solid-vacuum interfaces. Nonetheless, studies of the adsorption of water, hydrogen, oxygen, carbon monoxide, various organic molecules and other species at metal and semiconductor vacuum interfaces can provide information of help in understanding electrochemical interfaces. The interaction of water with such metals as gold and platinum is relatively weak at electrochemical interfaces, and hence, some similarities are expected between the behavior of various adsorbed neutral species such as hydrogen atoms and CO on these metals in the electrochemical and vacuum

environments. Such comparisons are more likely to be valid when the electrochemical interface is near the potential of zero charge and the potential gradient at the interface is small.

Particular types of experimental and theoretical information which can prove useful to the electrochemist include the energetics of the adsorption process, types of adsorption sites, configuration, electronic and vibrational properties of the adsorbed species and chemical modifications of the adsorbate attending the adsorption process. Most electrochemists concerned with various electrocatalysis processes already pay considerable attention to solid-gas catalytic literature and this trend is likely to increase.

V. SPECIFIC ELECTROCATALYTIC PROCESSES

Some typical electrocatalytic processes are listed in Table III. By far the most research effort has been applied to the hydrogen and oxygen electrode reactions. The most exciting development in applied electrocatalysis in recent years, however, has been the development of the dimensionally stable anode as a replacement for the carbon electrode for the generation of chlorine in the chlor-alkali industry. The catalyst for this reaction is ruthenium oxide, perhaps with additives, on a titanium substrate. In contrast to carbon anodes , the RuO_x/Ti electrode is not attacked at an appreciable rate and is dimensionally stable over years. Almost all of the Cl_2 produced electrochemically in the United States is generated with this electrode with large savings in energy because of the very low overpotential.

Our laboratory at Case has directed much attention to the hydrogen and oxygen electrode reactions and I shall emphasize these two areas of

electrocatalysis in the remainder of this lecture.

A. The Hydrogen Electrode Reaction

Hydrogen generation on various electrode surfaces is generally considered to involve the following steps:

I. Discharge: $H^+ + e^- \rightleftharpoons H_{ads}$ (1)

II. Recombination: $2\ H_{ads} \rightleftharpoons H_2$ (2)

III. Ion-plus-atom: $H_{ads} + H^+ \rightleftharpoons (H\text{-}H)^+_{ads}$ (3)

$(H\text{-}H)^+_{ads} \xrightarrow{e^-} H_2$ (3a)

In recent years some general insight has been achieved into the relationship of hydrogen electrode kinetics to hydrogen adsorption energies. For a given step the exchange current density is related to the standard free energy of adsorption of the particular type of adsorbed hydrogen involved in this step ($\Delta G°$). This dependence is represented by the familiar volcano-shaped curves (37-39) shown in Figure 2 according to Parsons (37) for the three reaction steps just listed. The flat portion of the curves corresponds to the Temkin region of the adsorption isotherm. In constructing the volcano curves, the cathodic and anodic transfer coefficients have been taken to be 1/2. This may be open to question for Reactions II and III. Arguments have been put forth (40), based on Bond's model of non-activated adsorption of hydrogen (type C) (41), that the free energy of activation for Reaction II approaches the free energy change for this step on some metals. Further, it is likely that the activated state $(H\text{-}H)^+$ for Reaction III involves the direct interaction of both hydrogens with the surface rather than an end-on interaction of an H-H intermediate.

Consequently, the transfer coefficient α for Reaction III may also approach unity rather than 1/2. Under such circumstances, the volcano curves take on the form (40) indicated in Figure 3, using a combination of Breiter's data (42) and Ludwig's data (40) as a few calibration points.

The experimentally observed behavior of hydrogen overpotential on various metals correlates reasonably well with Figure 3. Metals such as Hg, Tl, Zn, Cd and Pb, which adsorb hydrogen only weakly (large positive values of $\Delta G°$), have low values for the apparent exchange current density, Tafel slopes (dE/d log i) of -2.30 (2 RT/F), and Reaction I rate controlling. Metals such as Pt and the Pt family with $\Delta G°$ values close to 0 have high apparent exchange current densities and kinetics which indicate that Reaction II follows Reaction I and is rate controlling. Metals such as Mo, Ta and W, which strongly adsorb hydrogen and have very negative values of $\Delta G°$, again have low exchange current densities and kinetics which indicate Reaction III follows Reaction I.

An important implication of the volcano curves is that it is unlikely a catalyst will be found with an overall exchange current density higher than that for Pt since this metal has $\Delta G°$ close to 0. The main thrust of applied research on hydrogen electrocatalysts should be the finding of catalysts with higher exchange currents per unit cost and resistance to poisoning and to loss of area when used in high area forms.

Various authors have examined the discharge step I theoretically (for a review, see ref. 44). Bockris, Matthews and Srinivasan (45,46) have proposed the model in Figure 4 in which the proton is transferred over a barrier representing the intersection of two Morse curves. The vertical transition ΔE_0 corresponds to the transfer of an electron from

the Fermi level of the metal to the H_3O^+ ion with no change in the reaction coordinate. Radiationless electron transfer by tunneling occurs at the intersection of the two Morse curves, from the metal to the vibrationally excited H_3O^+. The various electron energy levels in the metal correspond to translation vertically of the Morse curve for the initial state. The principal levels contributing to the discharge current are those within kT of the Fermi level. This model yields reasonable predictions for the kinetics of the discharge step.

Various electrochemists have considered proton tunneling through the potential energy barrier rather than transmission over the barrier. These include Bockris and his coworkers (45,46); Christov (47-49); Conway and Salomon (50,51); Dogonadze, Kuznetsov and Levich (52-54); Kharkats and Ulstrup (55). All of the treatments involve questionable assumptions. The extent to which proton tunneling is involved in the discharge process is very sensitive to the barrier thickness as well as height. Isotopic studies of hydrogen discharge on mercury, however, do provide evidence that proton tunneling is involved (21,22).

Hydrogen electrode kinetics are of special interest on Pt because of its high catalytic activity. Various workers have found a Tafel slope for the cathodic branch of -2.30(RT/2F) or -30 mV/decade and high exchange current densities (e.g., $\gtrsim 10^{-2} A/cm^2$). Two explanations have been advanced for this behavior. Schuldiner (56) and Bockris et al. (57) have used a mechanism involving Reactions I and II (discharge followed by atomic recombination) with Reaction II rate controlling. Breiter has proposed pure diffusion control involving dissolved H_2 (58). On the basis of ultrasonic and rotating disk-ring measurements, Yeager et al. (43,59,61) have proposed

that the cathodic process is controlled by combined H_2 diffusion and recombination kinetics. Parsons (37) and Krishtalik (60) have offered theoretical arguments for desorption by Reaction II as rate controlling.

The anodic oxidation of H_2 exhibits first order dependence on H_2 concentration, and most workers consider the dissociative-adsorption of H_2 (the reverse of the recombination of Reaction II) as rate controlling. Here again, however, the high exchange current density makes it difficult to examine the kinetics without transport of dissolved H_2 to the electrode surface being the predominant control, even with the rotating disk electrode technique, particularly with Pt electrodes which have relatively high area, and hence high activity, as a result of repeated cycling to anodic potentials prior to the H_2 oxidation measurements. The current-potential data from rotating disk data are very well fitted with equations involving combined kinetic and molecular H_2 diffusion control with the atomic recombination step rate controlling. With Langmuir behavior, the current potential data for the anodic and cathodic branches is

$$\ln X = -\frac{2F\eta}{RT} + \ln X_o \tag{4}$$

$$X = i/(1-\exp\frac{2F\eta}{RT}) \tag{4a}$$

$$\frac{1}{X_o} = \frac{1}{i_o} + \frac{1}{i_d} = \frac{1}{i_o} + \frac{1}{B\sqrt{\omega}} \tag{5}$$

where η is the overpotential, i_d is the anodic limiting current density for H_2 transport, i_o is the exchange current density, ω is the rotation rate, B is a constant dependence on the H_2 diffusion coefficient and concentration, and the other symbols have their usual meaning. Equation (5) has been tested for Pt by Ludwig et al. (43) using the rotating disk data and fits the

data quite well (see Figure 5). The slope is essentially -2.30(RT/2F) over seven decades. The rotation rate dependence of the function X_o indicates that i_o is of the same order as i_d under most circumstances.

A problem associated with H_2 formation with the kinetics controlled by Reaction II is that the Tafel linearity with a slope of -2.30(RT/2F) is to be expected only with low H(ads) coverage. On the other hand, various electrochemical measurements, including impedance (66), linear sweep voltammetry (63,64) and charging curves (66,67) indicate that total H(ads) coverage is already close to unity at the reversible potential. This problem can be resolved by assuming that two types of H(ads) are involved in the overall electrode process and that the adsorbed hydrogen involved in Reaction II is at low coverage, as suggested by Schuldiner (62).

The question remains open as to what type of adsorbed hydrogen is involved in the desorption Reaction II on platinum. It is unlikely that the lower coverage H involved in this step corresponds to any of the hydrogen peaks observed by linear sweep voltammetry and other chemical techniques on Pt. Nonetheless, it will be helpful to understand the various factors contributing to up to several hydrogen peaks observed in the voltammetry curves (63). Figure 6 indicates some of the peaks found for Pt in 0.1 M HF and the effects of adding H_2SO_4 (64). Various explanations have been proposed for the several peaks including different adsorption sites on a given single crystal surface, a distribution of crystallographic surfaces, induced heterogeneity associated with hydrogen adsorption itself and anion adsorption which induces heterogeneity by blocking sites to varying degrees and perturbing adjacent sites. The pronounced dependence of the hydrogen electrosorption on the type and concentration of anion (Figure 6) indicates

that hydrogen adsorption-desorption are coupled to anion desorption-adsorption.

