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LA THÈSE A ÉTÉ  
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MODIFICATION OF THE SURFACE OXIDE FILMS  
ON NOBLE METALS FOR ELECTROCATALYSIS

by

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A thesis submitted to the School of Graduate Studies  
in partial fulfillment of the requirements  
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## PREFACE

In recent years, electrochemistry has provided some of the most interesting advances in the surface science of metals and in catalysis at their surfaces.

The present work described in this thesis covers two main topics in these fields: first the study of formation and growth of monolayer and multilayer oxide films on Ir and Pt, and the effects of anions on these processes; and secondly the examination of the oxide films, which can be formed in a controllable way at Ir electrodes, as electrocatalyst surfaces for the anodic  $\text{Cl}_2$  evolution reaction. The latter topic is also related to the technological advances which have been made in recent years with regard to development of so-called dimensionally-stable-anodes (D.S.A.<sup>®</sup>) for the chlor-alkali industry, based on a  $\text{RuO}_2$  coating on Ti. These electrodes give very favourable, low overpotential behaviour for  $\text{Cl}_2$  evolution, providing substantial electrical energy savings in the chlorine industry as well as a corrosion resistant anode material. The present work shows that Ir oxide films have many of the interesting characteristics of the previously investigated  $\text{RuO}_2$  films, and some novel features in addition.

The original work to be described in this thesis is conveniently divided into four chapters entitled:

- (a) Development of a Minicomputer Based System for Cyclic-Voltammetry Studies;
- (b) The Electrochemical Behaviour of Iridium Electrodes;
- (c) Electrocatalytic Effects of Modified Iridium Oxide Anodes on  $\text{Cl}_2$  Evolution Kinetics; and

(d) Effect of  $\text{Cl}^-$  ion on Surface Oxide Formation at Pt.

Some of the work has already been published or submitted for publication, and other papers are in preparation, as follows:

- (a) The Role of Ion Adsorption in Surface Oxide Formation and Reduction at Noble Metals: General Features of the Surface Process, H. Angerstein-Kozłowska, B.E. Conway, B. Barnett and J. Mozota, J. Electroanal. Chem., 100 (1979) 417.
- (b) Enhanced Electrocatalysis for Chlorine Evolution on Oxidized Ir and Ru Anodes Modified by Potential Cycling, J. Mozota, M. Vuković and B.E. Conway, J. Electroanal. Chem., 114 (1980) 153.
- (c) The Use of a Minicomputer for Data Collection and Treatment in the Study of Electrochemical Surface Processes, J. Mozota, B. Barnett, D. Tessier, H. Angerstein-Kozłowska and B.E. Conway, Anal. Chim. Acta, Sect. Comp. Tech. and Optim., in press (1981).
- (d) Modification of Electrocatalysis for Anodic Chlorine Evolution on Electrochemically Conditioned Oxide Films at Iridium Anodes, J. Mozota and B.E. Conway, J. Electrochem. Soc, submitted for publication.
- (e) The Electrochemical Behaviour of Ir Electrodes. Part I: Monolayer Stage and Transition to the Thick Film State, J. Mozota and B.E. Conway, in preparation.
- (f) The Electrochemical Behaviour of Ir Electrodes. Part II: Thick Oxide Films, B.E. Conway and J. Mozota, in preparation.
- (g) The Effects of  $\text{Cl}^-$  Ion on Surface Oxide Formation at Pt, B.E. Conway and J. Mozota, in preparation.

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ABSTRACT

The general aims of the work reported in this thesis were to take advantage of the rather unique oxidation behaviour of Ir metal electrode surfaces on which controllable degrees of thin and thick film oxidation can be achieved, thus giving the possibility of using such controllably modified oxide films in a study of an anode catalysed reaction such as  $\text{Cl}_2$  evolution.

The full study of these effects required (a) a characterization of the states of monolayer and thick-oxide films at Ir, (b) the effects of  $\text{Cl}^-$  ion on the formation, reversibility and stability of oxide films at Ir, and comparatively at Pt and (c) steady-state studies of anodic  $\text{Cl}_2$  evolution on a range of anodically conditioned oxide films formed at Ir electrodes.

The opportunity also existed to apply a new PDP-11/34 minicomputer system to on-line data acquisition and processing in cyclic-voltammetry experiments, e.g. in the Ir oxide formation and reduction studies. The procedures developed are described in this thesis.

This abstract is therefore given in four sections, covering the four respective parts of the work, mentioned above, which will be described in Chapters III, IV, V and VI as follows:

(a) Procedures for on-line acquisition and processing of data from controlled potential (linear potential sweep and cyclic-voltammetry) experiments on electrode surface processes by means of a PDP-11/34 minicomputer are described. Advantages of this procedure over regular recordings of current-potential or current-time traces on an oscilloscope are discussed and exemplified by selected experimental results;

(b) The electrochemical behaviour of Ir electrodes was studied both for the formation of monolayer surface oxide and for the thick oxide film which show

reversible oxidation/reduction currents due to redox processes involving two or more oxidation states of Ir in the film.

At the monolayer stage, Ir was found to behave like any other platinum metal. However, under conditions to be described here, a thick oxide film develops on the surface of Ir anodes whose properties and characteristics can be understood in terms of a model involving the change of conductivity of the oxide film as a function of applied potential. A growth mechanism is proposed based on the same model. Electrochemical, optical and spectroscopic evidence, together with the results obtained in kinetic studies of the  $\text{Cl}_2$  and  $\text{H}_2$  evolution reactions on these surfaces, confirmed the validity of the model.

(c) Studies on  $\text{Cl}_2$  evolution kinetics on Ir anodes on which oxide films of various thicknesses from a monolayer upwards were formed by a potential cycling programme, are reported. The multilayer oxide films were of the kind that exhibit reversible oxidation/reduction processes. The kinetic experiments conducted in aq. KCl at pH 2 give  $\log [\text{current density}]$  vs overpotential relations having a constant Tafel slope of  $2.3 \text{ RT/F}$  for all anode oxide surfaces prepared, indicating that the  $\text{Cl}_2$  evolution mechanism is independent of the thickness of the oxide film produced. However, the apparent exchange current densities increase in an almost linear way with thickness. The latter behaviour is attributed to an increase in the real area of the electrode available for  $\text{Cl}^-$  discharge, coupled possibly with improved electrocatalysis, e.g. on account of changes that can arise in the band-structure of the oxide. Increases of  $\text{Cl}_2$  evolution rate of up to 180x, at a given overpotential, are found.

Effects of  $\text{Cl}^-$  adsorption on the development of the initial monolayer of oxide of Ir were also studied and compared with the behaviour at Pt.  $\text{Cl}^-$  adsorption is found to inhibit the formation of the thick oxide films at Ir.

(d) The effect of  $\text{Cl}^-$  adsorption on the monolayer surface oxidation processes at Pt at low temperature, i.e. 213 K, was also studied and compared to that at 298 K. The importance of comparing data on the basis of total initial oxide coverage was stressed and demonstrated. A value for the parameter  $g$ , characterizing lateral interactions in the 2-dimensional monolayer oxide film was calculated by an analytical approach. The reversible component of Pt surface oxide reduction at low coverages, ca.  $< 15\%$ , was clearly distinguishable and was found, surprisingly, not to be selectively blocked by the presence of  $\text{Cl}^-$  ion at low concentrations of the latter.

A special potential-time programme was developed to study the effect of  $\text{Cl}^-$  ion on the kinetics of growth of Pt oxide at constant potential; the advantages and limitations of this procedure were also discussed. Pt oxide growth at constant potential appears to obey a direct logarithmic law in time, with a slope  $dq/d(\log t)$  dependent on the growth potential,  $E_a$ .  $\text{Cl}^-$  ion lowers the rate of growth but the direct logarithmic relation in time is maintained.

Interesting effects were observed under conditions where  $\text{Cl}^-$  blocking and oxide growth are competing processes, i.e. at low  $\text{Cl}^-$  concentrations and for high values of the anodic growth potential,  $E_a$ .

## CHAPTER I

### GENERAL INTRODUCTION:

### ELECTROCATALYSIS AND OXIDE FILMS

#### 1.1. INTRODUCTORY REMARKS

In recent years, the electrochemical behaviour of the Pt group metal, iridium, has attracted much interest in electrode process research because of its ability to develop, under the proper conditions, thick oxide films which can undergo reversible changes of oxidation state. Also, the solid state and surface properties of these oxide films can be somewhat controlled by means of various experimental conditions.

Films of this oxide, like those of  $\text{RuO}_2$  and some other oxides, are found to be excellent electrocatalytic substrates for reactions such as  $\text{Cl}_2$  and  $\text{O}_2$  evolution, and the oxidation of various organic molecules.

Electrocatalysis is a topic of current importance owing to its relation to energy storage and conversion problems, e.g. in the fields of fuel-cell research, electrochemical technology, development of advanced batteries, etc., in these times when a perceived energy crisis has arisen.

Studies in electrocatalysis imply the search for new substrates or the modification of existing ones to increase the rate of a certain reaction (at a given potential) or to improve its selectivity or current efficiency. Examples of varying electrocatalytic activity of electrode materials for a given reaction are shown in Table I, where the exchange current density,  $i_0$ , for the hydrogen evolution reaction on various substrates is seen to change by a factor as large as  $10^9$  in going from Hg to Pt, while the selectivity for oxidation of ethylene clearly depends on the substrate. Similar variations

TABLE I  
EXAMPLES OF ELECTROCATALYSIS

(a) EXCHANGE CURRENT DENSITY,  $i_0$ , FOR THE  $H_2$  EVOLUTION REACTION

| METAL | $-\log i_0$ ( $A\ cm^{-2}$ ) in 1 M $H_2SO_4$ |
|-------|-----------------------------------------------|
| Pd    | 3.0                                           |
| Pt    | 3.1                                           |
| Rh    | 3.6                                           |
| Ir    | 3.7                                           |
| Au    | 5.4                                           |
| Ti    | 8.2                                           |
| Mn    | 10.9                                          |
| Pb    | 12.0                                          |
| Hg    | 12.3                                          |

(b) OXIDATION OF ETHYLENE

| METAL | $-\log i_0$ ( $A\ cm^{-2}$ ) | PRODUCT  |
|-------|------------------------------|----------|
| Pt    | 9.0                          | $CO_2$   |
| Pd    | 9.0                          | Aldehyde |
| Rh    | 10.3                         | $CO_2$   |
| Ir    | 10.1                         | $CO_2$   |
| Au    | 9.7                          | Aldehyde |

are found for  $O_2$  evolution kinetics.

Electrocatalysis is a special example of heterogeneous catalysis since it occurs at an interface but with the added controllable variable, the electrical field across the interface, which can be accurately modulated.

The same factors that are of importance in heterogeneous catalysis, e.g. electrical, geometric and electronic properties, are also relevant in the case of electrocatalysis. In any heterogeneous system, such as a solid catalyst in contact with its substrate, there are normally substantial interfacial potential differences of 0.5 to 1.0 V over distances of ca. 0.1 - 0.2 nm but they are not controllable nor directly measurable. At an electrocatalyst interface, however, such potential differences are controllable and measurable relative to a reference potential difference established at a second electrode in the system. This controllability of the interface potential difference provides the opportunity for variation of electron density at the surface of the electrocatalyst and the population of cations and anions in the interphasial region, as well as changes in solvent orientation.

Although much work has been done in recent years, and many empirical correlations have been formulated, it has not been until recently that, with the help of modern spectroscopies, e.g. AUGER, LEED, XPS, and advanced microscopy, SEM, fundamental aspects of electrocatalysis, at the atomic level, have been probed.

More detailed knowledge of the kinetics of the growth of ridium oxide films presents the possibility that such films can be modified in controllable ways and the observed electrocatalysis related to the surface modifications achieved. This process is nevertheless complex, and requires the understanding of many parameters, as follows:

(a) As the electrocatalysed reaction, such as  $Cl_2$  evolution, normally

proceeds on a surface that is totally or partially covered by an oxide film, the latter becoming the catalytic surface, a knowledge of the properties and characteristics of the oxide film is paramount for better understanding of anodic electrocatalysis.

(b) Most of the reactions of interest involve the chemisorption of the reactant and/or intermediate species, which undergo chemical or electrochemical transformations at the surface; thus, the interaction between the various reactive species and the surface, reflected by the adsorption properties of the latter, has to be studied.

(c) The effect of anions on the electrochemical behaviour of metals is well known, especially with regard to the way anions block and delay surface oxide formation, or enhance or reduce corrosion rates. In some cases, such as  $\text{Cl}_2$  evolution, the reacting species itself is an ion that has a strong interaction with the surface. In other systems, the ions present in the supporting electrolyte may exert this kind of influence. In general, the study of the ion/surface system is a complementary requirement to the understanding of the process as a whole.

(d) Another important factor to be taken into account in the study of electrocatalytic factors is the question of real area increase vs. improved intrinsic electrocatalysis when a series of electrocatalytical preparations is being compared. While the former factor is of technological importance, the latter is of more basic significance, and both have to be separated and identified if quantitative understanding of electrocatalytic phenomena is to be achieved.

## 1.2. OBJECTIVES OF THIS INTRODUCTORY CHAPTER

As the subject of this work is the study of the electrocatalysis of the  $\text{Cl}_2$  evolution reaction at modified oxide anodes, as well as the investigation of the electrochemical behaviour of Ir metal together with a

study of the effect of  $\text{Cl}^-$  ion on the reversibility of formation and of growth of oxide films at Pt and Ir anodes, this introductory chapter will be structured as follows:

- (a) A discussion of the formation of thin and thick oxide films under potentiodynamic and potentiostatic conditions on Ir, Pt (as a reference metal for comparison with the behaviour of thin films at Ir) and Ru, Rh and Os (to provide comparative examples of metals that develop thick oxide films similar to those which can be formed at Ir);
- (b) An overview of the effect of adsorbed ions (usually anions) on the electrochemical behaviour of metals and on the kinetics of electrode processes;
- (c) A brief review of previous work on electrocatalysis in the  $\text{Cl}_2$  and  $\text{O}_2$  evolution reactions at oxide surfaces. Although the present work is restricted to a study of the  $\text{Cl}_2$  evolution reaction, some data on the  $\text{O}_2$  evolution reaction serve comparative purposes, since both processes occur under similar conditions on anode oxide film covered surfaces; and
- (d) An examination of the factors that account for the observed electrocatalytic properties of oxide surfaces, especially the geometric and electronic ones, together with a discussion of the main properties of the oxide/metal and oxide/electrolyte interfaces in terms of ion and electron transport, conductivity, crystallinity, potential distribution, etc.

### 1.3. THIN AND THICK FILMS ON NOBLE METALS

As discussed by Conway et al.(1) most noble metals behave in a remarkably similar general way in cyclic-voltammetry experiments. Thus, it is usually observed that a region of so-called underpotential deposition (upd) and ionization of H species (except at Au), is followed by a double-layer charging region and then by a region of underpotential deposition of OH species; the oxide film is further oxidized as more positive potentials

are attained. At the latter potentials, when  $O_2$  evolution commences, the oxide film is normally one or two layers thick and is reduced in the cathodic scan with more or less hysteresis, depending on the prior conditions of oxide film formation, as shown in Fig. 1 for the case of Pt.

The differences that are observed between the behaviour of different metals, or of the same metal in different electrolytes, are partly due to the interaction of the metal with H and O species and partly to the effect of adsorption of ions from the solution.

Under certain conditions, most noble metals can develop films thicker than 1 or 2 layers. Pt and Au grow such films only under extreme conditions, i.e. with long polarizations at high anodic potentials, with very low current efficiencies, and only to eventual thicknesses of up to ca. 60 layers. Such films on Pt and Au show very irreversible reduction behaviour. On the other hand, Ir, Ru, Rh and Os are known to develop, under the proper conditions, oxide films up to hundreds of layers thick, which exhibit large reversible anodic/cathodic currents for oxidation/reduction processes within the film.

All these films have, in general, good electronic conductivity, instead of the well known insulating characteristics of thick oxide films that can be formed at the base metals. Thus, they can sustain electron-transfer processes at their surfaces by rapid electron transport across the film.

We shall now present a critical review of the previous work on noble metals with regard to their electrochemical, and especially oxidation, behaviour, to establish the basis for subsequent discussion of the new work on Ir electrodes.

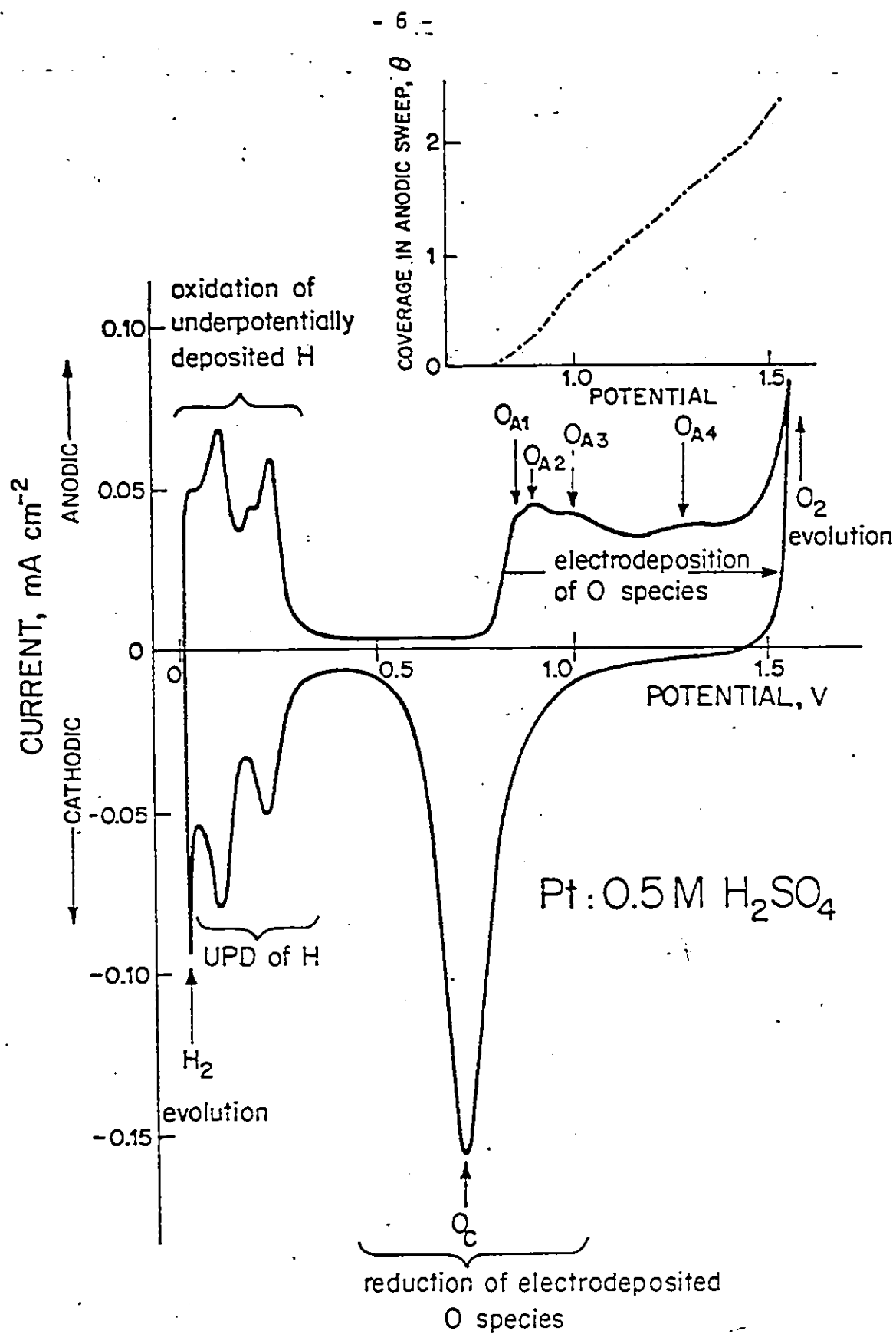


Fig. 1: Typical potentiodynamic current-potential profile at Pt in 0.5 M H<sub>2</sub>SO<sub>4</sub>. O<sub>A1</sub>, O<sub>A2</sub>, etc. refer to distinguishable stages of Pt surface oxide formation.

### 1.3.1. Pt Electrodes

Amongst the noble metals, Pt has been the most widely studied, partly because of its favourable electrocatalytic properties and also because of its corrosion resistance that makes it a "relatively simple" system for experimental study, although its sensitivity to impurities has tarnished the quality of much previous research. Its potential use as an electrocatalyst has, however, been hindered by its high price.

Work on Pt, as on other noble metals, can be divided chronologically into two parts: the earlier work up to the early 1960's, carried out by means of charging curves, and the modern approach using the cyclic-voltammetry technique developed by Will and Knorr (2), together with more recent optical and spectroscopic studies.

Frumkin et al. (3), as early as 1934, studied the behaviour of Pt in acid solutions and reported the existence of three regions in the charging curve that were associated with the following processes: H deposition/ionization, double-layer charging and metal surface oxidation.

However, in other work done at that time, rather puzzling and conflicting results were reported (4,5) that can now be understood on the basis of the known effects of impurities in solution, which were, very likely, significant also in the early work. Thus, it is known that Pt is extremely sensitive to impurities, one of the more common of which is dissolved  $O_2$  that can be eliminated by  $N_2$  bubbling. Other impurities are probably trace organic compounds, difficult to eliminate.

The effect of these impurities was minimized by Frumkin et al. (3) by use of large-area platinized Pt electrodes, and later by Ershler (6), who used large-area electrodes to obtain a large surface/solution volume ratio.

With regard to the amounts of surface oxide formed and reduced at Pt, various authors (7-11) have reported that the ratio of anodic to cathodic charge for oxide formation/reduction was  $> 1$ , and in some cases equal to 2 (8) but, as was discussed by Gilman et al. (12), a ratio of 1 is obtained for the potential range 0.95 to 1.6 V,  $E_H$  if the solution is free from impurities, the extra anodic charge observed in early work being the result of the oxidation of organic contaminants and/or the co-evolution of  $O_2$ .

The study of oxide growth at constant potential also led to inconsistent results. Some authors reported a limiting oxygen coverage (13-15),  $\theta_0$ , and others found no limiting value for  $\theta_0$  (16-18). Here it should be noted that electrochemical monolayer oxide growth is extremely sensitive to the presence of impurities, especially when the oxide is grown by holding the anodic potential constant for long periods of time ca.  $> 10$  s; this can account for discrepancies between various authors' results.

In general, the early work provided a qualitative idea of the oxidation behaviour of Pt metal but, because of the integral character of the charging curve method, many fine details of the behaviour were not observable; thus, Fig. 2 shows how a featureless charging curve compares with a cyclic-voltammetry profile for Pt over the same potential range.

With the development of cyclic-voltammetry, which is a differential technique, it has become possible to study surface processes at metal electrodes with much improved resolution. Thus, the charging curve method measures  $\int i \cdot dt$ , which is proportional to coverage of an electrodeposited species as a function of potential, whereas the cyclic-voltammetry method measures  $i$  as  $i = C \, dV/dt \equiv q_1 \, (d\theta/dV) \, (dV/dt)$ , so that the differential coefficient,  $d\theta/dV$ , of the electrochemical isotherm for the deposited species

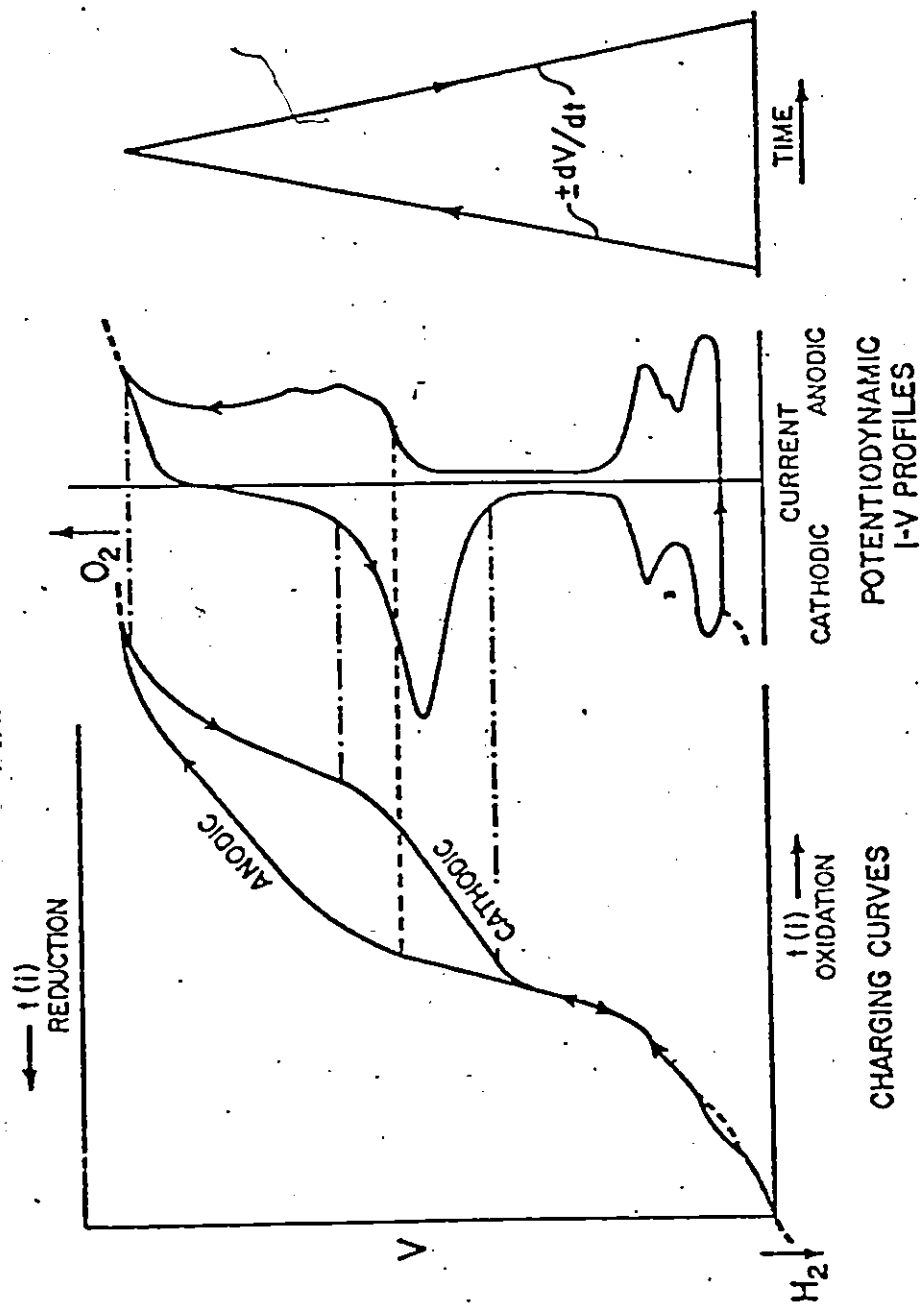


Fig. 2 Schematic comparison of current-potential relations for surface oxide formation and reduction, and for H desorption and ionization at a Pt electrode as generated by galvanostatic charging and potentiodynamic sweep methods.

is directly measured as a function of potential  $V$ ;  $q_1$  is the charge for deposition of a monolayer ( $\theta = 1$ ) of the electroactive species involved.

Thus, it was found (19) that the H deposition/ionization region is resolvable into 4 ~ 5 peaked regions, and that the formation of the monolayer of oxide also takes place through several distinguishable states, while the reduction of the oxide species occurs in an apparently "single" peak, which is however resolvable into various components under certain conditions, e.g. in low  $T$  and high sweep-rate experiments, (see chapter 6).

Will and Knorr (10) observed a ratio of  $Q_0/Q_{2H} = 1$  for Pt at 1.4 V,  $E_H$  in acid solution, indicative of a PtO monolayer. Conway et al. (19-21), using pyrodistilled water (22) to prepare ultra-pure solutions, reported the formation of a PtOH monolayer at 1.1 V,  $E_H$ . Further oxidation of this material to PtO becomes completed at 1.4 V,  $E_H$  and finally a PtO<sub>2</sub> monolayer is attained with an "apparently" limiting coverage at higher potentials, as discussed by Biegler, Rand and Woods (23).

In order to account for the multiplicity of states in the formation of the PtOH monolayer, Angerstein-Kozłowska et al. (19), and Tilak et al. (21), from this Laboratory, proposed that the upd of these species occurs in successive distinguishable sublattices with lattice stoichiometries of Pt<sub>4</sub>OH, Pt<sub>2</sub>OH and PtOH, respectively. Model calculations on sublattices, compared with the experimental behaviour, substantiated this idea. The existence of distinguishable sublattices of adsorbed species has also been proven by Hubbard et al. (24) in their study of I adsorption on Pt by LEED.

The irreversible reduction of the oxide monolayer was accounted for, by the same authors (19), on the basis of a place-exchange mechanism leading to decreased lateral repulsion in the monolayer and consequent formation of a more stable two-dimensional reconstructed O/Pt lattice.

This idea of place-exchange had been first discussed by Sato and Cohen (25) for the case of formation of Fe oxide, and applied by Reddy et al. (26) to Pt. Also, Conway et al. (19) extended their electrochemical investigations by means of optical reflectivity measurements which indicated reversible optical behaviour in the anodic formation and cathodic reduction of the surface oxide at Pt up to 15% of a monolayer, as expected since the turnover (place-exchange) process is not needed at low coverages to stabilize the structure. At coverages > 15%, irreversible optical behaviour was found, corresponding to the observed electrochemical irreversibility.

Simultaneously, Vetter and Schultze (27) carried out important work on oxidation of Pt, although their conclusion that a high field ionic transport ("Mott-Cabrera") mechanism was involved in the formation of the first one or two layers of oxide, is hard to understand due to the high conductivity of Pt oxide films (28) and the absence of a materially thick oxide layer.

These authors also found a logarithmic law in time for the growth of the oxide at constant potential over a range of milliseconds to 1000 seconds, while Gilroy et al. (29) had earlier observed the same behaviour over a more restricted time range. Later on Gilroy (30) extended his work and confirmed the results of Vetter and Schultze (27).

We can conclude that more work is needed to settle the differences arising from the results of various authors, and one important step in this direction has been the use of ultra high-purity solutions prepared by pyro-distilled water in the method described by Conway et al. (22). The development of sophisticated function generators, capable of establishing complex potential vs time programmes, has also been very important since it allows better control to be maintained, electrochemically speaking, over

the processes that take place during an experiment on electrode surfaces.

Although the above discussion was restricted to the monolayer oxide at Pt, it is to be noted that upon polarization at or near potentials where  $O_2$  evolution occurs, a thicker phase-oxide develops, as has been reported by various authors (31-34).

Such an oxide-film at Pt was noticed in 1963 by Shibata (35) when he observed that if a constant anodic current of  $0.1 \text{ A cm}^{-2}$  was applied to a Pt electrode at  $T > 298 \text{ K}$  for various lengths of time, e.g. 0.25 to 24 hours, a marked arrest was observed on the cathodic oxide film reduction curve in the potential region for H deposition; the charge passed in this region increased with time of prior anodic polarization, i.e. of film formation.

In 1967, he reported (36) that this kind of oxide film would not grow at temperatures below 295 K, and extended his study of this interesting behaviour in 1977 (37) by proposing a model to account for these experimental observations. In this model, two types of oxide, " $\alpha$ " with a maximum thickness of 3 monolayers and located at the electrolyte side of the interface and " $\beta$ " with a thickness of up to 60 layers, between the metal substrate and the  $\alpha$  oxide, were proposed. The  $\alpha$  oxide was much more conducting (conductance "identical" to that of Pt metal) than the  $\beta$  oxide (specific conductance =  $1.1\text{--}2.1 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ ) and resembled, in its behaviour, the regular "PtO" formed on Pt metal under cyclic-voltammetry conditions with the anodic potential taken to ca.  $1.4 \text{ V, } E_H$ ; thus, it was cathodically reducible in a single peak at the same potential as that of the monolayer oxide of the metal. On the other hand, the  $\beta$  oxide did not undergo reduction until the cathodic potential was more negative than  $0.35 \text{ V, } E_H$ , i.e. the potential at which H<sup>+</sup> deposition commences on the bare metal.

An elegant experiment in 1978 (38) involving the adsorption of  $I^-$

on Pt, with its related blocking of the H deposition, confirmed the importance of adsorbed H in the reduction of the  $\beta$  oxide. Thus, a model was proposed where the  $\beta$  oxide is regarded as being sandwiched between the metal and the  $\alpha$  oxide; the latter becomes reduced to Pt metal and H species are deposited on this surface and then participate in the reduction of the  $\beta$  oxide.

### 1.3.2. Ir Electrodes

In some respects the anodic oxidation behaviour of Ir is similar to that of Pt and in other respects to that of Ru, Rh and Os. Further details of previous work on Ir will be presented in section 4.2 in relation to new work described in this thesis.

### 1.3.3. Ru Electrodes

Ruthenium is to be regarded as a noble metal according to its Pourbaix diagram (39), although less so from the point of view of stability than Rh, Pd, Ir and especially Pt. However, under anodic polarization in acidic or alkaline media, it undergoes dissolution (40) and if the conditions are appropriate (41) it develops, like Ir, a thick oxide film exhibiting large reversible redox currents that transform the cyclic-voltammetry  $i$  vs  $V$  profile into a featureless "sausage", exhibiting reversible anodic/cathodic currents corresponding to a large pseudocapacitance over a wide potential range, 0.0 - 1.4 V,  $E_H$ .

The latter behaviour makes the study of this metal quite complex, since it is difficult to extract much information from the system without developing the thick oxide film and, once this happens, the  $i$  vs  $V$  profile becomes devoid of any detail.

In 1963, Stoyanovskaya et al. (42,43) studied Ru by the method of charging curves, determining that in acidic solution the onset of oxidation occurs at 0.8 V,  $E_H$  [which is incorrect; as was established later, e.g. (1)].

V

As they increased the potential in the anodic direction, the oxide became more irreversibly formed and at  $E_a = 1.4 \text{ V}$ ,  $E_H$ ,  $O_2$  was evolved and a straw-yellow solution resulted, due to dissolution of some Ru as  $RuO_4^{-2}$ .

Later, in 1966-67, Llopis et al. (44-45) investigating the passivation and corrosion of Ru in HCl, noted that the metal corrodes by the formation of  $[RuCl_6]^{-3}$  and/or  $[RuCl_6]^{-2}$ , with  $Cl^-$  ion enhancing the dissolution rate; formation of  $RuO_4^{-2}$  species occurs at high anodic potentials. Under certain conditions, they observed the electrode to become passivated by a film "several molecules" thick.

Radiochemical studies of the corrosion of the metal in 2 and 4 M HCl at 323 K under passive conditions (46), indicated a rate of corrosion of  $8 \mu A \text{ cm}^{-2}$ , corresponding to good corrosion protection by the oxide film.

Eighner in 1967 (47) confirmed the Pourbaix diagram for Ru in basic media by studying the electrochemistry of various Ru couples at a Pt electrode and the behaviour of a Ru wire in 4N NaOH. He noticed, again, the dissolution of the metal via  $RuO_4^{-2}$  at high anodic potentials, and the rapid passivation, coupled with commencement of  $O_2$  evolution, indicating that the oxide film has a lower overvoltage for that reaction than the bare metal. Thus, this could be described as the first observation of the electrocatalytic properties of Ru oxide films.

Burke and O'Meara (48), studying the oxygen electrode reaction at Ru, pointed out some of the features of the  $i$  vs  $V$  profile for Ru in 1 M  $HClO_4$  at 298 K. Unfortunately, the thick oxide which exhibits the featureless  $i$  vs  $V$  profile was evidently already on the surface of the electrode (a common problem in the early literature on Ru, as will be discussed also for the case of Ir, section 4.2).

The importance of  $\text{RuO}_2$  films was stressed by Trasatti et al. (49) in 1971, when chemically formed  $\text{RuO}_2$ , prepared by thermal decomposition of  $\text{RuCl}_3$  in air, was proposed as a new electrode material with promising electrocatalytic properties and excellent long-term stability. Remarkable similarity between the  $i$  vs  $V$  profile of the thermally prepared oxide and that of the film electrochemically formed on Ru was observed, which led to a growing interest in the study of the electrochemical behaviour of that metal.

The first study, where the monolayer stage of surface oxide film formation at Ru was properly investigated was carried out by Hadži-Jordanov et al. (50) in 1975, in this Laboratory. They showed that, as with most other noble metals, Ru exhibited a H deposition/ionization region, a region where further oxidation of the OH species to O species and higher oxides occurs and, in the cathodic scan, a region for the removal of the deposited oxide associated with a large hysteresis between oxide formation and reduction processes. They also showed that unless proper precautions were taken, the featureless symmetrical  $i$  vs  $V$  profile, corresponding to the thick  $\text{RuO}_2$  films, was obtained.

Similar results were published by Burke et al. (51) a year later for the case of electrodeposited Ru. In their study, the influence of potential, time and nature of the electrolyte on the extent of anodic film formation was investigated. They observed that the film grows at constant anodic potential and proposed the formation of a phase oxide of continuously increasing thickness, under a programme of cyclic polarization.

A detailed study of the state of electrodeposited H at Ru electrodes, to determine the possibility of using the H ionization charge as an "internal

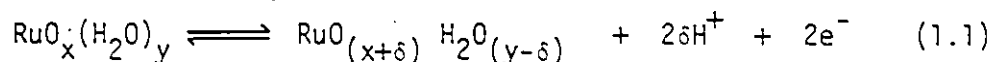
standard" for area determination, as at Pt or Ir (52,53), was performed by Hadži-Jordanov et al. (54), in this Laboratory. Reflectance measurements, coupled with results obtained on Ru surfaces prepared in various ways, indicated the presence of adsorbed as well as absorbed H, thus making it impossible to use the H charge at Ru for the intended purpose of real area evaluation.

Parallel to the interest in electrochemically grown  $\text{RuO}_2$ , much work has been carried out on the properties of thermally prepared films deposited on various substrates, e.g. Ti bearing a  $\text{TiO}_2$  film. This interest arises from the excellent electrocatalytic properties that are found with Ru/Ti electrodes. In the 1960's, De Beer (55-57) developed the so-called D.S.A<sup>®</sup> electrodes based on a  $\text{RuO}_2$ - $\text{TiO}_2$  coating on a Ti substrate, which have proven to be one of the most important technological discoveries in electrochemistry, in particular for the chlor-alkali industry where most of the existing plants have switched to D.S.A<sup>®</sup> electrodes for  $\text{Cl}_2$  evolution. De Beer holds most of the patents related to these electrodes (55-57). Much of the fundamental work in this area has been carried out by Trasatti et al. (58,59) and by various groups of Japanese workers (60-63). A more detailed discussion of this topic will be presented in the section on electrocatalysis in the anodic  $\text{Cl}_2$  evolution reaction.

Spectroscopic techniques were applied by Michell et al. (64) to the study of oxidation of Ru; they combined cyclic-voltammetry with X-ray emission spectroscopy and electron micrography in a study of the characteristics of the oxide film, its thickness, stoichiometry, species present and oxidation/reduction mechanism. Their results indicate that electrodes of various kinds, e.g. made of foils, formed by electrodeposition, chemically/electrochemically treated, thermally formed, etc., behave alike with the exception that the

observed currents differ on account of differences in surface roughness determined by the preparation technique.

The observed dissolution rate for Ru under a cyclic potential programme up to  $E_a = 1.5 \text{ V}, E_H$ , was found to be  $3.08 \text{ mg cm}^{-2} \text{ cycle}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  at  $298 \text{ K}$ ; this value decreased substantially when the electrode became covered by the oxide film. The nature of the oxide appears to be hydrated  $\text{RuO}_2$  in an amorphous state and the observed currents are due to a reaction involving proton ejection/injection in the oxide lattice, such as



They also concluded that all the oxide film was involved in the electrochemical redox process, although Trasatti et al. (58), pointed out that, in the case of thermally prepared  $\text{RuO}_2$ , only 6-7% of the layer is actually electrochemically active. It is our feeling that the conclusion of Michell et al. (64) is inaccurate, due to a gross underestimate of the oxide thickness because of the compact character of the outer region of the oxide layer that can be seen in SEM studies.