In an attempt to resolve this problem, various electrochemists have examined hydrogen electrosorption on single crystal Pt. Will (65) examined the low index planes (100), (110) and (111) and found the same two major peaks on these three orientations although the relative heights depended on the crystal orientation. The single-crystal Pt electrodes studied by Will probably did not expose a single crystallographic surface. The distribution of crystallographic surface planes depends on the overall orientation and the extent to which the surface has been cycled to anodic potentials. Will arrived at the conclusion that the strongly adsorbed hydrogen peak corresponding to IV, IV' in Figure 6 is on the(100) plane and the weakly adsorbed peaks I, I' is on the (110) plane. Rather analogous results have been reported by Bronel et al. (68) for the (100) and (111) Pt surfaces. These workers used electron microscopy to establish that the surfaces were facet-free. Kinoshita and Stonehart (69) have examined hydrogen adsorption on dispersed Pt as a function of crystallite size and found a dependence which they interpret as further evidence that the multiple peaks result from different surface crystallographic structures.

In contrast, Bagotzky et al. (70) and Conway et al. (63) have concluded from their single crystal Pt studies that there is little difference in the hydrogen adsorption on the (100) (110) and (111) planes. Conway et al. (63) attributed the multiple peaks principally to induced heterogeneity arising from collective long range electronic interactions.

The probability is high in all of the single crystal studies just cited that the surface prevailing during the electrochemical measurements

does not correspond to a single crystal plane. Even if the Pt crystal has only one plane predominant before the electrosorption measurements, these workers generally cycled their electrodes to anodic potentials in the anodic film region to oxidize or desorb interferring surface contaminants and this procedure is likely to cause restructuring.

Recently several groups have attempted to devise techniques which permit the introduction of a single crystal surface of predominantly one plane and free of impurities into an electrochemical environment with a minimum possibility of restructuring and contamination. In the USA these include A. Hubbard (71,72) at the University of California at Santa Barbara, J.A. Joebstl (73,74) at Fort Belvoir, P. Ross (75,76) at the Lawrence Berkeley Laboratories and our group (30,31,77) at Case Western Reserve University. Each group has turned its attention to the (100), (110) and (111) planes of Pt and first established that the surface is predominantly one plane using low energy electron diffraction (LEED) and free of surface impurities down to a few percent of a monolayer using Auger electron spectroscopy.

The key features of the techniques used in our laboratory by O'Grady et al. (30,31,77) with the equipment in Fig. 1 are vacuum transfer; thin-layer electrochemical cell techniques to avoid contamination; and introduction of the Pt single crystal surfaces into the electrolyte at controlled potentials in the hydrogen adsorption region. In the cyclic voltammetry studies of hydrogen electrosorption, the potential range is restricted to +0.05 to 0.50 V vs. RHE to reduce any possible restructuring. The voltammetry curves on the single crystal Pt surfaces retract with repeated cycling, starting with the very first sweep. If the voltage sweep is

extended into the anodic film formation region to ≥ 1.4 V vs. RHE, the hydrogen adsorption region changes significantly with new peaks appearing or very minor peaks becoming major peaks, depending on the original surface. This is probably the result of restructing although the possibility exists that oxygen has been irreversibly adsorbed into sites within the surface layer.

On the (100) Pt surface, Hubbard et al. (72), Ross (75,76) and our group (30,31) find one predominant peak (Fig. 7) corresponding to the strongly adsorbed hydrogen peak on polycrystalline Pt in acid solutions. The LEED pattern for the Pt (100) indicates a 5 x 20 overlayer. This surface probably reverts to (1x1) in contract with the electrolyte. On the (111) surface, our group finds only a minor peak corresponding to weakly adsorbed hydrogen while Ross and Hubbard et al. report a major peak. The source of this discrepancy is not fully clear but may be caused by the cycling of the electrode to anodic potentials in the case of Ross's work and possibly also that of Hubbard et al. Alternatively our Pt (111) surface may have some of the sites blocked by an impurity such as carbon.

With the sulfuric acid electrolyte, it was not possible to volatilize the residual electrolyte off of the single crystal surface without encountering an oxidizing range of sulfuric acid concentrations. More recently, Arthur Homa, a graduate student in my group, has repeated these studies with 0.1 M HF as the electrolyte. This acid is completely volatilizable and does not specifically adsorb. Thus it has been possible to examine the LEED patterns and Auger spectrum following the electrochemical measurements. The post electrochemical LEED patterns are usually of reasonably good quality with the same symmetry as for the original surfaces. Small

amounts of carbon, up to 10%, are usually found with the Auger examination. This carbon is believed to originate from CO released from ion pumps during the pumping out of the ultra pure argon support gas following the electrochemical measurements and not to have been present during these measurements.

The voltammetry results in the 0.1 M HF are very similar to those in the 0.05 M H_2SO_4 on the (111) and (110) (1x2) surfaces with only one H adsorption peak on each surface and the H coverage much lower than a monolayer. The (100)-(5x20) surface also shows only one principal peak but a sharp cathodic spike appears in the anodic sweep (Fig. 8). This spike remains to be explained but may be caused by surface restructuring. Repeated cycling of the three low index surfaces to potentials well in the anodic film region produces large increments in the peaks on these low index surfaces, disappearance of the cathodic spike on the (100) surface and voltammetry curves resembling those of Ross and the Hubbard group. We do not believe that these large changes are the result of the stripping of a minor carbon impurity but rather are related to some special role of oxygen in the hydrogen adsorption process. Rather similar results with cycling for polycrystalline platinum treated in high vacuum have been reported by the Soviet Academy Institute of Electrochemistry in Moscow (78).

Note is taken of the very unusual results for hydrogen voltammetry curves on Pt (111) found by J. Clavilier et al. (79,80) and described by Roger Parsons in his Palladium Award address before this Society. This strange behavior is difficult to explain either as the true situation or as an artifact.

In perspective, it appears that the question of hydrogen adsorption on

single crystal Pt surfaces is still not a settled issue experimentally. Similar anomalous results for hydrogen adsorption on Pt single crystal surfaces are also to be found in the solid-gas phase literature.

B. The Oxygen Electrode

The oxygen electrode reactions are even less well understood than for the hydrogen electrode. The pronounced irreversibility of the oxygen electrode reactions at moderate temperatures has complicated mechanistic studies. The exchange current densities for the oxygen electrode are very low -- typically 10^{-10} to 10^{-11} A/cm^2 on an effective catalytic surface such as platinum at room temperature. Consequently, the current densities near the reversible potential are generally too low to permit measurements under conditions where the kinetics are sensitive to the reverse as well as forward reactions. Further, the experimentally accessible portions of the cathodic and anodic branches of the polarization curves are sufficiently separated in potential that the surface conditions differ very substantially. Therefore, the cathodic and anodic processes under these conditions are probably not the reverse of each other. To complicate the situation further, the oxygen electrode reactions may proceed through a large number of pathways. This explains why the mechanisms of O_2 generation and reduction are still not fully understood even on platinum, the most extensively used and most studied O_2 electroreduction catalyst. I shall address only the question of the catalysis of the O_2 reduction reactions:

Oxygen reduction is usually considered to proceed by two pathways:

1. <u>The peroxide pathway (the series process)</u>:

$$\begin{array}{ccc} HOH + O_2 & \xrightarrow{2e^-} & HO_2^-(ads) + OH^- \\ & \searrow^{2e^-} & \rightleftarrows \\ & & HO_2^- + OH^- \end{array} \qquad (6)$$

The peroxide is then either electroreduced further to OH^- or catalytically decomposed; i.e.,

a. <u>peroxide reduction</u>

$$\begin{array}{ccc} HOH + HO_2^- & \xrightarrow{2e^-} & \\ \rightleftarrows & & \\ HOH + HO_2^-(ads) & \xrightarrow{2e^-} & 3\ OH^- \end{array} \qquad (7)$$

b. <u>peroxide catalytic decomposition</u>

$$\begin{array}{ccc} 2\ HO_2^- & \longrightarrow & \\ \rightleftarrows & & \\ 2\ HO_2^-(ads) & \longrightarrow & 2\ OH^- + O_2 \end{array} \qquad (8)$$

The overall reaction is the 4-electron reduction reaction

$$O_2 + 2\ H_2O + 4e^- \longrightarrow 4\ OH^- \qquad (9)$$

regardless of whether the peroxide elimination occurs via reaction 7 or 8 since the O_2 resulting from reaction 8 is recycled through reaction 6.

2. <u>The direct 4-electron pathway</u>:

This pathway involves a series of steps in which O_2 is reduced to OH^- or water without hydrogen peroxide being produced in the solution phase. This does not mean that the reduction process does not involve an adsorbed peroxide intermediate but rather than the reduction does not involve any adsorbed intermediate which leads to appreciable peroxide in the solution phase. When both pathways are operating on a given electrode surface, the reduction is referred to as involving parallel mechanisms.

The distinction between these two pathways mechanistically can be quite diffuse since the question of whether a peroxide adsorbed intermediate desorbs or not can depend on various impurities in the electrolyte as well

as electrode potential and temperature. An adsorbed peroxide state is very likely involved in the direct 4-electron pathway as well as the peroxide pathway. The classification of the pathway as "direct 4-electron" then may depend on whether the peroxide desorption proceeds to a significant extent. This may depend on the type of site. Two sets of sites may each support the reaction through essentially the same surface reaction pathway but differ in the extent to which the peroxide desorbs from each. If the desorption is very slow or thermodynamically unfavorable from one set of sites but not another, the O_2 reduction will proceed by the so called "parallel" pathways.

Illustrations of catalysts on which the peroxide pathway is clearly predominant include carbon, graphite and gold in alkaline electrolytes while the direct 4-electron pathway is predominant on clean platinum surfaces and also certain transition metal macrocyclics. In the presence of impurities peroxide pathway a can become predominant even on platinum.

Under some circumstances it is possible that the superoxide species $O_2^{\cdot -}$ may be formed in the outer Helmholtz plane by outer sphere electron transfer. This ion is formed as a reasonably stable entity during O_2 reduction in aprotic solvents (see e.g., ref. 81-84) and probably in carbonate melts (85). The superoxide ion also has been proposed to be formed in aqueous solutions on Hg (85,86), and amalgamated gold (87) and carbon paste (88) cathodes in the presence of surface active agents. In the absence of adsorbed organic species, however, it does not appear in alkaline solutions that an $O_2^{\cdot -}$ species in the solution phase contributes significantly to the observed current (89).

C. The Specific Adsorption of O_2 Molecules

The search for effective 4-electron catalysts is guided by the models in Fig. 9 for the interaction of O_2 and related oxygen species with adsorption sites. O_2 reduction in aqueous solutions requires a strong interaction with the electrode surface for the reaction to proceed at a reasonable rate. Three types of interactions have been proposed. Partial charge transfer is probably involved with each of these models. The Griffiths model(112) involves a lateral interaction of the π-orbitals of the O_2 interacting with empty d_{z^2} orbitals of a transition element, ion or metal atom with back bonding from at least partially filled d_{xz} orbitals of the transition element to the π^* orbitals of the O_2. A strong metal-to-oxygen interaction results in a weakening of the O-O bond and an increment in the length of this bond. Sufficiently strong interaction of this type may lead to the dissociative adsorption of O_2 with probably simultaneous proton addition and valency change of the transition element in the manner represented by Pathway I in Fig. 9 followed by reduction of the $M(OH)_2$ to regenerate the catalyst site. Sandstedé et al. (91,92) have attempted to explain oxygen reduction with square pyramidal Co(II), Fe(II) and Fe(III) complexes as well as on the thiospinels on the basis of such π bonding.

With most transition metal catalysts, the most probably structure for O_2 adsorption is the Pauling model (93) in which the π^* orbitals of O_2 interact with d_{z^2} orbitals of the transition metal. The square pyramidal complexes of Fe(II) and Co(II), which have good activity for O_2 reduction in acid solutions, appear to involve such an end-on interaction on the basis of esr and other evidence (94). This adsorption of O_2 is expected to be accompanied by at least a partial charge transfer to yield a superoxide

and then peroxide state, as represented by Pathway II in Fig. 9. The adsorption of the O_2 on the square pyramidal complexes of Fe(II) and Co(II) may lead directly to the superoxide state. With somewhat similar oxyhemoglobin complexes of iron, various workers have proposed that O_2 binding to the iron involves O_2^- or $O_2^=$ states with Fe in the III valent state (95-97). The change in valency state of the transition metal coupled with the change in O_2 oxidation state during formation of the O_2 adduct corresponds in principal to the redox electrocatalyst concept proposed by Beck et al. (98,99).

The further reduction of the O_2 beyond the peroxide state requires rupture of the O-O bond. Such can occur in Pathway IIB through the formation of $O^{\bar{\cdot}}$ or $HO\cdot$ free radicals in solution or the simultaneous reduction bond cleavage (electrochemical desorption) to yield H_2O or OH^-. Neither of these processes are likely to be sufficiently fast at practical operating potentials for O_2 cathodes. The free energies of formation of the $O^{\bar{\cdot}}$ and $HO\cdot$ free radicals in solution are just too high.

Pathway III in Fig. 9 provides an alternate means for bringing about rupture of the O-O bond through the formation of an O-O bridge. Such a mechanism may come into play with the proper surface spacing of transition metal atoms or ions in a metal, oxide, or thiospinel or in a bimetal complex such as a macrocycle. The formation of the bridge species also requires that the two metal species have partially filled d orbitals to participate in bonding with the π^* orbitals of the O_2. Bimetal macrocyclic complexes with the proper M-M distance have been synthesized (e.g., see ref. 100-103) and appear to occur naturally in hemeythrin.

For any of the pathways in Fig. 9, considerable questions exist as to

the reversibility of the O_2 adsorption step at the rather high rates involved with practical O_2 cathodes. For O_2 to bond to M^z will generally require the replacement of a water molecule or anion of the electrolyte -- a situation which would normally be expected to be unfavorable to O_2 unless the O_2 adduct has a pronounced dipolar character ($M^{z+1}O\text{-}O^-$) (104,105).

Of the various possibilities for catalysts which promote the 4-electron reduction, the transition metal macrocyclics appear particularly promising. In the work in our laboratory these are adsorptively attached to high area conducting substrates, as monolayers. The water soluble iron tetrasulfonated phthalocyanine (Fe-TSPc) (Fig. 10) strongly adsorbs on graphite and at monolayer levels has high activity for the overall 4-electron reduction of O_2 in neutral and dilute alkaline electrolytes. The catalytic activity per unit surface area is higher than for platinum. Rotating disk-ring electrode measurements indicate no detectable peroxide over a substantial potential range (106). The principal problem is the stability of the iron macrocyclic in concentrated caustic and acid solutions. In contrast to the Fe-TSPc, the adsorbed Co-TSPc catalyzes the reduction of O_2 to the peroxide (106,107).

The interaction of the adsorbed Co-TSPc and Fe-TSPc with the substrate electrode surface (graphite, Pt and Au) has been studied using visible reflectance spectroscopy (108) (see Fig. 11). The reflectance spectra of the adsorbed Fe-TSPc and Co-TSPc monolayers undergo substantial changes at constant potential with the introduction of O_2 into the electrolyte. We believe this is caused by the formation of an O_2 adduct with the adsorbed species. The Raman spectra of the Co-TSPc (Fig. 12) has also been obtained with this complex adsorbed on silver, which provides a large surface en-

hancement of the Raman signal (15). Further work is needed to interpret the Raman spectra and their potential dependence. On the basis of the strong adsorption and the Raman data, we believe that the Co-TSPc is adsorbed on the silver as shown by model C in Fig. 13 with one of the Co-TSPc units in the O_2 bridge dimer interacting directly with the metal substrate. We do not yet have Raman data for the Fe-TSPc but suspect that the adsorption may be in a similar configuration. Dimeric -O-O- complexes have been proposed in aqueous solutions for both the Fe-TSPc and Co-TSPc, principally on the basis of the UV-visible absorption spectra. The -O-O- bridged complex would be a likely candidate in the case of the adsorbed Fe-TSPc to explain the 4-electron reduction. The Co-TSPc apparently also forms such a bridge but because of its redox properties or some other factors, does not undergo reduction via a 4-electron pathway (107).

Collman, Anson and their coworkers (109) have recently synthesized covalently linked face-to-face dicobalt prophyrin dimers with the proper spacing to form a Co-O-O-Co bridge. With relatively thick layers of this complex graphite, rotating disk-ring electrode measurements also indicate a 4-electron reduction in acid electrolytes, verifying that the bridged complex can promote the overall 4-electron reduction. The complexes of Collman et al., however, are expensive to synthesize with many steps while the approach involving adsorbed solubilized complexes is not.

While these are encouraging fundamental developments in O_2 electrocatalysis, it is difficult to translate them into practical electrodes, principally because of catalyst stability problems. Research is in progress at Case to establish whether other macrocyclic catalysts affording M-O-O-M bridging may have greater stability.

ACKNOWLEDGEMENT: The research sited in this address in the awardee's laboratory in the field of electrocatalysis has been carried out by a number of former and present graduate and postdoctoral students, whose names in most instances are in the cited publications. Most of the credit for this work belongs to them.

The Office of Naval Research has supported the awardee's research in the field of electrocatalysis continuously since 1952 and is gratefully acknowledged. The awardee also is pleased to acknowledge support for the research on O_2 electrocatalysis in more recent years from the U.S. Department of Energy, the Electric Power Research Institute, NASA and several companies including Diamond Shamrock, General Motors, Union Carbide and the International Nickel Company.