Hadži-Jordanov et al. (41), in this Laboratory, continued their work on this area, with an investigation of the reversibility and growth behaviour of surface oxide films at Ru. Their main conclusions were: confirmation of the previously discussed (50) monolayer behaviour; growth of the phase oxide due to incomplete reduction of oxide species formed in every anodic cycle; the redox reaction in the film is  $\text{Ru(III)/Ru(IV)}$ ; the effect of  $\text{Cl}^-$  ion on the monolayer stage is to make the profile more similar to that of other noble metals in acid media; the overall behaviour of Ru is thus similar to that of Ir.

Finally, in 1979, Burke et al. (65) studied Ru anodes in basic

solution and concluded that, although the behaviour of the electrode in this medium is similar to that in acid, the corrosion rates of the metal and the oxide are greatly enhanced due to the more facile formation of solution-soluble ruthenate species.

#### 1.3.4. Rh and Os Electrodes

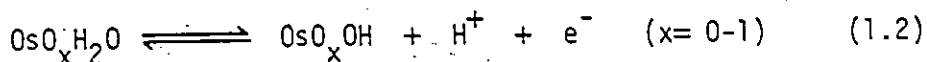
The observation that Ir and Ru can develop, under certain conditions, thick oxide films of technological and basic importance, led to the study of other Pt metals, such as Rh and Os, in an attempt to reproduce the behaviour of Ru and Ir.

Rh and Os have not been subject to many studies but in the period 1965-1976, Vovchenko et al. (66,67) and Appleby et al. (68) carried out some work on hydrogen adsorption on Os electrodes and found, as on Ru, a large overlap between the H deposition/ionization region and the onset of up of OH species.

Later, it was shown (69) that the onset of oxidation occurred on Os at lower positive potentials than for any other Pt metal, and that the voltammogram for Os was rather featureless. The corrosion studies of Colon et al. (70) indicated dissolution of the metal as  $\text{OsO}_4^{-2}$  at high anodic potentials, and that passivation could be achieved by increasing the acidity or decreasing the chloride concentration of the electrolyte.

In 1978, Colon et al. (71) studied the electrochemical behaviour of electrodeposited Os in HCl and  $\text{HClO}_4$ , dilute enough to minimize corrosion effects; their conclusions were as follows: the electrode develops very quickly a thick oxide film similar to that at Ru and Ir; the oxidation reaction for the film formation is  $\text{Os}/\text{OsO}_2$ ; the dissolution process at high anodic potentials involves  $\text{OsO}_2/\text{OsO}_4^{-2}$ ; no condition could be found where the electrode

was free from the thick oxide film; the reaction in the film is proposed to be



Finally, the same authors continued their investigation of this metal in 1980 (72) by galvanostatic and potentiostatic measurements. They found that the growth of the film obeys the usual direct logarithmic law in time at constant potential and proposed two different types of oxide: a thicker one, capable of undergoing reversible redox behaviour and a thinner one, irreversibly deposited and slowly reduced, responsible, they supposed, for the growth of the film by its slow penetration into the co-existing thicker oxide layer.

In the case of Rh, various authors studied the formation and reduction of oxide films on this metal in acid media by means of galvanostatic transients in the 1960's (73-76). It was concluded that the oxidation occurs, as with other noble metals such as Pt, via RhOH species, reversibly deposited and removed, RhO species irreversibly reduced and Rh<sub>2</sub>O<sub>3</sub> as the final stable form of the oxide. It was observed that the oxidation/reduction charge ratio,  $Q_a/Q_c$ , was greater than 1 but this was accounted for by Rand and Woods (75) in terms of some anodic metal dissolution. Hydrogen deposition/ionization and double-layer charging regions were observed, the latter somewhat obscured by the onset of oxidation and the irreversibility of oxide reduction.

However, in 1978, Burke et al. (77) showed that the behaviour of Rh in basic media parallels that of Ir in acid solutions, i.e. a thick oxide film can be developed on the surface and involves a bulk process with proton transfer, as with Ir and Ru. The layer is porous and poorly adherent, and the dependence of the growth on various experimental conditions is similar

to that for Ir films to be discussed in section 4.2. As for the latter metal, the increased charge capacity is restricted to the oxide region and the H deposition/ionization and double-layer charging regions remain essentially unchanged, regardless of oxide thickness.

Finally, Gottesfeld in 1980 (78), studied the Rh oxide film with respect to its electrochromic properties and concluded that the behaviour in basic media was remarkably similar to that of Ir oxide films in acid.

#### 1.4. ION EFFECTS IN ELECTRODE SURFACE PROCESSES

The electrochemical behaviour of a metal is greatly influenced by the presence and nature of ions in solution (1), either those from the supporting electrolyte or those which are the reacting species. This is because many types of ions, especially anions, interact with the metal surface more or less strongly, depending on properties such as size, charge, donicity, solvation, as well as such experimental conditions as concentration, temperature and charge on the metal.

Ions may influence electrode kinetics or the formation of oxide films in several ways:

- (a) They may cause a change on the value of the  $\phi_2$  potential\* at the inner Helmholtz plane (IHP) or the  $\phi_1$  potential\* at the outer Helmholtz plane (OHP);
- (b) They may cause surface blocking by competitive adsorption;
- (c) They may affect the transition state of the reaction, if it occurs in the IHP, both sterically and electrostatically;
- (d) If the adsorbed ion is also the reacting species, its  $\Delta G_{ads}^0$  will vary as a function of its coverage  $\theta$ , and  $\theta$  is usually a  $f(V)$ ;
- (e) They may influence the kinetics of metal/oxygen turnover (place-exchange) in oxide film growth and ageing processes; and

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\*These are the well-known designations of the inner and outer layer potentials in the Stern-Grahame treatments of the double-layer.

(f) They may affect the state of adsorbed and oriented water at the metal surface.

In the field of electrode kinetics, Frumkin (79) and later Iofa et al. (80) studied the effects of specifically adsorbed anions of the halide series on the kinetics of the  $H_2$  evolution reaction at Hg. They found a diminution of the overvoltage for the reaction in the presence of these ions in the following sequence:  $I^- > Br^- > Cl^-$ , which parallels the strength of specific adsorption of these ions.

The effects disappeared at sufficiently high cathodic potentials, where the anions become desorbed due to the strong negative charge density on the metal. They accounted for the results on the basis of changes in the  $\phi_1$  potential.

Parsons (81) later introduced a theory that took into account the interaction between the adsorbed ion and the transition state of the reaction, characterized by an "activity coefficient", and applied it successfully to the results of Frumkin and Iofa (79-80).

Many more studies of the influence of ions on electrochemical kinetics have been carried out by various authors (82-86); three main cases have emerged:

(a) Redox reactions, such as  $Eu(II)/Eu(III)$ , that are assumed to occur at or near the OHP, and for which adsorbed ions can have no effect whatsoever;

(b) Reactions that take place at the OHP, as in the h.e.r case treated by Frumkin where the effect of the ions is simply an electrostatic one due to a change in the  $\phi_1$  potential.

(c) Reactions occurring at the IHP, as treated in Parsons' theory of the h.e.r, where the adsorbed ions not only modify  $\phi_2$  and determine  $\phi_1$ , but they

interact with the transition state of the process. In this case, the reactant is also adsorbed and blocking effects are also usually important.

In the case of formation of thin oxide films or "upd" monolayer processes, the effects of ions, especially anions, are mainly as follows(1):

- (a) They increase the irreversibility of the upd of OH species;
- (b) They probably increase the rate of place-exchange processes by a local field effect. Thus, if the oxide coverage relative to adsorbed anion coverage can be described by an isotherm such as:

$$\frac{\theta_{ox}}{(1-\theta_{ox}-\theta_A)} = K_c \exp(zVF/RT) \exp(-g\theta_{ox}-g'\theta_A) \quad (1.3)$$

Then, at quite low coverages of oxide as  $\theta_{ox} \ll 1$ , the equation becomes:

$$\theta_{ox} = K_c \underbrace{(1-\theta_A)}_{\text{blocking effect}} \exp(zVF/RT) \underbrace{\exp(-g'\theta_A)}_{\text{local field effect}} \quad (1.4)$$

in which blocking and local interaction effects can be distinguished. Cations, on the other hand, tend to have a stabilizing effect on the unrearranged species and thus slow down place-exchange processes and hence film growth; and

- (c) Anions determine, to a great extent, the peak multiplicity observed in the reduction of oxide species, i.e. the distribution of reversible and irreversible components which may be experimentally distinguished, e.g. at Pt and Au in cathodic sweep  $i$  vs  $V$  profiles.

The effect of anions on the electrochemical behaviour of noble metals will be examined in the present work with respect to the role of  $Cl^-$  ion on the upd of monolayer oxide species at Ir and its effect on the growth of Pt oxide at constant potential and under low temperature conditions.

### 1.5. ELECTROCATALYSIS IN THE $\text{Cl}_2$ AND $\text{O}_2$ EVOLUTION REACTIONS

Interest in the electrocatalytic properties of oxide films is centered on two anodic reactions,  $\text{O}_2$  and  $\text{Cl}_2$  evolution, which are both of technological importance as well as of basic interest. The role of the state of anodic oxide films in the Kolbe reaction has also been considered.

Although the respective thermodynamic potentials for the  $\text{Cl}_2$  and  $\text{O}_2$  reactions are:

$$E_{\text{O}_2} = 1.230 - 0.059 \text{ pH} + 0.015 \log p_{\text{O}_2} \quad (1.5)$$

and

$$E_{\text{Cl}_2} = 1.359 + 0.0295 \log p_{\text{Cl}_2} - 0.059 \log a_{\text{Cl}^-} \quad (1.6)$$

the overvoltage for the  $\text{Cl}_2$  evolution reaction, on most substrates, is smaller than that of the  $\text{O}_2$  evolution reaction. Thus, in  $\text{Cl}^-$  solution sufficiently concentrated,  $\text{Cl}_2$  evolution occurs before  $\text{O}_2$  evolution. Nevertheless, at high enough current densities, analysis of the gaseous products indicates some (2~5%) parallel evolution of  $\text{O}_2$ .

While the  $\text{Cl}_2$  evolution reaction uses the oxide film simply as a substrate for adsorption of  $\text{Cl}^-$  intermediates in the reaction pathway, the  $\text{O}_2$  evolution reaction appears to involve the film in such a way that, under certain conditions, it undermines the oxide's stability. Also, because  $\text{O}_2$  evolution usually occurs at higher anodic potentials than those for  $\text{Cl}_2$  evolution, the structure of the film and the species present can change on account of the larger metal/oxide/electrolyte potential difference. Any changes in film properties during the  $\text{O}_2$  evolution are reflected in changes of Tafel slopes and discontinuities in the kinetic behaviour of the reaction.

In 1976 Buckley and Burke (87) studied the  $\text{O}_2$  evolution reaction

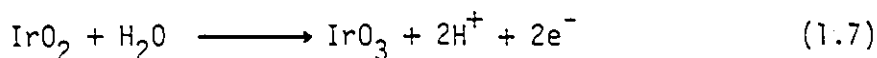
on Ir oxide films and found three Tafel regions in the potential range 1.5-2.0 V,  $E_H$ , having slopes of 0.054, 0.112 and 0.127 V, respectively. They also observed that the currents at constant overpotential followed this order:  $Ir_{acid} \gg Ir_{base} \gg Pt_{acid} > Pt_{base}$ . A decrease in the activity of the film with time expressed as the variation of current at constant overpotential, was also observed and attributed to uptake of O species, leading to transformation of a surface layer to a more stable, less active, oxide film.

In 1978, Gottesfeld et al. (88) compared  $O_2$  evolution kinetics at Ir "metal" (i.e. on the monolayer surface oxide) with the kinetics on thick (250 nm)  $IrO_2$  films and found an increase of 5-10 times in the current at constant overpotential in going from monolayer-oxidized metal to a thick oxide film. They also detected a change in the Tafel slope, that for the process on the thick oxide film being lower. The loss of activity with time was explained, as above, by supposing that the film aged at constant potential, rendering it less active.

The importance of a non-stoichiometric, mixed-valence oxide was also stressed by these authors, who pointed out that the presence of an oxide film, by itself, is not enough for good electrocatalysis, since similar studies on thinner films at Pt revealed a diminished activity compared to that at the bare metal. Thus, "the right type of oxide", catalytically speaking, has to be formed.

In 1979, Frazer and Woods (89) showed that an Ir oxide electrode polarized for up to 2 hours at constant anodic potentials up to 1.55 V,  $E_H$  did not suffer any modifications in its film. This enabled them to correlate the observed initial  $O_2$  evolution currents at a constant potential of 1.55 V,  $E_H$ , with the various charges associated with the bulk oxide layer redox

process in films formed to various thicknesses in a cyclic polarization regime; a linear relationship was found between the  $O_2$  evolution currents and the oxide redox charges. Since the constancy of the H deposition/ionization and double-layer charge seem to indicate no area change (this will be discussed in detail later), they proposed a mechanism similar to that of Lodi et al. (90) and Burke et al. (91) for  $O_2$  evolution on  $RuO_2$  films, involving decomposition of bulk oxide species within the oxide structure, according to the following scheme (as written by the authors (89)):



to account for the increase in current with increasing thickness, in terms other than an area change.

Similar studies were made simultaneously on  $RuO_2$  films. Thus, Trasatti and Buzzanca (49) observed at this electrode the lowest overvoltage ever for the  $O_2$  evolution reaction. Lodi et al. (90) proposed a mechanism for this reaction at  $RuO_2$  substrates, similar to that of Burke et al. (91), discussed above. ESCA evidence that indicated the presence of Ru(IV) species in the oxidized surfaces supported the mechanism (91).

Burke and O'Sullivan (92) also found the thick oxide film at Rh to be a good electrocatalyst for  $O_2$  evolution and attributed the observed effects to area increases due to microcrystallinity of the oxide layer and to the ease of formation of unstable surface species at the thicker oxides. However, they failed to account for the constancy of the H and double-layer regions, which is also evident at Rh oxide films, regardless of film thickness. Both

these ideas have been critized by various authors (53,89,93).

Much work has been done on the  $\text{Cl}_2$  evolution reaction in the case of oxidized Ru electrodes, mainly because of their importance to the chlor-alkali industry, which represents a 3 billion dollars per year business. The work has been mainly directed towards the behaviour of thermally formed oxides of Ru on Ti substrates, the D.S.A<sup>®</sup> type electrodes developed by De Beer (55-57). However, as we shall see, electrochemically grown oxide films also have excellent electrocatalytic properties and allow better control to be maintained over the characteristics of the films, which is of importance for basic research studies in this area.

Since the early 1900's, the chlor-alkali industry used graphite electrodes for the  $\text{Cl}_2$  evolution reaction. These anodes were plagued by many problems including short life-time, contamination of the  $\text{Cl}_2$  product by chlorinated hydrocarbons, CO and  $\text{CO}_2$ , interference with the performance of the diaphragm on the cell and technical problems associated with frequent reinstallation and machining of the electrodes.

In 1913, Stevens (94) started the modern metal anode technology by using Pt-coated tungsten anodes but it was not until the 1950's-1960's, with the development of the D.S.A<sup>®</sup> electrodes by De Beer (55-57), that the industry became of age.

Almost all possible combinations of oxides and substrates have been tested since the De Beer discovery, possibly to circumvent De Beer's patents (which can prove to be difficult, since he himself tested and patented many formulations) and partly to improve even more the performance of the cell anodes. It should be mentioned that newer technologies such as SPE (Solid Polymer Electrolyte) membranes could lead to a situation where noble metals, such as Pt, could be used as electrocatalysts, regardless of the

cost, due to the improved performance of the cell as a whole. One such example was announced recently by DeNora Industries, although the details were kept secret.

From a fundamental point of view, interest in the  $\text{Cl}_2$  evolution reaction has been directed towards the elucidation of the mechanism of  $\text{Cl}_2$  formation as a function of the state of the anode surface and to an explanation of the observed electrocatalytic properties of various substrates in this reaction.

Work in this area is complicated by the following problems:

- (a) Changes of the anode structure during  $\text{Cl}_2$  evolution at constant applied potential due to oxide growth, increase in the oxidation state of the species on the film with increasing applied potential, etc;
- (b) Increased corrosion of most films in  $\text{Cl}^-$  media;
- (c) Co-evolution of  $\text{O}_2$  at higher overpotentials; and
- (d) Influence of  $\text{Cl}^-$  ion on the properties of the anode oxide films when they are grown or formed in the presence of this ion.

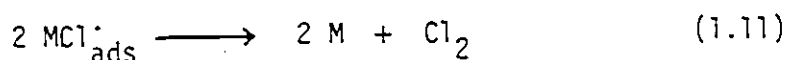
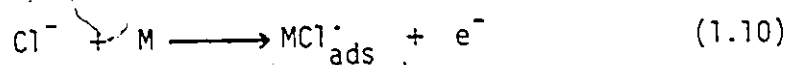
Co-evolution of  $\text{O}_2$  was a matter of great concern in the early work. Thus, Hickling (95) and later Tedoradze (96) studied this problem and concluded that no  $\text{O}_2$  evolution takes place at Pt before  $\text{Cl}_2$  evolution commences. Under commercial conditions, however, the current efficiency is 96~98% for the  $\text{Cl}_2$  evolution reaction. As a  $\text{Cl}^-$  ion solution becomes diluted with continuous electrolysis,  $\text{Cl}_2$  evolution is less predominant and the partial current for  $\text{O}_2$  evolution becomes larger.

That the electrocatalysis is associated with the oxide film (rather than the metal) on the surface of  $\text{Cl}_2$ -evolving anodes, was recognized by Littauer (97) and later by Yokoyama and Enyo (98), but the role of the surface oxide was only clearly proven by Conway and Novak (99,100), in this Laboratory,

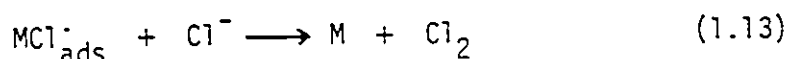
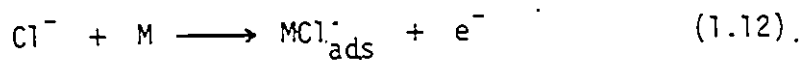
in their comparative studies on Pt, using water and an anhydrous solvent,  $\text{CF}_3\text{COOH}$ , to obtain an oxide-free surface at which the kinetics of  $\text{Cl}_2$  evolution could be comparatively studied.

In the case of metals such as Pt, where a monolayer oxide film is involved,  $\text{Cl}^-$  ion is known to block its formation, but an oxidized surface can be prepared in a  $\text{Cl}^-$ -free environment and then transferred to the reaction vessel with  $\text{Cl}^-$  present (100).

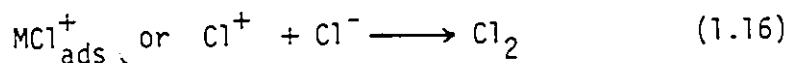
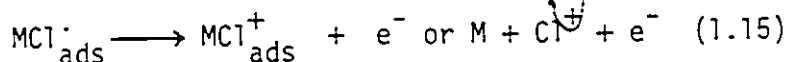
Two main reaction mechanisms for the  $\text{Cl}_2$  evolution reaction have been formulated: the so-called Volmer-Tafel mechanism



and the Volmer-Heyrovsky mechanism



A third possibility was considered by Kristhalik (101) involving the chloronium ion



This last pathway was also considered by Enyo and Yokoyama (102) for  $\text{Cl}_2$  evolution on  $\text{RuO}_2$ , but the basis for this mechanism has been questioned by various authors (99,103).

Chang and Wick (104) studied the kinetics of  $\text{Cl}_2$  evolution on Pt and Ir, using the reaction order approach. They concluded that, on Ir "metal",

the reaction rate was controlled by the discharge of the  $\text{Cl}^-$  ion and that the mechanism was of the Volmer-Heyrovsky type. They observed curved polarization lines, as noted by other authors (98,105) and discussed by Todoradze (106) in terms of varying oxide coverage.

Yokoyama and Enyo (98) arrived at a similar conclusion, proposing a Volmer-Heyrovsky mechanism for Ir and a Volmer-Tafel one for Pt, both controlled by the rate of discharge of  $\text{Cl}^-$ . Nevertheless, the use of the reaction order approach, in the way employed, is questionable since the known competitive adsorption of  $\text{Cl}^-$  makes the  $\theta_{\text{Cl}}$  and  $\theta_0$  dependent on the  $\text{Cl}^-$  concentration, complicating the analysis, as discussed by Dickinson (107), Fajta and Fiori (108) and Conway and Novak (100). Problems in assignment of mechanism by Yokoyama and Enyo also arise because in the above and other studies, adsorption-controlled limiting currents are approached at high overpotentials, consistent with a recombination-controlled mechanism, as indicated later by the work of Conway and Novak (99) who developed a new characteristic kinetic plot for treating the applicability of a recombination-controlled mechanism.

Some other authors (98,109,110) have, however, also supported a discharge-controlled mechanism even when limiting currents were observed at high overpotentials. Conway and Novak (99) applied their analytical approach to their own data and to that of others obtained from the respective publications. For the case of Pt, most of the evidence points to the mechanism being the Volmer-Tafel one, with the rate controlling step being the recombination of adsorbed  $\text{Cl}^-$ .

For the case of Ir, the study is further complicated by the possibility of adventitious growth of a thick film on the electrode, e.g. during pretreatment procedures, as discussed in section 4.2. Most of the

work on Ir and IrO<sub>2</sub> anodes has been carried out without proper characterization of the anode surfaces prior to and after evolution of Cl<sub>2</sub>.

Thus, Arikado et al. (103) studied the Cl<sub>2</sub> evolution reaction on IrO<sub>2</sub> anodes and proposed a Volmer-Heyrovsky type of mechanism, discharge-controlled, but Kuhn et al. (111) found their data to be consistent with a Volmer-Tafel mechanism.

The Cl<sub>2</sub> evolution reaction at Ru is even more complex, since the oxide grows at constant potential and a thickened layer develops as Cl<sub>2</sub> evolution is taking place. As for the case of Ir, various authors have arrived at divergent conclusions regarding the reaction mechanism at Ru. Linear  $\eta$  vs  $\log i$  relationships were obtained, giving rather low Tafel slopes,  $b$ , of 0.030 to 0.040 V which can be explained in terms of a Volmer-Tafel, recombination-controlled mechanism ( $b = 0.029$  V) or by means of a Volmer-Heyrovsky pathway with the reaction between Cl<sup>-</sup> and adsorbed Cl<sup>-</sup> being rate controlling ( $b = 0.039$  V).

The electrocatalytic properties of these oxide anodes for Cl<sub>2</sub> evolution has been discussed, aside from surface area effects, in terms of weaker binding of the adsorbed Cl<sup>-</sup> to the oxide surface sites as compared with that to metal sites (103,112,113).

The role of surface defects, i.e. "active centers", has also been stressed by Trasatti et al. (90), although the exact meaning of "defects" is not clear in the context of the work.

The importance of the electronic configuration of oxide surfaces was evaluated by Arikado et al. (103) by relating the mechanism of the reaction at various oxide anode surfaces to the population of the  $t_{2g}$  and  $e_g$  levels of the d-band of the oxide. They found that some oxides with partially filled  $t_{2g}$  levels and empty  $e_g$  levels favour a Volmer-Heyrovsky mechanism, whereas

on oxides with half or just filled  $t_{2g}$  levels and partially filled  $e_g$  levels, the reaction tends to occur by the Volmer-Tafel mechanism. Their results are summarized in Table II.

Thus, in conclusion, it can be seen that the evidence regarding the mechanism of the  $Cl_2$  evolution reaction on various substrates is conflicting. Almost certainly this arises because the surfaces on which  $Cl_2$  was evolved were not properly characterized or prepared in the same states. This is particularly important when thick oxide films are involved.

A range of electrocatalytic activities of various oxide film surfaces is evident but the several possible origins of the observed behaviour, e.g. in terms of geometric or electronic factors, or even changes of real area, are difficult to assign unambiguously and, in some cases, difficult to distinguish.

## 1.6. ELECTROCATALYSIS AND OXIDE FILMS

### 1.6.1. Electrocatalytic Factors

As discussed previously (see page 2), the same factors that are of importance in heterogeneous catalysis, are also relevant in electrocatalysis. These factors can be divided into two main types: geometric and electronic.

The geometric factors in electrocatalysis include:

- (a) Lattice spacing and geometry of exposed surface planes (114,115);
- (b) Intersite distance (116);
- (c) Grain size (117);
- (d) Presence of steps, kinks and surface vacancies (118);
- (e) Presence of point defects (119); and
- (f) Presence of line defects (120).

They are of great importance when the breaking of bonds is the rate-determining step in a catalysed reaction, especially if steric effects are significant.

TABLE II  
Chlorine Evolution Mechanisms and Behaviour:

Summary of the reaction mechanism, d-electron configuration and exchange current density (ref. 103)

| Electrode                                            | Tafel slope | Mechanism        | d-electron configuration                    | $i_0$ (mA/100 $\mu$ F) |
|------------------------------------------------------|-------------|------------------|---------------------------------------------|------------------------|
| RuO <sub>2</sub>                                     | 2RT/3F      | Volmer-Heyrovsky | ( $t_{2g}$ ) <sup>4</sup>                   | 0.118                  |
| IrO <sub>2</sub>                                     | 2RT/3F      | Volmer-Heyrovsky | ( $t_{2g}$ ) <sup>5</sup>                   | 0.390                  |
| Eu <sub>0.1</sub> WO <sub>3</sub>                    | 2RT/3F      | Volmer-Heyrovsky | d <sup>0</sup> or ( $t_{2g}$ ) <sup>x</sup> | 0.019                  |
| Graphite                                             | 2RT/3F      | Volmer-Heyrovsky | -----                                       | -----                  |
| Pt/MnO <sub>2</sub>                                  | RT/2F       | Volmer-Tafel     | ( $e_g$ ) <sup>1</sup>                      | 0.410                  |
| Ti/PtO <sub>2</sub>                                  | RT/2F       | Volmer-Tafel     | ( $e_g$ ) <sup>x</sup>                      | 0.550                  |
| La <sub>0.6</sub> Sr <sub>0.4</sub> CoO <sub>3</sub> | RT/2F       | Volmer-Tafel     | ( $e_g$ ) <sup>0.4</sup>                    | 0.433                  |
| LaNiO <sub>3</sub>                                   | RT/2F       | Volmer-Tafel     | ( $e_g$ ) <sup>1</sup>                      | 0.144                  |

On the other hand, electronic factors are determined by:

- (a) The d-electron configuration and band structure (121);
- (b) The density-of-states function and its derivative at the Fermi level (122);
- (c) The electronic work function (123); and
- (d) In the case of semiconductors, the concentration of charge carriers (124) and their type, p or n, as well as band-bending at the surface.

These factors, to various degrees, determine the transient bonding of intermediates, and the interaction of the transition state with the surface, and thus influence the rate of the reaction.

Therefore a prerequisite in understanding electrocatalysis is knowledge of the reaction mechanism, which in some cases can prove to be the most difficult requirement, especially in the case of organic oxidations. Sometimes the most important effect of changing the electrocatalyst material for a given reaction is a change of mechanism that the modified catalyst brings about with an attendant change in rate.

In general, in an electrocatalytic study, it is obviously important to be able to modify one parameter of the substrate, while keeping the others constant, in order to assign reliably any observed effect(s) to the change in that particular property. For example, alloys and semiconductors offer excellent possibilities ~~for providing~~ a range of related electrocatalyst materials at which it is feasible to alter the electronic properties in a controlled manner (125), e.g. changing the d-character of the alloys or the concentration and/or nature of charge carriers in semiconductor materials.

A difficult and common problem arises on account of possible changes in real area that may occur when an electrocatalyst is modified. Since unambiguous determination of the real area is not always feasible, care has to be taken to identify and separate effects due to real area changes

(which are of technological importance) from any changes of intrinsic electrocatalytic activity (which are of more fundamental interest).

Also, although the modifications, e.g. of composition, are usually carried out on the bulk substrate, electrocatalysis takes place at the interface and thus involves many factors both in the electrochemical reaction itself and the surface structure of the electrode material. For example, further research in areas such as : understanding of transfer coefficients, structure of the double-layer, adsorption isotherms for charged and neutral species, etc., is needed if electrocatalyst modifications, leading to changed reaction mechanism and/or different adsorption conditions, are to be fully understood.

Fortunately, the modern spectroscopies provide means for probing structures and states of surfaces at the atomic level, and provide the much needed quantitative data on catalyst surface properties necessary for new developments in the subject.

#### 1.6.2. Role of Oxide Films in Electrocatalysis

In the case of anodic reactions, it was mentioned previously, that they normally occur on a surface that is totally or partially covered by an oxide film proven to be the catalytic substrate in various instances (97,99,100,106,126).

Oxide films influence the rates of reactions occurring on their surfaces in various ways:

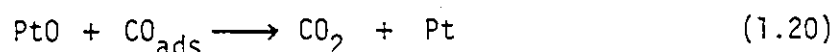
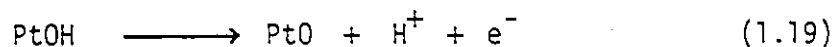
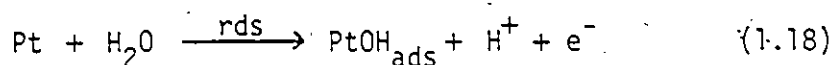
(a) By providing new adsorption sites of different energy and type from those on the metal itself (113);

(b) By blocking any other reaction that may previously have been taking place at lower potentials on the surface of the metal itself (passivation) (127);

(c) By presenting to the reacting molecule a mixed-valence system, with an electronic structure that favours or mediates electron transfer (128);

(d) By having sites of greater catalytic activity due to more favourable geometric factors (113); and

(e) By entering the reaction as a catalytic reagent, e.g. as in the case of CO oxidation on Pt where a possible pathway for the anodic reaction could be:



However, the ability of the oxide film to influence the reaction rate of a catalysed reaction in an electrochemical process depends, to a great extent, on its ability to support continuous charge transfer across the film. The latter is determined by three main factors:

(a) Thickness of the film;

(b) Structure of the film, i.e. whether it is compact, porous or homogeneous, etc.; and

(c) The electronic and/or ionic conductivity of the film (130).

These factors also determine the kinetics and mechanism of oxide film growth when the electrode is polarized anodically and thus how the thickness and properties of the oxide film may change with time during the course of some anodic reaction taking place at its surface.

When these factors are analyzed more closely, it becomes evident that they are interrelated. Thus, the thickness to which the oxide will effectively grow depends on the electronic and/or ionic conduction properties

of the film itself. Also, although the structure of the film depends to a great extent on the conditions under which it is grown, e.g. type of electrolyte, temperature, etc., it will also be influenced by the other two factors.

This conclusion, together with the fact that one of the most important developments in modern treatments of catalysis has been the better understanding of the "electronic factors" in catalysis in terms of localized and delocalized states in surfaces (131), d-orbital hybridization and emergence at surfaces (132) and the collective state of electrons in various levels (Band Theory (133)) in catalyst materials, indicates the importance of achieving an adequate description of the states of the outer electrons in oxide materials since they are responsible for conduction properties and for providing electron density for the transient bonding of intermediates in catalysed reactions.

#### 1.6.2.1. Electronic Theories of "Metallic" Oxides

There are two limiting treatments for the description of the outer electrons in solids: Crystal-field Theory and Band Theory.

Crystal-field Theory is based on the assumption that the electrons are localized about a particular atom due to weak interaction between that atom and its neighbors; on the other hand, Band Theory considers that the interaction is so strong that the electrons are essentially delocalized (collective electron theory).

##### 1.6.2.1.1: Band Theory

By considering strongly interacting electrons, a many-electron problem arises which is impossible to solve exactly. The usual approach to the solution of this type of problem is, however, to use the Hartree-Fock approximation to reduce the situation to that of one electron moving in a

periodic potential (Bloch waves).

When this is done (134-137), there are two main consequences:

- (a) The appearance of Brillouin zones; and
- (b) The appearance of energy bands of allowed states, separated by gaps of forbidden states.

Once this band system is filled with electrons according to Fermi-Dirac statistics, which take into account Pauli's exclusion principle, the highest occupied level at 0 K is called the Fermi level. If that level ( $E_F$ ) is in the middle of an allowed band, the solid is a conductor, if it is in the middle of a forbidden band, the material is an insulator or a semiconductor, depending on the band gap energy.

At temperatures  $> 0$  K, the width of the highest occupied state becomes  $50kT$ , since some electrons will occupy energy levels slightly higher than  $E_F$ . Then, as the temperature increases, a semiconductor can become more conducting by thermal excitation of valence electrons into the conduction band; other mechanisms for increased conductivity include photoexcitation and doping, i.e. the creation of extrinsic energy states near the valence or the conduction band that arise from electron acceptors or electron donors, respectively.

An important point which has to be mentioned is the fact that the energy of the different states depends on the symmetry direction of the unit cell (122). Thus, a more useful representation of the band structure is given by the density-of-states function which is averaged over all symmetry directions and (as will be shown later) can be related to bands of molecular orbitals formed by combination of the atomic orbitals of the cation(s) and anions(s) in the oxide primitive cell.

While Band Theory explains the observed properties of oxides

such as  $\text{ReO}_3$ ,  $\text{TiO}$  and  $\text{VO}$ , it fails to unify the experimentally observed properties of oxides in a given series such as  $\text{TiO}$ ,  $\text{VO}$ ,  $\text{CrO}$ ,  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{CoO}$  and  $\text{NiO}$ , where  $\text{TiO}$  has a conductivity of  $4.7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ ,  $\text{MnO}$  of  $10^{-15} \Omega^{-1} \text{cm}^{-1}$  and the other monoxides are insulators regardless of the fact that all have the same crystal structure, similar lattice parameters and melting points.

Similar effects are observed when the dioxides of the 3d, 4d and 5d transition metals are considered.

#### 1.6.2.1.2. Crystal-Field Theory

In Crystal-field Theory the electrons are considered localized and the energy of the atomic orbitals of the cation is disturbed by the near-neighbor atoms which interact with the center cation in a geometrically determined way, as is manifested in the known d-orbital splitting behaviour in tetrahedral or octahedral fields.

Although this approach has been rather successful in accounting for the properties of complexes of transition metals (138,139) and in explaining certain catalytic effects at surfaces where emergence of d-orbitals and d-character of the bonding have been correlated with catalytic effects (132,140), it does not allow the electrons the required freedom to conduct charge across the crystal nor does it explain certain observations that can only be understood in terms of a collective model.

Thus, many empirical approaches have been formulated (141-143) that have encountered limited success in attempts to describe the electronic structure of metallic oxides. However, Goodenough (144) developed a model that has been widely accepted as being presently the most accurate and useful one (145).

#### 1.6.2.1.3. Goodenough's Approach

Goodenough (144,146) based his model on ideas of chemical bonding and crystal structure, introducing a parameter,  $b$ , called the "critical distance" for cation-cation (c-c) or cation-anion-cation (c-a-c) interactions. He defined two classes of oxides: Class I, those where  $b$  is small and c-c interactions dominate the behaviour and Class II, where  $b$  is large and c-a-c interactions are responsible for the properties of the material.

Since Goodenough's approach will be used later on to account for the conductivity of  $\text{Ir}_2\text{O}_3$  and  $\text{IrO}_2$ , we shall give here only a brief description of the application of this model to  $\text{TiO}_2$  which crystallizes, like  $\text{IrO}_2$ , in the rutile structure, and for which considerable information exists in the literature (147-150). The case of  $\text{TiO}_2$  provides a model case for  $\text{IrO}_2$ , involved in the present work.

The rutile structure has tetragonal symmetry. The unit cell is a body-centered, perpendicular parallelepiped, the center and the corners of which are occupied by cations. Each cation is octahedrally coordinated by six anions, each of the latter being surrounded by three cations located in the corners of an equilateral triangle. The coordination number for cations is thus six and for anions three, the  $c/a$  ratio being 0.644.

According to Goodenough, the two  $e_g$ , one  $4s$  and the three  $4p$  orbitals of the cation form strong  $\sigma$  bonds with 6  $sp^2$  orbitals of the anion, and 6 additional  $\sigma^*$  antibonding states. Two of the  $t_{2g}$  orbitals combine with  $2p_\pi$  orbitals of oxygen atoms to form  $\pi$  and  $\pi^*$  states. The third  $t_{2g}$  orbital combines with another  $t_{2g}$  of another cation to give a  $t_{2g}$  bonding state. This bonding scheme is shown in Fig. 3.

The valence electrons available to fill the band structure are 4 from the Ti and 12 from the 2 oxygens; these fill completely the  $\sigma$  and  $\pi$

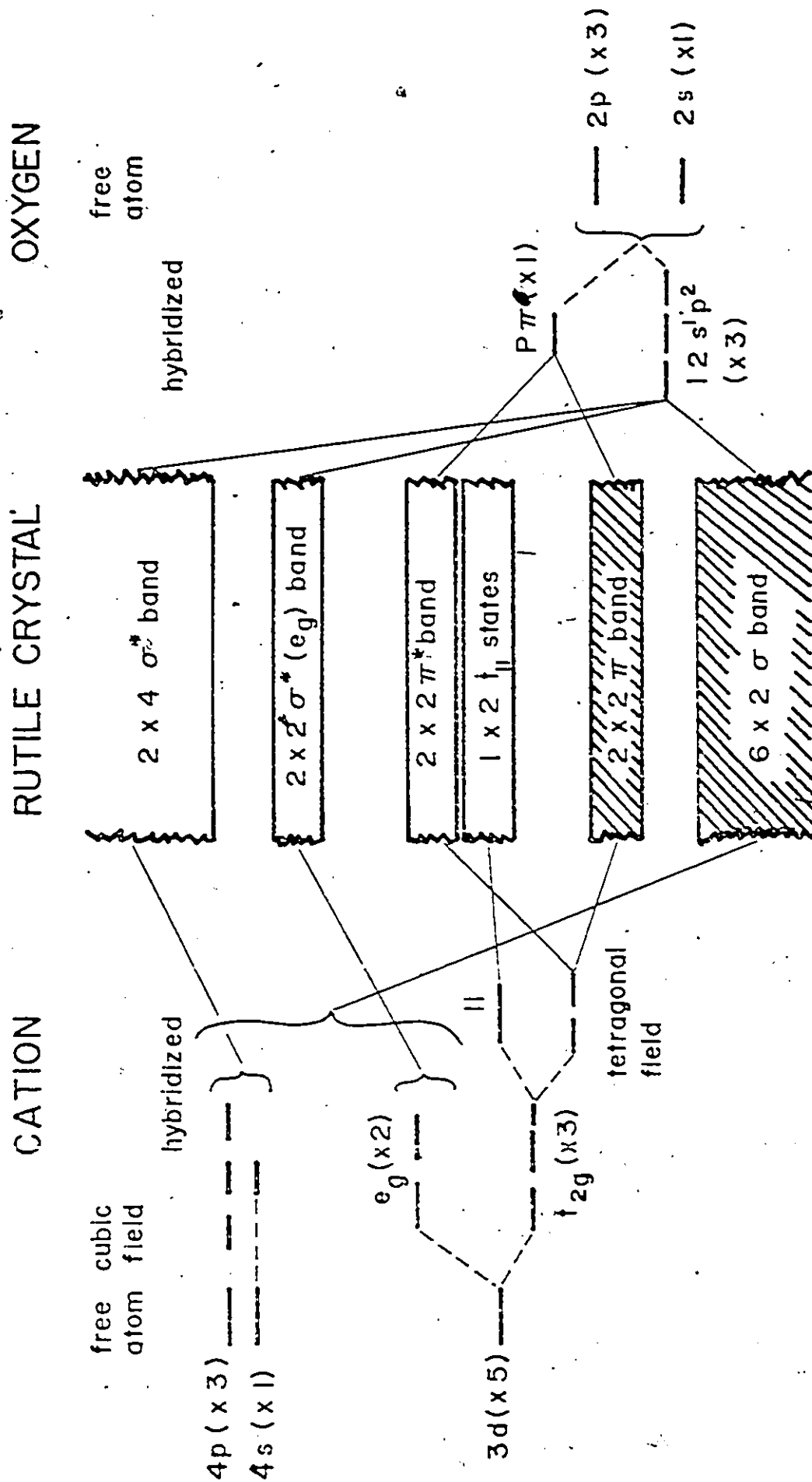


Fig. 3. Schematic band structure diagram for  $\text{TiO}_2$  showing filled valence bands and empty conduction bands (ref. 145).

bands and the high energy conduction bands remain empty, thus giving  $\text{TiO}_2$  its semiconducting properties because the energy of the band gap is such that at high  $T$ , conduction can occur (see Fig. 3).

The application of this model to various crystal structures gives the results shown in Fig. 4, in which it can be seen that as we progress from  $d^0$  to  $d^{10}$  along a transition series, successively higher energy states are filled, so that the conductivity properties of the oxide depend on whether the highest occupied state (i.e.  $E_F$ ) lies inside an allowed band or within a band gap.

#### 1.6.2.2. Potential Distribution Across Oxide Films

The way an applied potential difference is distributed across metal/oxide/electrolyte interfaces at anodized electrodes is very important for electrode processes at oxidized surfaces and depends on the electronic properties and thickness of the oxide film. It turns out to be very important in the present work on oxide films at Ir, as will be shown later.

Thus, if the oxide film is an insulator, as at the valve metals, most of the applied potential difference falls across the thin film, creating a high-field condition that results in oxide growth, if ionic transport across the film is possible (151,152).

If, on the other hand, the film is a good conductor, then the growth will stop since only a small field can be maintained across the film and electron transfer processes will preferentially occur at the oxide/electrolyte interface in the case of compact films or on the whole available surface in the case of porous oxides (the case in the present work at Ir).

In the case of semiconducting films, the behaviour is complicated by the appearance of a space-charge region near the surface, that can be modified by the creation of new surface states due to adsorbed species, e.g.

# Rhenium

## Trioxide

### (Perovskite)

### Corundum

### Rutile

### MO<sub>3</sub>

## MO

## M<sub>2</sub>O<sub>3</sub>

## MO<sub>2</sub>

## MO<sub>3</sub>

s

σ

σ

σ

e<sub>g</sub>

σ (e<sub>g</sub>)

σ (e<sub>g</sub>)

σ (e<sub>g</sub>)

t<sub>2g</sub>

t<sub>2g</sub>

π

π (t<sub>2g</sub>)

Bands  
or  
Levels

Bands  
or  
Levels

t<sub>2g</sub> (llc)  
Band or  
Levels

Bands  
or  
Levels

d<sup>10</sup>  
d<sup>9</sup>  
d<sup>8</sup>  
d<sup>7</sup>  
d<sup>6</sup> ..... PtO<sub>2</sub>  
d<sup>5</sup> ..... IrO<sub>2</sub>  
d<sup>4</sup> ..... RuO<sub>2</sub>  
d<sup>3</sup> ..... MnO<sub>2</sub>  
d<sup>2</sup> ..... CrO<sub>2</sub>  
d<sup>1</sup> ..... VO<sub>2</sub>  
d<sup>0</sup> ..... TiO<sub>2</sub>

P<sub>π</sub>

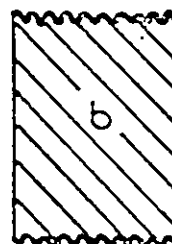


Fig. 4. Predicted Fermi levels for cation electronic configurations in various

crystal structures with examples from oxides having rutile structure (ref. 145).

ions from the electrolyte or intermediates in a reaction.

Even when the film is a conductor, its thickness and its structure (compactness or porosity) influence its behaviour. Thus, the film will have some finite resistance, so that part of the applied potential difference will be dropped across the film and this IR drop will be a linear function of the film thickness for homogeneous films.

In a general case, therefore, the applied potential difference will be distributed, according to the factors already discussed, across the interphase in the following way:

$$\Delta V = \Delta V_{M/O} + \Delta V_O + \Delta V_{dl} \quad (1.21)$$

$\Delta V_{M/O}$  and  $\Delta V_O$  are important with regard to film growth and related electronic and ionic transport across the film.  $\Delta V_{dl}$ , on the other hand, is necessary for any electron transfer process to take place at the outer surface of the oxide films (153,154).

The mechanism of electron transport across films also depends on thickness. While thin films can allow electron tunneling (155), thicker films require electron injection/ejection, coupled with ionic transport (156-158), to maintain electroneutrality of the system and provide charge transport.

#### 1.6.2.3. Laws for Oxide Film Growth

The laws of oxide film growth also depend strongly on the electronic properties of the film. Thus, the growth of insulating oxides seems to obey an inverse logarithmic law in time, while conducting oxides grow by a direct logarithmic law.

For conductive oxides, such as those at Pt and Au (29,159), the formation of the oxide is believed to occur by a place-exchange mechanism (26) at the metal/oxide interface. It should be mentioned, however, that

Damjanović et al. (160,161) favour a high-field assisted growth of oxide films at Pt (as proposed by Ord and Ho (162)) and found different laws for growth under constant current or constant potential conditions.

If the growth proceeds through a place-exchange mechanism, the free energy of activation for the process increases linearly with the thickness\* of the oxide; thus,

$$\Delta G^\ddagger = \Delta G_0^\ddagger + bD \quad (1.22)$$

where D is the thickness of the oxide and b is a constant.

In the absence of an anodic field, e.g. in the gas-phase oxidation of a metal surface, the rate of growth of the oxide is given by

$$\frac{dD}{dt} = A \exp [-(\Delta G_0^\ddagger + bD)/RT] \quad (1.23)$$

Rearranging and integrating for the boundary conditions  $D = 0$  at  $t = 0$  gives the relation

$$\exp (bD/RT) = \frac{bA}{RT} \exp (\Delta G_0^\ddagger/RT) t + 1 \quad (1.24)$$

If the time of growth is long enough, taking logarithms and rearranging, it is found that

$$D = \frac{RT}{b} \ln t + \frac{RT}{b} \ln \frac{bA}{RT} \cdot \frac{\Delta G_0^\ddagger}{b} \quad (1.25)$$

or

$$D = K \ln t + K' \quad (1.26)$$

which is a direct logarithmic law in time for increase of thickness.

When an anodic field falls across the oxide film, equation (1.26) can be modified as follows:

$$D = K \ln t + K' + \frac{cFV}{b} \quad (1.27)$$

---

\* A similar direct log relation for 2-dimensional oxide film growth arises if it is assumed that  $\Delta G$  is a linear function of coverage,  $\Delta G_\theta = \Delta G_0^\ddagger + g\theta$

where  $c$  is a constant and  $F$  the Faraday.

This linear dependence of  $D$  on  $\log t$  has been experimentally observed for Pt and Au (27,29,159) and will be discussed later in this thesis (Chapter 6.) with respect to the growth of Pt oxide at constant potential in the presence of  $Cl^-$  ion.

The inverse logarithmic law for the growth of insulating oxides is obtained (163-165) by considering the growth in terms of passage of ions over an energy barrier and the associated ionic transport across the film (166,167), following Mott and Cabrera's treatment (168,169).

Again, in the absence of an anodic field,

$$\frac{dD}{dt} = A \exp (- \Delta G_o / RT) \quad (1.28)$$

in the presence of an anodic field,  $E = \frac{D}{V}$ ,

$$\frac{dD}{dt} = A \exp (- \{ \Delta G_o - zaFE \} / RT) \quad (1.29)$$

can be written. After applying boundary conditions and manipulating the equations, the result

$$\frac{zaFV}{RTD} = \ln \frac{RT}{zaFV} - \ln a - \frac{\Delta G_o}{RT} - \ln t \quad (1.30)$$

where  $z$  is the charge on the ion and  $a$  is the half-barrier width ("half-jump" distance), is obtained.

According to eqn. (1.30), at constant  $V$  and  $T$ , the thickness  $D$  is inversely proportional to  $\ln t$ ; this is, of course, the inverse logarithmic law for the oxide growth.

For some metals, the growth of an oxide follows a "parabolic" law, as for the case of the valve metals under low field conditions (170); then the result is

$$D^2 = \frac{4AzaFVt}{RT} \exp(-\Delta G_0/RT) + \text{constant} \quad (1.31)$$

so that  $D$  is proportional to  $t^{1/2}$ . This result may also be observed for cases where diffusion of ions through the oxide controls the rate of growth (171). Frequently "parabolic" behaviour follows an initially logarithmic growth of the film.

It should be made clear at this point that it is found (see later) that the growth of Iridium oxide films cannot be analyzed in terms of any of the above treatments because it cannot be made to take place at constant potential. Rather the development of thick films appears to occur because of accumulation, on cycling, of incompletely reduced oxide species probably formed by the successive deposition of monolayers on the metal at the inside of the growing thick film, as will be discussed in Chapter 4.

#### 1.6.2.4. Solid-State Structure and Defects on Oxide Films

One last point requiring some comment is the solid-state structure of oxide films, i.e. their compactness and crystallinity, and the type of defects that oxide structures normally contain, since the latter especially can determine the mechanism of ionic transport across the oxide.

Oxide films can be classified according to limiting descriptions, e.g. crystalline or amorphous, and compact or porous. The particular structure of an oxide film depends to a great extent on the conditions under which the film is grown; for example, oxide films on Al can be prepared in compact or porous states depending on the nature of the electrolyte. In electrolytes where dissolution of the film is negligible, compact films are developed (172,173). In contrast, if the film dissolves, a porous system is formed by a redeposition and growth mechanism (174,175). The area accessible for reaction depends on these characteristics of the film. Thus, compact

films have areas comparable to those of the underlying substrate, while porous films can have areas much greater than that of the substrate metal.

The degree of crystallinity also varies from film to film. While some oxides, especially thin ones, grow epitaxially and in a highly crystalline way (176), most oxides tend to be amorphous (177), thus complicating the problem of correlating electronic properties with the results of the above mentioned descriptions of the outer electrons where crystalline ordering is assumed. In these cases, density and electronic properties of such oxides can be quite different from those of bulk oxides prepared by other methods (178), e.g. thermally, in an oxygen atmosphere.

Finally it has to be recognized that oxide films always contain structural imperfections. These defects can be classified into two main groups:

- (a) Defects of small size called point defects; and
- (b) Defects of larger size, e.g. dislocations and grain boundaries.

Point defects in the lattice can be classified into:

(a) Atomic defects:

(i) Native atomic defects:

- 1. Vacancies - Schottky defects;
- 2. Interstitial atoms or ions - Frenkel defects; and
- 3. Antistructural defects formed by incorporation of misplaced native atoms into some lattice sites.

(ii) Foreign atoms incorporated into the lattice.

(b) Electronic defects:

- (i) Quasi-free electrons;
- (ii) Quasi-free holes; and
- (iii) Polarons.

The larger defects, such as dislocations, can be of two main types: edge dislocations and screw dislocations.

The type of point defects and their concentration are important for ionic transport in the film (179-181), while larger size defects create sites of different energy on the oxide surface, and are normally related to high catalytic activity.

## CHAPTER II

### EXPERIMENTAL PROCEDURES

Since both surface processes (Ir and Pt oxidation) and continuous Faradaic processes ( $\text{Cl}_2$  evolution) were studied in this work, both non-steady state and steady-state techniques were employed. In the non-steady state experiments, the potentiodynamic sweep method (2,19) was mainly used and in some experiments, controlled potential measurements of oxide film growth were made. Details of procedures used are described below.

These approaches allow principally three types of critical data to be obtained: (a) the coverage or extent of oxide film formation at Ir or Pt as a function of potential, i.e. the charge isotherm; (b) the kinetics of

surface processes involved, from the dependence of peak potential on sweep-rate and (c) kinetics of slower oxide film growth processes.

The kinetics of  $\text{Cl}_2$  evolution were evaluated in the well known way from steady-state overpotential vs log (current density) relations.

### 2.1. Pt, Ir AND Ru ELECTRODES

Working electrodes were prepared from Engelhard high purity Ir and Pt wires, and from sections of zone-refined Ir and Ru rods cut with a diamond saw and polished by standard techniques.

The electrodes were sealed directly into soft-glass or Pyrex, or spot-welded to short tips of Pt and Ir, sealed into glass. Once made, the electrodes were stored in 98%  $\text{H}_2\text{SO}_4$ .

The oxidized Ir and Ru electrodes, with variable but controlled charge enhancement factors (CEF's), i.e. the extent to which the charge for oxidation processes in the film in the anodic sweep of a cyclic voltammogram exceeds that for initial monolayer formation on the bare metal, were prepared by electrochemical growth of the oxide film, using a cyclic-voltammetry programme, as will be discussed later.

### 2.2. REFERENCE ELECTRODES

For all experiments, a platinized Pt hydrogen electrode in the same solution as that under study was employed as a reference electrode. All potentials referred to in this thesis will be designated  $V, E_H$ , meaning volts vs a  $\text{H}_2$  electrode in the same solution.

### 2.3 SOLUTIONS AND SALTS

The salts utilized to prepare the various solutions were all A.C.S analytical grade and were recrystallized twice. BDH "ARISTAR" grade  $\text{HCl}$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  were used to prepare the acid solutions. Water used as a solvent was pyrodistilled following two regular distillations, the last

being from an alkaline permanganate still, according to the procedure described previously (22).

#### 2.4. EXPERIMENTAL CELLS

The cells employed in this work were all of the type shown in Fig. 5. The design of this cell allowed the required levels of solution purity to be achieved, as discussed in previous work from this Laboratory (22).

The  $N_2$  used to deoxygenate the solutions was purified in a conventional gas train (182) consisting of : molecular sieve (BDH type 4A),  $Mg(ClO_4)_2$ , Cu turnings at ca. 623 K (periodically regenerated by reduction with purified  $H_2$ ) and then through three traps cooled in liquid  $N_2$ , two of these containing activated charcoal.

#### 2.5. CLEANING PROCEDURES

The glass used to build the cells was initially soaked in concentrated  $CrO_3-H_2SO_4$  solution. The cells were stored filled with 98%  $H_2SO_4$ , which was poured away and the cell rinsed several times with pyrowater before the experiment was begun. Between experiments, the same procedure was followed.

#### 2.6. TEMPERATURE CONTROL

Experiments conducted at various temperatures, higher than 298 K, were performed by immersing the whole cell, including the reference electrode compartment, in a thermostated water bath, the temperature of which was controlled to  $\pm 0.1$  K by a HAAKE E2 circulating water heater.

Experiments conducted at low temperatures, down to ca. 213 K, were performed using an acetone-dry ice bath in a Dewar flask, in which the cell was immersed as in the higher temperature runs.

#### 2.7. ELECTRICAL CIRCUITRY

The basic instrumental arrangement and circuitry used in this

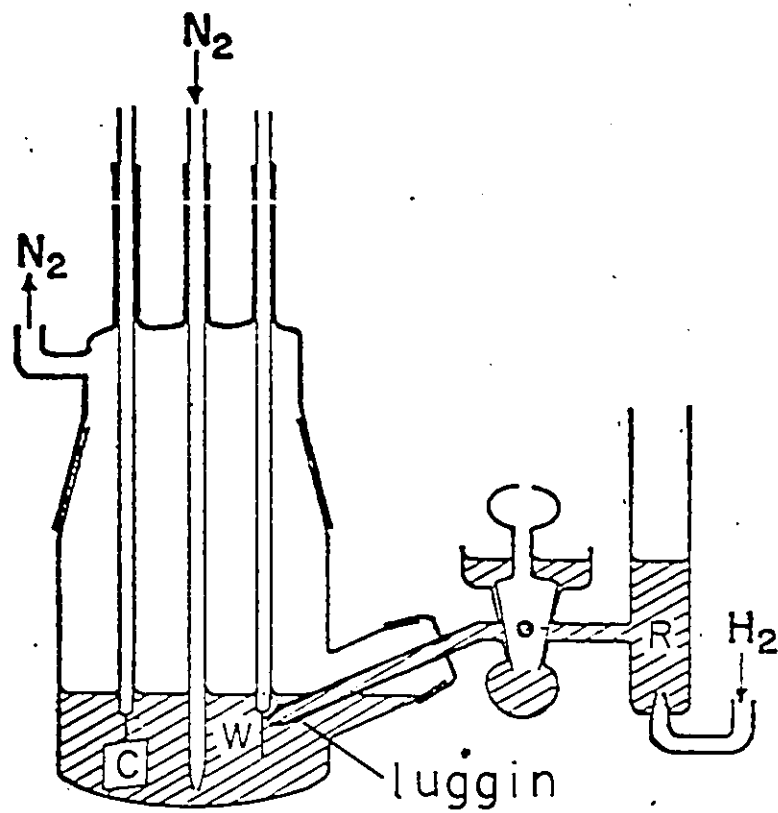


Fig. 5. Experimental Cell

work is shown in Fig. 6. The potential of the working electrode was controlled by means of a PAR 173 potentiostat according to a preselected programme set up by a TACUSSEL type GSATP function generator. The potential of the working vs the reference electrode was measured by means of a high-impedance electrometer probe supplied with the potentiostat. Current passing through the working-counter circuit was converted to potential by means of an accurate (Leeds and Northrup) ohmic transducer. The current vs potential profile was recorded on a Houston 2000 X-Y recorder, a Tektronix 5115 storage oscilloscope or on a Nicolet 1090A Explorer digital oscilloscope.

In some cases a minicomputer-based system, to be described in Chapter 3, was used to record the  $i$  vs  $V$  profile or  $i$  vs  $t$  data, and store and process it.

## 2.8. DETERMINATION OF ELECTRODE AREA

The area of the Pt and Ir electrodes was determined by measuring the H ionization charge as an internal standard. For Pt, a fractional coverage of H species equal to 1 was assumed in the usual way (52) to be attained at 0.0 V,  $E_H$  at the least positive end of the observable  $i$  vs  $V$  profile for H deposition/ionization over the potential range 0.45 to 0.0 V,  $E_H$ . This coverage corresponds to a charge of  $210 \mu\text{C cm}^{-2}$  (23). For Ir, this coverage was taken as 0.65 with respect to that of Pt, corresponding to H deposition/ionization between 0.065 and 0.450 V,  $E_H$ , as discussed by Woods (52).

Comparison of real and geometric areas gave roughness factors of 1.5 to 3, depending on the preparation technique. In the case of Ru, due to the overlap of upd of OH and H species, and to the presence of adsorbed as well as adsorbed H, the real area could not be determined reliably (54). Thus the currents for these electrodes are expressed as  $A \text{ cm}^{-2}$  (geometric area).

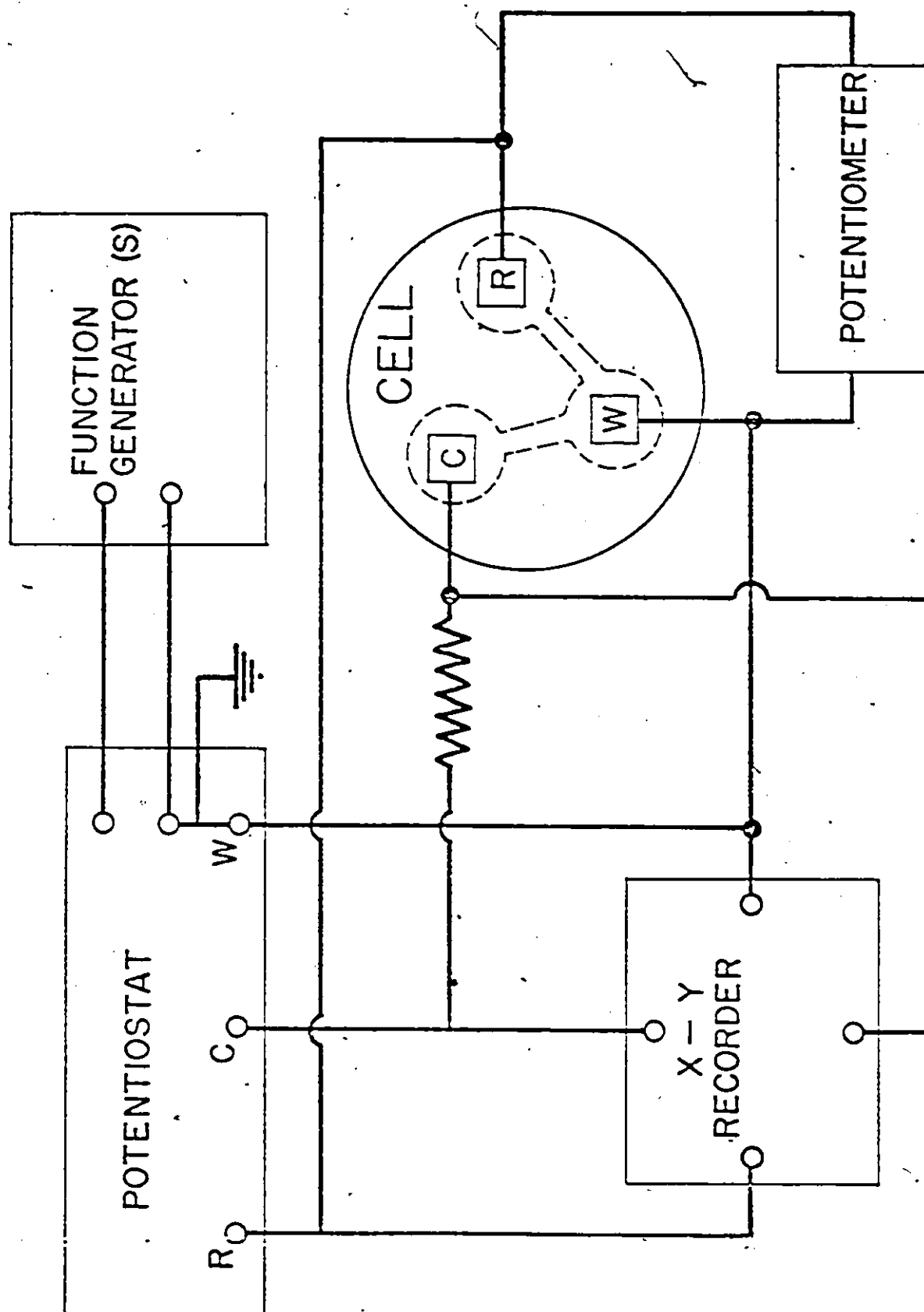


Fig. 6 Electrical circuitry employed in potentiodynamic sweep studies

## 2.9. POLARIZATION STUDIES

In order to determine the electrocatalytic properties of the electrodes under study, steady-state current vs potential relations for the  $\text{Cl}_2$  and  $\text{H}_2$  evolution reactions were obtained potentiostatically. The potential was stepped in increments of 0.010 V by means of a PDP-11/34 minicomputer based system (to be described in Chapter 3 ) and held for 10 s to allow current readings to be collected. A general programme allowing variable potential increments, as well as voltage offset and variable data collection times, is shown in Appendix I (page 217). Currents were recorded from a DANA 4200 digital multimeter for ascending and descending directions of potential change.  $\text{Cl}_{2(g)}$  or  $\text{H}_{2(g)}$ , at 100 KPa, was bubbled through the solution. All polarization data were corrected for IR drop, measured by means of a current interruption technique (183,184), since most of the electrode surfaces were active for  $\text{Cl}_2$  evolution and thus led to passage of appreciable currents,  $\sim 0.100 \text{ A cm}^{-2}$ .

The influence of mass transport in the  $\text{Cl}_2$  evolution reaction, was studied by means of a rotating Ir disk electrode provided by Dr. Tilak of Hooker Chemical Co.

## 2.10. $\text{Cl}^-$ ION ADSORPTION

Chloride ion adsorption experiments at Ir and Pt were performed in 0.5 M  $\text{H}_2\text{SO}_4$  by successive additions of known amounts of standard KCl solutions by means of a micrometer pipette fitted with 1 mm Teflon spaghetti tubing, terminating in a fine glass tip. The effects of  $\text{Cl}^-$  ion adsorption at the monolayer stage of surface oxidation of these electrodes were evaluated from observed changes of the Ir surface oxidation and of the Pt oxide reduction charges, respectively, measured from the cyclic-voltammograms taken after every addition of  $\text{Cl}^-$  ion, following a period of stirring by bubbled  $\text{N}_2$ .

### CHAPTER III

#### DEVELOPMENT OF A MINICOMPUTER BASED SYSTEM FOR CYCLIC VOLTAMMETRY STUDIES

##### 3.1. STATEMENT OF OBJECTIVES

In recent years, the use of computers in chemistry has rapidly increased, both for data acquisition and handling, and for numerical solution of problems. This has been facilitated by the development of micro and mini-computers available at reasonable prices and having performance exceeding that of some large-scale computers currently used only a few years earlier (185,186).

At the same time, the use of non-steady state techniques, such as cyclic-voltammetry, for the study of the electrochemistry of surface processes has opened up many new possibilities for data acquisition and interpretation (187).

Although, as will be discussed below, there are many uses for computers in the field of chemistry and, in particular, electrochemistry, few, if any, applications to the specific method of cyclic-voltammetry have been made, especially with regard to sampling and processing of (i,V) pairs of data during the course of experiments.

Also, industry-provided software suffers from the limitation of being too flexible, having to adapt itself to the applications of a variety of users. Hence, usually it is not 100% efficient for a particular, specific task.

It was therefore our purpose to adapt a PDP-11/34 minicomputer-based system and develop the necessary software for the purpose of data acquisition from and processing of cyclic-voltammetry experiments, and to

study the advantages and limitations of such a system as compared with traditional approaches, using experimental systems of interest in our laboratory in the present work.

### 3.2. PREVIOUS WORK

The application of computers in chemistry can be divided into the following areas:

- (a) Data acquisition, processing and storage (188-190);
- (b) Automatic experiment monitoring and control (191-193);
- (c) Simulation of behaviour of physical and chemical systems (194-197);
- (d) Data-bases for information retrieval (198,199); and
- (e) Educational purposes (200,201).

An excellent introduction to most of these topics can be found in Perrone and Jones' book (202).

Of the above mentioned areas, (a) and (b) are of particular interest to the electrochemist, and (c) is only starting to be developed due to the usually complex behaviour of most experimental systems.

In the field of data acquisition and treatment, Perrone and his group at Purdue University have carried out extensive work, especially in electroanalytical chemistry (203-205) and on a.c. impedance measurements (206).

The availability of A/D and D/A converters of various types has also started a trend towards "in-house" designed systems based on components available from various sources (188,207).

Important contributions have also been made by Bond et al. (190) on on-line fast Fourier transform Faradaic-admittance measurements, and by Alpen et al. (188) on a system for data acquisition in electrochemical systems.

On the other hand, in the field of automation of experiments,

Perrone et al. (203) have contributed much relevant work in recent years.

Other groups include those of Hampson et al. (208), Sierra-Alcazar et al. (189), Slaïma et al. (193), Mohilner (209) (who has been the leading contributor in the field of automated electrocapillarity measurements) and Chen (210) with his work in the area of ellipsometry and others (211-214), but their interest have been mostly directed towards situations where the events take place at a slow enough rate as to allow the computer-control system to respond accurately to the changes in the controlled variables.

In the particular case of cyclic-voltammetry, Breiter, as early as 1965 (215) described the use of a relatively primitive computer-based system for on-line collection of cyclic-voltammetry data with a paper-tape encoding system having obvious limitations with regard to sampling times. Since then Gosden et al. (207), Drake et al. (216) and Whiston et al. (217) have developed improved systems but their information lacks the detail needed to understand the different parameters of importance in the design and operation of such a system. It should also be mentioned that in all these systems the data are sampled as  $(i, t)$  pairs, while in the system to be described below,  $(i, V)$  pairs are collected for reasons to be discussed.

Last, but not least, the field of simulation is a very interesting and important one, in which advances are made slowly as the complexity of the model treated is increased to approach that of the real system. Along these lines, Conway et al. (218-221) published a series of papers directly related to the interpretation of cyclic-voltammetry results for surface processes; others (222-225) have explored similar approaches but, in this area, much remains to be done, e.g. with regard to simulation of oxide growth mechanisms, nucleation and hysteresis between oxide film formation and reduction processes, etc.

### 3.3. EXPERIMENTAL

#### 3.3.1. Electrochemical Aspects

Cyclic-voltammetry experiments were performed on systems of current interest in our Laboratory, in particular at Au electrodes in 1.0 M  $\text{HClO}_4$  and  $\text{Ba}(\text{OH})_2$  and at Ir in 0.5 M  $\text{H}_2\text{SO}_4$  at 298 K. Suitable potential-time programmes were chosen to illustrate the application of minicomputer procedures to the various types of experiments usually performed.

The techniques and equipment have been described previously elsewhere (1,2) and in this thesis (see Experimental section, chapter 2 ).

#### 3.3.2 Computer Aspects

##### 3.3.2.1 Hardware

The computer consisted of a PDP-11/34 mainframe with 32K words of RAM, a dual RX-01 floppy-disk drive (single-density), an RL-01 hard disk and a magnetic tape drive. Two peripheral units, a VT-55 (CRT terminal) and a LA-52, are available to interact with the computer.

The following interfaces were used to connect the computer to the laboratory set-up: AD11-K, 12 bits A/D converter with sample and hold circuitry and 16 channels single-ended or 8 channels in differential mode, an AA11-K, 12 bits D/A converter with 4 output channels and various signals to interact with storage oscilloscopes, and a KW11-K programmable clock connected by jumpers to the A/D converter board, to allow control of the sampling rate by clock overflow.

A block diagram of the computing and experimental set-up is shown in Fig. 7.

Additional circuitry could be added for sampling control by means of the Schmitt Trigger available in the AD11-K, that includes slope and level detection (inside broken lines in Fig. 7).

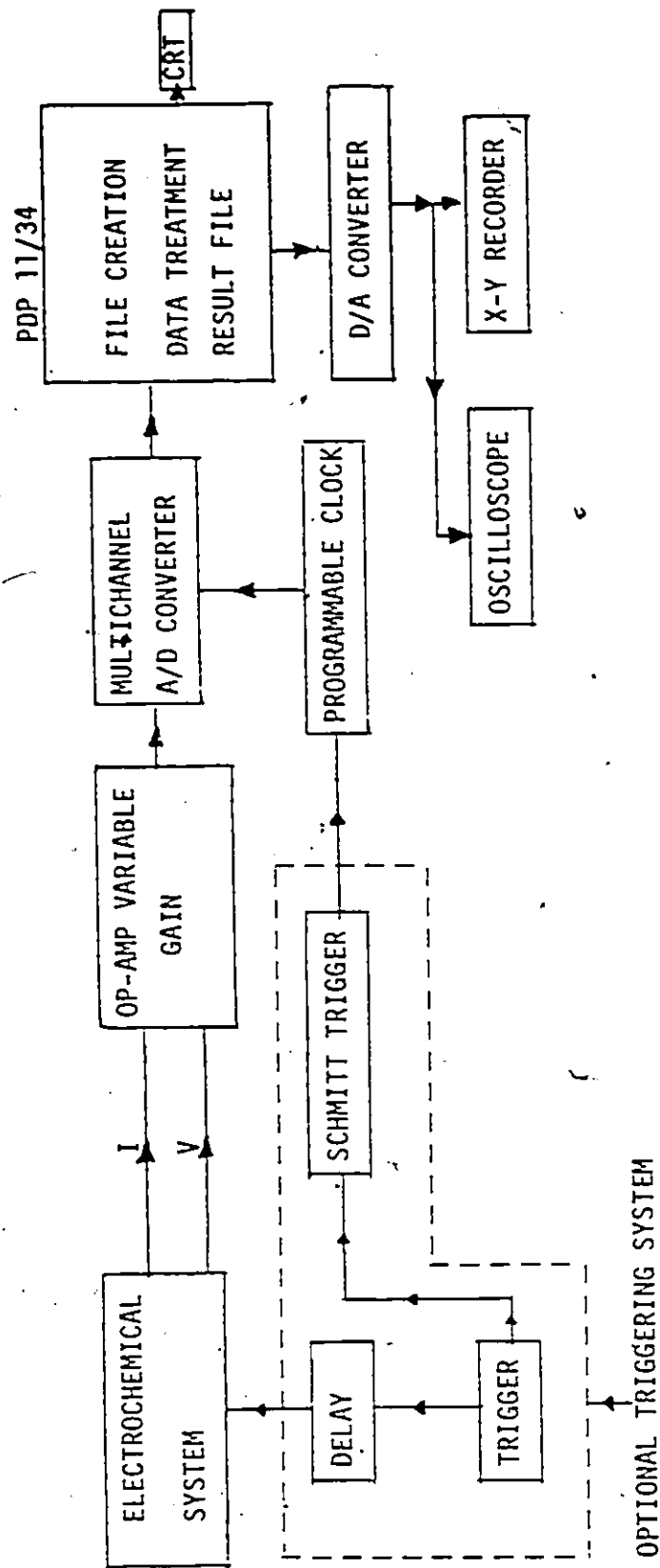


Fig. 7. Block diagram of experimental and computer hardware.

### 3.3.2.2. Software

The PDP-11/34 was supplied with an RT-11 single user system, with a foreground-background monitor that allows simple tasks, such as text editing, to be performed while another task is being carried out. A FORTRAN IV compiler and a MACRO-11 assembler are available for programming in both languages.

Programmes were written in FORTRAN and MACRO (PDP assembly language). FORTRAN sections of the programme handled the input of parameters and the creation of data files, while data acquisition, display and interface control were performed by FORTRAN-callable MACRO subroutines because of the need to manipulate the bits in the status register of the interfacing modules.

Arguments were passed between the main programme and the MACRO subroutines through the declaration of COMMON areas in a PSECT statement in the MACRO programme in order to free the working registers and for ease of programming.

Programmes for data collection, display and treatment are exemplified in Appendix I (page 217).

### 3.3.3. Procedure

In a typical experiment, the potential of the working electrode vs the reference electrode, and the resulting current in the working-counter circuit, transformed to a potential difference by means of an ohmic transducer, were fed through operational amplifiers, Tektronix AM 501, (acting as non-inverting amplifiers of variable gain) to the A/D converter by means of an H322 distribution panel. Shielded cable was used to minimize noise pick-up. The signals were fed in a differential mode.

The signal gain at the amplifier stage was limited by the maximum input range of the A/D converter which in the present system was + 5 to - 5 V.

The sampling rate was determined by software programming of the KW11-K clock. This has fixed crystal-controlled frequencies of 60 Hz, 100 Hz,

1 KHz, 100 KHz and 1MHz, and provision for obtaining any desired frequency through software programming of the clock counter buffer.

Once the data had been collected and stored, plotting by means of the D/A converter was made on an X-Y recorder with software control of the plotting speed, chosen sufficiently low that writing errors were avoided. Normally  $i$  vs  $V$  or  $i$  vs  $t$  was plotted.

### 3.4. RESULTS AND DISCUSSION

The results obtained will be discussed in terms of (1) optimization of input parameters; (2) exemplification of treatment of various types of transient profiles derived from electrochemical experiments; (3) noise level problems and (4) advantages of a computer-based system over conventional methods of data recording and analysis.

#### 3.4.1. Input Parameters

A number of input parameters must be optimized in order to utilize fully the capabilities of the A/D converter without degrading the data. These include:

##### 3.4.1.1. Rate of Sampling

Theoretically this should be determined by the rate at which the event takes place but in practice it is limited by hardware and software capabilities.

On the hardware side, it has to be recognized that the A/D converter has a finite "throughput time", which includes sample and hold, interchannel settling and A/D conversion time, typically 20  $\mu$ s. This couples with software delays such as flag testing and loading of status registers which in our case adds another 20  $\mu$ s, to give a maximum sampling rate ( $msr$ ) given by

$$msr \text{ (Hz)} = 1/\text{time delays (s)} = 25 \text{ KHz} \quad (3.1)$$

The practical sampling rate used depends on the resolution of the A/D converter and the sweep-rate at which the experiment is being conducted. Since the A/D converter has a data register that is 12 bits long, it can only store  $2^{12}$  values, i.e. 4096 integers (from 0 to 4095, maximum integer is  $2^{12} - 1 = 4095$ ). Then the resolution of the converter ( $r$ ) is given by

$$r = \frac{\text{Voltage range (mV)}}{2^{12}} = \frac{+5V - (-5V)}{4096} \approx 2.5 \text{ mV} \quad (3.2)$$

In sampling a linear potential ramp, the change in potential,  $\delta V$ , accompanying the passage of an increment of time,  $\delta t$ , is given by

$$\delta V \text{ (mV)} = \text{sweep-rate (mV s}^{-1}\text{)} \times \delta t \text{ (s)} \quad (3.3)$$

so that, combining the resolution of the A/D converter and the fastest sampling time, it follows that the limit of sweep-rate that can be handled for potential sampling at increments of 2.5 mV is given by

$$\text{Sweep-rate limit} = \frac{2.5 \text{ mV}}{40 \times 10^{-6} \text{ s}} = 60 \text{ V s}^{-1} \quad (3.4)$$

therefore, any linear potential ramp with sweep-rate  $> 60 \text{ V s}^{-1}$  will be sampled at potential intervals greater than 2.5 mV, as given by equation (3.4). If two channels are sampled, which is the case when  $i$  vs  $V$  profiles are to be recorded, the highest sweep-rate that can be handled, when sampling is to be made every 2.5 mV will be halved.

It is possible to improve the resolution by means of amplification of the  $V$  signal, so that consecutive  $V$  points that would normally be separated by only 1 mV, and thus would be below the resolution of the A/D converter, are in practice separated by 1 mV multiplied by the amplification factor.

However, this improvement in resolution reduces the limit of sweep-rate that can be handled for potential sampling at increments of 1 mV, as given by equation (3.4)

#### 3.4.1.2. Mode of Sampling

Sampling can be performed in several modes determined chiefly by the individual preference with regard to the desired display of data and type of information required. For cyclic-voltammetry experiments, however, sampling alternate values of  $i$  and  $V$  is convenient so that the profile can be later displayed in the same way that it is normally recorded, viz. as  $i$  vs  $V$ .

A problem arises in the sampling of  $i$ - $V$  pairs as follows: after a sample  $V_i$  has been taken, the current sampled next,  $i_i$ , does not correspond to  $V_i$  but to  $[V_i + (\text{sampling time} \times \text{sweep-rate})]$ . Thus, a correction has to be introduced by means of software instructions before the data are treated further.

In sampling  $i$  vs  $t$  relations, triggering of the collection routine at an accurately known potential value on the potential ramp is necessary in order to assign correct values of potential corresponding to those of time on the time axis, as determined by the sweep-rate.  $i$  vs  $V$  sampling simplifies the circuit and does not require any knowledge of the ramp slope.

Nevertheless, in some cases such as IR drop determination or recording of current or potential decay curves, it is obvious that sampling directly in time is required.

#### 3.4.1.3. Synchronization of Sampling

In the study of a current response which is stable repetitively in time with respect to a periodic potential programme, triggering the initiation of  $i$  vs  $V$  sampling is not necessary, rather only the time interval between samples need be controlled.

The AD11-K sampling was timed by means of overflow pulses from the clock. In the repetitive mode, the clock counts at a predetermined rate until the previously loaded clock count buffer goes to zero. Then an overflow

pulse triggers the AD11-K which collects a sample and the initial value of the counter is reloaded and the process repeated.

For collection of one-shot  $i$  vs  $t$  or  $V$  vs  $t$  transients, triggering of the initiation of sampling is required and can be conveniently achieved by means of Schmitt trigger (ST) circuits on the KW11-K which start the clock when the input potential to the ST crosses a predetermined threshold in a specified direction. A delay circuit may be needed in order for the ST to be triggered slightly before the transient signal is presented, so that the initial part of the transient may be obtained (this feature, also known as "negative" triggering, is available in digital oscilloscopes and transient recorders, where a portion of the memory is continuously sampled and stored and when the trigger signal initiates the sampling of the transient signal, the rest of the memory is filled with data. Thus, a similar approach can also be used with the computer based system, through appropriate software instructions, which eliminates the need for additional circuitry). Once sampling has been initiated, timing proceeds as outlined above.

#### 3.4.1.4. Number of Samples

This depends primarily on (a) the type of experiment [continuous sweeping contrasted with holding the potential constant at the end of a sweep (anodic or cathodic) for programmed periods of time]; (b) the number of sweeps to be recorded (in the event of optimization through signal averaging) and (c) memory limitations of the storage device. Typically we have found that approximately 4000 points ( = 16 blocks ) is a convenient sample number, with the data being stored as integers to minimize file size.