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TABLE 1. Non-traditional Techniques for the Study of Electrochemical Interfaces and Adsorption at Such Interfaces

Presently used techniques

1. Optical
   a. ultraviolet-visible and infrared spectroscopy
      - specular reflectance (external, internal)
      - diffuse reflectance
      - transmission through optically transparent electrodes
      - ellipsometry - as a spectroscopic tool

   b. Raman spectroscopy

   c. photoassisted processes, including photoemission

2. Mössbauer spectroscopy

3. acoustoelectrochemical techniques

4. electron spin resonance

Promising techniques

1. EXAFS

2. NMR
   - broadline
   - high resolution

TABLE II. Ex-situ Electron and Ion Techniques for the Study of Electrochemical Interfaces

Ex-situ

Electron physics

- X-ray photoelectron spectroscopy (XPS)
- Ultraviolet photoelectron spectroscopy (UPS)
- Auger spectroscopy
- Electron eneergy loss spectroscopy
- Low energy electron diffraction (LEED)
- Reflection high energy electron diffraction (RHEED)
- Inelastic electron tunneling
- Transmission electron microscopy - diffraction

Ion

- Ion scattering spectroscopy
- Secondary ion mass spectroscopy

TABLE III. Typical Electrocatalytic Reactions

1. The hydrogen electrode reaction

$$H_2 \rightleftharpoons 2\ H^+ + 2\ e^-$$

2. The oxygen electrode reaction

$$O_2 + H_2O + 4\ e^- \rightleftharpoons 4\ OH^-$$

3. Chlorine generation

$$2\ Cl^- \rightleftharpoons Cl_2 + 2\ e^-$$

4. Organic oxidations

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6\ H^+ + 6\ e^-$$

$$C_3H_8 + 6\ H_2O \rightleftharpoons 3\ CO_2 + 20\ H^+ + 20\ e^-$$

5. Organic synthetic reactions

Kolbe reaction: $R\text{-}CO_2^- \longrightarrow 2\ CO_2 + RR + 2\ e^-$

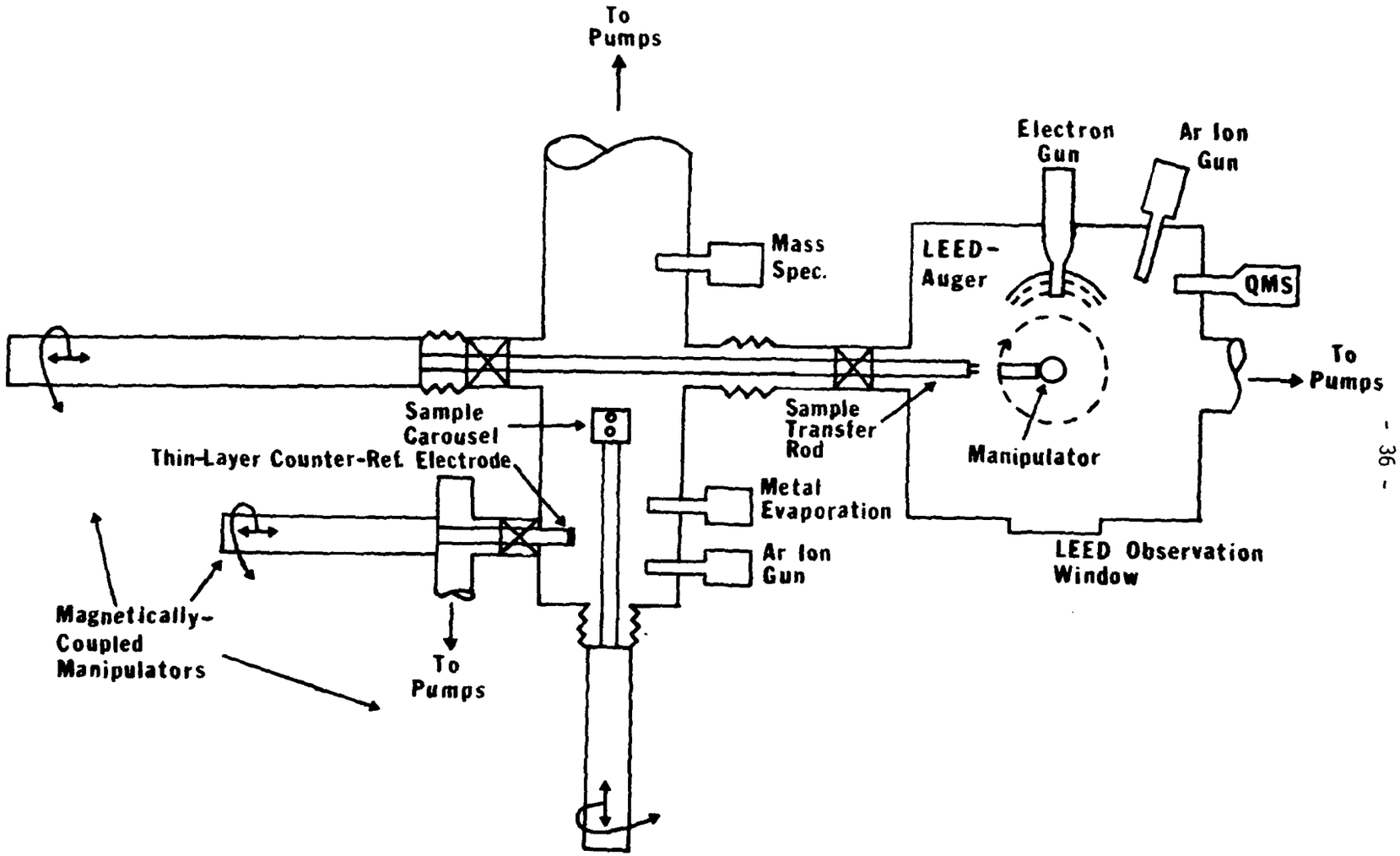

FIG. 1. LEED-AUGER-THIN LAYER ELECTROCHEMICAL CELL SYSTEM WITH SPECIAL TRANSFER SYSTEM (36).

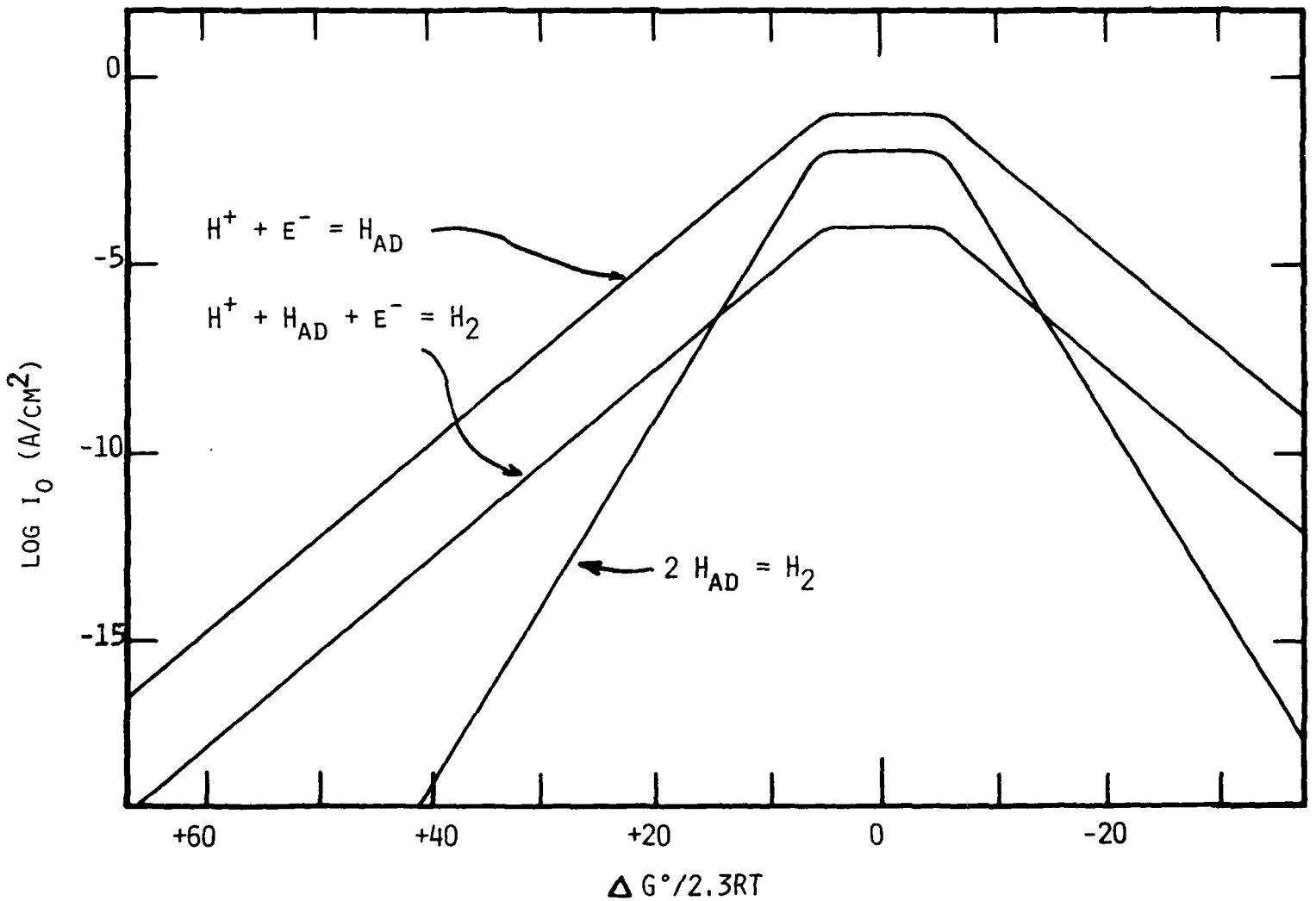

Fig. 2. Volcano curves for the exchange current densities of the hydrogen electrode component steps vs. the standard free energy of adsorption of hydrogen (39). Transfer coefficient for each process: $\alpha = 1/2$.