#### 3.4.2. Typical Profiles

Figs. 8 to 14 show sets of results obtained for several different types of experiments which serve to illustrate the usefulness and capabilities

of the computer-based method. The salient features of these  $i$  vs  $V$  profiles will be briefly discussed below, as each illustrates a different advantage or capability of the computer and emphasises the versatility of the technique. Where possible, directly photographed oscilloscope traces are displayed for comparative purposes together with the  $i$  vs  $V$  profiles recorded and played back by means of the computer on large-scale graphs at a low writing speed.

Types of experiments and results will now be considered.

#### 3.4.2.1. Work at Various Sweep-Rates

Fig. 8 shows results of a typical study of the effect of varying the sweep-rate ( $s$ ) on the surface oxide formation and reduction behaviour of Au (1) in 1 M  $\text{HClO}_4$ , keeping  $i/s$  (which gives the capacitance (226)) constant in the range of  $s = 0.5$  to  $10 \text{ V s}^{-1}$ . The behaviour at higher sweep-rates was not included here because of the relatively large IR drop which then arises at appreciable surface oxide coverages ( $\theta_0 \sim 0.5$ ). The behaviour at lower sweep-rates is discussed later with respect to background noise.

#### 3.4.2.2. Systematic Variation of the Anodic End Potential

Fig. 9 shows the results of an experiment of this type carried out at  $10 \text{ V s}^{-1}$  on Au in 1 M  $\text{HClO}_4$ . The resolution demonstrated here on the X-Y recorder output is strikingly superior to that obtainable on the oscilloscope trace. Note that the trace thickness on the storage scope used routinely obliterates detail in "crowded regions"; it is evident from Fig. 9 that this is not a problem at all on the recorded output of  $i$  vs  $V$  data, processed by the computer.

#### 3.4.2.3. Fast Sweep-Rate Work

Fig. 10 shows an  $i$  vs  $t$  profile for the double-layer charging region of the  $i$  vs  $V$  profile on Au in 0.2 M  $\text{Ba(OH)}_2$  at  $50 \text{ V s}^{-1}$  where only a small amount of surface oxide is allowed to form. This example illustrates

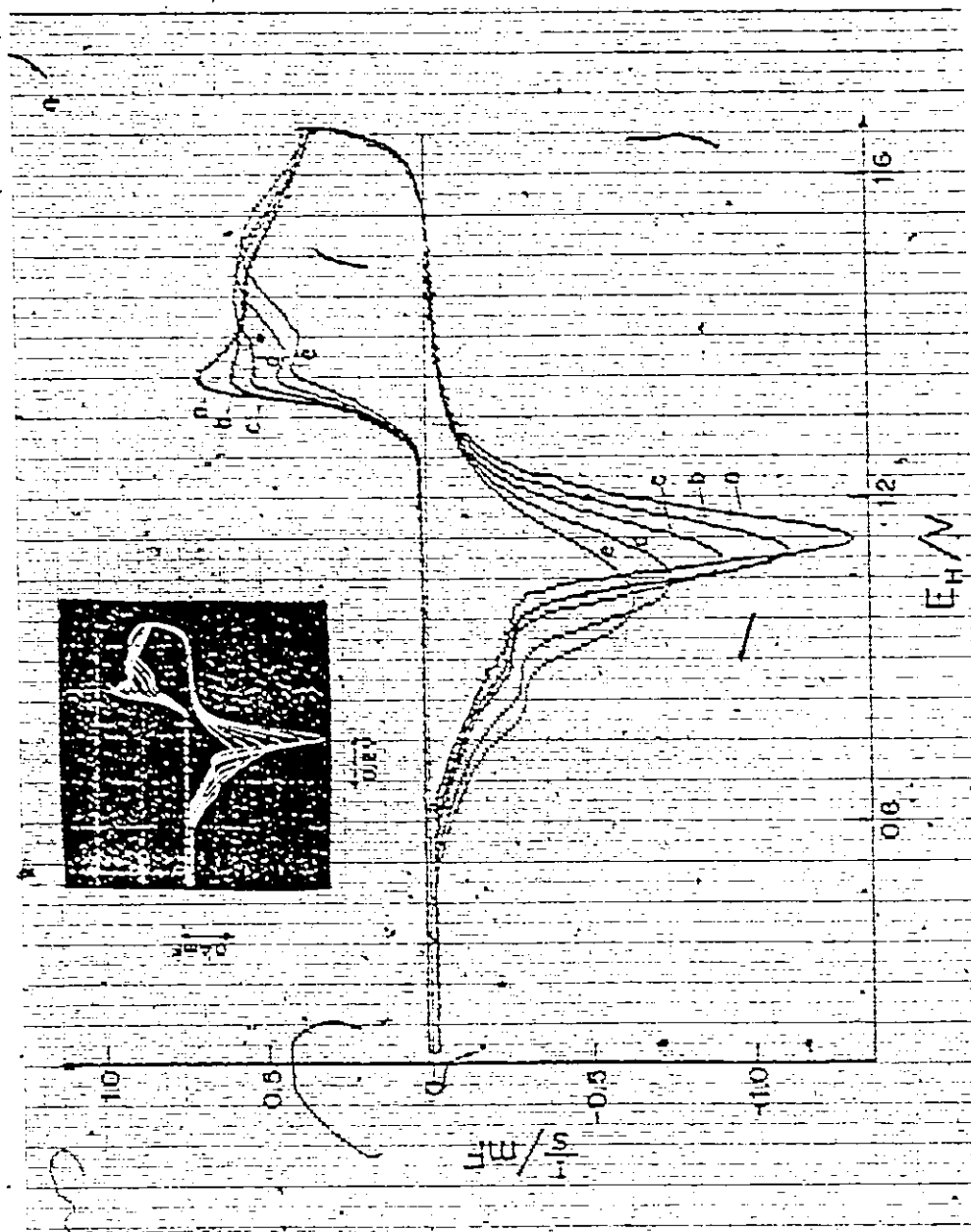


Fig. 8. Comparison of cyclic-voltammetry  $i/s$  vs  $V$  profiles for Au in 1 M HClO<sub>4</sub> at 298 K collected and plotted through the computer, with directly recorded oscilloscope traces: (a) 0.5; (b) 1; (c) 2; (d) 5 and (e) 10 V s<sup>-1</sup>.

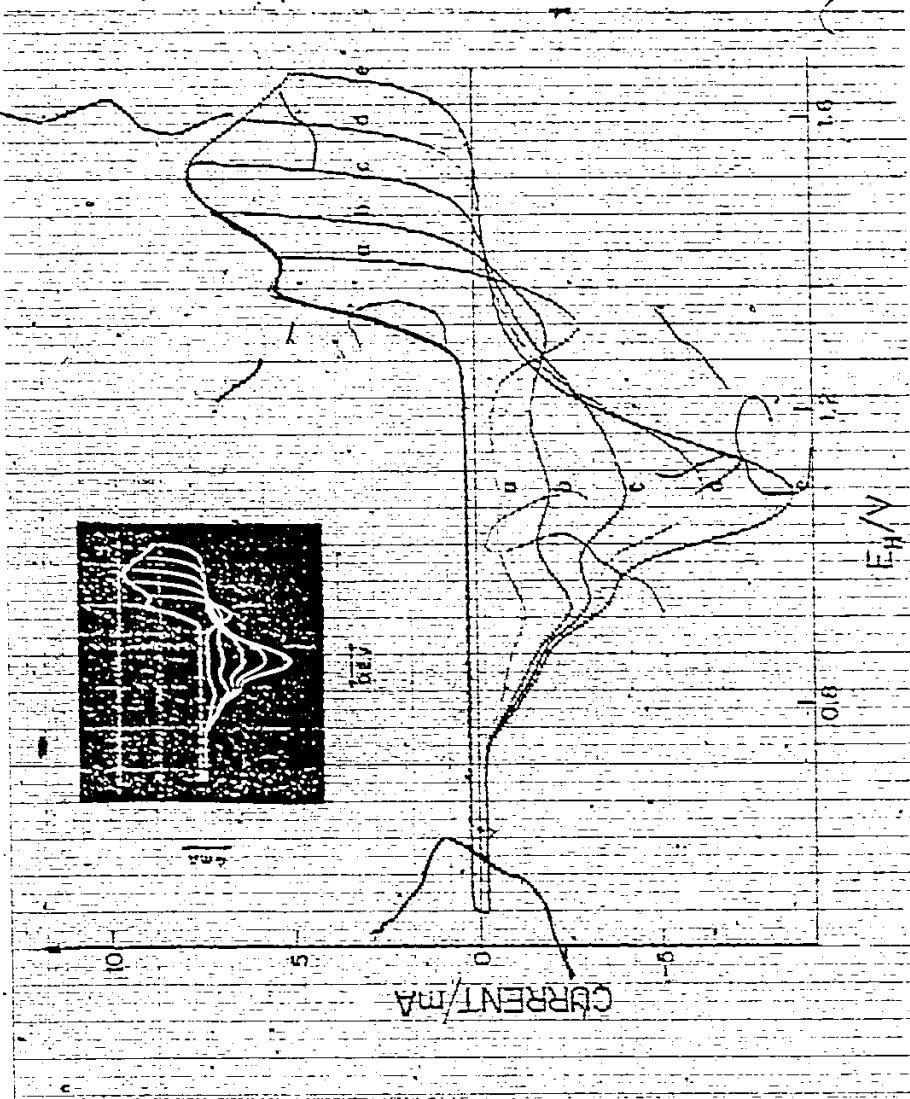


Fig. 9. Cyclic-voltammetry  $i$  vs  $V$  profiles for Au in 1 M HClO<sub>4</sub> at 10 V s<sup>-1</sup> and 298 K, with variable anodic end potential, collected and plotted through the computer, compared with directly recorded oscilloscope traces: (a) 1.415; (b) 1.475; (c) 1.540; (d) 1.600 and (e) 1.665 V,  $E_H$ .

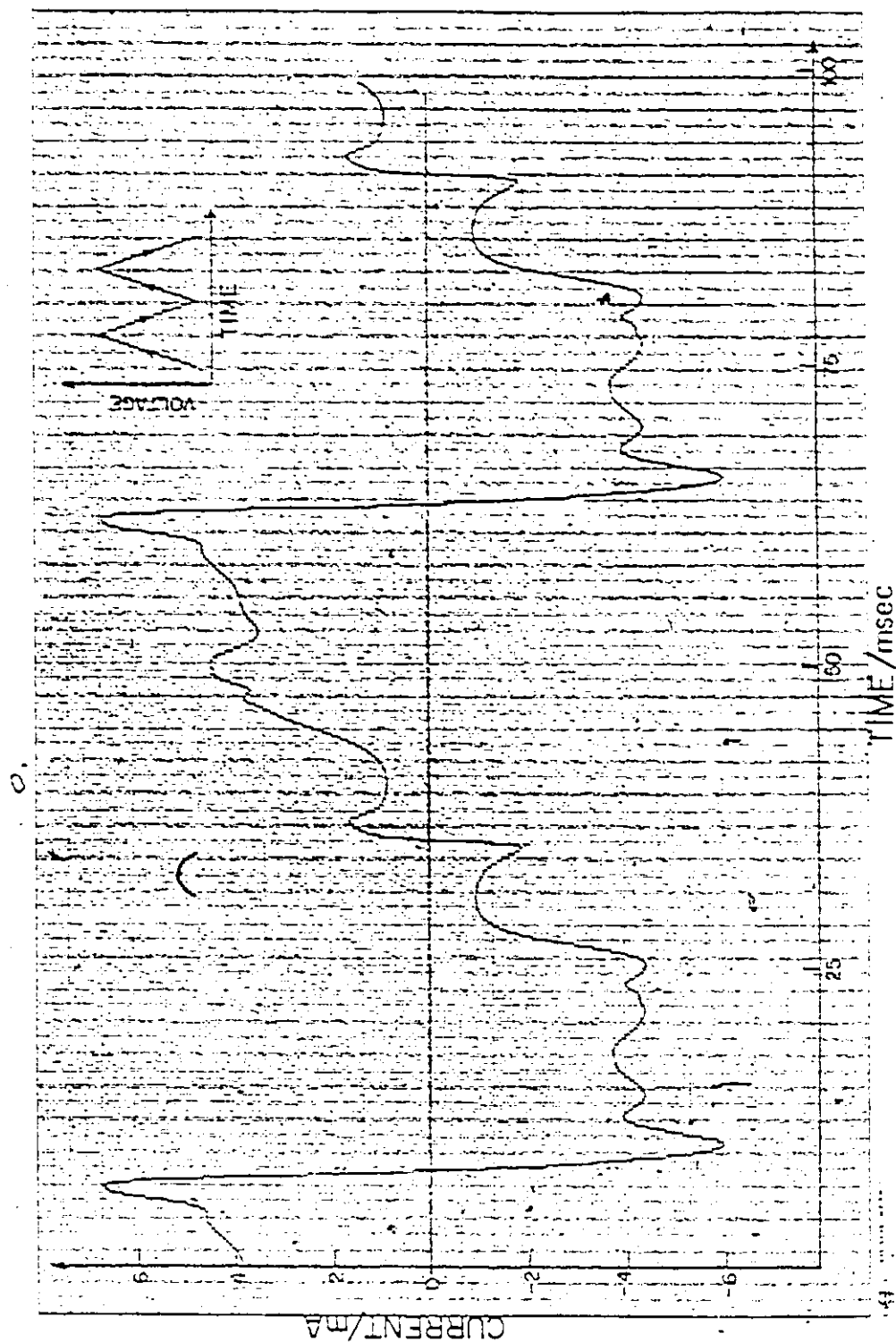


Fig. 10. Computer-collected and plotted  $i$  vs  $t$  profiles for Au in 0.2 M Ba(OH)<sub>2</sub> at 50 V s<sup>-1</sup>

and 298 K, obtained in cyclic-voltammetry between potentials  $E_a = 1.252$  and

$$E_c = 0.040 \text{ V}, E_H.$$

the applicability of the method to experiments at higher sweep-rates.

#### 3.4.2.4. "Holding" Experiments

Experiments where the end potential of the anodic sweep is "held" or maintained constant for programmed periods of time, are called "holding" experiments. Fig. 11 shows the  $i$  vs  $V$  profiles obtained on Au in 1 M  $\text{HClO}_4$  at  $2 \text{ V s}^{-1}$  where the anodic end potential limit was maintained for 0 (multisweep), 0.1, 0.5, 1 and 2 s. Again the resolution obtained on the X-Y recorder output is seen to be substantially superior to that on the oscilloscope, especially in detecting small, but significant, changes in relatively crowded regions of the profile which are not distinguishable on the concomitant oscilloscope trace (note especially the  $O_{A2}$  and  $O_{C2}$  regions; cf. ref 1).

Fig. 12 presents an expanded view of the computer-plotted profile with a holding time of 0.5 s and shows how the  $i$  vs  $t$  decay curve can also be easily observed.

#### 3.4.2.5. Data Treatment

Fig. 13 shows an  $i$  vs  $V$  profile for Ir in 0.5 M  $\text{H}_2\text{SO}_4$  at  $0.05 \text{ V s}^{-1}$  [due to the fact that the thick oxide, showing reversible redox processes, is present on the surface of this electrode (see section 4.3), the current signal is high enough not to be disturbed by noise problems, as will be discussed below]. The corresponding charge isotherm, determined by computer integration of the  $i$  vs  $V$  profile, is plotted together with the latter profile with appropriate software-determined scales for each of the plots. The charges for the anodic and cathodic profiles were obtained separately by the integration procedure discussed below.

The integration was performed by means of the FORTRAN subroutine QSF from the FORTRAN Scientific Subroutine Package provided by Digital. This

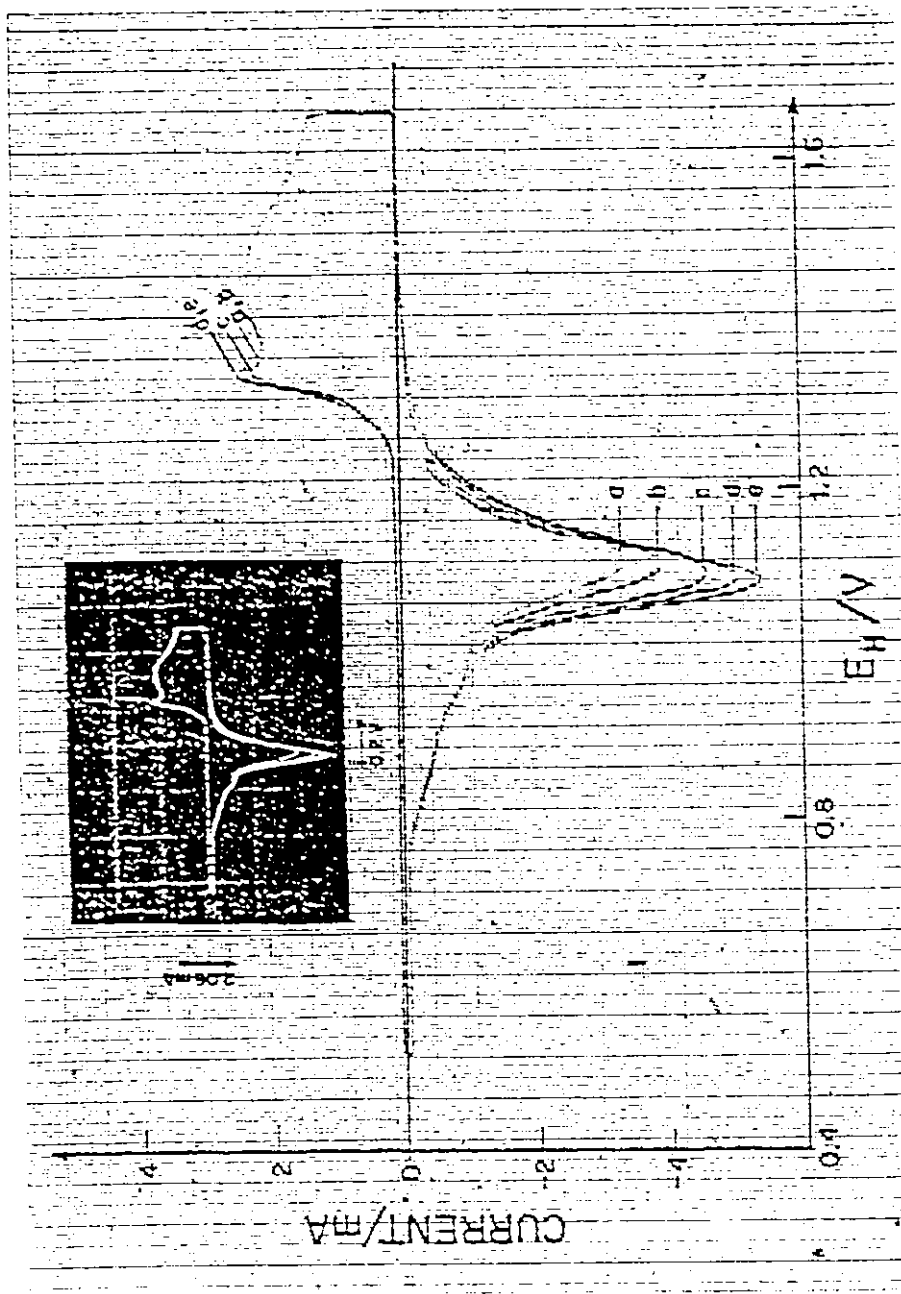


Fig. 11. Successive anodic and cathodic  $i$  vs  $V$  profiles for linear potential sweep at Au in 1 M HClO<sub>4</sub> at 2 V s<sup>-1</sup> and 298 K, collected and plotted through the computer, compared with directly recorded oscilloscope traces, with arrest ( $\tau$ ,s) of potential at 1.622 V,  $E_H$  for (a) 0.0; (b) 0.1; (c) 0.5; (d) 1.0 and (e) 2 s.

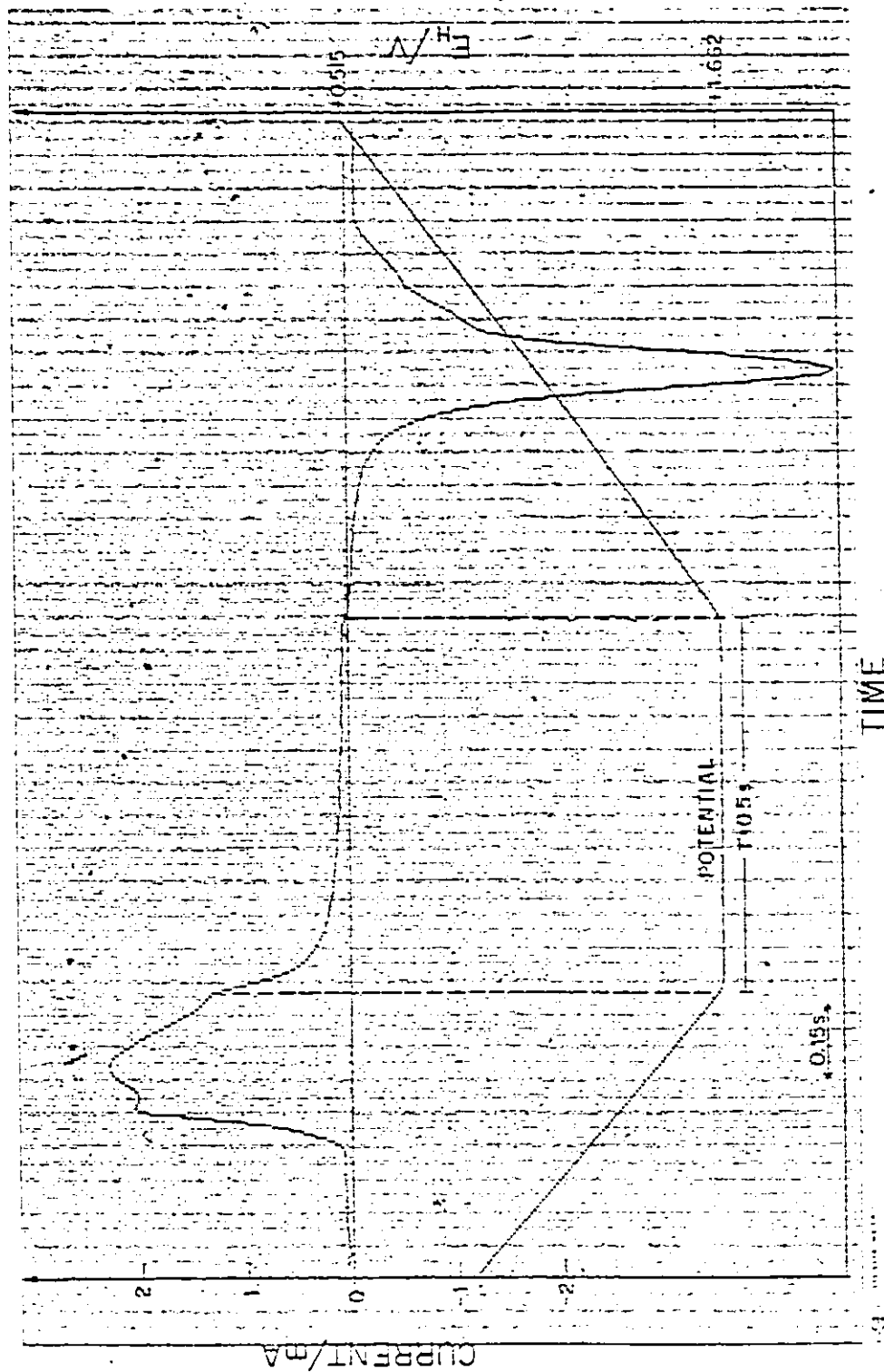


Fig. 12. Computer collected and plotted  $i$  vs  $t$  response to anodic and cathodic linear potential sweeps for Au in 1 M  $\text{HClO}_4$  at  $2 \text{ V s}^{-1}$  and 298 K, with an arrest for 0.5 s at 1.622 V,  $E_H$ . This plot also shows the current decay on holding the potential at  $E_a$ .

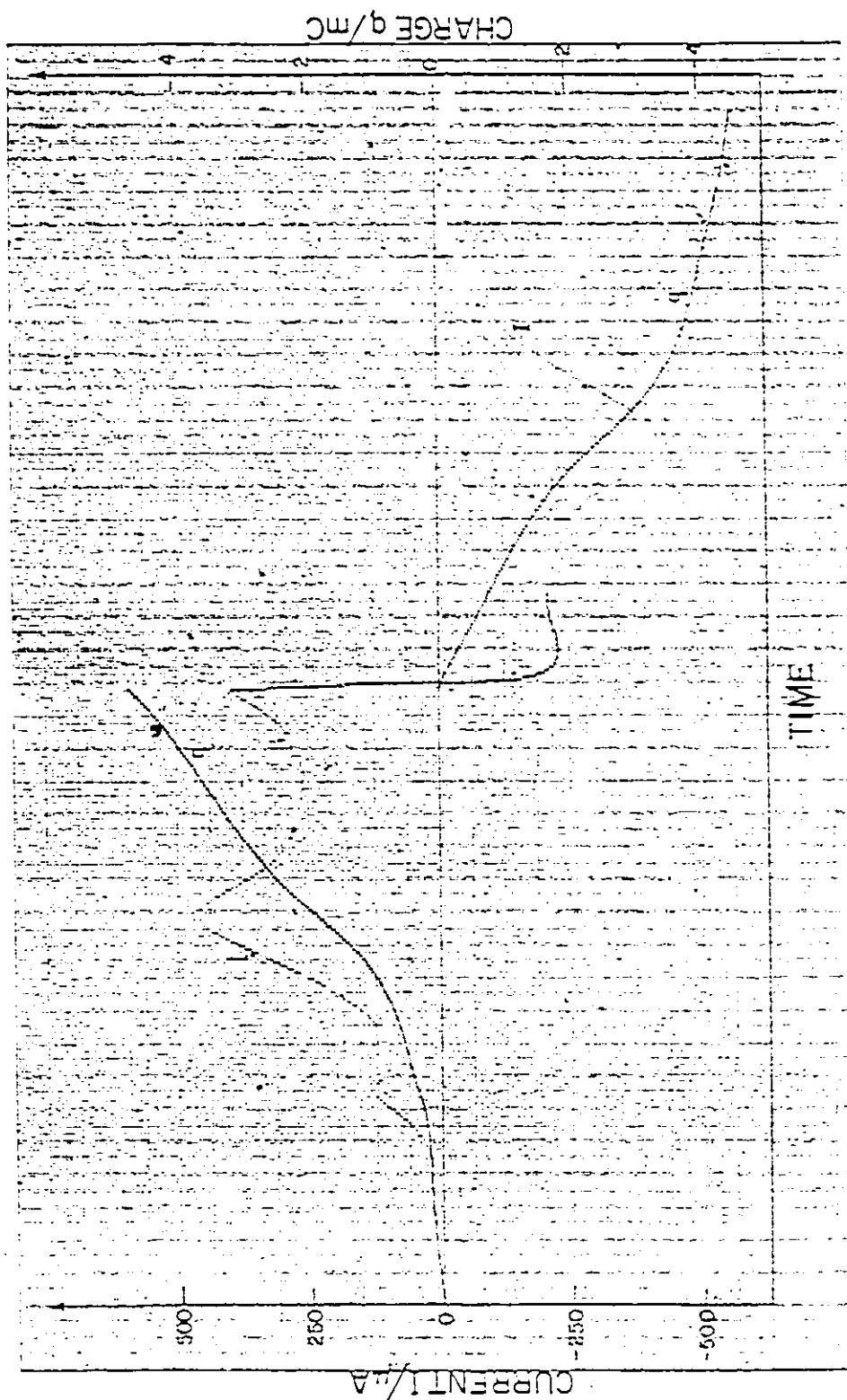


Fig. 13. Computer-collected and plotted  $i$  vs  $t$  anodic and cathodic profiles for Ir in 0.5 M  $H_2SO_4$  at  $0.050 V s^{-1}$  and 298 K, together with the computer calculated and plotted charge isotherm ( $q$ ) for these profiles.

subroutine utilizes Simpson's rule, together with Newton's rule (227,228), to integrate equidistant data values (in our experiments, collected at constant intervals  $\Delta V$  or  $\Delta t$ ).

#### 3.4.2.6. Noise Level

Experiments at  $s < 0.5 \text{ V s}^{-1}$  tend to have a higher noise level than those carried out at higher  $s$  values because of the relation between  $i$  and  $s$ . Thus, at lower  $s$ , the  $i$  signal is relatively smaller and amplification does not help because the signal-to-noise ratio is low and fixed, so that the noise becomes amplified with the signal, unless a signal-averaging procedure is applied to a repeated set of sweeps.

For  $s \leq 0.05 \text{ V s}^{-1}$ , as applies in Fig. 14 for Ir in  $0.5 \text{ M H}_2\text{SO}_4$  at  $0.05 \text{ V s}^{-1}$ , a 60-cycle filter can be effectively used to record an excellent, undistorted noise-free  $i$  vs  $V$  profile of the monolayer stage of surface oxidation at Ir (see section 4.3). For values of  $s$  beyond  $0.1 \text{ V s}^{-1}$ , however, such a filter will distort the  $i$  vs  $V$  profile to an unacceptable extent. While an X-Y recorder can be used without a filter because some damping of the noise is achieved on account of mechanical inertia, the computer samples both the signal and the noise giving profiles that are unacceptable if a filter cannot be used in this range of values.

Some approach to a solution of this problem can be made by design of alternate filters (digital or analogue ones) as well as by multiple sweep collection, followed by signal averaging as is done in reflectance work (229).

#### 3.5. CONCLUSIONS

It is apparent that a computer-based system can be utilized with advantage in routine experimental cyclic-voltammetry work over the traditional methods employing analogue or digital oscilloscope recording, or the use of transient recorders.

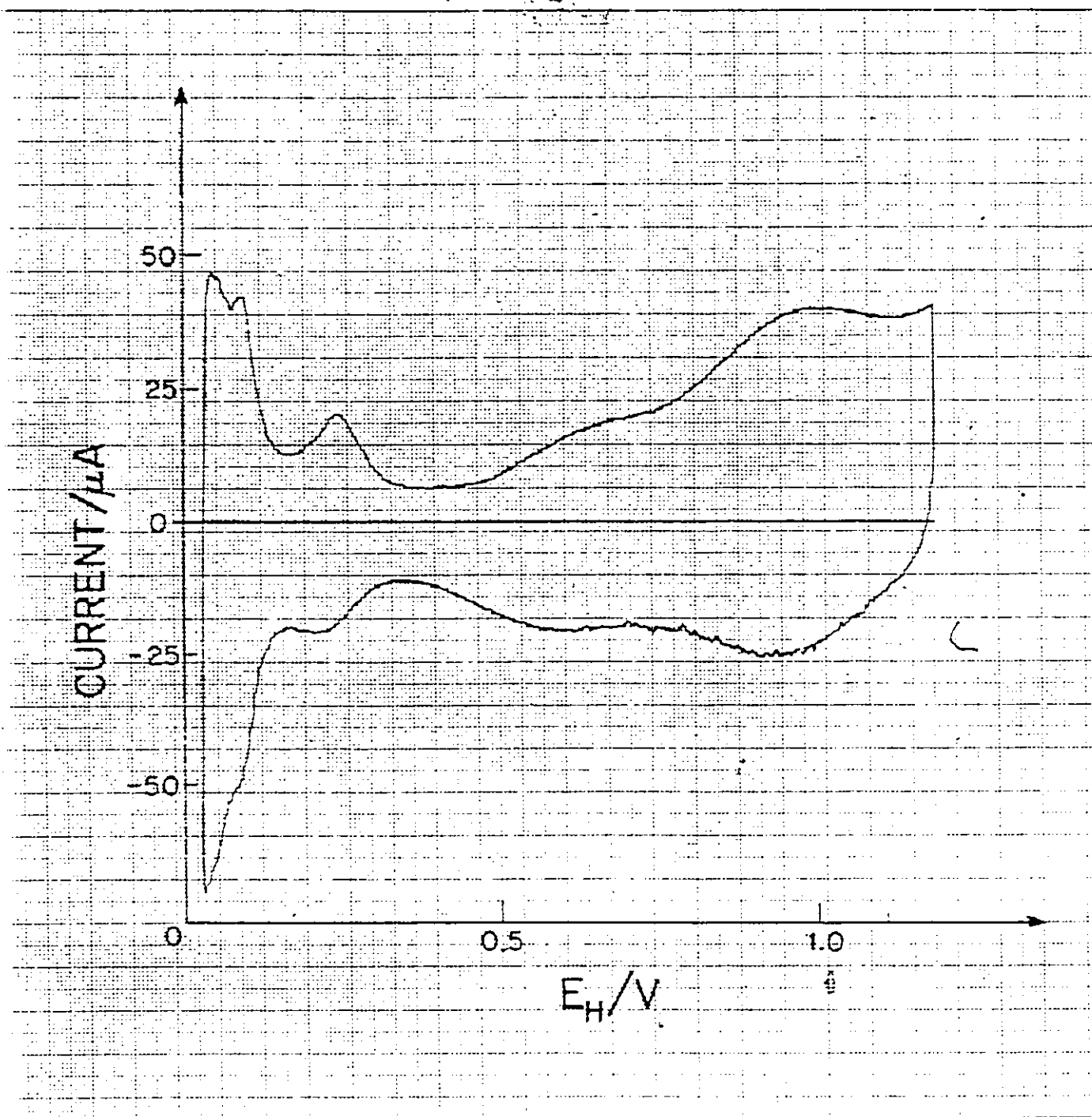


Fig. 14. Computer-collected and plotted  $i$  vs  $V$  profile for Ir in 0.5 M  $H_2SO_4$  at  $0.050 V s^{-1}$  and 298 K.

Some of the advantages of the computer-based data collection and treatment system are:

(a) High resolution of transient or repetitive non-steady state signals allows small but significant differences in  $i$  vs  $V$  profiles to be detected better than is possible on storage oscilloscopes;

(b) Computer calculation of derived quantities, such as the charge isotherm for an electrochemical surface process, determination of peak parameters (230) and treatment of data in general can be done accurately and rapidly;

(c) Output of the collected data at low, error-free writing speeds on to an X-Y recorder allows manual calculation of diagnostic parameters (230), superposition of experimental data and calculated results, as well as scaling up of data obtained under various conditions, and at various times, for comparison or publication purposes;

(d) "Safe" storage of results in the short and long term, e.g., on magnetic tape, can be easily realized; and

(e) Other possibilities include automatic IR correction, multistate (19) curve deconvolution or simulation procedures and applications to the study of diffusion-controlled processes by means of cyclic-voltammetry. For the latter type of application, the data processing programmes will, of course, be different from those employed for treatment of surface processes.

## CHAPTER IV

### THE ELECTROCHEMICAL BEHAVIOUR OF IRIIDIUM ELECTRODES

#### 4.1. INTRODUCTION

The element Iridium, was discovered in 1802 by Smithson Tenant. Its name comes from the greek word "iris", because of the "iridescent" colors of some of its derivatives.

It is a noble metal, with a natural abundance of  $< 10^{-7}\%$  of the earth's crust (231), where it is present primarily as sulphides, since its oxides are not thermodynamically stable.

It is obtained mainly as a by-product of Pt extraction by thermal decomposition of ammonium chloriridate at the end of the Pt separation process, its purity at that stage being of 99.9%.

Iridium chemistry is centered around the I, III and IV oxidation states. It has a d-electron configuration of  $5d^9$ , in its zero oxidation state instead of the expected  $5d^7, 6s^2$ .

As in the case of Pt, its favourable corrosion resistance and electrocatalytic properties, somewhat offset by its price, have led to a great deal of work on the electrochemistry of Ir electrodes, specially in recent years.

The study of Iridium in electrochemistry can be divided into two main periods: firstly, prior to 1968, when the thick oxide of Ir, with reversible characteristics was first noticed by Stonehart, Angerstein-Kozłowska and Conway (20); and secondly, later studies, mainly since 1972.

#### 4.2 PREVIOUS WORK

Iridium has specially interesting characteristics with regard

to its electrochemical oxidation behaviour. Under certain conditions it behaves like any other Platinum metal and exhibits an irreversible formation and reduction of a monolayer surface oxide. However, when the conditions are modified, it can develop an oxide film hundreds of nm thick that exhibits reversible oxidation/reduction currents in cyclic-voltammetry but these currents do not correspond to formation of the oxide from the metal or reduction of the oxide to the metal. They are currents for a solid-state redox process within the thick film (232). Other metals such as Ru, Rh, Os and W can be made to behave in a similar way (50,51,72,77,233).

Because this thick film is quite stable and can only be removed under extreme conditions such as potential cycling in strong  $\text{H}_2\text{SO}_4$  or by subjecting it to anodic polarization at potentials greater than 1.7 V,  $E_H$  for extended periods of time, extreme care has to be taken when studying this metal to achieve the desired reproducible states of the oxide film. Thus, the early literature and unfortunately some of the papers in recent years are full of examples of this problem.

In the early 1960's, Will and Knorr (2) and Breiter et al. (234-236) studied the behaviour of Ir electrodes under potentiodynamic conditions with regard to the formation and reduction of very thin oxide films (i.e. with the oxide at more or less the monolayer stage), and the H deposition/ionization behaviour at the electrode surface. Unfortunately, their voltammograms show clearly the presence of a film thicker than a monolayer on the Ir surface, so that the real formation/reduction of the oxide monolayer was not really characterized in that work.

In 1972, Capon and Parsons (237) noted that the thick film did not develop in 5 M  $\text{H}_2\text{SO}_4$ , so they were able to observe, for the first time, the true oxide monolayer profile for an Ir electrode, and showed that under

the effect of potential cycling, a thicker oxide film could be developed, exhibiting reversible anodic/cathodic, oxidation/reduction currents.

That Ir exhibits a reversible redox behaviour, quite different from that of Pt, was first noticed by Stonehart et al. (20) in this Laboratory. The reversibility of the film was initially studied by means of reflectivity experiments in work by Gottesfeld and Conway (238).

This reversible behaviour of iridium oxide films attracted most of the subsequent interest so that the monolayer stage was not further investigated until the present work was carried out.

Various Russian workers (239-244) have been active in this field, carrying out studies on ion adsorption at the surface of Ir electrodes and on the formation and reduction of oxide layers, but there is a complete lack of consistency in that body of work, since the initial state of the electrode surfaces varies widely from publication to publication, i.e. films of different thicknesses were evidently already present on the Ir surfaces, rendering the results of these workers on Iridium oxidation behaviour quite inconclusive.

In 1973, Schubert et al. (245), by means of Field Ion Microscopy, studied the anodic oxide film formed on Ir electrodes. They observed that, in 1M  $\text{H}_2\text{SO}_4$  below 0.5 V,  $E_H$  no oxide was detectable, at 1.0 V,  $E_H$  a monolayer of oxide was present on the surface and at potentials in the  $\text{O}_2$  evolution region, thicker films were clearly indicated, with the (111) plane being especially resistant to oxide film formation. The films were amorphous and the metal/oxide interface was very sharp.

A number of important papers appeared in 1974: Otten and Visscher (246,247) studied the film growth by ellipsometry and proposed a "pit model" to account for the experimental results. This model was later proven

incorrect by Gottesfeld et al. (88) in a more detailed analysis of the ellipsometric data.

Rand and Woods (248) obtained the first  $i$  vs  $V$  profiles for the oxide monolayer in 0.5 M  $H_2SO_4$  and pointed out the importance of proper care in the pretreatment of the electrodes. They determined the dissolution rate for Ir under cyclic-voltammetry conditions as being equivalent to  $50 \mu C cm^{-2} cycle^{-1}$  and pointed out that the monolayer of nominal IrO was completed at about 1.5 V,  $E_H$ .

They also remarked on one of the most surprising features of the thick film state of oxidized Ir, that is the constancy of the H ionization charge and of the double-layer charging current, independent of the huge increase in oxidation/reduction charge that takes place at more positive potentials upon prolonged cycling. Rand and Woods (248) tried to explain this effect on the basis of a very porous structure that allowed the electrolyte to reach bare metal patches at the metal/oxide interface where H deposition/ionization could take place, but they could not account for the unchanged double-layer charging region which implied that a negligible area increase had taken place during the development of the thick film.

As in the case of Pt, the use of the H ionization charge as an internal standard for determining the real area of Ir electrodes at the monolayer stage, was suggested by Woods (52). It was shown that this procedure is satisfactory provided the integration of the  $i$  vs  $V$  profile for H charge is carried out between 0.06 and 0.45 V,  $E_H$  and that a coverage,  $\theta_H$ , by H species, relative to that on Pt taken as 1, of 0.65 is assumed.

The effect of various experimental parameters on the growth of the thick oxide film was studied by Buckley and Burke (249). They found that previously formed oxide could be irreversibly lost when the electrode

was polarized at  $E_a > 1.7 \text{ V}, E_H$  for various lengths of time, that the rate of growth of the film on cycling at  $0.1 \text{ V s}^{-1}$  was  $13.3 \mu\text{C cm}^{-2} \text{ cycle}^{-1}$  and that  $\text{Cl}^-$  ion did not have any effect on the anodic/cathodic cycle charge or on the reversible behaviour of the thick oxide films. On the basis of these observations, they proposed that the growth was due to accumulation of an incompletely reduced oxide species and that the reversible behaviour of the thick oxide films was due to a change of oxidation state of Ir species in the oxide which was not reduced to Ir metal [cf. Gottesfeld(88)] on the cathodic cycles.

To account for the H and double-layer region behaviour, a model involving reduction of the outer layer of oxide to Ir metal [i.e. forming a sandwich in which most of the oxide remains between the Ir metal substrate and the reduced exterior of the film, similar to that in Shibata's model for thick films on Pt (37)] capable of acting as sites for H deposition, was proposed.

Buckley and Burke (249) also noted for the first time that, on cycling, the oxide films exhibited electrochromic properties, i.e. a change of color on changing the applied potential difference or corresponding oxidation state of the film.

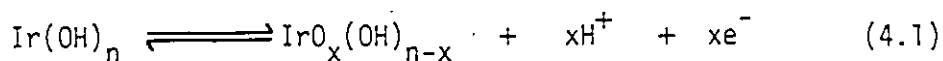
Later, in 1976, they extended their work to include the study of the influence of the anodic/cathodic end potentials in the potential-sweep programme on the growth of the thick films (250). They observed negligible growth in basic media but this has been proven to be incorrect, since other work (93), including that described in this thesis, has shown that the oxide film can, in fact, be grown in basic pH solutions.

The nature of the oxide species constituting the film was studied by Rand and Woods (251) using X-Ray Electron Spectroscopy, and by Kim et al.

(276) by means of ESCA. Both groups concluded that "IrO<sub>2</sub>" species are present at anodic potentials, > ca. 1.0 V, E<sub>H</sub>, and that "IrO<sub>3</sub>" species are present at higher anodic potentials, > ca. 1.6 V, E<sub>H</sub>, i.e. when the film begins to dissolve. SEM studies performed by Rand and Woods showed a porous film that becomes loose with increasing thickness.

A mechanism of oxide growth was proposed in 1978 by Arvia et al. (252) that accounted for some, but not all, of the experimental facts. Their model is based on two interfaces, metal/oxide and oxide/electrolyte, operating simultaneously to allow transport of electrons and ions in and out of the film. Incomplete reduction of an anodically formed species, coupled with the breaking of "metal-metal bonds" to generate new sites for H deposition was supposed to account for the continuous growth and for the constancy of the H ionization region charge. However, the complete scheme is rather elaborate and involves many species and reactions, some of which are improbable and tend to obscure the intended explanation.

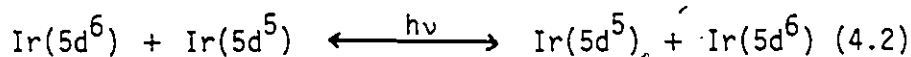
The electrochromic properties (EC) of the Iridium oxide film were investigated by Gottesfeld et al. (253) at Bell laboratories with regard to its possible use as a display device as described in the corresponding patent (254,255). They proposed a mechanism coupling proton transfer with oxidation of Ir species in the oxide film, similar to that for WO<sub>3</sub> (255,256) electrochromism, to account for the observed effects on the basis of results obtained in buffered/unbuffered solutions at pH 3.5. Thus, the redox reaction would be as follows, noting the required role of protons:



Later studies by McIntyre et al. (257) confirmed that the EC reaction involves a change of oxidation state of the film of 1, and that the

species involved are Ir(III)/Ir(IV) hydrated oxides, as shown by Raman and XPS data (258).

The coloration is attributed to an intervalence transition of the type:



in a mixed valence oxide, involving the injection of holes into the  $5d_{t_{2g}}$  sub-band of the oxide.

A controversy developed at that time between Gottesfeld and McIntyre (259), and Rice, Beni and Shay (260,261) as to the actual mechanism of the electrochromic reaction: the latter authors invoked  $\text{OH}^-$  transfer based on results obtained in non-aqueous acidic media, where no EC effect was observed by them, in relation to the behaviour in non-aqueous basic media where an EC effect was evident.

On the other hand, Gottesfeld et al. (259) were not able to obtain an EC effect in  $\text{Li}^+$  solutions without any protons; they demonstrated the necessity for  $\text{H}^+$  by experiments with buffered/unbuffered, stirred/unstirred solutions, where they distinguished two processes for the coloration of the film: a fast one associated with the use of bound water as the source of protons, together with those available at the oxide/electrolyte interface and a slower one involving diffusion of ionic species from the electrolyte. McIntyre et al. (257) by means of Rutherford back-scattering experiments, also ruled out the possibility of  $\text{OH}^-$  being the species involved in the EC reaction.

While Beni and Shay (261) also attempted to model their results after two reactions; in their case pH-dependent, their work has an obvious flaw in the assignment of peak potentials as a function of pH that led them

to erroneous conclusions.

This controversy is still alive with both sides publishing results that seem to support their respective viewpoints (262-266). One of the factors complicating the interpretation of the results is the porosity and high degree of hydration of the film, which makes it difficult, if not impossible, to eliminate the effects due to bound water. Also, the importance of free access of the electrolyte into the pore system implies that studies performed in organic solvents are difficult to interpret because of the possible blocking, by the solvent molecules, of the pore system.

The nature of the oxide films at Ir was studied by Gottesfeld et al. (88) by means of ellipsometry. They found that the oxide (once formed) remains present, even at cathodic potentials, where it is very slowly reduced but never back to the bare metal.

The effect of  $\text{H}_2\text{PO}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{HSO}_4^-$  ions on the electrochemical behaviour of Ir oxide films was mentioned in a preliminary note by Arvia et al. (267) but an observed increase in charge in the H deposition/ionization region with cycling indicates probably the presence of impurities, which could have affected the results.

Finally, in 1980, McIntyre et al. (257) calculated and proved conclusively that the EC reaction involves  $1\text{ e}^-$  and that all the film is active (at least at the thickness studied by them, ca. 295 nm). They utilized a stripping technique to remove the oxide film and to determine the oxide's weight, SEM observations to estimate the oxide thickness and cyclic-voltammetry to obtain the total charge corresponding to the EC process. The density of the hydrated oxide, which was indicated as  $\text{IrO}_2$ , was found to be  $2.0\text{ g cm}^{-3}$ , compared with that of bulk  $\text{IrO}_2$  which is  $11.68\text{ g cm}^{-3}$ .

Later, two very important contributions appeared (266,268),

the results of which will be utilized subsequently in this thesis to support a model for the oxide behaviour developed in the present work.

First, an a.c. impedance study of the oxide film indicated a change in conductance(268) from  $< 10^{-2} \Omega^{-1} \text{ cm}^{-2}$  (units as in reference 268) in the bleached state (reduced) to  $> 10^2 \Omega^{-1} \text{ cm}^{-2}$  for the colored (oxidized) form. Also the infinite frequency capacitance,  $C_{\infty}$ , was found to be potential-dependent, i.e. it had a value of  $60 \mu\text{F cm}^{-2}$  at  $0.4 \text{ V}, E_H$  and of  $760 \mu\text{F cm}^{-2}$  at  $1.0 \text{ V}, E_H$  for an oxide film 150 nm thick. These results were used by Gottesfeld (266) to interpret the observed behaviour of the  $\text{Fe(CN)}_6^{-3}/\text{Fe(CN)}_6^{-2}$  redox couple at a rotating Ir disc electrode compared to that on an Iridium oxide disc electrode, in terms of the change in conductivity of the oxide as a function of the applied potential difference.

#### 4.3. THE MONOLAYER STAGE OF Ir OXIDATION

As noted in section 4.2, although Ir has been the subject of many papers in recent years, the main interest has been centered on understanding the growth and properties of thick oxide films that can be developed on Ir under certain conditions, similar to those which can be formed at Ru, Rh, Os and W (50,51,72,77,233).

Very few studies have, however, dealt with the thin, monolayer type film, and those that have been addressed to the behaviour of the monolayer surface oxidation stage (2,234,237,239) have, it appears, encountered the problem that the initial surface already had an oxide film on it, thicker than a monolayer, formed during electrode pretreatment cycles.

This has led to some conflicting results (235,236,240,241) with regard to the electrochemical behaviour of Ir at the monolayer stage, which has been elucidated in the present work, where Ir electrodes have been studied in the monolayer state of oxidation by taking extreme care in the preparation

and pre-treatment of the electrodes in order to avoid the development of the thicker oxide films which show reversible behaviour.

The importance of obtaining, reproducibly, the monolayer stage of Ir electrodes, lies not only in the interest of studying that particular case (to place the behaviour of the metal in the proper perspective when compared to the behaviour of other Pt-group metals) but with respect to the accurate determination of growth of the thick film at the early stages.

#### 4.3.1. Results and Discussion

##### 4.3.1.1. H Deposition/Ionization Region

Ir electrodes, under potentiodynamic conditions, present a potential region for H deposition/ionization that spans the potential range 0.060 V,  $E_H$  to 0.45 V,  $E_H$  in 0.5 M  $H_2SO_4$  at 298 K. On the anodic side, there are 3 H-ionization peaks clearly distinguishable, labelled  $H_{A1}$ ,  $H_{A2}$  and  $H_{A3}$  (Fig. 15) and a fourth peak that appears as a shoulder on  $H_{A3}$  and will be referred to as  $H_{A4}$ . This peak is better resolved at higher sweep-rates or lower temperatures (52). Due to overlap of the reduction of oxygen species (see below) with the H-deposition region, the cathodic side of the profile is less clearly resolved, unless the anodic end potential of the sweep is limited to a low value, e.g. up to 0.6 V,  $E_H$ . Under such conditions,  $H_{C2}$  and  $H_{C3}$  are clearly distinguished but  $H_{C1}$  is obscured by the onset of  $H_2$  evolution and  $H_{C4}$  is again noticeable as a shoulder of  $H_{C3}$ .

The coverage of the adsorbed H species in this potential range in acid solution has been estimated (52) as 0.65 of a monolayer, with respect to that at Pt, the latter having a charge of  $210 \mu C cm^{-2}$  (23) at full coverage.

The evaluation of the coverage for solutions of higher pH is complicated by the overlapping of the onset of up of OH species [as in the case of Ru in acid media (54)], although a clear redistribution of the

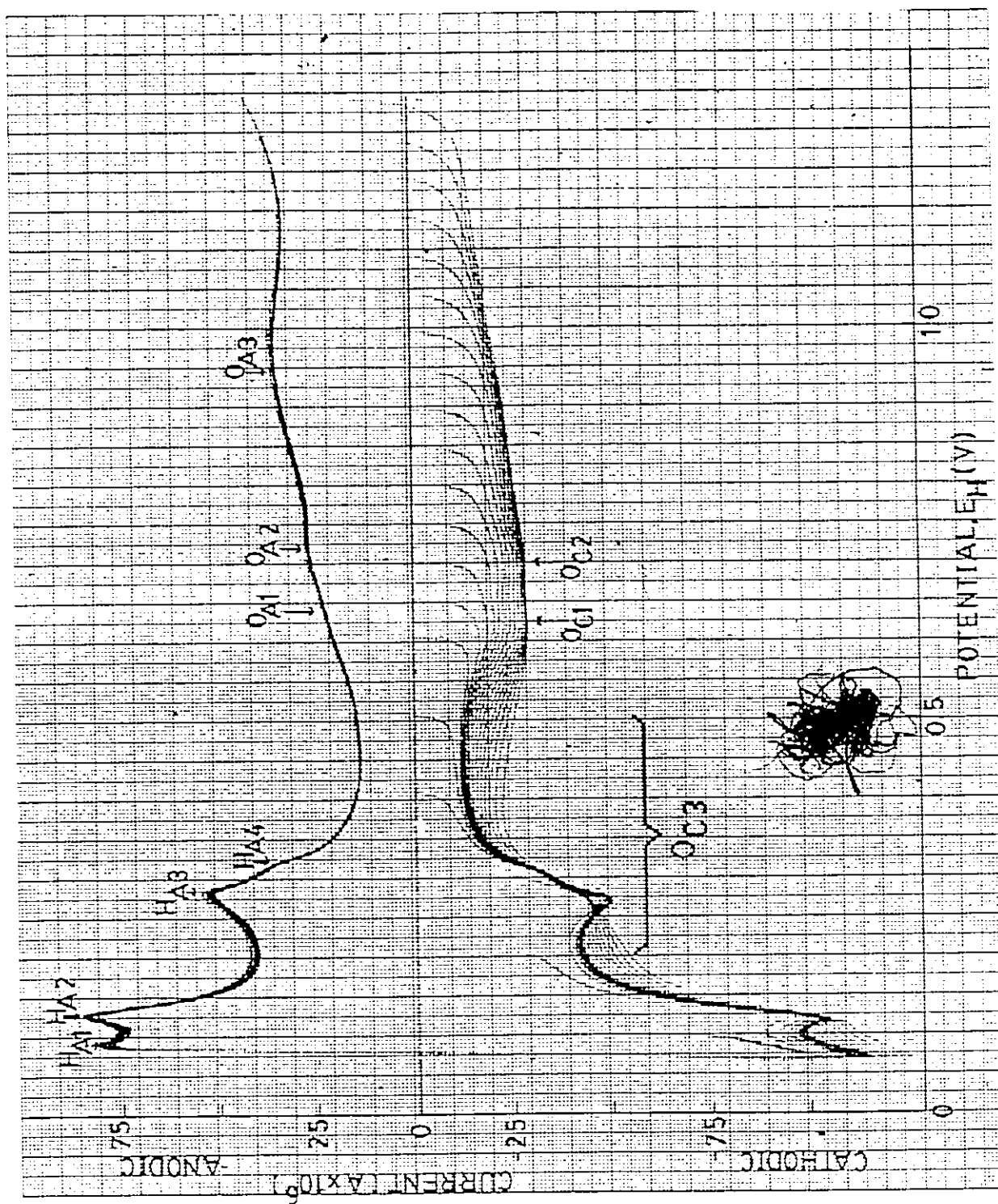


Fig. 15. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir electrode at  $0.100 \text{ V s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  at  $298 \text{ K}$ .

adsorbed H amongst the different peaks is evident in Figs. 16 and 17, where the change in the  $i$  vs  $V$  profile in that potential region can be appreciated for  $5 \times 10^{-3}$  M  $H_2SO_4$  and 0.1 M  $Na_2CO_3$ .

The potentials at which the H peaks appear are also a function of the electrolyte (due to anion adsorption effects) as shown in Table III. Since the H deposition/ionization reaction is expected to have the same pH dependence as that of a hydrogen electrode in the same solution, the observed dependence of peak potential ( $E_p$ ) has to be attributed to the following factors:

(a) The effect of adsorbed ions, since upon increasing the pH, the  $H_2$  region moves to the negative side of the p.z.c\*, thus changing the ion adsorption properties of the surface;

(b) Since the half-width of the peaks also appears to change as a function of pH, it is likely that the interaction parameter,  $g$ , has been altered; in fact the broader peaks observed in base indicate a stronger repulsive interaction, or a less favorable attractive one. It has to be noted, however, that the broadening could also be due, partly, to increased irreversibility of the process, as indicated by the difference between the apparent peak potentials for the anodic and cathodic components of, e.g.  $H_{A3}/H_{C3}$  which is 0.045 V in 0.5 M NaOH while it is only 0.010 V in 0.5 M  $H_2SO_4$ .

(c) As pH is increased (Table III), the nature and the concentration of the anions are also usually changed.

(d) Change in the energy of the M-H bond due, or leading to, a combination of any of the previous factors.

The shape and potential for the  $H_{A3}$  peak, which is clearly resolved from its neighbors in 0.5 M  $H_2SO_4$ , presents an interesting opportunity to

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\* p.z.c.(potential of zero charge).

TABLE III  
PEAK POTENTIALS ( $V, E_H$ ) FOR IONIZATION OF STATES OF ADSORBED H AT Ir

| SOLUTION                       | $H_{A1}$ | $H_{A2}$ | $H_{A3}$ | $H_{A4}$ |
|--------------------------------|----------|----------|----------|----------|
| 0.5 M $H_2SO_4$                | 0.080    | 0.115    | 0.270    | 0.300    |
| $5 \times 10^{-3}$ M $H_2SO_4$ | 0.090    | 0.160*   | 0.295    | n.d      |
| 0.5 M $Na_2CO_3$               | 0.140    | 0.240    | 0.320    | n.d      |
| 0.5 M NaOH                     | 0.125    | 0.235    | 0.315    | n.d      |

n.d : not distinguishable

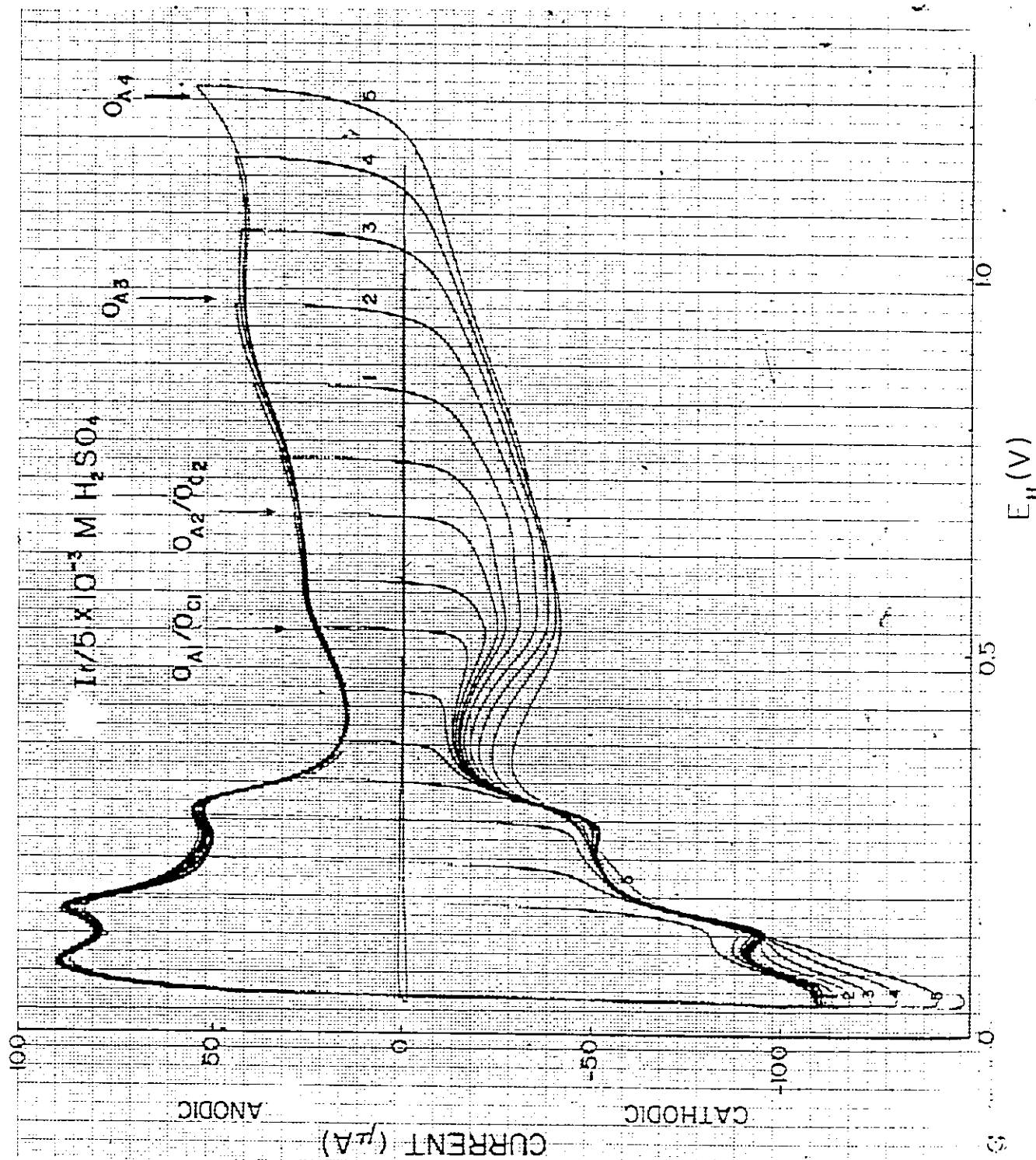


Fig. 16. Cyclic-voltammogram  $i$  vs  $V$  profile for Ir electrode at  $0.050 \text{ V s}^{-1}$ ,  $298 \text{ K}$  in

$5 \times 10^{-3} \text{ M H}_2\text{SO}_4$ .

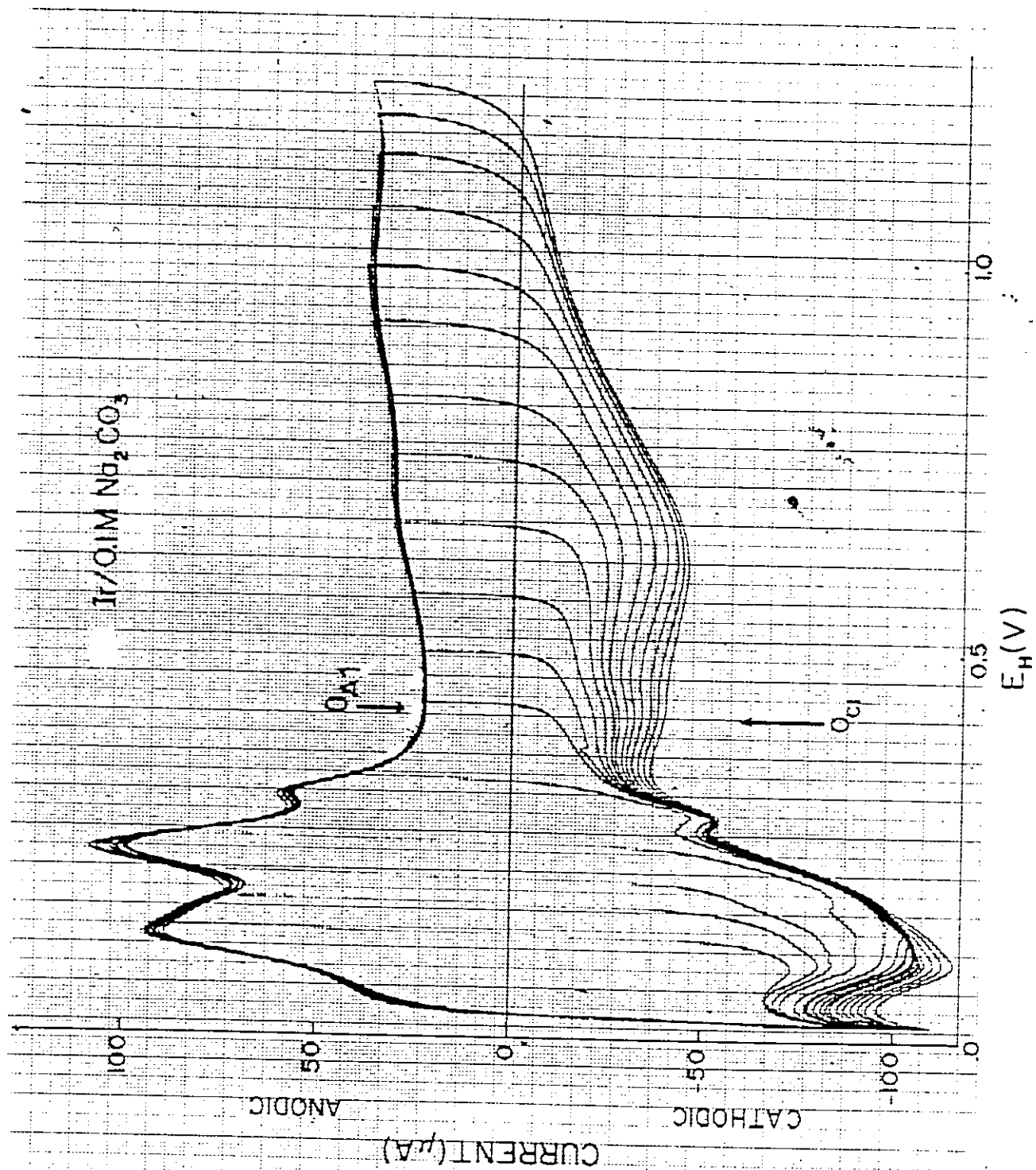


Fig. 17. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir electrode at  $0.050 \text{ V s}^{-1}$ ,  $298 \text{ K}$  in  $0.1 \text{ M Na}_2\text{CO}_3$ .

evaluate the parameters discussed by Conway et al. (218) as being characteristic of a  $1 e^-$  surface process and defining the transition (218) between a reversible and an irreversible surface reaction under the influence of increasing sweep-rate. Such results are shown in Table IV, and the behaviour of the diagnostic parameters, i.e. the capacitance at the peak maximum,  $C_p$ , the half-width of the peak,  $\Delta V_{1/2}$ , and the peak potential,  $E_p$ , as a function of sweep-rate ( $s$ ) is shown in Fig. 18a.

As can be seen, although the values differ somewhat from the theoretically predicted ones, partly due to difficulties in evaluating the parameters from a real  $i$  vs  $V$  profile where overlapping of peaks is always present, the agreement and the trend is rather good between the experimentally determined values and the calculated ones for the model reaction, (218). The  $C_p$  values are somewhat smaller in the experimental case because, as discussed previously, the  $\theta_H$  reaches only 0.65 of a monolayer in the case of Ir, while the calculated  $C_p$ 's are based on a  $\theta_H = 1$ . A normalizing correction factor of  $1/0.65$  can be easily applied.

Angerstein-Kozłowska and Conway (230) also discussed the significance of the limiting sweep-rate,  $s_0$ , corresponding to the exchange current density,  $i_0$ , below which a surface process is reversible.

A related value,  $s'_0$ , is obtained by extrapolation of anodic and cathodic peak potentials as a function of  $\log s$  to a common point, with appropriate allowance for interaction effects (230).

A general expression for the relation between  $s_0$  and  $s'_0$  was derived by the above authors as:

$$\log s_0 = \log s'_0 - \log \left[ 1 + \frac{g}{2} (1 - \theta_{p,irrev}) \right] + \frac{g}{4.6} (\theta_{p,irrev} - \frac{1}{2}) - \frac{V^0}{2.3} b \quad (4.3)$$

Thus, for  $g = 0$ , as seems to be the case for the  $H_{A3}/H_{C3}$  processes in this system,  $\log s_0 = \log s'_0$ . The result of this graphic approach is shown in

TABLE IV  
Diagnostic Parameters for a  $1e^-$  Surface Reaction

| PARAMETER            |        | THEORY (ref. 218)<br>$1e^-$ process, $g = 0$ | EXPERIMENTAL<br>HA3, 0.5 M $H_2SO_4$ |
|----------------------|--------|----------------------------------------------|--------------------------------------|
| $C_p$ , $F\ cm^{-2}$ | rev.   | $2.14 \times 10^{-3}$                        | $6.7 \times 10^{-4}$                 |
|                      | irrev. | $1.57 \times 10^{-3}$                        | $5.53 \times 10^{-4}$                |
| $\Delta V_{1/2}$ , V | rev.   | 0.091                                        | 0.110                                |
|                      | irrev. | 0.126                                        | 0.145                                |
| $d(E_p)/d(\log s)$   | rev.   | 0                                            | 0                                    |
|                      | irrev. | 0.118                                        | 0.092                                |

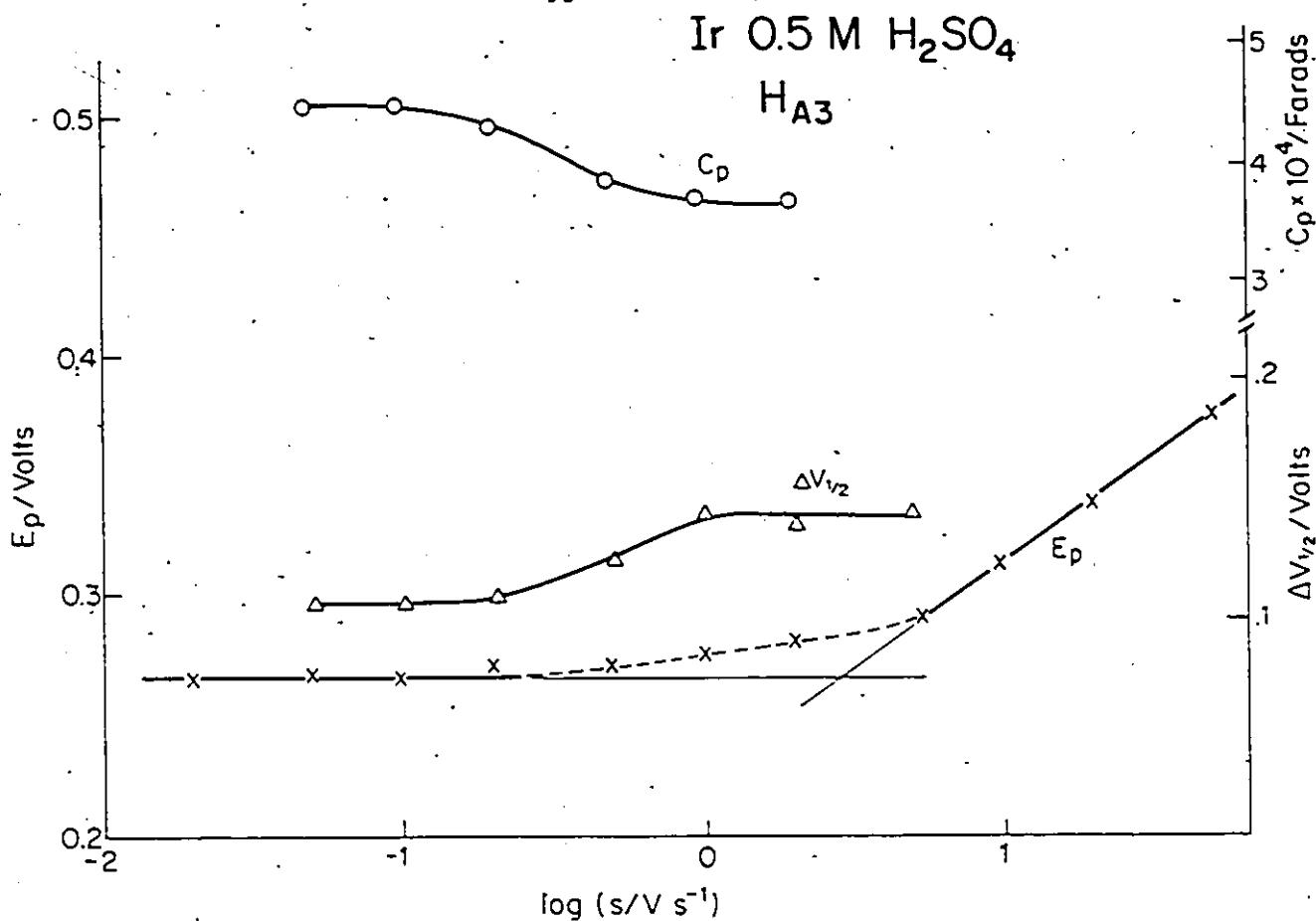


Fig. 18a. Dependence of characteristic parameters ( $C_p$ ,  $\Delta V_{1/2}$ ,  $E_p$ ) on  $\log s$ , for H<sub>A3</sub> region at Ir in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 298K.

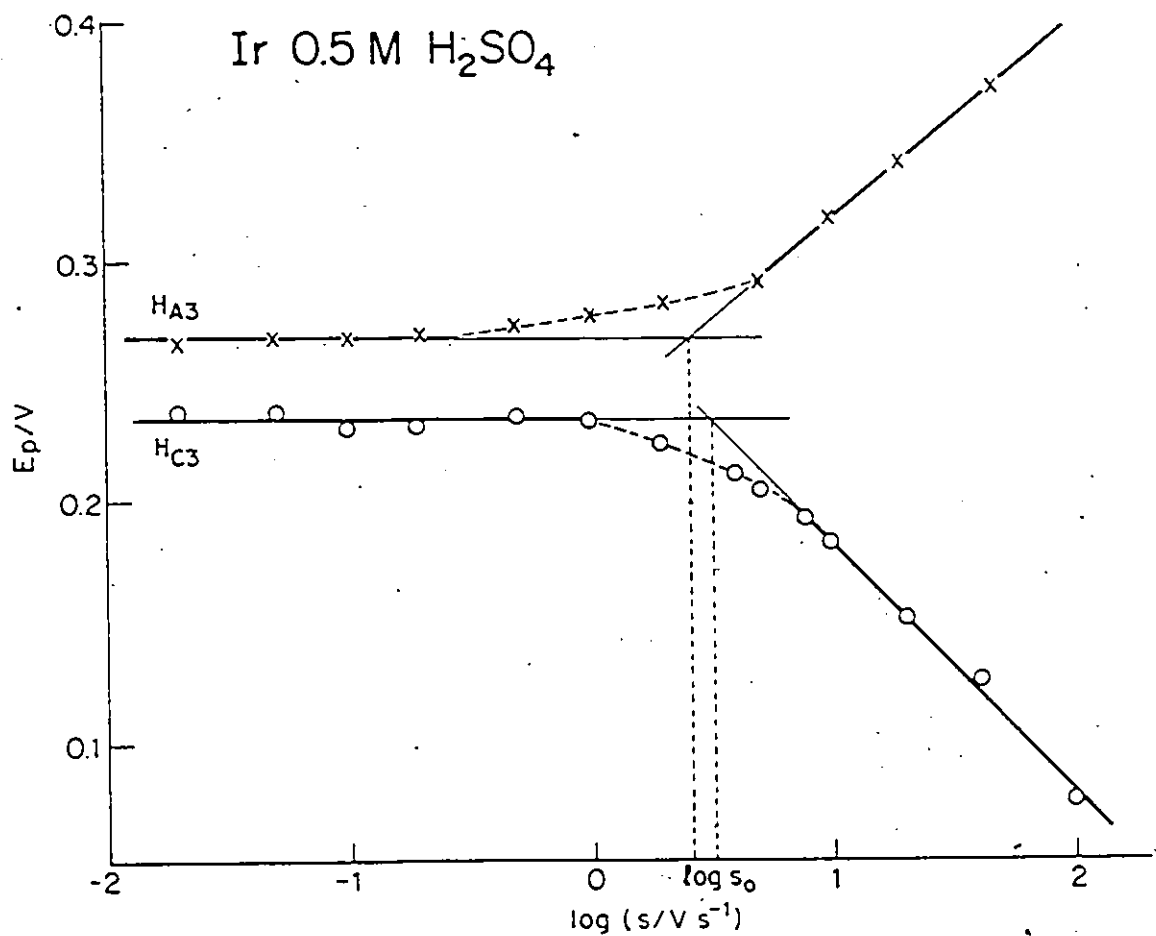


Fig. 18b. Evaluation of  $s_0$  and Tafel slope for H<sub>A3</sub> region at Ir in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 298K.

Fig. 18b, where it can be seen that  $s_0 = 2 \text{ V s}^{-1}$ .

#### 4.3.1.2. Double-Layer Charging Region

As can be seen from Figs. 15-17, the double-layer charging region is partially obscured by overlap with the currents for final desorption of H species and the onset of upd of OH species, this overlap being more significant in basic solutions, where the onset of surface oxidation is shifted to less positive potentials (see below) and where there is no distinguishable double-layer charging region (Fig. 17).

Nevertheless, even in 0.5 M  $\text{H}_2\text{SO}_4$ , where the double-layer region appears to be resolved, a calculation of the capacitance of the double-layer, based on the observed current and the relation  $C = i/s$  indicates a value of  $93 \mu\text{F cm}^{-2}$  which is rather large, since the technique used to prepare the electrodes does not roughen the surface to such an extent. This result implies that another process, e.g. onset of upd of OH species, already begins to take place over that potential range.

This was proven to be the case by Mozota and Conway (269), in their work on the effect of  $\text{Cl}^-$  ion on the monolayer stage of surface oxidation of Ir where, as the concentration of  $\text{Cl}^-$  was increased, the onset of upd of OH species was shifted to more positive potentials, revealing a real double-layer charging profile giving a capacitance of  $30 \mu\text{F cm}^{-2}$ , in agreement with values previously determined for similar Ir surfaces (246,247) with roughness factors of 1 to 2.

On the cathodic side in the double-layer region, currents larger than the conjugate anodic ones indicate a component due to irreversible reduction of the previously deposited monolayer oxide species, as will be discussed later.

#### 4.3.1.3. Formation and Reduction of Monolayer Oxide Films at Ir:

##### Reversibility and Hysteresis

Under cyclic-voltammetry conditions, as the potential of an Ir electrode in 0.5 M  $\text{H}_2\text{SO}_4$  at 298 K increases in the anodic direction up to a maximum of 1.3 V,  $E_H$  (to avoid growth of thick oxide films), two broad peaks are clearly distinguishable at potentials of ca. 0.7 and 0.975 V,  $E_H$  (Fig. 15). According to the charge isotherm (Fig. 19), they correspond to the upd of OH species, the monolayer of which is completed (according to the charge evaluation,  $\theta_{OH} = 1$  at  $210 \mu\text{C cm}^{-2}$ ) in the range 1.1-1.2 V,  $E_H$  (as at Pt), i.e. after the capacitance maximum of the most anodic peak,  $O_{A3}$ . Extension of the anodic end potential of the cyclic programme to values  $> 1.3 \text{ V}, E_H$ , up to 1.6 V,  $E_H$  indicates completion of a monolayer of "IrO" at about 1.4 V,  $E_H$  and leads into the transition from monolayer to thicker oxide formation that eventually becomes associated with large, reversible oxidation/reduction currents due to redox processes within the film, together with growth of the latter, if cycling is continued.  $\text{O}_2$  evolution takes place at potentials higher than 1.6 V,  $E_H$ .

The first, broad, anodic peak is seen to be composed of two peaks, clearly distinguishable on the cathodic side of the  $i$  vs  $V$  profile (Figs. 15-17). The system for labelling the peaks will be the one described by Conway et al. (19) for the case of Pt and applied by Angerstein-Kozłowska et al. (1) to Au and other noble metals. Thus, the first broad anodic peaks will be designated  $O_{A1}, O_{A2}$  and the corresponding cathodic ones  $O_{C1}, O_{C2}$ . The third (broad) anodic peak will be referred to as  $O_{A3}$  and its associated reduction region, which appears over a broad potential range, at less positive potentials, will be designated  $O_{C3}$  (see Fig. 15).