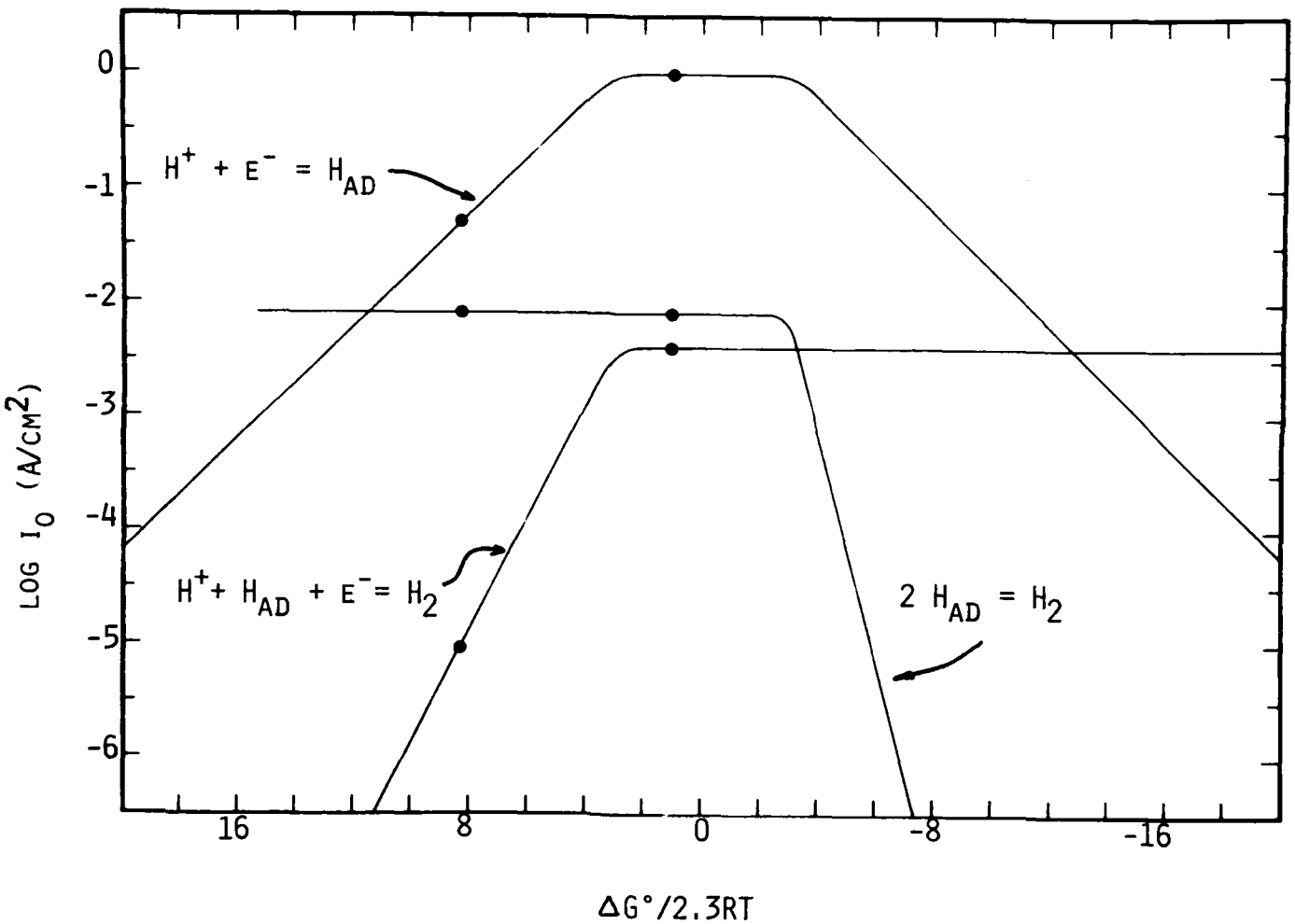

Fig. 3. Volcano curves (40) in 3 M HCl with $\alpha_I = 1/2$ for the discharge reaction; $\alpha_{II} = 1$ for the recombination reaction; and $\alpha_{III} = 1$ for the ion-plus-atom reactions.

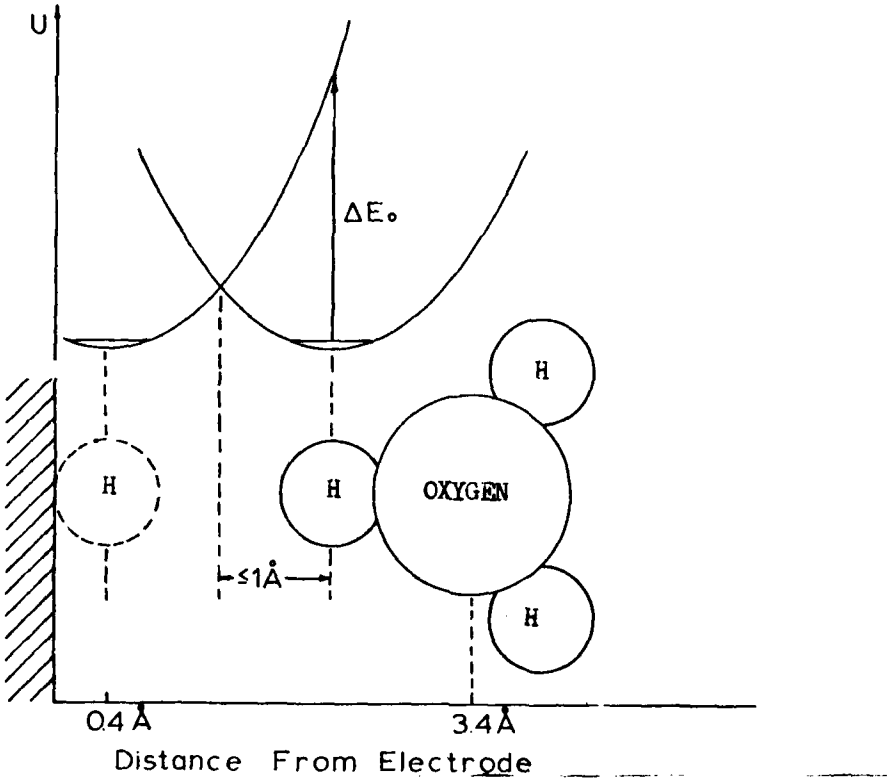

Fig. 4. Potential energy surfaces in the Bockris-Matthews model for proton discharge (110).

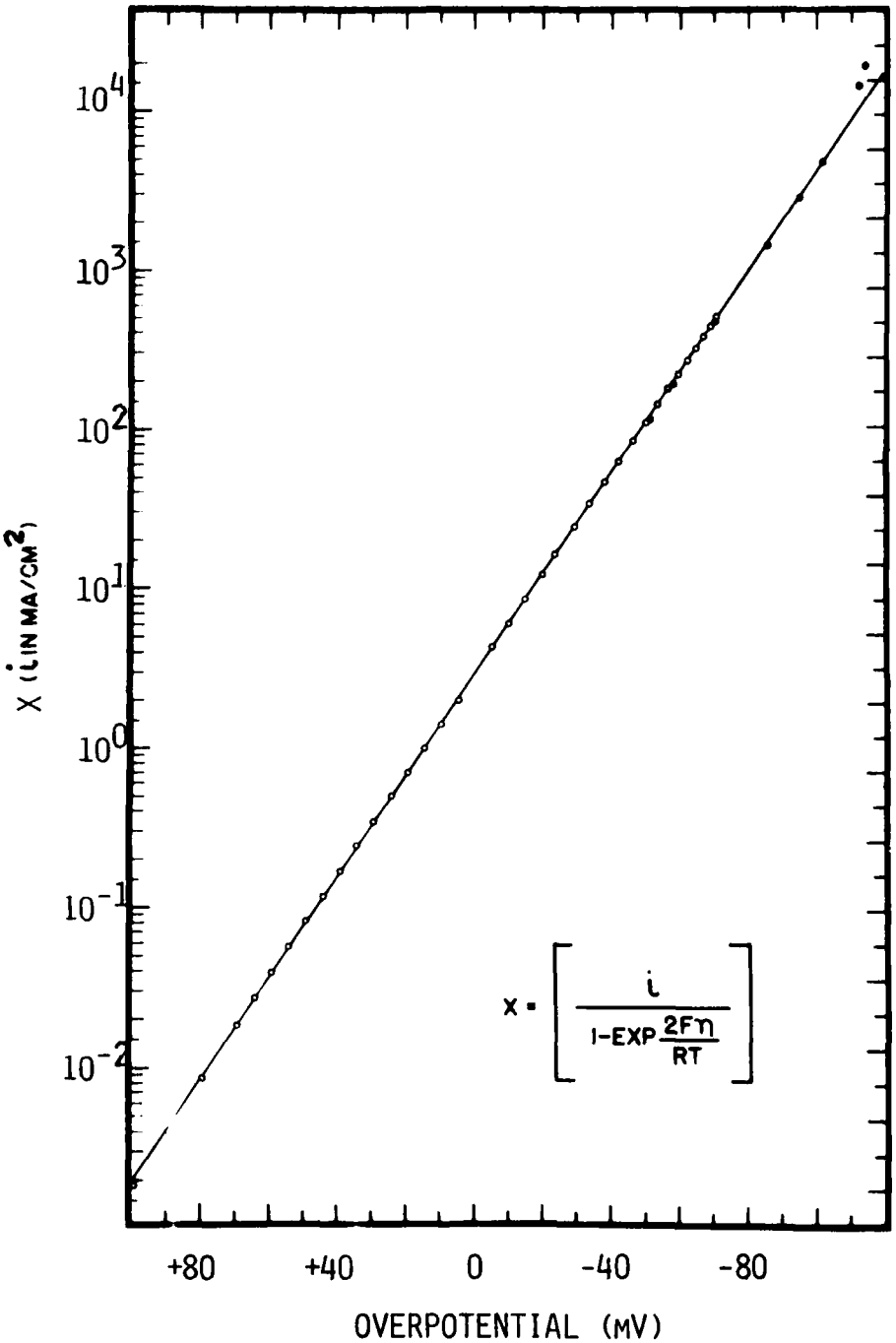

Fig. 5. Hydrogen electrode kinetics on Pt (43). Rotating disk electrode. Rotation rate: 187 Hz; T = 26°C; 6.1 M HCl (H_2 saturated).