When the sweep proceeds in the cathodic direction, it can be seen

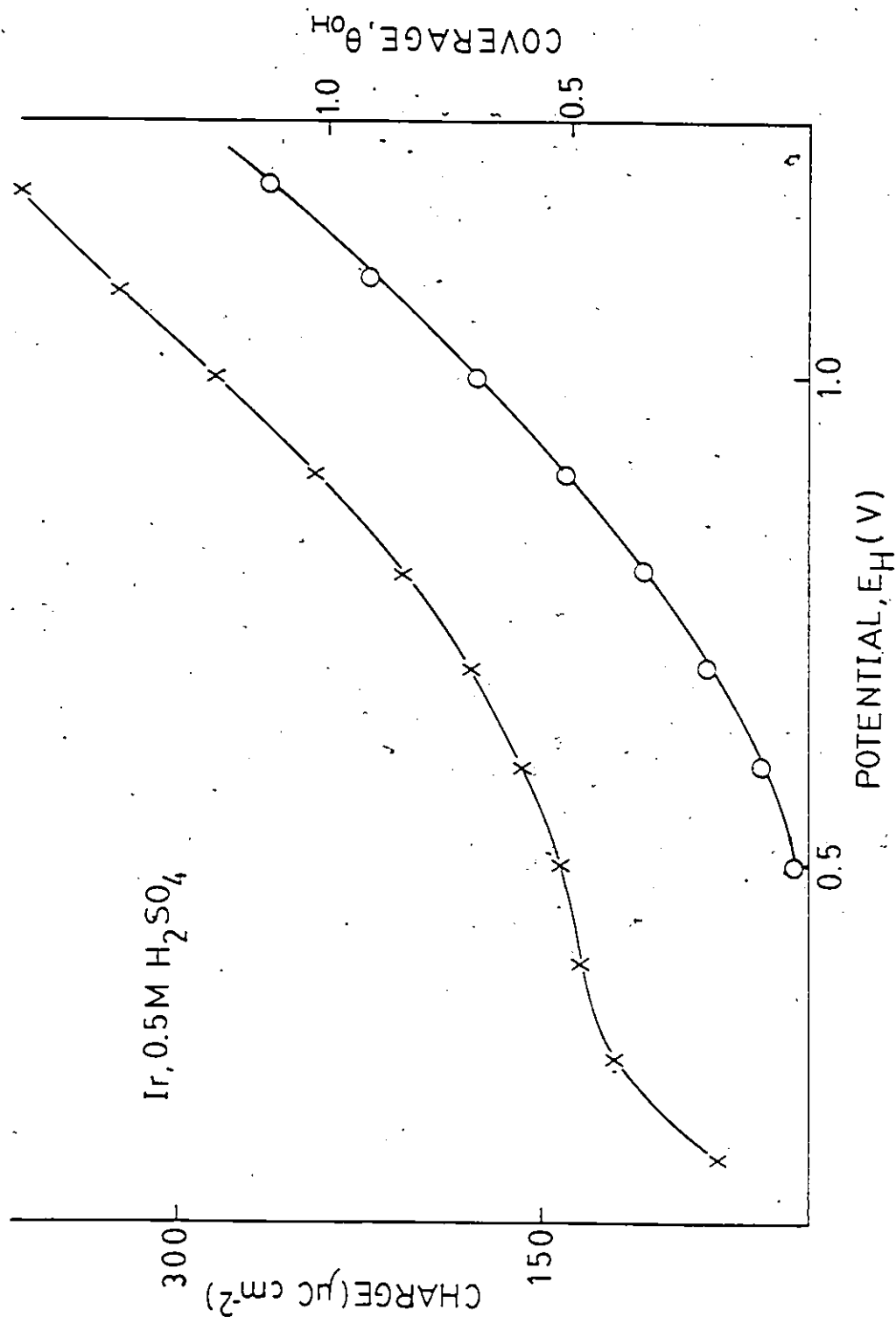


Fig. 19. Charge isotherm for Ir oxidation in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 298 K at 0.100 V s<sup>-1</sup>: (X) total charge; (O) coverage of OH species (θ<sub>OH</sub>).

that while the species deposited in the  $O_{A1}$ ,  $O_{A2}$  regions are reduced in an almost reversible way, the reduction of  $O_{A3}$  species does not occur in a single peak, but it takes place, with much hysteresis, in a broader potential region that overlaps with the double-layer and H deposition regions, indicating strong irreversibility of the reduction process (Fig. 15).

As the coverage of IrO increases and as higher oxidation states are attained, e.g.  $Ir_2O_3$ , these species are seen to be reduced also with great hysteresis, overlapping the H deposition region and causing diminution of the coverage by oxide species reduced in the  $O_{C1}$ ,  $O_{C2}$ , regions (see Fig. 20).

The peak multiplicity observed in the upd of an OH monolayer was interpreted by Conway et al. (19,21) in terms of the formation of a succession of sublattices, namely: " $M_4OH$ ", " $M_2OH$ " and " $MOH$ " as the monolayer became completed ( $\theta_{OH} \rightarrow 1$ ). The existence of such sublattices has been recently proven by Hubbard et al. (24) using LEED to study the case of I adsorption on Pt from the gas phase. Comparison of the theoretical predictions of Conway et al. (21) with the experimental results for PtOH monolayer formation gave excellent agreement and exemplified the importance of the  $g$  parameter in fitting the simulated  $i$  vs  $V$  profile to the experimental one.

In the case of Ir, although the multiplicity is not as well resolved as at Pt, it is nevertheless evident (e.g. see Fig. 15); the differences arise from the broadness of the peaks, which indicates stronger repulsion between the deposited OH species\*. However, quantitative evaluation of the

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\* Probably due to a stronger M-OH bond that is associated with an increased charge on the OH, i.e. a difference of electrosorption valency with respect to that for OH on Pt, Au, etc. This is consistent with the onset of upd of OH species taking place at Ir at potentials less positive than those at Pt.

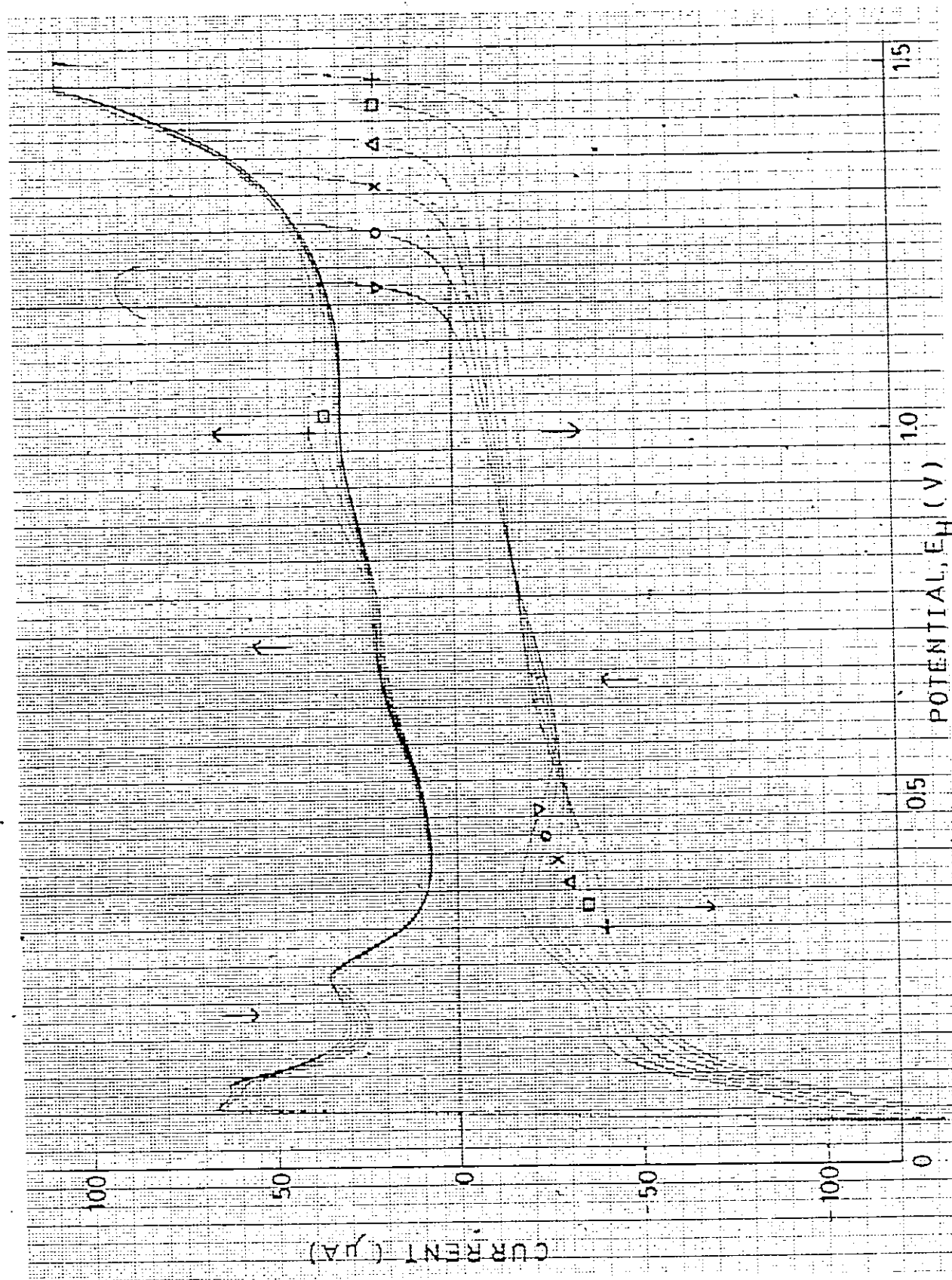


Fig. 20. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir in  $0.5 \text{ M H}_2\text{SO}_4$  at  $0.100 \text{ V s}^{-1}$ ,  $298 \text{ K}$ , with variable anodic end potential: (v) 1.205; (o) 1.290; (x) 1.355; ( $\Delta$ ) 1.415; ( $\square$ ) 1.475 and (+) 1.525 V.  $E_H$ . Arrows indicate directions of change of profile with increasing anodic end potential

charges for the distinguishable regions of the  $i$  vs  $V$  profile at Ir show that the coverage,  $\theta_p$ , at the peak maxima are lower for Ir than for Pt. Table V compares the  $\theta_p$  values for these two metals.

The idea of increased repulsive interactions between the deposited OH species is also supported by the fact that, at coverages  $\theta_{OH} > \text{ca. } 0.3$ , the deposited species are reduced with appreciable hysteresis ( $O_{A3}$  peak/ $O_{C3}$  region), consistent with a high degree of turnover (place-exchange) associated with a more stable two-dimensional lattice (cf. the behaviour of Pt electrodes: ref. 21).

It is however puzzling that the reduction of this rearranged or place-exchanged surface oxide does not occur in a "single-peak" as at Pt\*, Au or other noble metals, but instead appears to be smeared out over a broad range of potentials.

The lower coverages attained over the  $O_{A1}$  and  $O_{A2}$  regions, as well as the weaker effects of ion adsorption at Ir (Chapter 5), allow the reduction of OH species at  $\theta_{OH} < 0.3$  to occur in a more reversible way than those at Pt.

Thus, it can be concluded that the scheme suggested by Angerstein-Kozłowska et al. (1) in this laboratory, for the formation/reduction of monolayer surface oxide on noble metals, can be applied to the case of Ir, as exemplified in Scheme I (page 97).

More information about the behaviour of the monolayer surface oxide film at noble metals can usually be obtained by studying the film formation/reduction kinetics at constant current or constant potential. However, such experiments cannot be made unambiguously in the case of Ir since, if the reduction of the anodically formed oxide is carried out at

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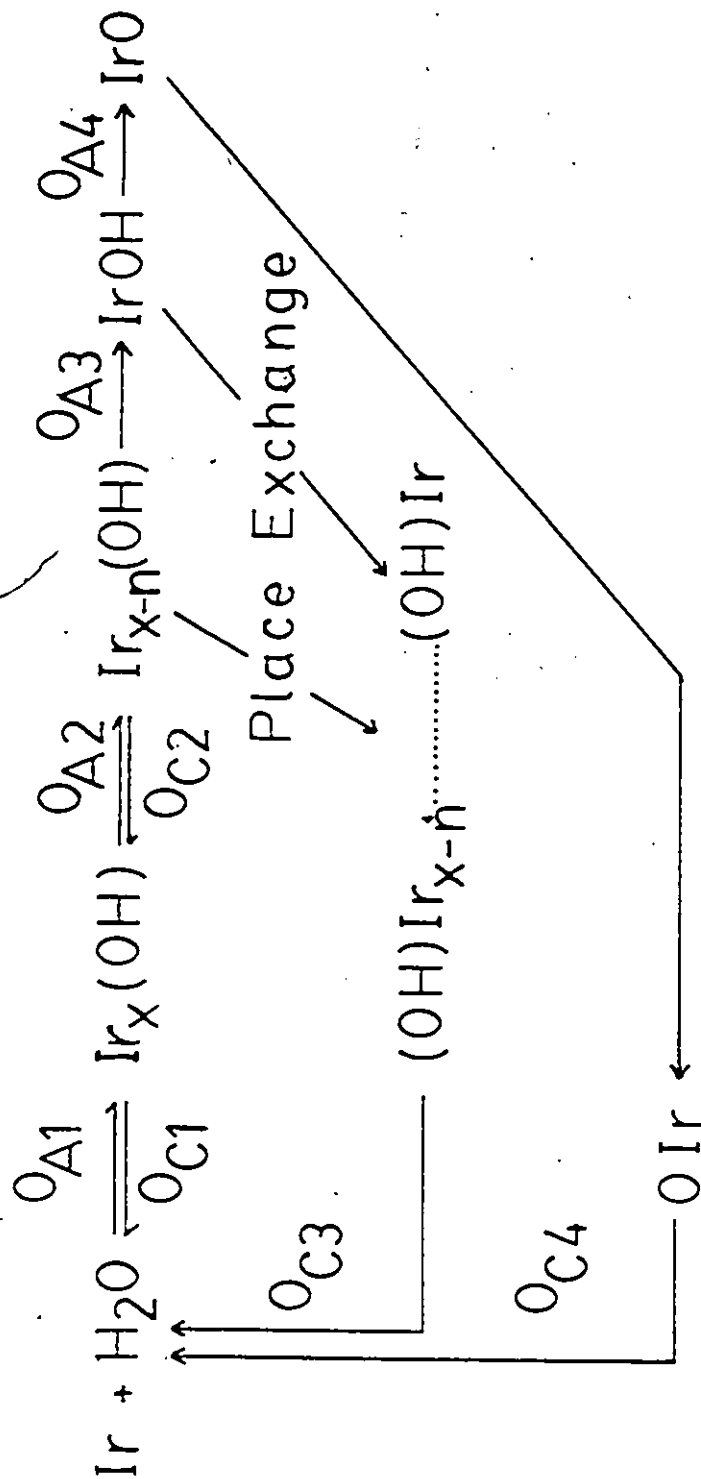
\* The "single" peak, often observed at Pt, is in fact resolvable into at least two regions, depending on conditions (see Chapter 6). Similar behaviour is found at Au (1).

TABLE V

Surface Oxide Coverages,  $\theta_p$ , up to Capacitance Maximum

| Metal | Region        |               |               |
|-------|---------------|---------------|---------------|
|       | $\theta_{A1}$ | $\theta_{A2}$ | $\theta_{A3}$ |
| Pt    | 0.15          | 0.40          | 0.78          |
| Ir    | 0.10          | 0.18          | 0.54          |

# SCHEME I Cycle of Processes in Ir Monolayer Oxidation



constant current, the oxide reduction current component overlaps with the double-layer charging and H deposition current components; on the other hand, if the reduction is observed by means of the sweep method, the extra oxide formed on holding at constant potential does not get completely reduced in one sweep but in two or three successive ones, thus making it difficult to identify the charge component due to reduction of the extra oxide in both methods.

Nevertheless, qualitative examination of the cathodic sweep after variable times of application of a constant anodic end potential, indicate preferential growth of the irreversibly reduced component; this is consistent with observed ageing phenomena, such as increased metal/oxygen turnover, found on other noble metals (ref. 1).

A further point should be mentioned and that is the question of charge balance between the anodic and cathodic sweeps. Iridium is known to dissolve anodically to a small extent under potentiodynamic conditions if the anodic end potential is more positive than ca. 1.16 V,  $E_H$ , the latter being the  $E_{rev}^0$  value for the Ir/aquo.Ir(III) couple. Thus, the anodic charge  $Q_a$  will always tend to be greater than the cathodic charge  $Q_c$  and the  $\Delta Q = Q_a - Q_c$  will be a measure of the amount of metal dissolved. Values for  $\Delta Q$  were observed in the range of  $10-20 \mu C cm^{-2} cycle^{-1} \approx 10 ng cm^{-2} cycle^{-1}$  in 0.5 M  $H_2SO_4$  with  $E_a = 1.3 V, E_H$  which compare with the reported value (232) of  $38 ng cm^{-2} cycle^{-1}$  with  $E_a = 1.54 V, E_H$ , the sweep-rate being  $0.05 V s^{-1}$  in both cases. In 0.5 M  $Na_2CO_3$ , the rate of dissolution appears to be smaller, of the order of  $5 ng cm^{-2} cycle^{-1}$ , under similar conditions to those for the acid solution experiments.

#### 4.3.1.4. Role of Adsorbed Ions in the Observed Behaviour

It was mentioned previously that adsorbed ions have a marked

effect on the behaviour of metal electrodes under cyclic-voltammetry conditions.

As studied by various authors (270-275) and demonstrated for all noble metals by Angerstein-Kozłowska et al. (1), adsorbed ions play a role in the following processes which influence the development of oxide films:

- (a) Competition between adsorption of ions and electrodeposition of OH and O species;
- (b) Displacement of the potential range for deposition of H and OH species;
- (c) Change of inner-layer potential;
- (d) Rate of turnover, growth and ageing processes; and
- (e) State of adsorbed water at the surface.

The extent of ion adsorption effects will be determined by the strength of the interaction between the ion and the metal compared to the interaction between OH or H species with the metal, and also by the potential range of the oxidation/reduction region with respect to the p.z.c.. This is because the latter does not depend on pH, while the other processes such as oxide deposition/removal and H ionization/deposition are a function of pH. Thus, in basic media, noble metal surfaces are probably relatively free from adsorbed anions, except for cases of strong specific adsorption.

A further point is that a metal surface which, for thermodynamic reasons is relatively easily oxidized, i.e. at low positive potentials relative to 0 V,  $E_H$ , will suffer less competition from anion adsorption than a metal which requires higher positive potentials for surface oxidation to commence. This is one of the reasons for the differences of behaviour and of sensitivity to anions of Ir vis a vis Pt (see Chapters 5 and 6).

Inspection of the  $i$  vs  $V$  profiles in Figs. 15-17, indicates:

- (a) The onset of upd of OH species is shifted towards more positive values in the order:  $0.5 \text{ M H}_2\text{SO}_4 \approx \text{HClO}_4 > 0.5 \times 10^{-1} \text{ M H}_2\text{SO}_4 > 0.5 \times 10^{-3} \text{ M}$

$\text{H}_2\text{SO}_4 > 0.1 \text{ M Na}_2\text{CO}_3 \approx 0.5 \text{ M NaOH}$ ;

(b) The reversibility of  $\text{O}_{\text{A1}}/\text{O}_{\text{A2}}$  processes increases in the opposite order, i.e.  $\text{Na}_2\text{CO}_3 > \text{H}_2\text{SO}_4$ ;

(c) The hysteresis associated with  $\text{O}_{\text{A3}}$  also increases as in (b); and

(d) Anion effects on the H deposition/ionization (as were discussed in section 4.3.1.1) similar to those at Pt.

However, anion effects with the above electrolytes are much smaller than those exerted by ions such as  $\text{Cl}^-$  and  $\text{Br}^-$  which are known to interact strongly with metal surfaces due to greater donicity of lone pairs.

In the present studies (53) of the effect of  $\text{Cl}^-$  ion on the monolayer stage of Iridium oxidation in relation to the investigation of the electrocatalytic properties of  $\text{IrO}_2$  films for the  $\text{Cl}_2$  evolution reaction (see Chapter 5 ), it was shown how the charge isotherm for up of OH species depends on the concentration of  $\text{Cl}^-$  ion, since the amount of deposited oxide decreases markedly with increasing  $\text{Cl}^-$  concentration. Similar results are obtained in the presence of  $\text{Br}^-$  ion, although the latter is even more effective than  $\text{Cl}^-$  ion in blocking oxide formation and H deposition.

The growth of the oxide under constant potential conditions can also be followed quantitatively in the presence of halide ions, where the growth and the blocking processes compete with each other. In this case, the result is essentially the same as in the absence of these ions, namely that the growth of the irreversibly reduced component is favored but inspection of the  $i$  vs  $V$  profiles for both cases, i.e with and without halide ions, indicates that the latter greatly increase the irreversibility of the reduction of the deposited oxide species (see chapter 6, where such effects were studied with  $\text{Cl}^-$  at Pt).

#### 4.3.1.5. Transition Between Monolayer and Thick Film States

When an Ir electrode is cycled or pulsed (246,248,249) between the appropriate limits, i.e.  $E_a^* > 1.3 \text{ V, } E_H$  and  $E_c^* < 0.2 \text{ V, } E_H$  in  $0.5 \text{ M H}_2\text{SO}_4$  at  $298 \text{ K}$ , the monolayer oxide film (designated as State A) is replaced by a thicker oxide (labelled State M) capable of undergoing reversible redox processes in the bulk of the film. This film grows continuously with cycling at a rate depending on various parameters which will be discussed later in section 4.4.

Once this transition takes place, lowering of the anodic end potential in the cycles leads to slower growth or even to a decrease in the anodic/cathodic charge ratio associated with the processes in the film, but the original A-state is never regained unless the electrode is polarized at  $E_a > 1.7 \text{ V, } E_H$  for the necessary length of time (i.e. the thicker the oxide layer to be removed, the longer the polarization time required) or cycled in  $98\% \text{ H}_2\text{SO}_4$ , i.e. under conditions for which the film is known to dissolve or fail mechanically (250). The latter effect occurs because of  $\text{O}_2$  evolution.

The A-state i vs V profile, together with the first few cycles leading to the M state in  $0.5 \text{ M H}_2\text{SO}_4$ , is shown in Fig. 21. The main features of the transition,  $A \rightarrow M$ , are:

(a) Almost no change on the H desorption and double-layer charging regions (a rather puzzling effect that remains even at high film thicknesses, viz.  $500 \text{ nm}$ ; this will be discussed later);

(b) Appearance of a sharper peak in the potential region of  $\text{O}_{A1}/\text{O}_{A2}$ , which will be labelled  $\text{O}_{A,1,2,r}$  (the "r" indicates that it is associated with the thick films exhibiting reversible behaviour), the charge of which increases and the potential for which becomes more positive with successive cycles;

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\*  $E_a$  and  $E_c$  are used to represent the anodic and cathodic end potentials of the linear potential sweep, respectively.

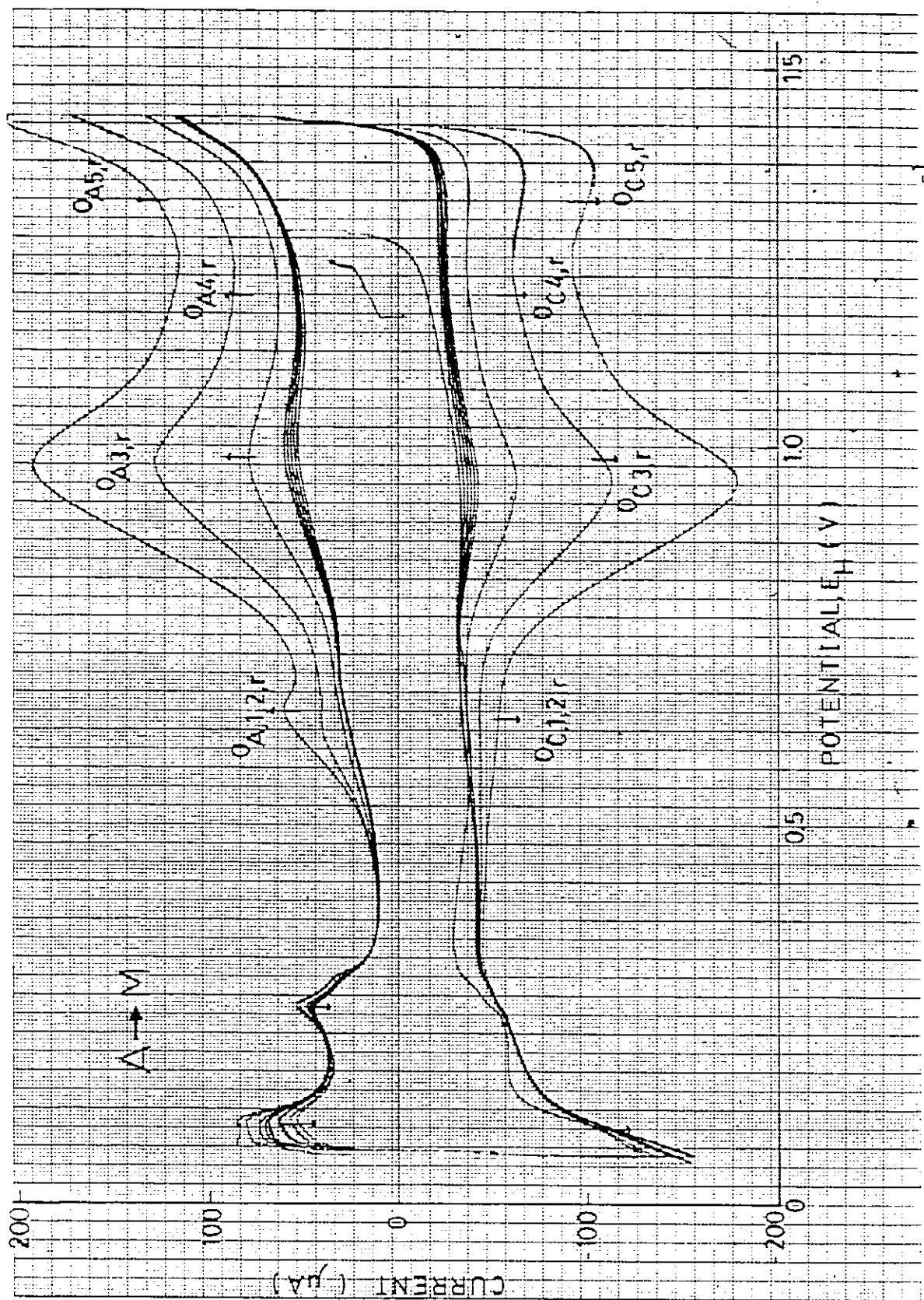


Fig. 21. Series of cyclic-voltammetry  $i$  vs.  $V$  profiles for Ir in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 0.100 V s<sup>-1</sup>, 298 K,

showing the transition between states A and M. Arrows indicate direction of change of the profile with continuous cycling and the main peaks are labelled as discussed in sect. 4.3.1.5.

(c) Development of a reversible series of current peaks at about 1.0 V,  $E_H$ , to be referred to as  $O_{A3,r}$  and  $O_{C3,r}$ , the charges of which increase continuously and the potentials for which remain fairly constant until the film has grown to thicknesses of ca. > 100 layers;

(d) A charge increase in the region 1.2-1.4 V,  $E_H$ , associated with a reversible system labelled  $O_{A4,r}/O_{C4,r}$ ; and

(e) The appearance of a shoulder at  $\sim 1.45$  V,  $E_H$  clearly distinguishable when the film becomes thicker (see later, Fig. 22) labelled  $O_{A5,r}$  which appears at potentials below those for commencement of  $O_2$  evolution. Also a corresponding  $O_{C5,r}$  peak can be resolved which can be partially obscured by the reduction of previously evolved  $O_2$ .

These features, as well as their change with oxide thickness, depend on various growth parameters, including the nature of the electrolyte. These effects, together with a detailed discussion of the mechanism of oxide growth, will be presented in the next sections.

#### 4.4. THICK OXIDE FILMS ON IRIDIUM

As described previously (p. 101), when an Ir electrode is cycled between the appropriate limits (to be discussed below), its  $i$  vs  $V$  profile undergoes drastic changes, the main one being the appearance of large reversible oxidation/reduction currents at potentials higher than ca. 0.7 V,  $E_H$ .

As the cyclic programme of potential change is continued, the charge associated with the reversible processes continuously increases, while that of the region of deposition/ionization of H species and double-layer charging below 0.7 V,  $E_H$  appears to remain constant. This latter effect is one of the most interesting features of the behaviour associated with the thick films which can be developed at Ir and Rh (78).

The understanding of the mechanism for oxide growth is important

both for technological and basic reasons. On the one hand, the thick oxide films formed at Ir are of interest because of their electrochromic properties (259), which makes them suitable as display devices (254); on the other hand, because of their large active area, interesting electrocatalytic properties arise, as will be discussed for the cases of  $\text{Cl}_2$  [Chapter 5 and cf. (53)] and  $\text{O}_2$  evolution (88).

The fact that Ir, Ru, Os, Rh and W (50,51,72,77,233) develop similar thick oxide films, under similar conditions and with related properties, implies that any knowledge gained in the study of Ir oxide films will also contribute to the understanding of anodic oxide film formation at the above metals.

Finally, as will be discussed later (Chapter 5), formation of the oxide films under cyclic conditions allows the films to be modified in a controllable way, which is one of the main requirements in an electrocatalytic study.

Unfortunately, the same characteristics that make this system rather special, i.e. development of large charge values associated with reversible redox processes in the film, also make the system difficult to study, since the  $i$  vs  $V$  profile maintains constant features (unlike the case of Pt), under the influence of the usual perturbation programmes, at least until CEF's > 150 are achieved. Thus, although the  $i$  vs  $V$  profiles are not as featureless as those for Ru, the amount of electrochemical information that can be obtained from them is rather restricted and other techniques such as SEM, ESCA and AUGER analysis have to be used to complement the electrochemical results.

The first step towards obtaining data that could lead to formulation of a growth mechanism was to study the effect of various

experimental conditions on the rate of growth of the oxide film.

#### 4.4.1. Dependence of the Rate of Growth of Thick Ir Oxide Films on Various Experimental Parameters

In general, regardless of the effect of a particular experimental condition, the growth of Ir oxide films proceeds in the way illustrated in Figs. 22 and 23 for 0.5 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{Na}_2\text{CO}_3$  solutions, respectively.

Once the A  $\rightarrow$  M transition has taken place (section 4.3.1.5), the state of the electrode will be designated as M, until the electrochromic effect is observable at CEF's  $>$  ca. 50. Then the electrode state will be referred to as "MB", because of the apparent metallic  $\rightarrow$  black change in coloration as potential is cycled. When high oxide thicknesses are achieved (CEF's  $>$  150-200), the electrode always appears black and this state will be referred to as state "B".

It should be mentioned that the difference between states M, MB and B is due only to the optical properties of the electrode, which are a reflection of the oxide thickness and of the efficiency of the redox process taking place in the oxide film. Thus, in all these states, the oxide species (involving various valence states of Ir) present in the film are proposed to be identical at any given potential, except perhaps those in the monolayer oxide.

##### 4.4.1.1. Effects of Anodic and Cathodic End Potential

In order to determine the effect of the anodic and cathodic end potential in a repetitive sweep on the rate of growth, the Ir oxide films were developed in 0.5 M  $\text{H}_2\text{SO}_4$  at 298 K and at a sweep-rate of  $0.100 \text{ V s}^{-1}$ . The growth was monitored by measuring the current at the capacitance maximum ( $I_p$ ) of  $\text{O}_{\text{A3,r}}$ , i.e. at  $\approx 1.0 \text{ V}, E_H$ , every 5 cycles for 20 cycles and then varying the corresponding end potential by a fixed increment of voltage while

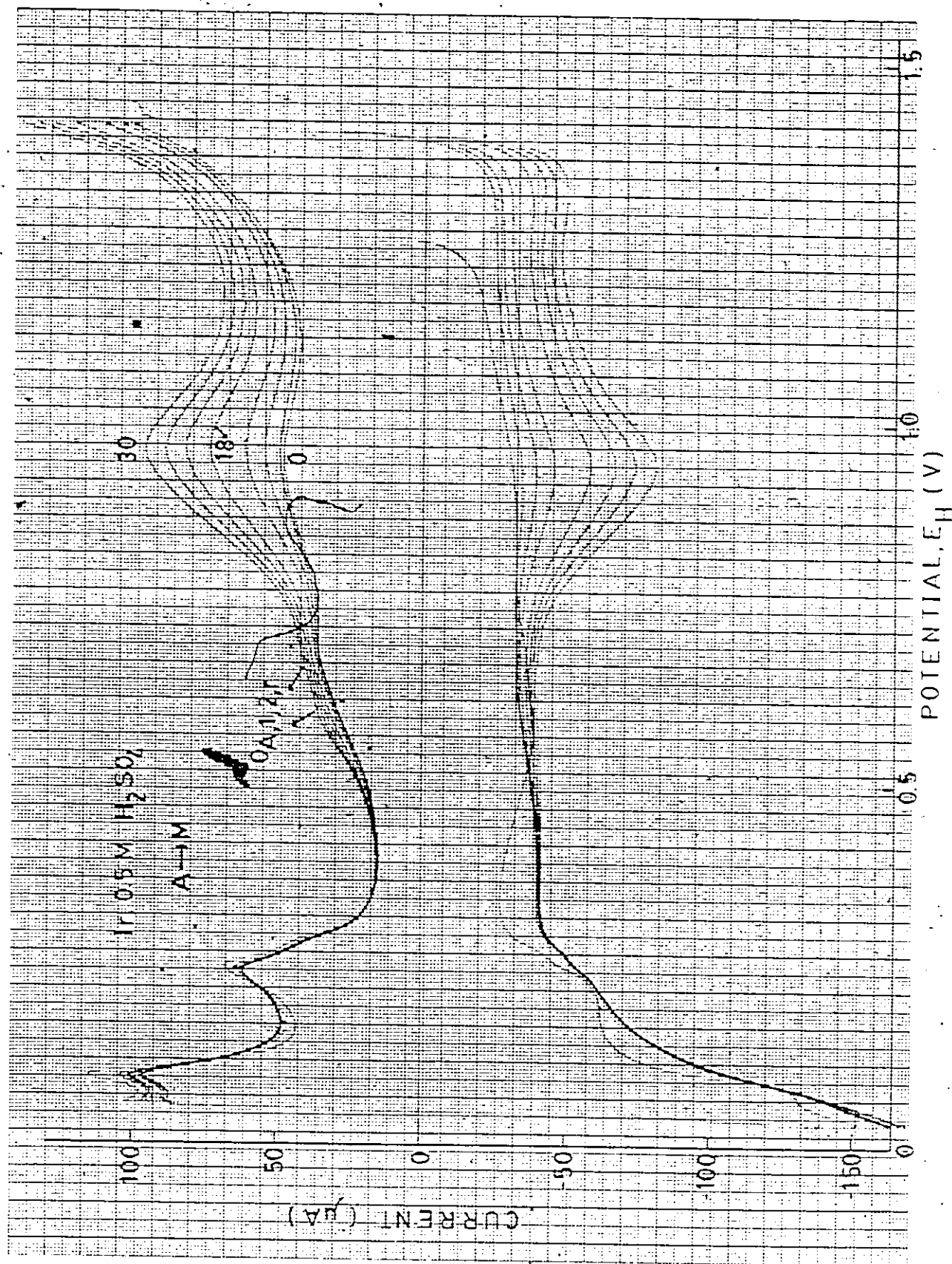


Fig. 22a. Series of cyclic-voltammetry  $i$  vs  $V$  profiles for Ir in 0.5 M  $H_2SO_4$  at  $0.100\text{ V s}^{-1}$ , 298 K, showing the change of the profile on cycling, due to the development of the thick oxide film at Ir, for 0-30 cycles, as indicated in the figure.

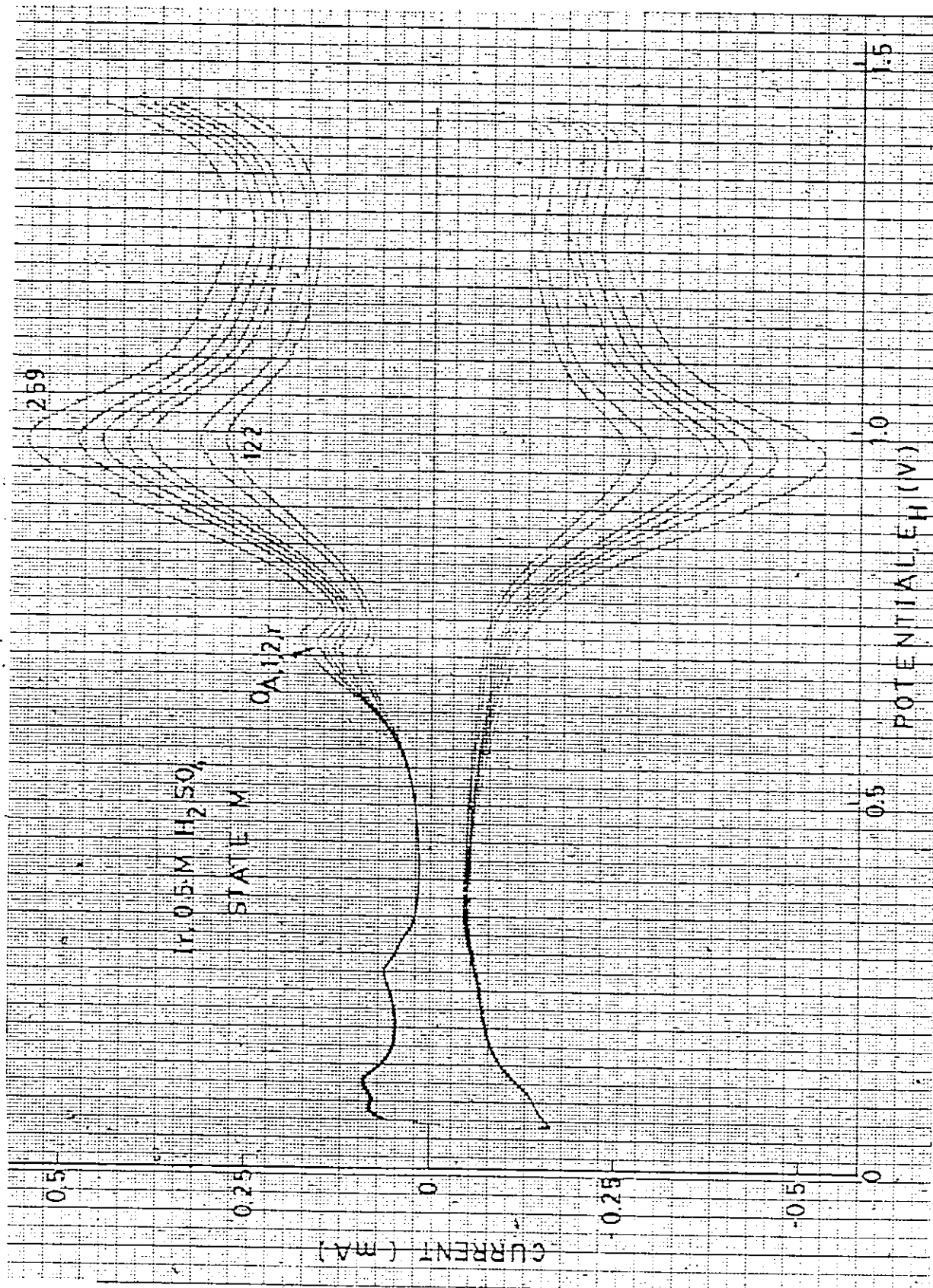


Fig. 22b. Conditions as in Fig. 22a, but for 122-252 cycles as indicated in the figure.

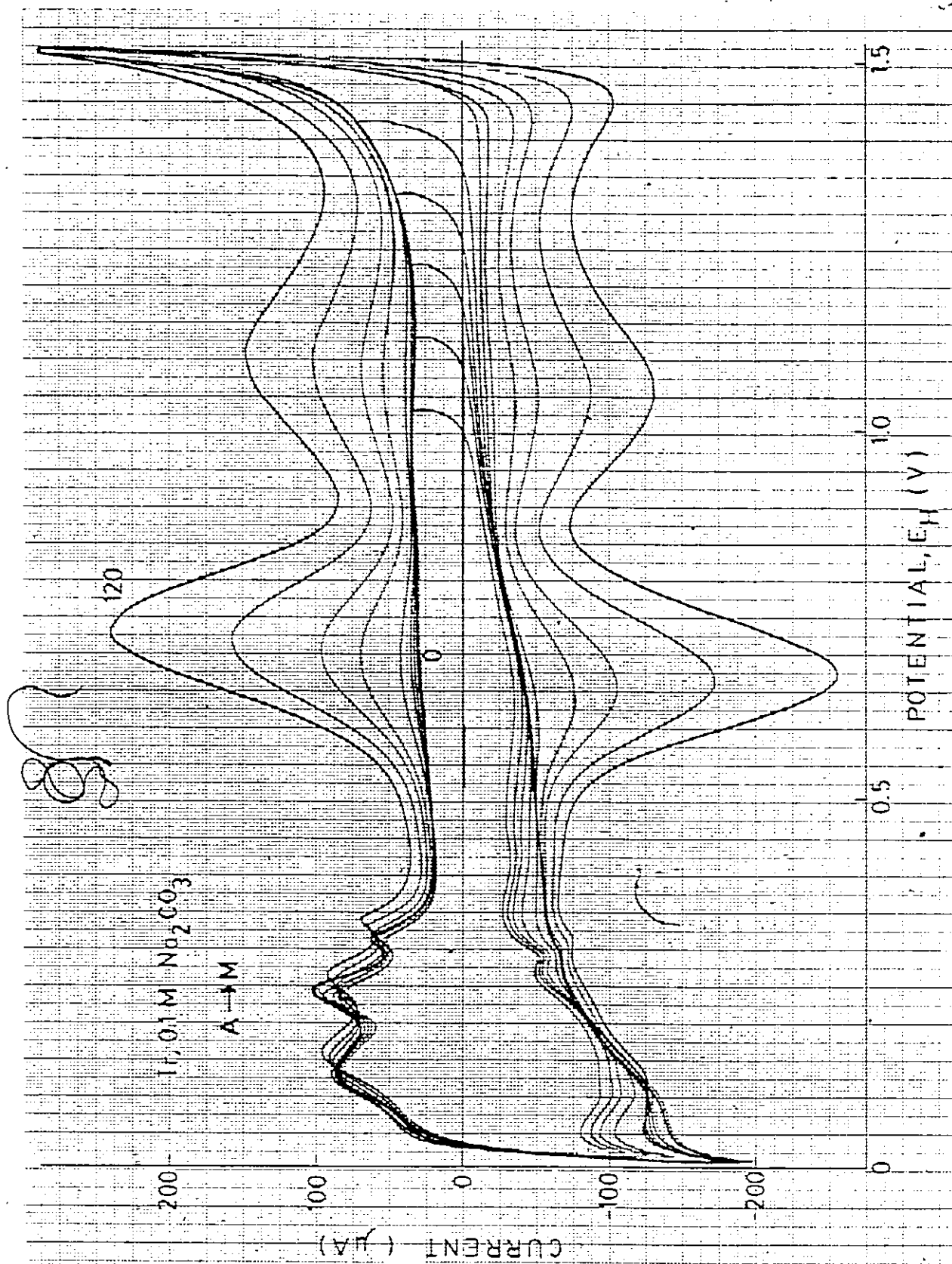


Fig. 23a. Series of cyclic-voltammetry  $i$  vs  $V$  profiles for Ir in  $0.1 \text{ M Na}_2\text{CO}_3$  at  $0.100 \text{ V s}^{-1}$ ,  $298 \text{ K}$ , showing the change of the profile on cycling, due to the development of the thick oxide film at Ir, for 0-120 cycles, as indicated in the figure.

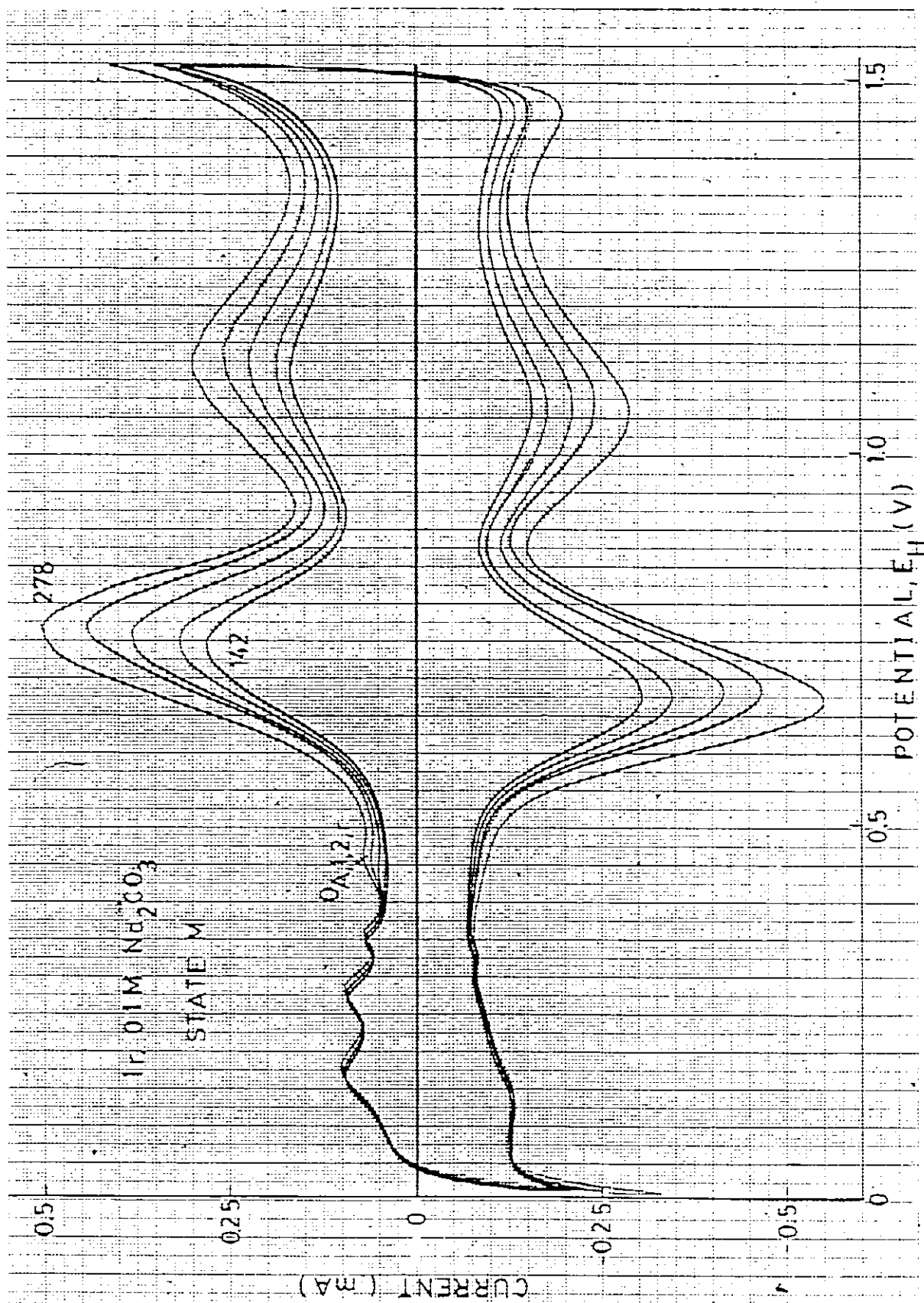


Fig. 23b. Conditions as in Fig. 23a, but for 142-278 cycles as indicated in the figure.

scanning the potential region of interest. The linearity of the growth for every end potential was established by graphical means, and the total growth in a given experiment was well within the linear region of the growth curve, as shown later (Fig. 28).

The results obtained are shown in Fig. 24. It can be seen (Fig. 24) that there appears to be an optimum anodic potential ( $E_{a, \text{optimum}}$ ) at which the rate of growth is a maximum and that as  $E_a > E_{a, \text{optimum}}$ , the rate of growth decreases markedly, presumably due to some corrosion of the film by dissolution and involvement of the film itself in the  $O_2$  evolution reaction.

It is also apparent (Fig. 24) that there is an optimum cathodic end potential ( $E_{c, \text{optimum}}$ ), although in this case for  $E_c < E_{c, \text{optimum}}$  the rate of growth tends to level-off, as expected, since the oxide cannot dissolve at these cathodic potentials and  $H_2$  evolution (as will be discussed later) takes place only at the Metal/Oxide interface and thus does not disturb the bulk of the film, unlike  $O_2$  evolution which is assumed to involve the film itself.

The existence also of threshold potentials, viz.  $E_a$  and  $E_{c, \text{minimum}}$  required for growth to start at all, in both the anodic and the cathodic ends of the sweep also indicates the need for a certain state of oxidation or a certain coverage by oxide species to be achieved (at  $E_a$ ), as well as the requirement for partial reduction of anodically formed species at the cathodic end ( $E_c$ ), with large hysteresis, by an electrochemical mechanism or assisted by electrodeposition of H species (at  $E_c$ ).

It should also be noted that if a film is grown to a certain thickness and then the end potential of the anodic or the cathodic sweep is decreased below  $E_{\text{minimum}}$ , a decrease in charge is observed, associated with a corresponding decrease in thickness. This again stresses the fact

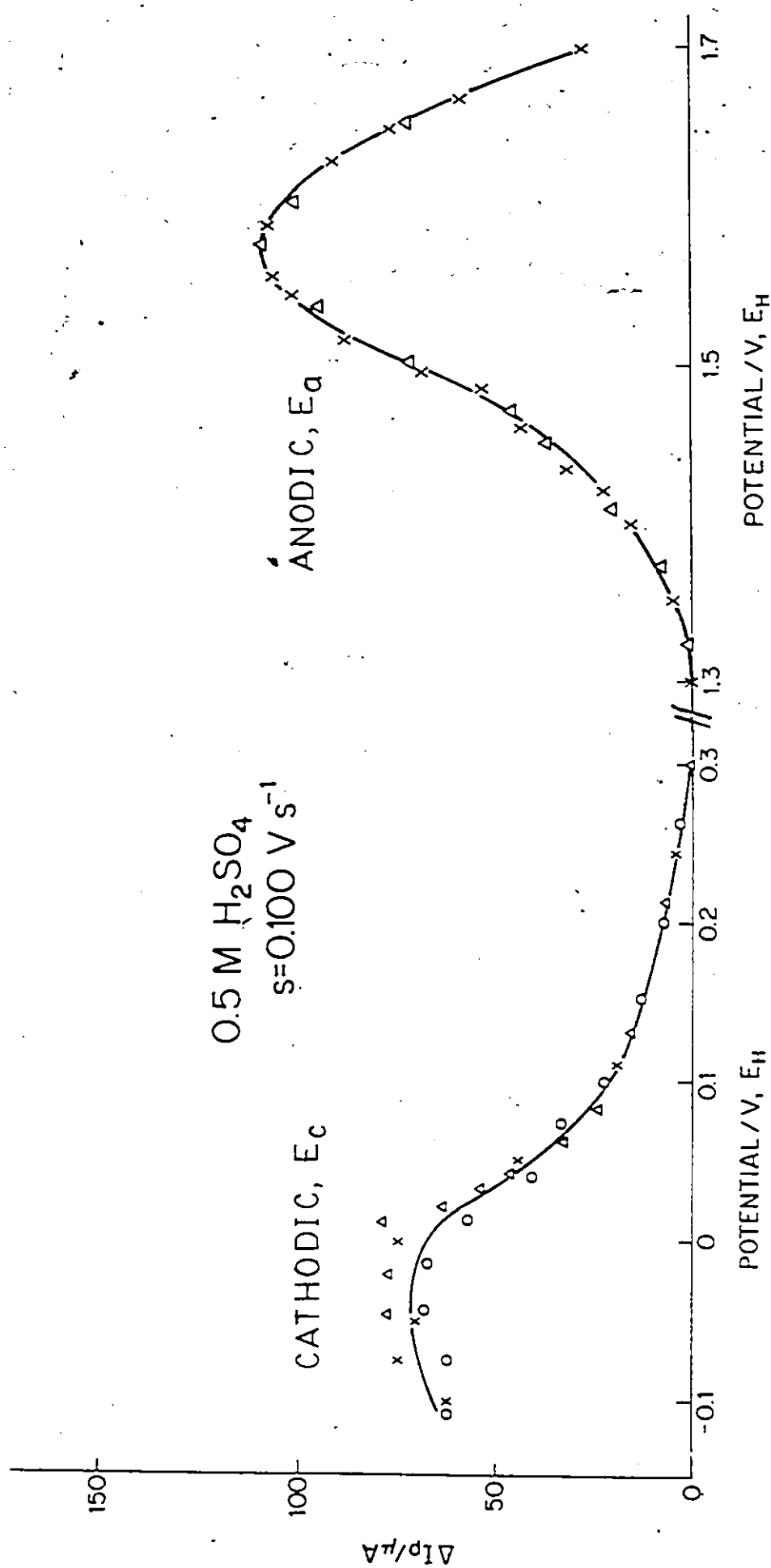


Fig. 24. Dependence of the rate of growth of Ir oxide films on the anodic,  $E_a$ , and cathodic,  $E_c$ , end potentials of the sweep, in 0.5 M  $\text{H}_2\text{SO}_4$  at  $0.100 \text{ V s}^{-1}$ , 298 K. Growth measured as  $\Delta I_p$  for 20 cycles between set  $E_a$  and  $E_c$  limits.

that the oxide film is slowly dissolving, probably by a chemical reaction, at the same time that it is being formed, but the original A state is never regained.

#### 4.4.1.2. Type and Concentration of Supporting Electrolyte

In Fig. 25 is shown the dependence of the rate of growth on the anodic end potential of the sweep on the type of electrolyte, namely 0.5 M  $\text{H}_2\text{SO}_4$ , 1M  $\text{HClO}_4$  and 0.5 M  $\text{Na}_2\text{CO}_3$ . Results in 0.5 M NaOH are not shown owing to the extremely slow rate at which growth takes place in that medium.

As can be seen, the rate of growth at any given potential decreases in the order  $0.5 \text{ M } \text{H}_2\text{SO}_4 > 1\text{M } \text{HClO}_4 >> 0.5 \text{ M } \text{Na}_2\text{CO}_3 >> 0.5 \text{ M } \text{NaOH}$ . While the shape of the function (Fig. 25) and the  $E_{a,\text{optimum}}$  are similar for both acid electrolytes, they are different for the case of  $\text{Na}_2\text{CO}_3$ , where the  $E_{a,\text{optimum}}$  is displaced to less positive potentials and the width of the peak-shaped relation is smaller than that for the acid media.

The difference in the rate of growth between  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  is due, probably, to increased solubility of the oxide in the  $\text{HClO}_4$  solution and also to the type of anion present,  $\text{HSO}_4^-$  vs  $\text{ClO}_4^-$ . The latter effect probably arises because the anion is involved in the growth mechanism, e.g. anion migration is necessary to maintain the electroneutrality of the system. Buckley et al. (250) pointed out the importance of the anion in discussing the results they obtained in solutions of  $\text{H}_2\text{SO}_4 + x \text{ Na}_2\text{SO}_4$ . They found that on increasing the concentration of  $\text{Na}_2\text{SO}_4$ , the rate of growth decreased. This can only be understood on the basis of a change in the anion responsible for the ionic migration, which is most likely  $\text{HSO}_4^-$  in acid solutions and becomes  $\text{SO}_4^{2-}$  when the concentration of  $\text{Na}_2\text{SO}_4$  is increased.

It has also been observed that increasing the acid concentration decreases the rate of growth, presumably due to increased dissolution of the

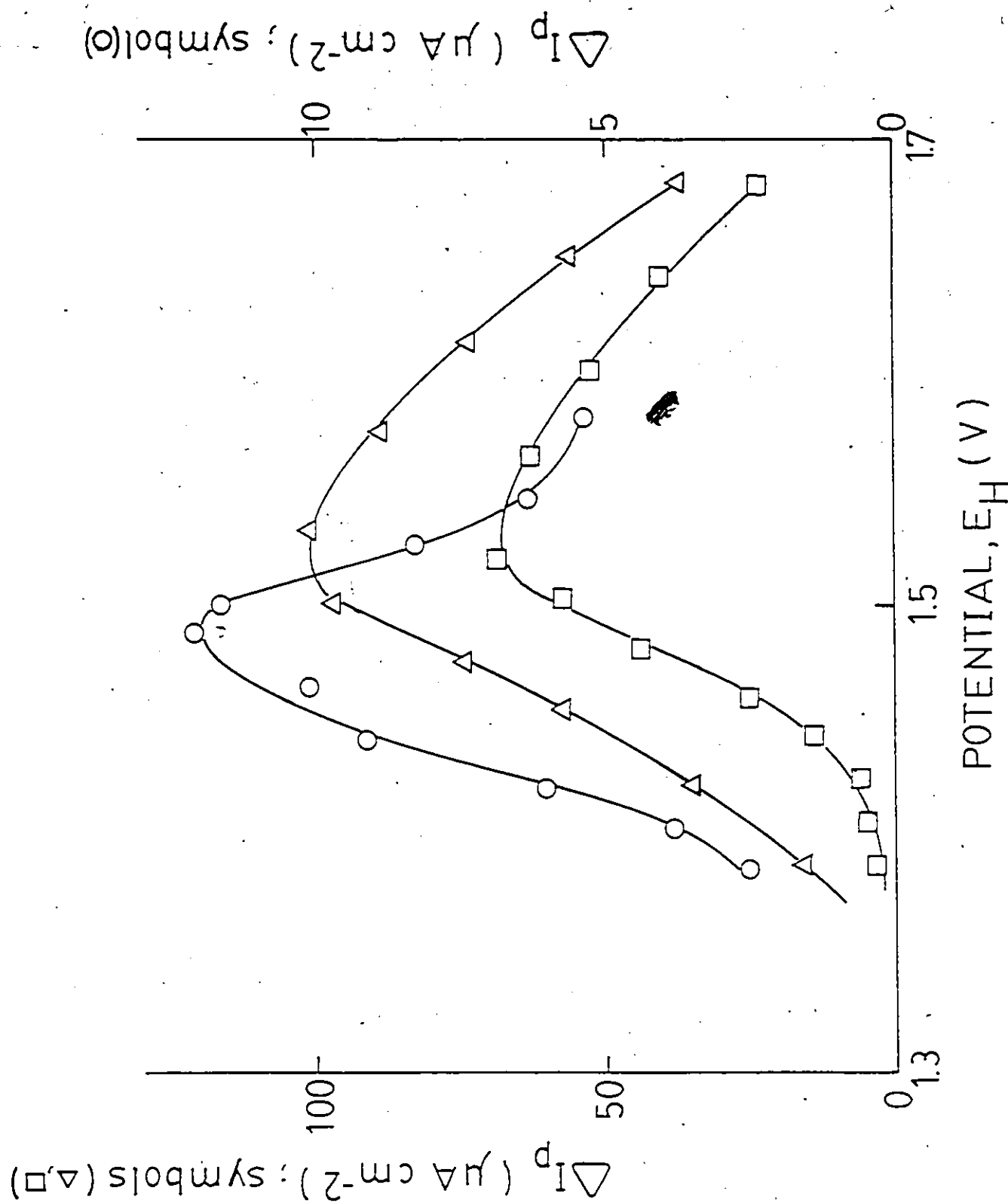


Fig. 25. Dependence of the rate of growth of Ir oxide films on the anodic end potential, and the type of electrolyte, at  $0.100 V s^{-1}$ , 298 K. (o)  $0.5 M Na_2CO_3$ ; ( $\Delta$ )  $0.5 M H_2SO_4$  and ( $\square$ )  $1 M HClO_4$ .

oxide.

As mentioned above, the behaviour in the case of  $\text{Na}_2\text{CO}_3$  is quite different from that in acid media. This effect is also clear in the dependence of the rate of growth on the cathodic end potential of the sweep, where the  $E_{c,\text{optimum}}$  in  $\text{Na}_2\text{CO}_3$  solutions is displaced to more negative potentials. This global shift of both curves in the negative direction indicates a pH dependence of the rate of growth which correlates with the unusual pH dependence of the peak potentials to be discussed later.

The very slow rate of growth in NaOH, attributed by some authors to increased oxide dissolution (250) is more likely to be due to increased difficulty in breaking the M-M bond or even to the fact that, in the absence of strongly adsorbed anions, the turnover process is slower since it cannot be assisted by adsorbed anions, thus giving rise to a slow growth reaction. The solubility explanation is apparently incorrect, since an oxide formed in  $\text{H}_2\text{SO}_4$  and then transferred to NaOH, can be cycled in the latter medium for a long period of time, > ca. 10 hours, without an appreciable loss of charge.

#### 4.4.1.3. Effect of Sweep-Rate

On varying the sweep-rate ( $s$ ), while keeping all the other conditions constant, the rate of growth of the oxide film varies as indicated in Fig. 26, for two different anodic end potentials. Thus, while the rate of growth is fairly constant at  $s < 0.100 \text{ V s}^{-1}$ , it decreases as a linear function of  $\log s$  as  $s$  is increased. The observed effect could be due to two factors: First, as  $s$  is increased, there will be shorter time available for turnover of the oxide species to occur before they are reduced. This tends to make the amount of oxide that is not reduced, and thus able to incorporate itself into the film, smaller. Secondly, the surface oxidation peaks become irreversible at high  $s$ , thus effectively making a given chosen end potential thermodynamically less positive.

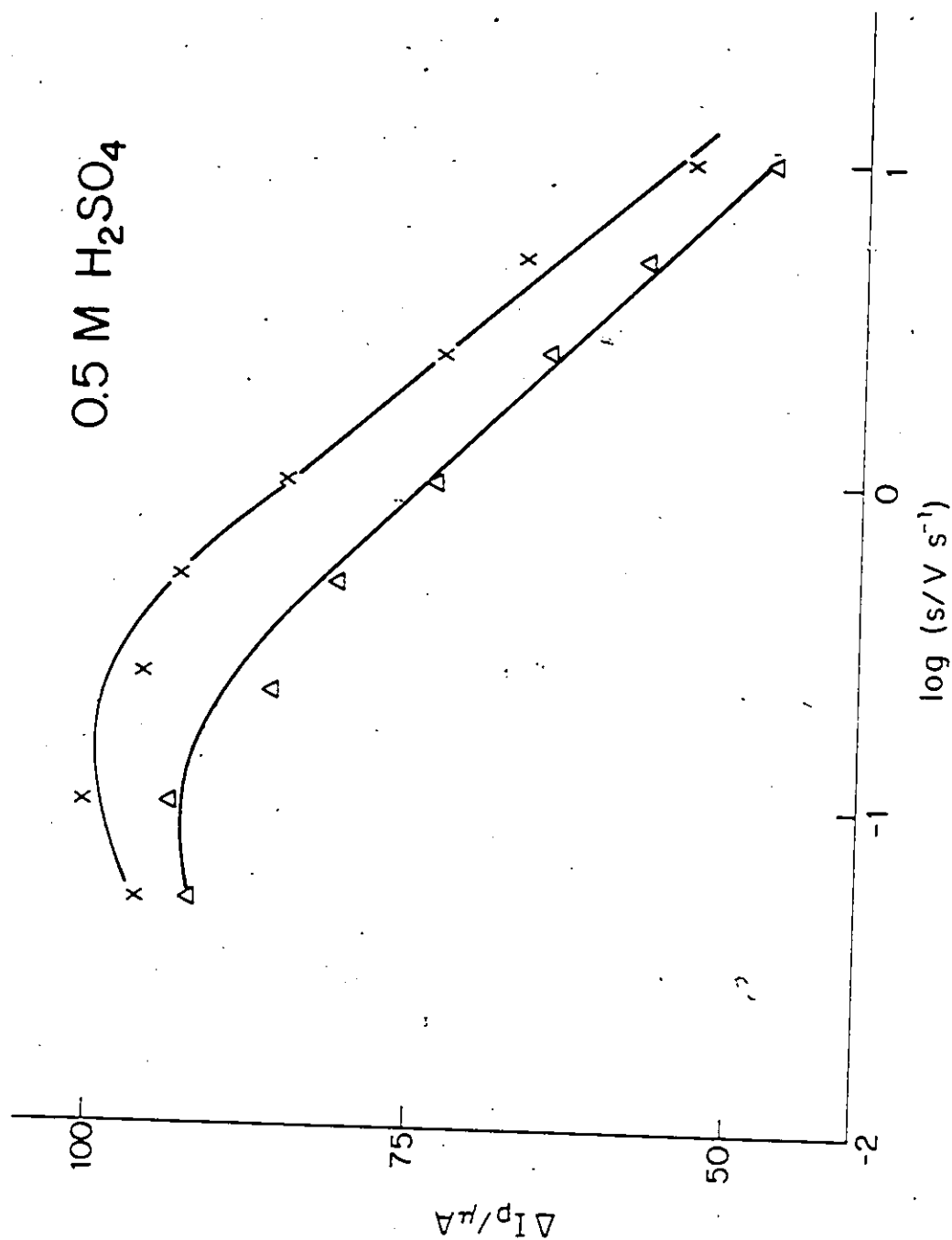


Fig. 26. Dependence of the rate of growth of Ir oxide films on  $\log$  (sweep-rate), in 0.5 M  $\text{H}_2\text{SO}_4$ , 298 K, for two anodic end potentials,  $E_a$ : (x) 1.500 and ( $\Delta$ ) 1.475 V,  $E_H$ .

The latter effect is based on the idea that the monolayer surface oxidation processes observed in the A state are still operating at the Metal/Oxide interface beneath the thickening film and are responsible for the growth of the film but are obscured by the large redox currents for the film process itself. This is supported by the fact that all the peaks observed in states M, MB and to some extent B, are rather reversible (with the exception of  $O_{A,1,2,r}$ , which will be proven later not to be involved in film growth), i.e. their peak potentials are constant with  $s$  up to  $s \geq 10 \text{ V s}^{-1}$ . Therefore, the observed effect of  $s$  cannot be attributed to the influence of increasing  $s$  in any of the reversible processes occurring in the film.

A last factor involves the possibility that, as the oxide is not epitaxially grown, increase of sweep-rate could induce faster dissolution due to greater stress (176) during oxide formation but this factor is probably a minor one, since the observed linear dependence of rate of growth on  $\log s$  hints that a process whose properties are also linear in  $\log s$  is responsible for the experimental behaviour, i.e. the irreversibility of the oxidation peaks as  $f(s)$ .

#### 4.4.1.4. Temperature Effects

The temperature dependence of the rate of growth in  $0.5 \text{ M H}_2\text{SO}_4$  at  $s = 0.100 \text{ V s}^{-1}$ , for the range  $298 \leq T \leq 340 \text{ K}$ , presents a shallow maximum around  $308 \text{ K}$ , while at  $T > 308 \text{ K}$  the rate of growth decreases quite markedly and eventually at  $T > 345 \text{ K}$ , the thick oxide does not grow any further and, if present on the surface, it dissolves away (74). These effects are associated with two competing processes: one is the increase in the rate constant for the processes involved in oxide formation with increasing temperature and the other is an increase in the dissolution rate of the oxide, both chemically and electrochemically, and finally because the  $\text{O}_2$  evolution reaction, which involves the oxide film itself, occurs at less positive potentials at higher temperatures.

#### 4.4.1.5. Rotating Disc Experiments

Although no change in rate of growth can be detected by stirring the solution with  $N_2$  with respect to the rate observed in quiescent solutions, it has been suggested (257), because of the porous structure of the oxide films as seen under the SEM, that a dissolution/redeposition growth mechanism possibly takes place. A study of the rate of growth as a function of rotation speed of an Ir disc electrode was therefore carried out in order to elucidate the role, if any, of dissolution and redeposition of Ir species in solution on the rate of growth of the oxide film.

The results are shown in Fig. 27 and, as can be seen, no trend in the slope, i.e. rate of growth, can be observed with respect to the rotation frequency,  $\omega$ . The spread of the slopes of the relation in Fig. 27 for the various  $\omega$  values is smaller than the calculated standard deviation,  $\sigma$ , of the data. Thus, it can be concluded that dissolution/redeposition is not involved in the growth mechanism at the early stages of film formation. It is possible that such processes could play a role once the film achieves a certain thickness, but then such processes would be undetectable in the above experiment due to the insensitivity of the processes taking place inside the pore system to electrode rotation or bulk solution stirring.

#### 4.4.1.6. Experiments at constant potential

When the anodic end potential of the sweep is maintained constant for a controlled period of time, the oxide film on Ir does not continue to grow, regardless of the length of the holding period, e.g. up to 2 h; and only undergoes minor changes during this time. If the  $E_a > 1.6 \text{ V}, E_H$ , then some dissolution of the oxide takes place.

On the other hand, when the cathodic end potential is held constant, the oxide film does not get reduced back to the bare metal, nor is it lost mechanically, regardless of the rate of  $H_2$  evolution. The only appreciable

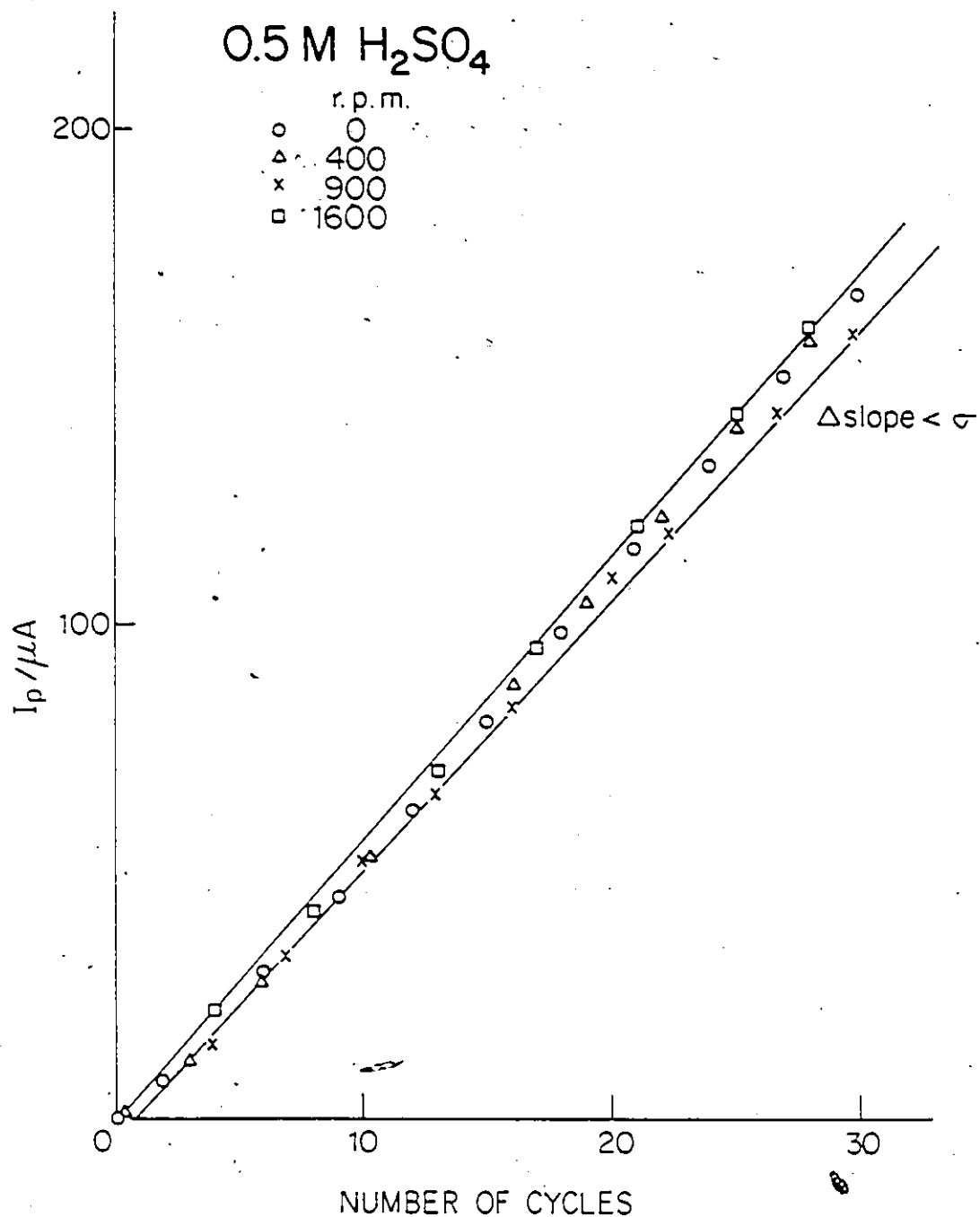


Fig. 27. Growth of an oxide film on a rotating Ir disc electrode as a function of the number of cycles, for various frequencies of electrode rotation,  $\omega$ , (values as shown), in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 0.100 V s<sup>-1</sup>, 298 K.

change is that once the potential sweep is resumed in the anodic direction, there is an increase in charge in the  $O_{A,1,2,r}$  region, and a certain increase in the  $O_{A3,r}$  region, while the rest of the profile, including that for the cathodic scan, remains constant. After two or three sweeps, the  $i$  vs  $V$  profile returns to its original shape.

#### 4.4.1.7. Effect of $Cl^-$ ion on Oxide Film Growth

As will be discussed later in more detail (Chapter 5), the presence of  $Cl^-$  ion inhibits the  $A \rightarrow M$  transition. However, once the oxide has been developed in the absence of  $Cl^-$  ion, the addition of  $Cl^-$  to the electrolyte indicates that the ion has no effect whatsoever on the charge or shape of the profile at potentials  $> 0.7 V, E_H$ , as expected since the oxide does not get reduced back to the metal in every cycle and  $Cl^-$  ion is known to exert its influence by adsorption at the metal in the monolayer stage of surface oxidation (see Fig. 50, page. 166). However, the  $Cl^-$  ion clearly blocks the deposition of H species in a similar way to that seen for the "monolayer" processes at Ir before thick film formation has occurred.

Once the thick oxide film is present on the surface, no further growth can be achieved in the presence of  $Cl^-$  ion. This inhibition of the growth reaction arises either from blocking of oxidation of bare metal sites needed for continuous growth or by blocking of deposition of H species which could play a role in the growth mechanism, as proposed by Shibata (38) for the case of thick oxide films at Pt.

#### 4.4.2. Oxide Growth Law

The current at the peak of the capacitance maximum at ca.  $1.0 V, E_H$ , i.e.  $O_{A3,r}$  region, is plotted as a function of the number of cycles in Fig. 28 for the case of  $0.5 M H_2SO_4$  at  $298 K$  and for a sweep-rate of  $0.050 V s^{-1}$ .

As can be seen, the extent of growth ( measured by the CEF) initially increases linearly in time ( as shown for the first 500 cycles).

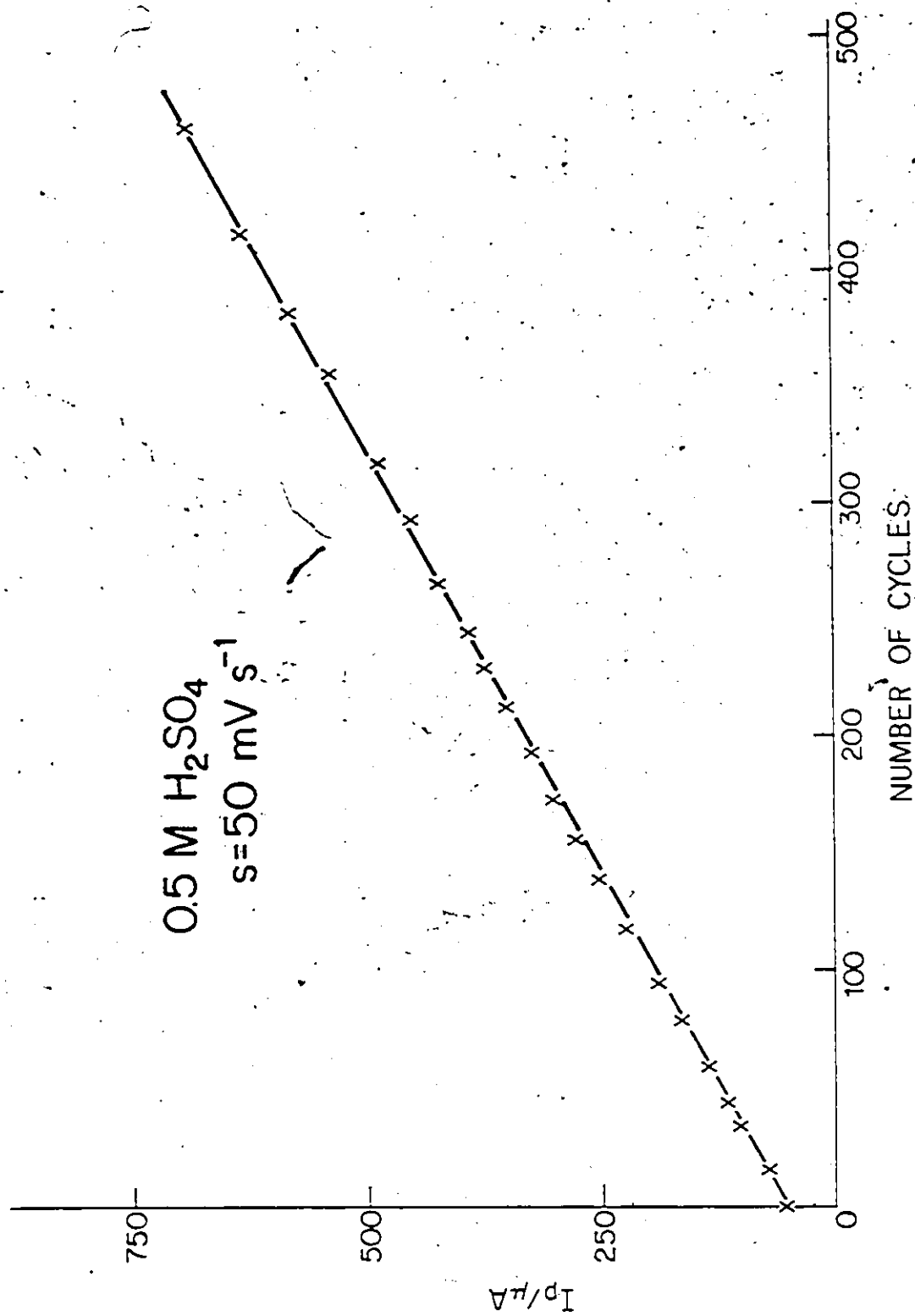


Fig. 28. Growth of an Ir oxide film as a function of the number of cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 0.050 V s<sup>-1</sup>, 298 K, under continuous cycling between E<sub>a</sub> = 1.465 V and E<sub>c</sub> = 0.055 V, E<sub>H</sub>.

This linear behaviour, that extends up to ca. 1000 cycles, can be described by an equation of the form

$$I_p = A \cdot \# \text{ cycles} + I_{p,0} \quad (4.4)$$

where A is a function of the electrolyte and depends on the other experimental conditions previously discussed. After 1000 cycles, the film growth starts to level off in a parabolic way as the film continues to thicken further. Limiting values were observed for film thicknesses but no correlation could be found between this phenomenon and the other experimental conditions. Behaviour limited by anion and  $H^+$  diffusion in pores is probably involved when appreciable film thicknesses are developed.

This general behaviour was expected since the growth of the film is presumably due to accumulation of oxide species that are not completely reduced in each cathodic sweep. Thus, as long as mass-transport or IR drop problems do not become limiting factors because of film thickness, oxide accumulation proceeds in the same fashion; since the growth rate is not very large, i.e. the rate of growth in 0.5 M  $H_2SO_4$  at  $s = 0.050 \text{ V s}^{-1}$  is about  $13.3 \mu\text{C cm}^{-2} \text{ cycle}^{-1}$  which is about 6% of a monolayer of OH species, growth can continue undisturbed, until the limitations mentioned above for thicker films begin to interfere with the growth process.

#### 4.4.3. Optical Studies of Iridium Oxide Films

Iridium oxide films prepared under various conditions were examined by means of optical and scanning electron microscopies.