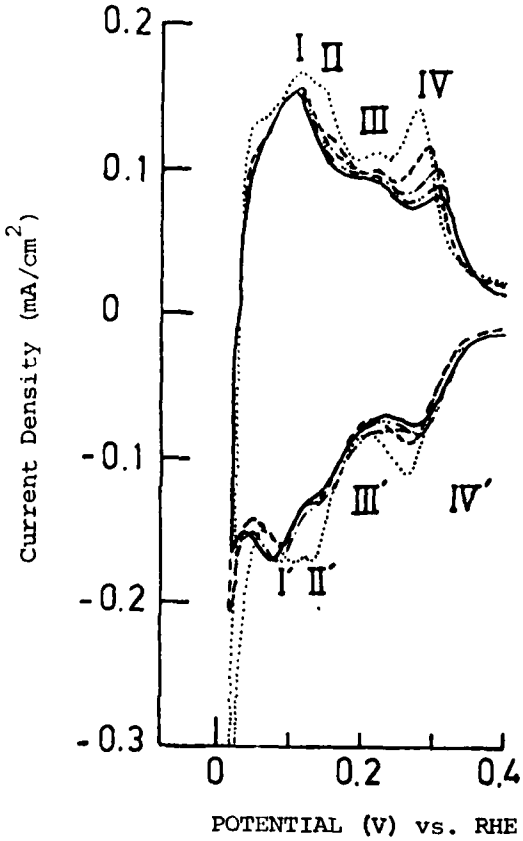

Fig. 6. Voltammograms for Pt in 0.1M HF with various concentrations of H_2SO_4 added. —— 0.1M HF, —·—·— 0.1M HF + 5 × 10^{-5}M H_2SO_4, —·— 0.1M HF + 5 × 10^{-4}M H_2SO_4, — — — 0.1M HF + 5 × 10^{-3}M H_2SO_4, . . . 0.1M HF + 5 × 10^{-2}M H_2SO_4.

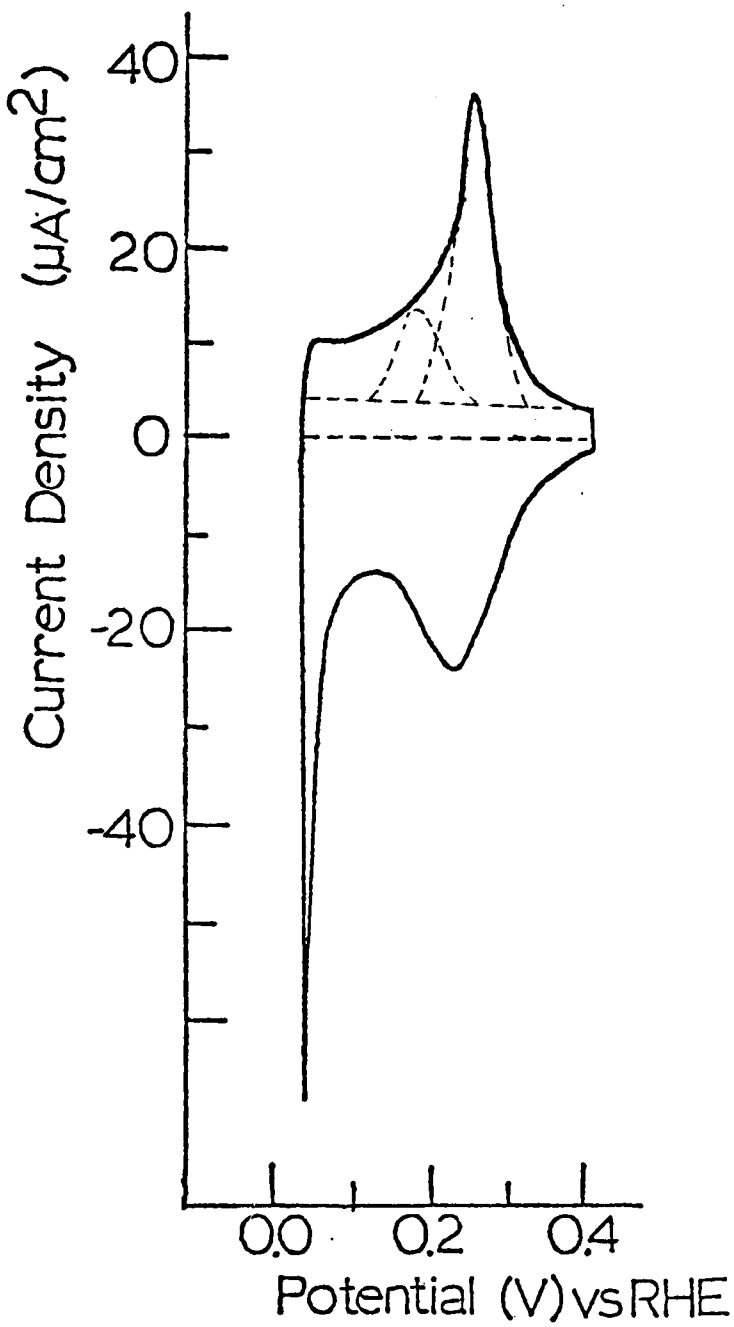

FIG. 7. VOLTAMMOGRAM FOR PT (100)-(5x20) IN 0.05 M H_2SO_4. SWEEP RATE: 50 MV/S. T = 25°C (30).

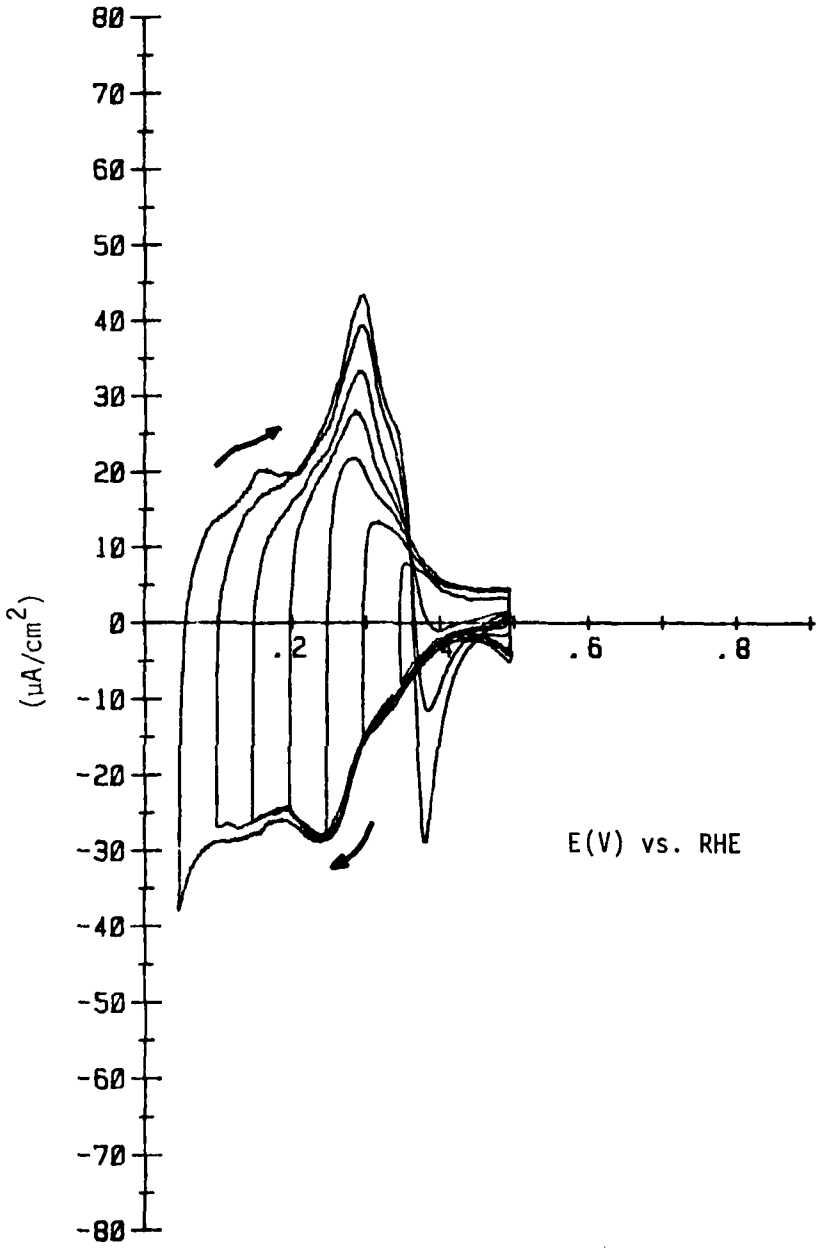

FIG. 8. VOLTAMMOGRAM FOR PT (100)-(5x20) IN 0.1 M HF. SWEEP RATE: 50 MV/S. T = 25°C.

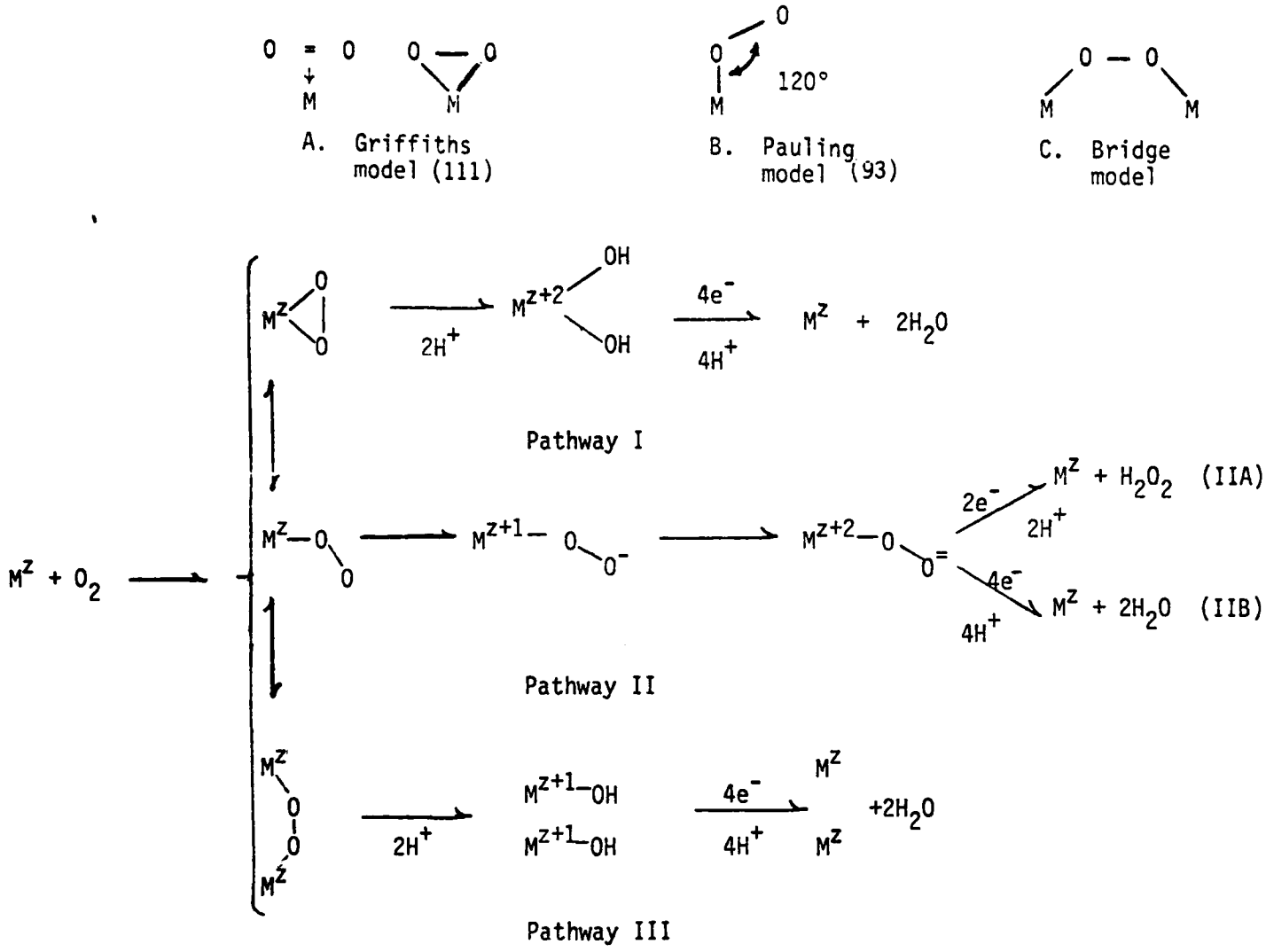

FIG. 9 . REACTION PATHWAYS FOR O_2 ELECTROREDUCTION IN ACID ELECTROLYTES [YEAGER(111)].

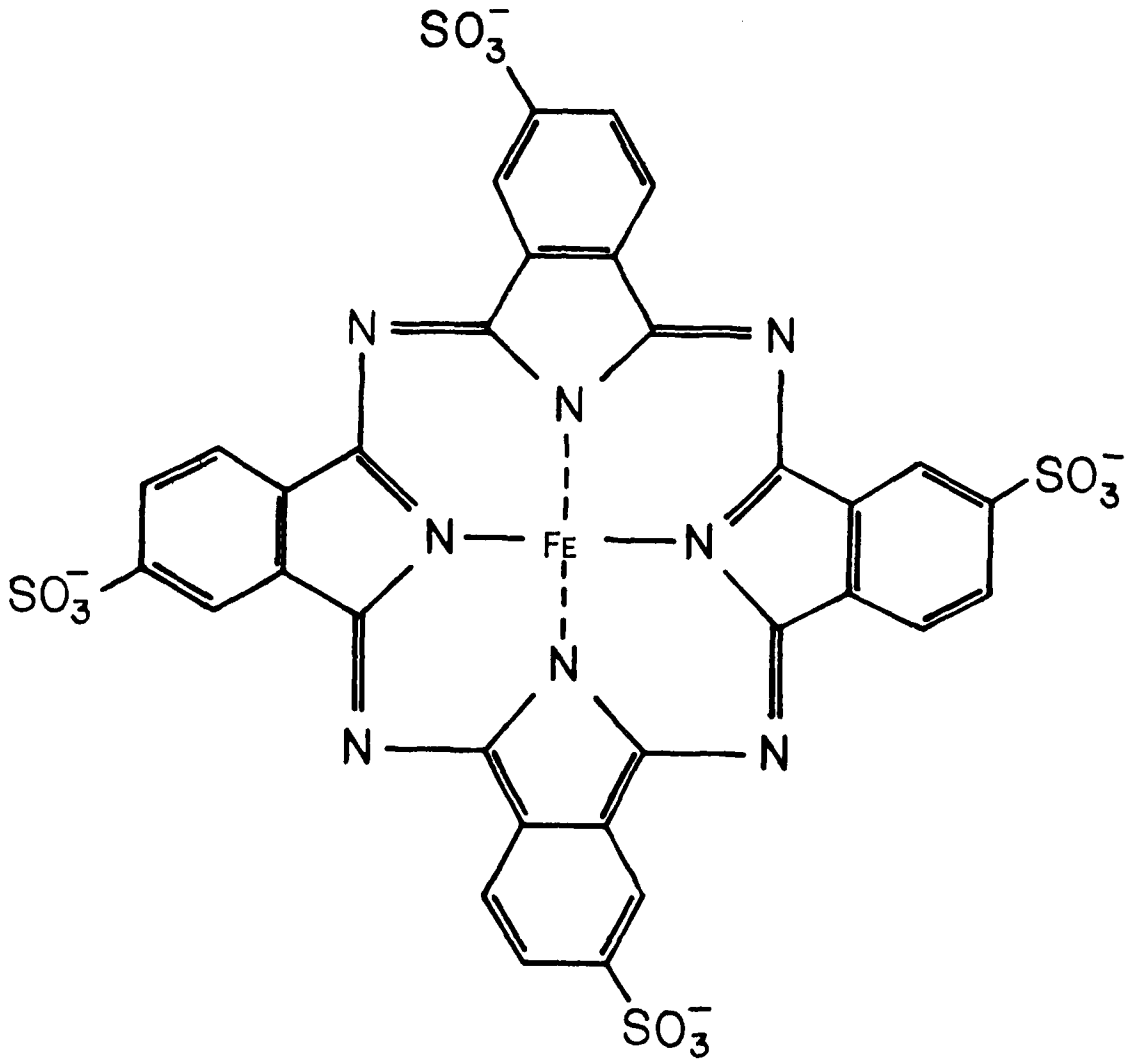

FIG. 10. THE MOLECULE: COBALT TETRASULFONATED PHTHALOCYANINE (CoTSPc)

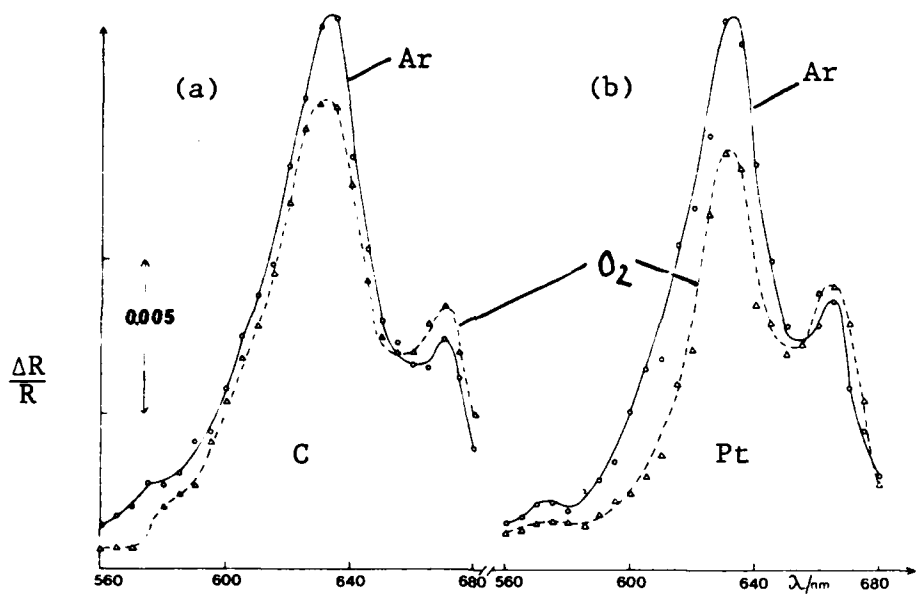

Fig. 11 Reflectance spectra of Fe(III)-TSPc in 0.1 M NaOH adsorbed at basal plane of stress-annealed pyrolytic graphite electrode at 0.90 V (a) and at Pt electrode at 0.70 V(b) with Ar(——) and O_2 (---) saturated solutions. Perpendicular polarization (108).

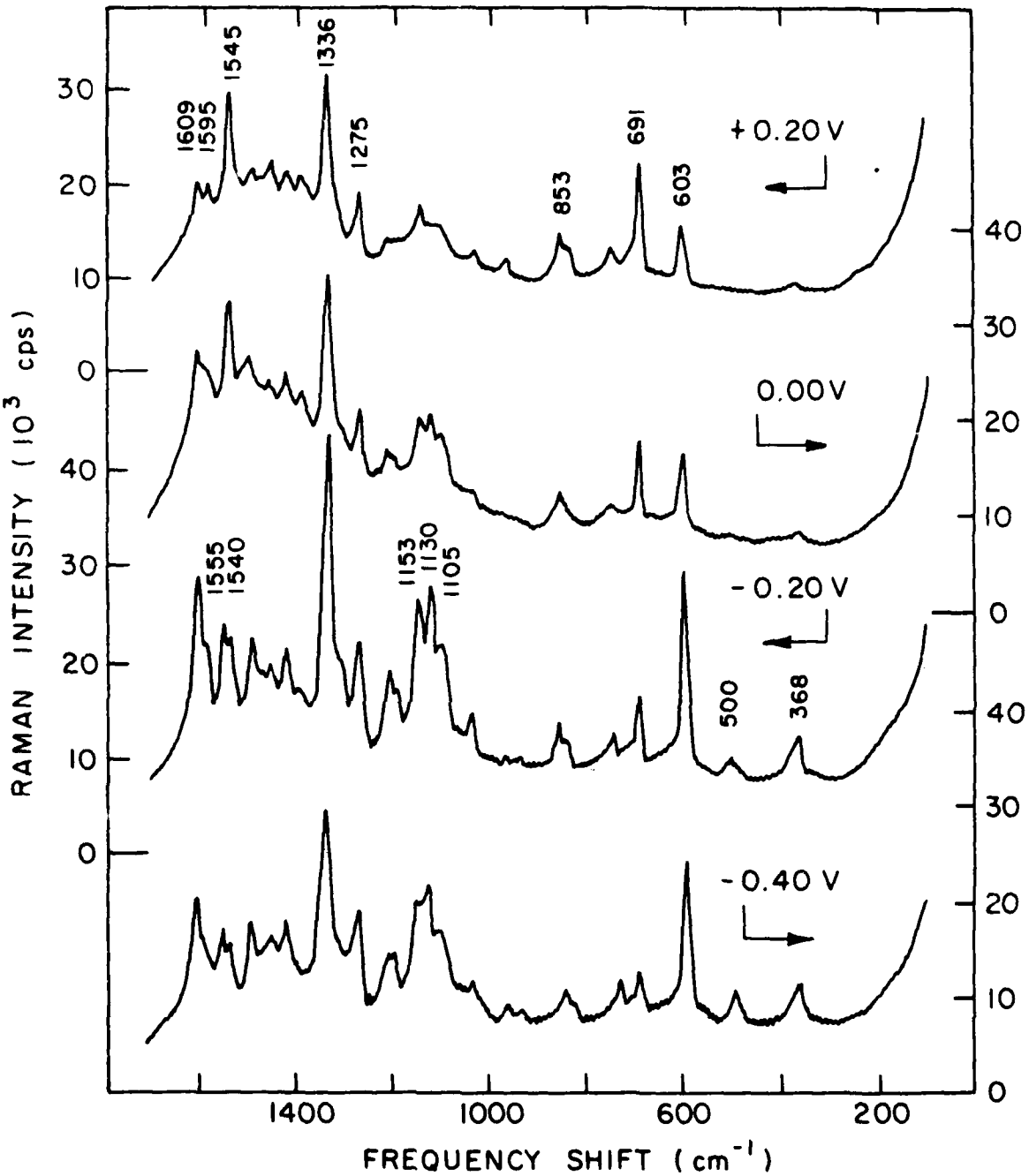

FIG. 12, RAMAN SPECTRA OF CoTSPc ADSORBED ON AN Ag ELECTRODE FOR DIFFERENT ELECTRODE POTENTIALS IN 0.05 M H_2SO_4 + 10^{-5} M CoTSPc; 514.5 NM; POWER AT THE SAMPLE 50 MW.(15).

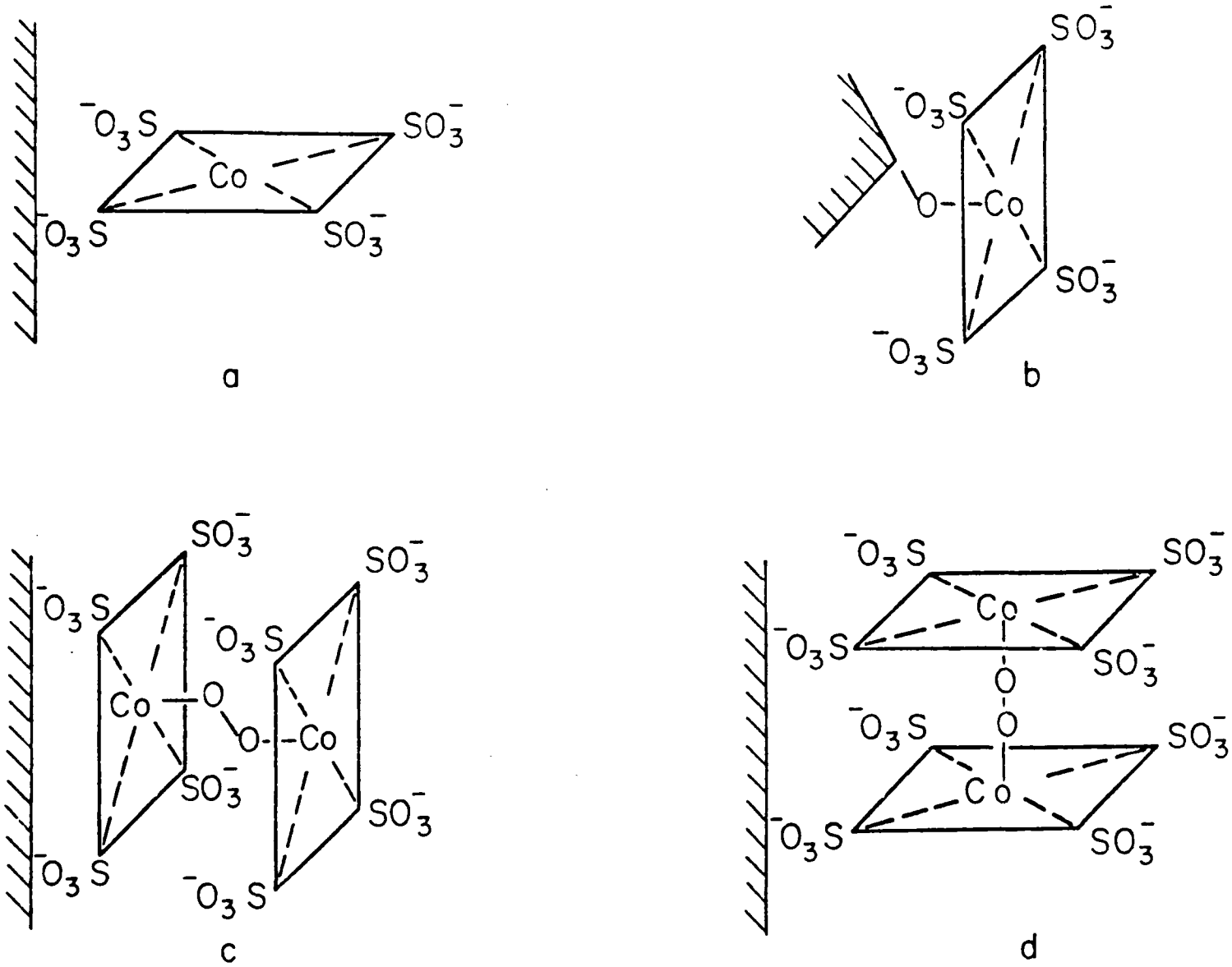

FIG. 13. POSSIBLE CONFIGURATIONS FOR CoTSPc ADSORBED ON AN ELECTRODE SURFACE (15).

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