The surface characteristics of the electrochemically grown films were found to be dependent mainly on oxide thickness. Thus, the oxide layer appeared initially as a continuous smooth film showing some cracking and a great deal of apparent porosity, as shown in Fig. 29a. As the oxide film thickness becomes increased, cracking of the film is observed (Fig. 29b),

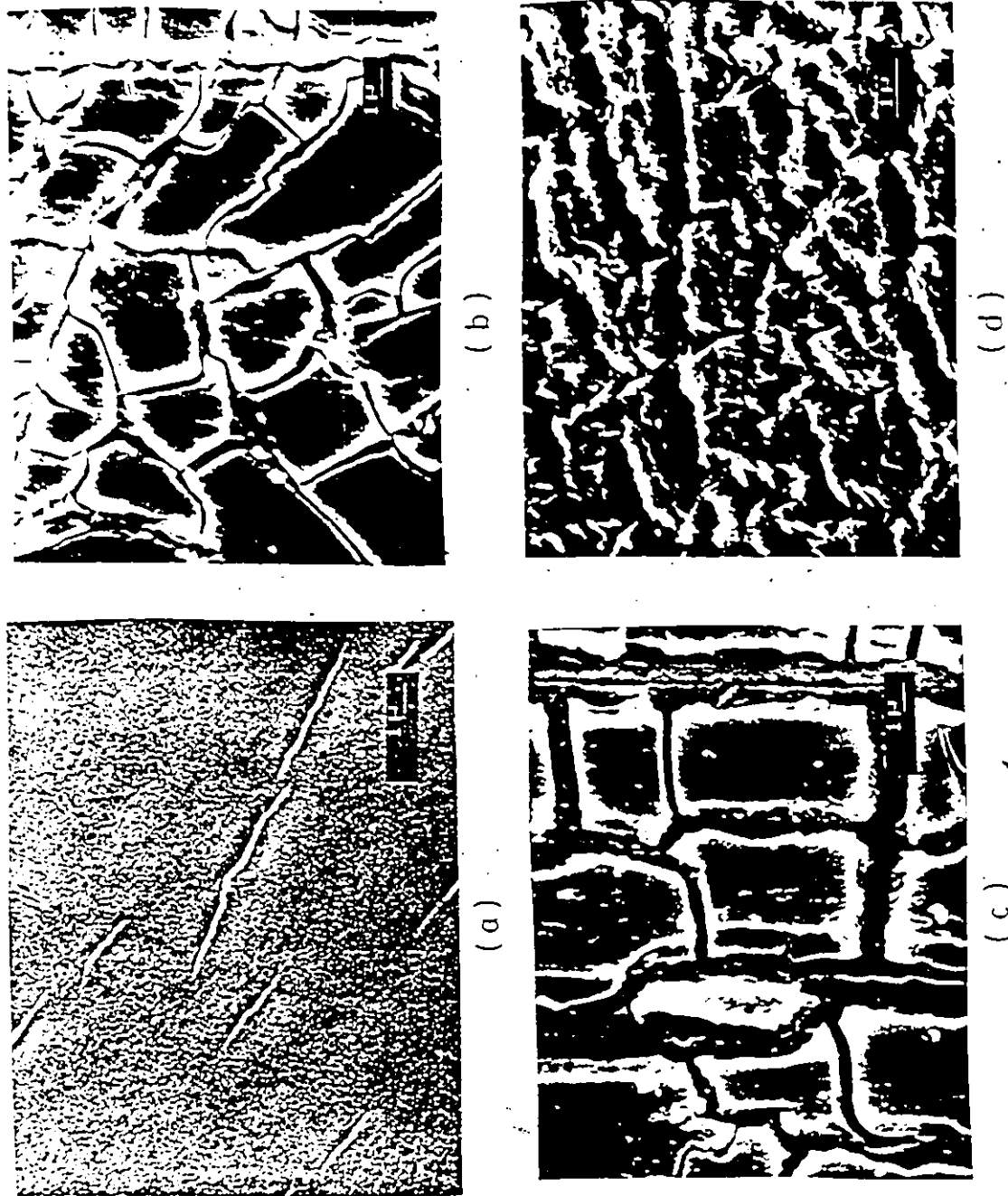


Fig. 29. SEM micrographs of Ir oxide films: (a) thin oxide film ( $CEF = 20$ ) showing small amount of cracking and a large density of macropores; (b) thicker oxide film ( $CEF = 50$ ), showing widespread cracking and a smooth outer surface; (c) and (d) thicker oxide films ( $CEF$ 's 100 and 87 respectively) showing wide cracks between oxide pieces, roughness of the substrate and top layer of the oxide.

probably due to stress created by the large amount of electrolyte inside the film, and the difference of lattice constants of the  $\text{IrO}_2$  film and the Ir substrate. However, the surface of the oxide species appears relatively smooth, as shown in Fig. 29b/.

For thicknesses of  $\sim 1 \mu\text{m}$  or CEF's  $> 100$ , the film consisted of islands of oxide separated from each other by wide cracks (Figs. 29c,d); at the same time, the surface of the oxide appeared rougher than before, as also seen in Figs. 29c,d.

That the cracking effect was not an artifact, due to the vacuum conditions in the SEM chamber, was confirmed by optical microscopy. Electrodes bearing freshly prepared oxide films were observed under the Nomarski optical microscope while still wet and the cracking of the film was already evident.

These electrochemically grown films were quite different from the films of  $\text{IrO}_2$  that can be prepared thermally by exposing an electrode to a gas flame. The surface of the thermal oxide is shown in Fig. 30a where grain boundaries are clearly detectable but are absent in the electrochemically prepared oxides.

The oxide films, regardless of thickness, appear to follow the substrate topography, as shown in Figs. 30b,c. The former figure shows the surface of an oxide film thinner than that of Fig. 30c; the substrate can be clearly seen in regions where the oxide fell-off and it appears to be very rough. In the case of Fig. 30c, the oxide appears to have a thickness of  $\sim 1 \mu$  and is evidently becoming detached from the surface. The latter effect probably originates from the effects of  $\text{O}_2$  evolution on that oxide. It seems that the  $\text{O}_2$  evolution reaction involves species in the film and causes film dissolution and mechanical failure. However, this effect gives us an opportunity to examine the film and the underlying substrate in an excellent

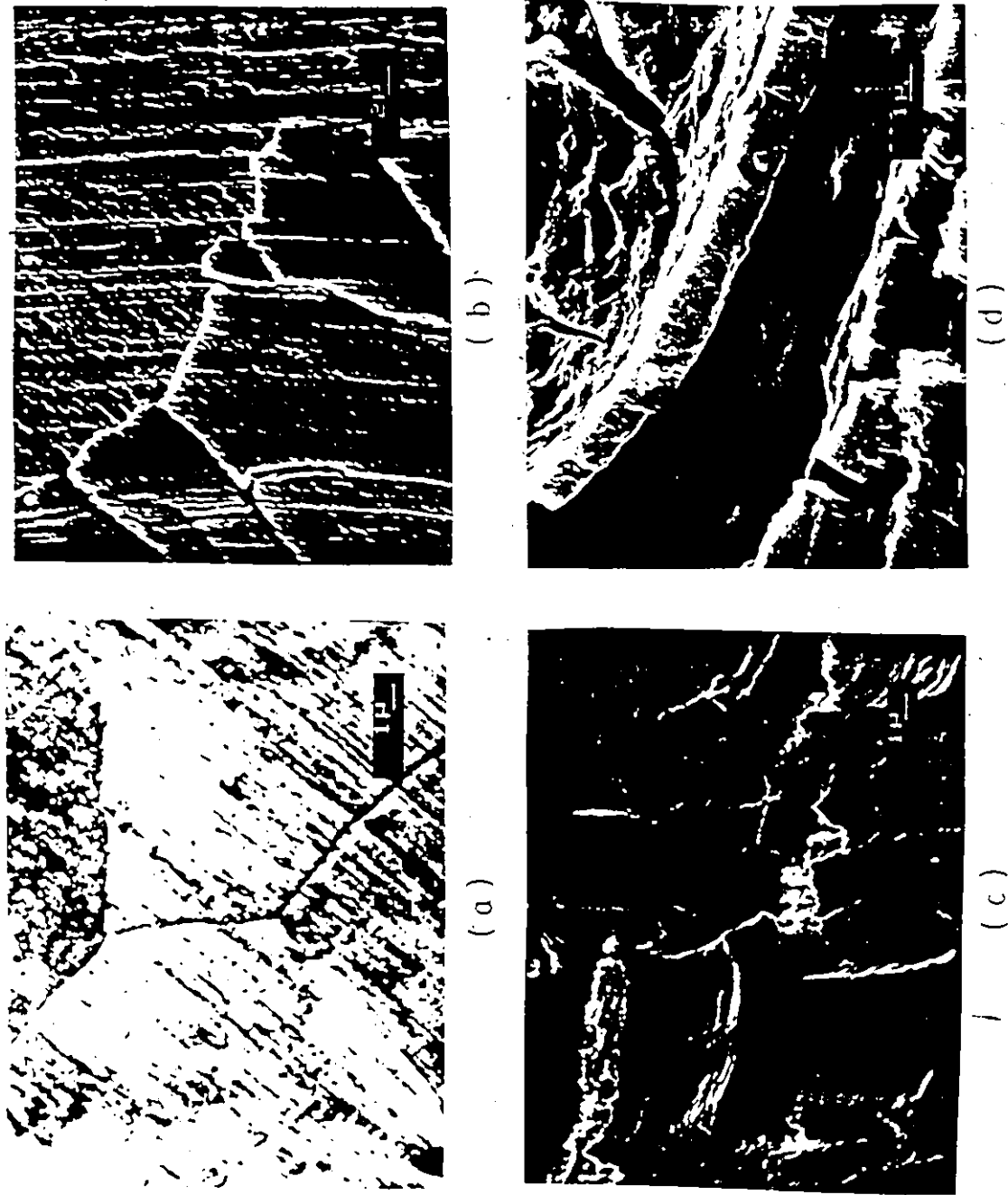


Fig. 30. SEM micrographs of Ir oxide films: (a) thermal oxide formed under a gas flame, showing grain boundaries; (b) thin oxide film, showing how the film follows the substrate topography; (c) thicker oxide film, ca.  $1\mu\text{m}$ , lifting-off from the surface due to  $\text{O}_2$  evolution; and (d) higher magnification of the surface shown in (c). Roughness of the oxide layer and of the underlying substrate can be seen.

way, as is seen from Fig. 30d, where the roughness and macroporosity of both the oxide and the substrate are evident. The substrate can be better seen at higher magnification, as in Fig. 31a.

Because of these observations, efforts were made to determine if the underlying substrate was actually metal or an oxide layer. For this purpose the surface of a sample, where a wide crack existed between two oxide patches, was mapped for the presence of O by means of X-Ray emission spectroscopy. As shown in Fig. 31b, there is a clear difference between the amount of oxygen in the two regions, the quantity being larger on the oxide pieces; however some O signal is still clearly seen from within the crack.

Similarly, when the substrate where the oxide had peeled-off and the oxide itself are both analyzed by XES, the results indicate the presence of  $16 \pm 6$  atomic percent oxygen in the substrate region and  $75 \pm 20$  atomic percent oxygen in the oxide region. The latter result suggests, as expected, an  $\text{IrO}_2$  stoichiometry, the large uncertainty being due to the lack of appropriate standards. However, the former value indicates that some O is present on the substrate.

By the same technique, XES, it was determined that the oxide film contains some S, probably due to incorporation of  $\text{SO}_4^{2-}$  from the electrolyte during the oxide growth. By comparing the two XES spectra corresponding to the substrate and to the oxide, a peak at 2.29 eV, characteristic of a KA line of S, was visible only for the case of the oxide. A standardless analysis of the peak indicated about 8 atomic percent of S in the sample, assuming Ir to be the only other constituent.

This is a rather interesting result, since the presence of S in the oxide film has been previously suggested (257) but, to our knowledge, this is the first experimental confirmation of this effect.

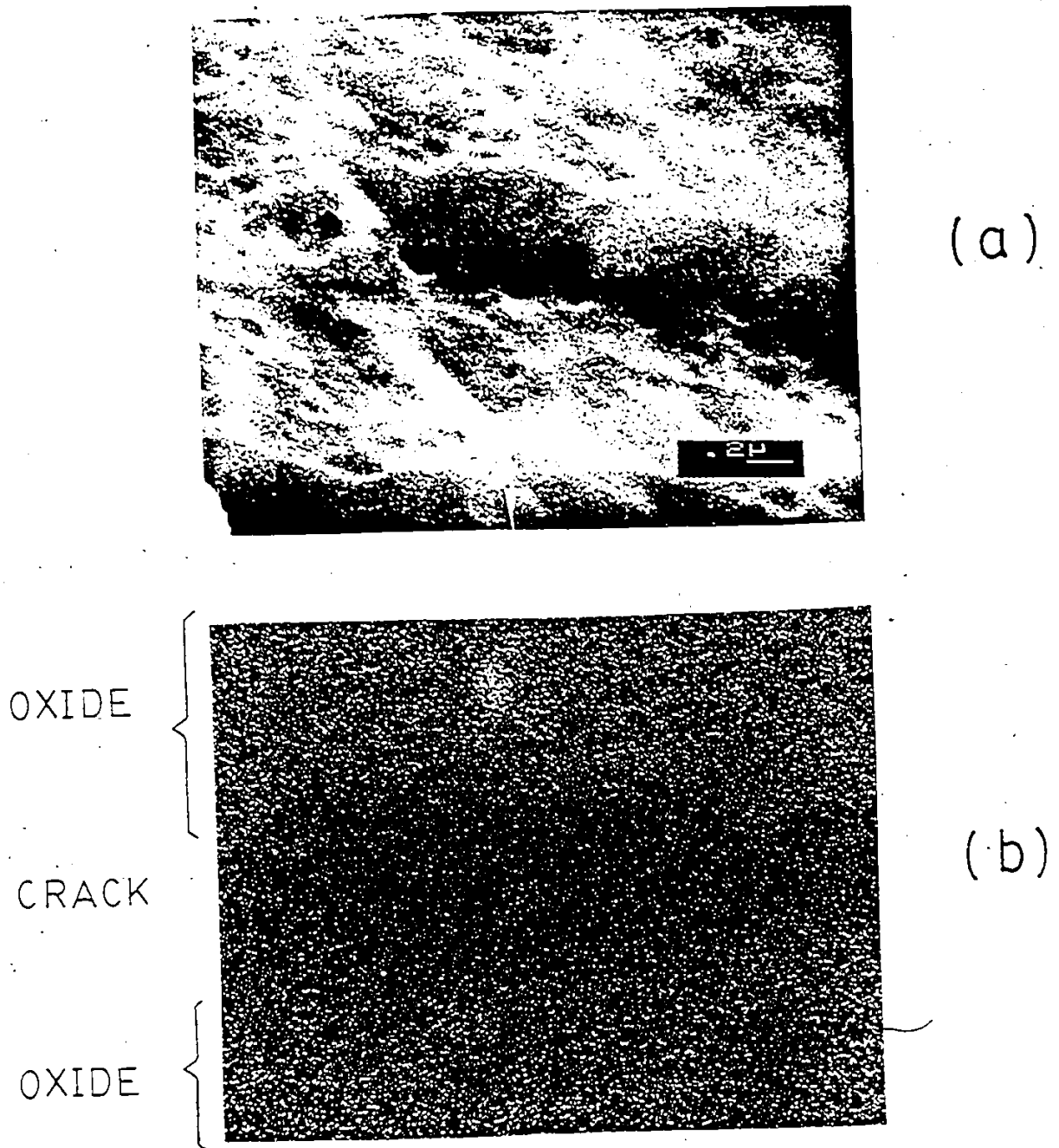


Fig. 31. (a) SEM micrograph of the surface shown in Fig. 30d, at higher magnification to indicate the underlying substrate morphology. (b) Oxygen mapping of an oxide film sample, similar to that shown in Fig. 29c. The oxide and the substrate showing in the cracks were both analyzed. Notice lower density of O signals from the material inside the cracks.

#### 4.4.4. Spectroscopic Studies of the Iridium Oxide Films

In order to complement the electrochemical and optical results, the iridium oxide films ~~were~~ subjected to analysis by ESCA and AUGER spectroscopies at the N.R.C Laboratories by Dr. D.Mitchell.

The samples were two Ir disks on which thick oxide films of different thicknesses had been prepared. The electrochemical characteristics of both samples, A and B, are shown in Table VI.

The appearance of both samples under the SEM indicated that sample A (Fig. 32a) consisted of oxide islands exposing an underlying substrate which could be roughened metal covered by a certain amount of oxide. Sample A had an apparent oxide thickness of ca. 500 nm. Sample B showed a more uniform oxide layer covering the surface (Fig. 33a); however, the layer exhibited widespread cracking and was thinner than that on the A sample. The thickness of the oxide on the B sample could not be estimated by SEM but due to the 2:1 ratio in CEF's between samples A and B the thickness of sample B should have been ca. 250 nm.

The general AUGER and ESCA scans (Figs. 34a,b) indicated the presence of Ir, oxygen and a small amount of carbon located in inclusions in the surface; the C probably arises from the diamond saw used to cut the Ir discs from an Ir rod.

The ESCA survey for both samples (Figs. 35 a,b) indicated no appreciable difference between them, thus the O 1s and Ir 4f 5/2, 7/2 spectra were consistent with the presence of IrO<sub>2</sub>. Based on Au 4f 7/3 = 83.8 eV

| sample    | A     | B      |
|-----------|-------|--------|
| O 1s      | 530.9 | 531.13 |
| Ir 4f 7/2 | 62.00 | 61.95  |

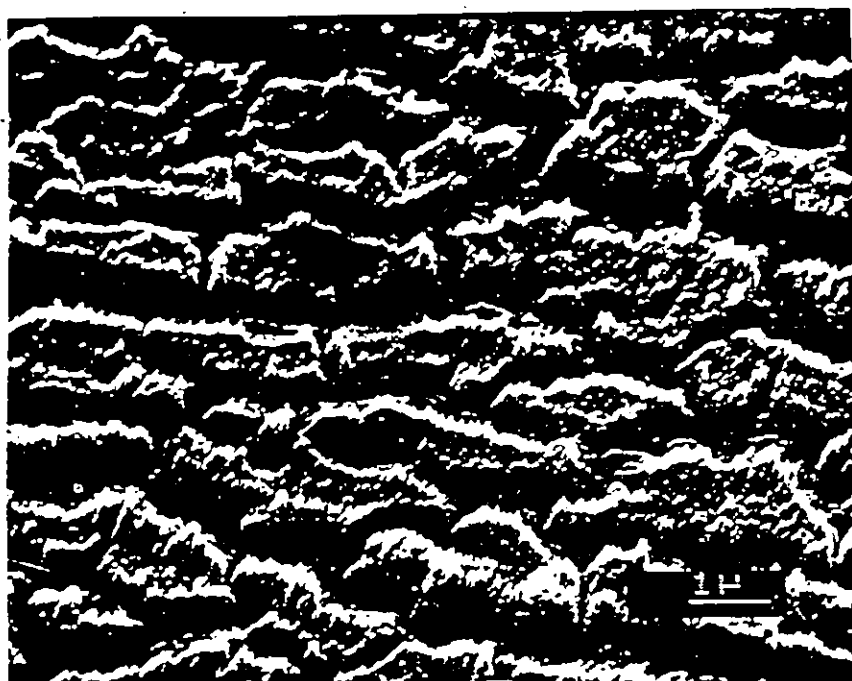
TABLE VI

FORMATION CONDITIONS AND ELECTROCHEMICAL CHARACTERISTICS OF  
THE OXIDIZED Ir SAMPLES USED FOR SPECTROSCOPIC ANALYSIS

| <u>QUANTITY</u>        | <u>SAMPLE A</u> | <u>SAMPLE B</u> |
|------------------------|-----------------|-----------------|
| $E_c (V, E_H)$         | 0.061           | 0.061           |
| $E_a (V, E_H)$         | 1.467           | 1.467           |
| $s (V s^{-1})$         | 0.100           | 0.100           |
| T (K)                  | 298             | 298             |
| Growth time (min)      | 977             | 380             |
| Cyclic programme       |                 |                 |
| terminated at          | $E_a$           | $E_c$           |
| Optical appearance     |                 |                 |
| (freshly prepared)     | black           | metallic        |
| Charge ( $C cm^{-2}$ ) | 0.0184          | 0.00888         |
| CEF                    | 87              | 42              |
| Electrolyte            | 0.5 M $H_2SO_4$ | 0.5 M $H_2SO_4$ |
| Thickness ratio        | 2               | 1               |



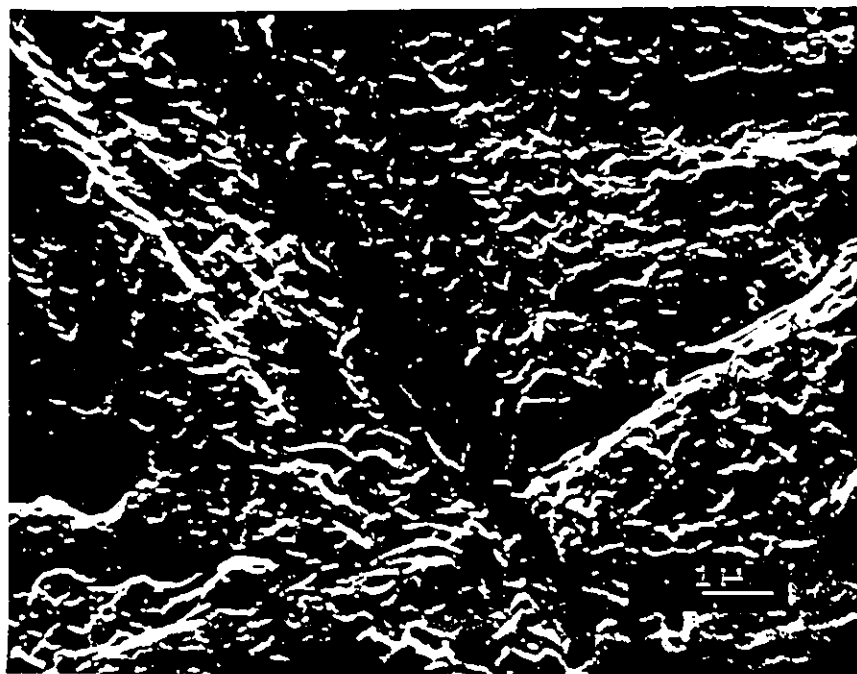
(a)



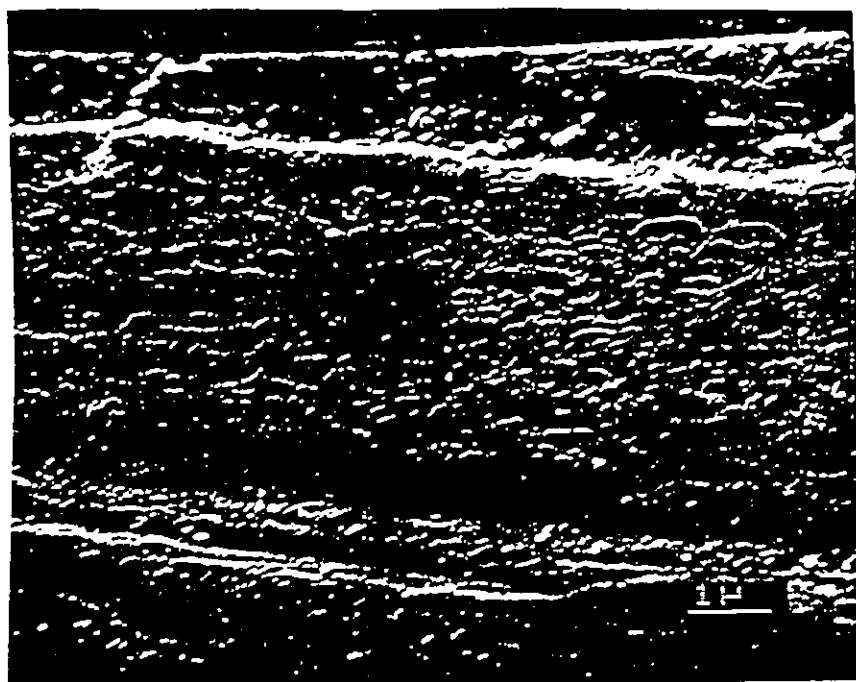
(b)

Fig. 32. SEM micrographs of sample A, used for spectroscopic studies:

- (a) oxide freshly formed; and
- (b) after sputtering.



(a)



(b)

Fig. 33. SEM micrographs of sample B, used for spectroscopic analysis:  
(a) oxide freshly formed; and  
(b) after sputtering.

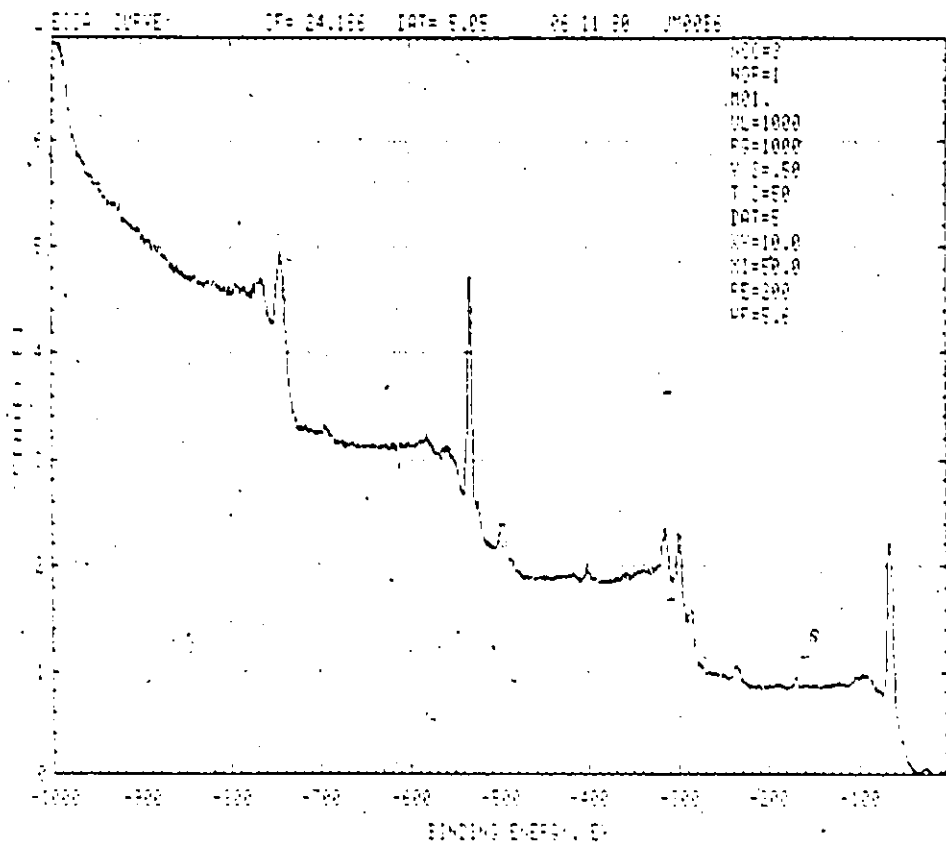


Fig. 34a. General ESCA survey of sample B.

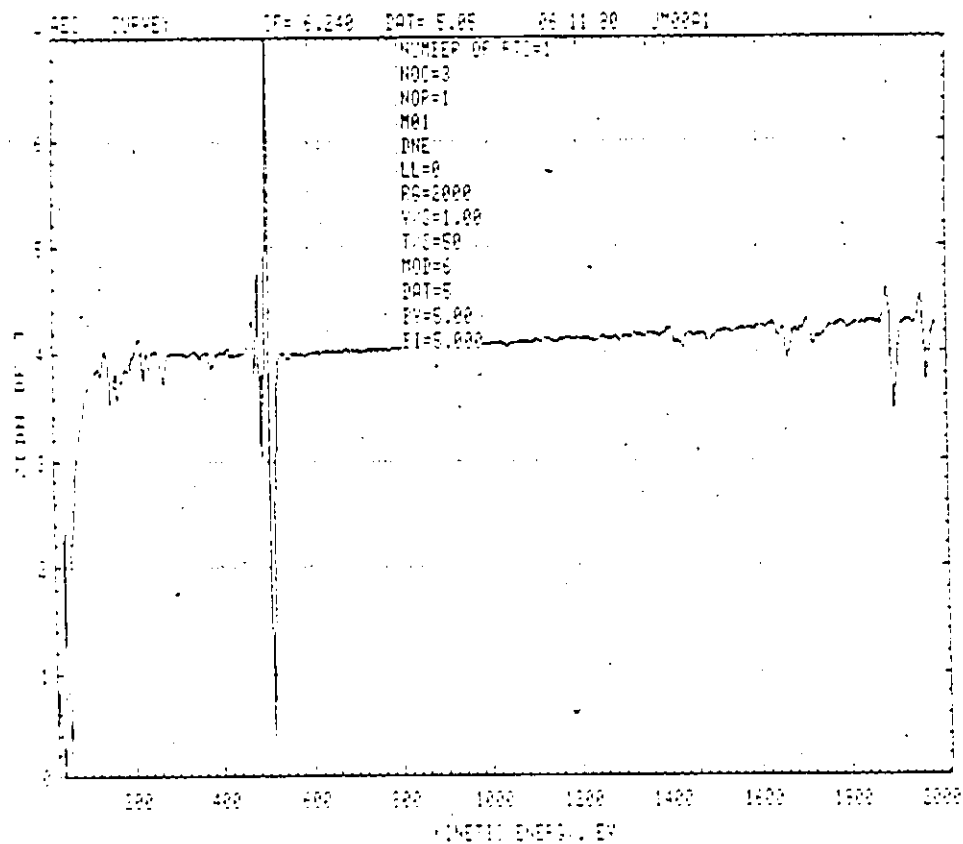
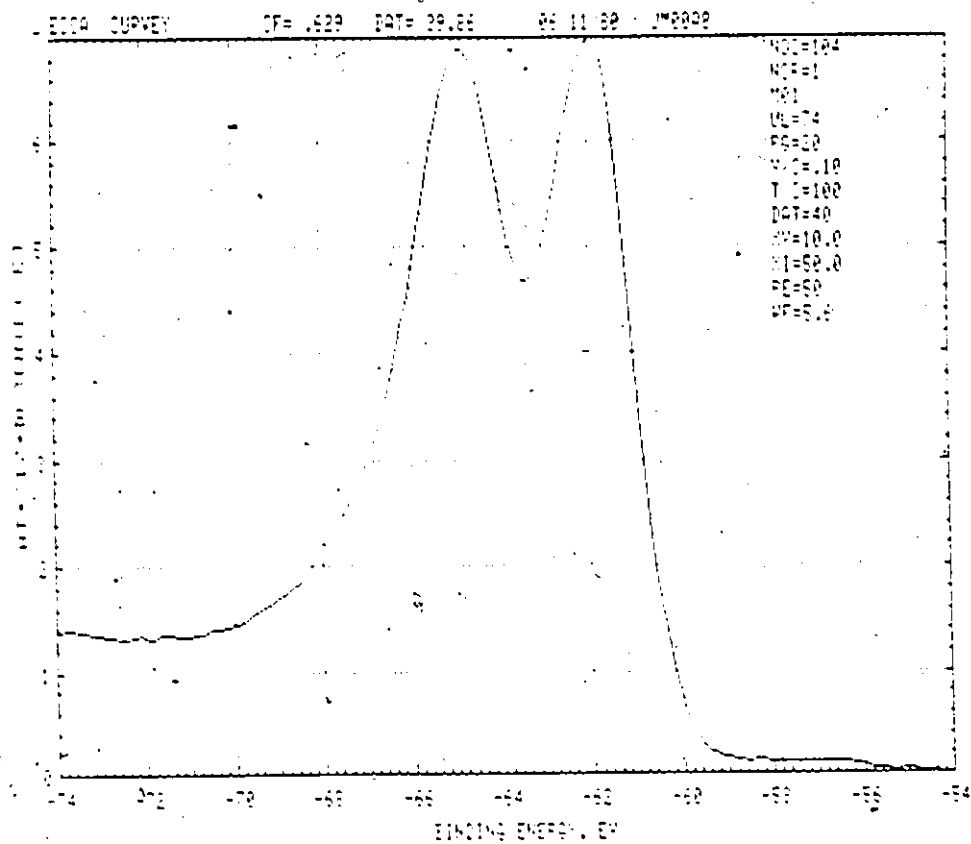
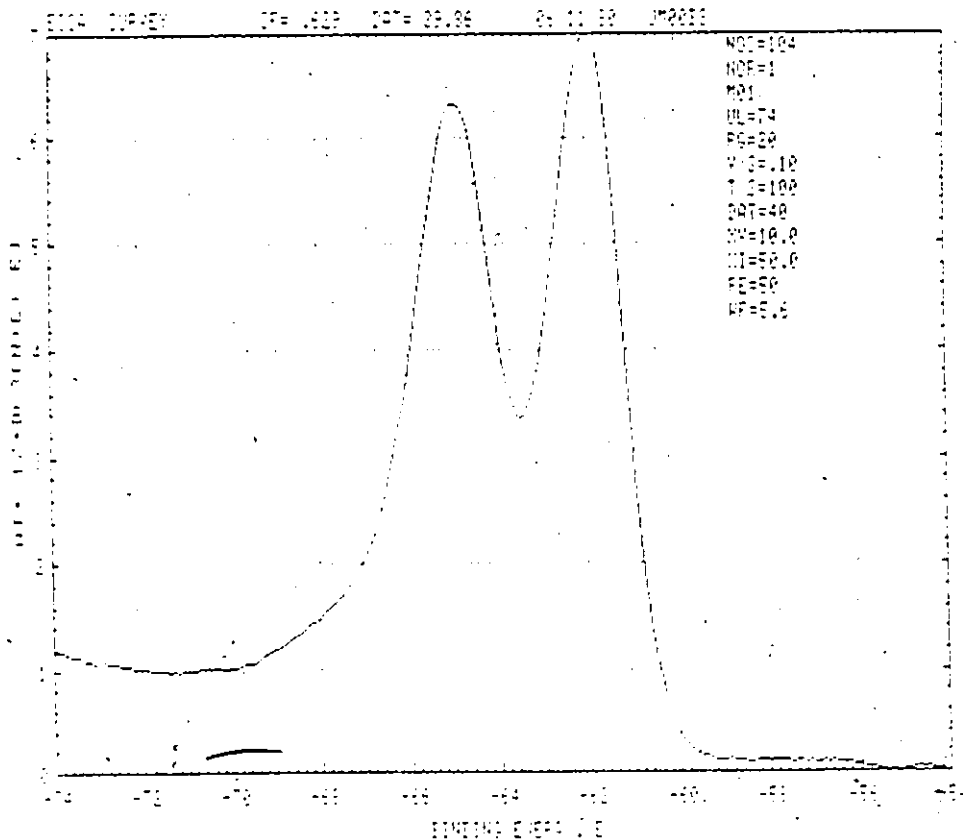


Fig. 34b. General AUGER survey of sample A.



(a)



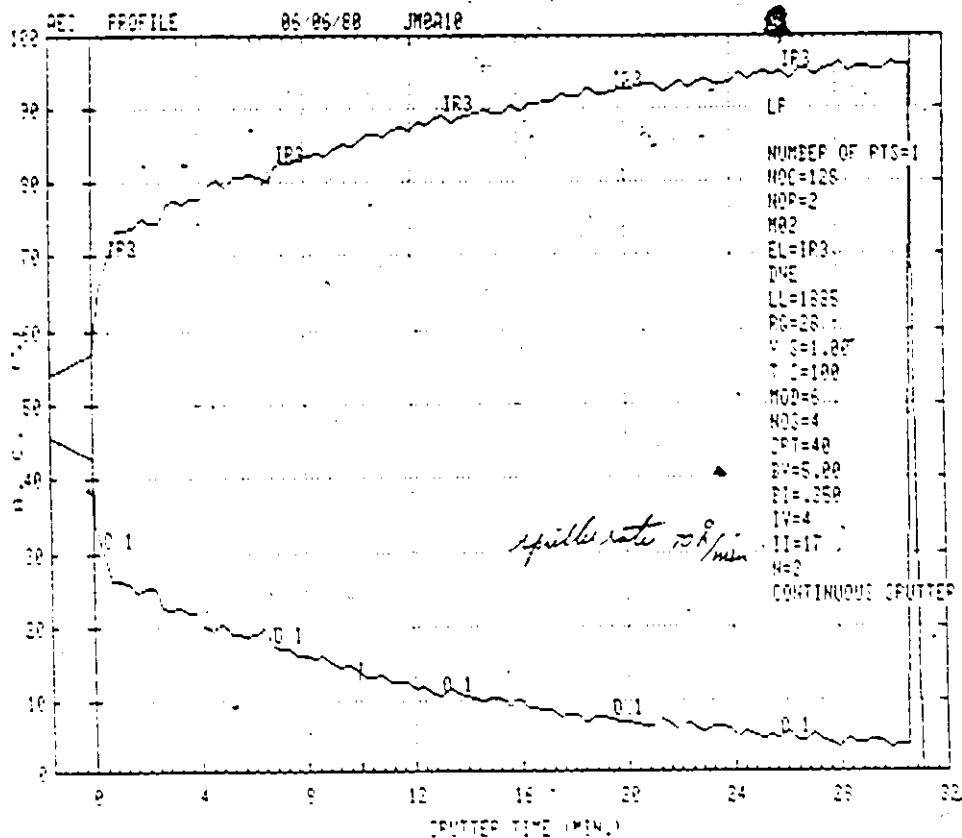
(b)

Fig. 35. ESCA spectrum of (a) sample A and (b) sample B, in the Ir 4f 7/2 region.

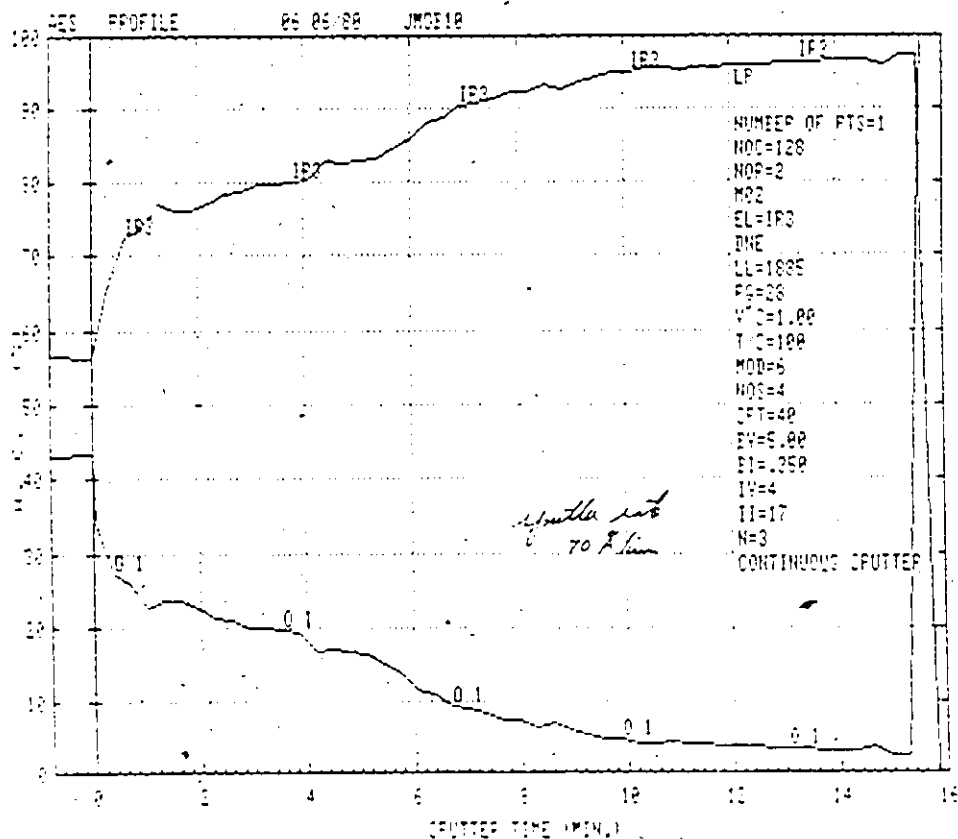
It should be noted that after a certain time of exposure in the air, sample B, which had been removed from the cell at the cathodic end of the sweep, lost its metallic appearance and turned bluish-black, presumably because  $\text{IrO}_2$  is the most stable form of Iridium oxide. This transformation is possible on account of the great amount of water that the oxide film contains.

The Auger sputtering profiles for both samples (Figs. 36a,b) indicated that the oxide layer was non-uniform in both cases. The estimated oxide thicknesses according to the sputtering times were given as 70 nm for sample A and 40 nm for sample B but, because of lack of knowledge of the density of the oxide and extent of porosity of the samples, the sputtering rate could have been overestimated. However, even when the reported film thicknesses appear to be smaller than the ones expected according to the SEM observations and to the results of other authors for similar oxide films (257,259,265), the ratio is still close to 2:1.

An interesting aspect of the properties of the film was observed when samples were examined under the SEM after the sputtering experiments had been performed on them : thus, because the metal and the oxide are assumed to sputter at about the same rate, a sputtered sample should retain the initial topography of the sample. This is observed in Figs. 32,33 where the sputtered surfaces of samples A and B are shown (Figs. 32b,33b). As can be seen, the appearance of the sample is maintained in the sputtered material but all the oxide had been removed. This was confirmed by means of in-situ X-Ray analysis of the samples which indicated that no O was present in the sputtered section of the sample. From the unsputtered region of the sample, a large O signal was detected.



(a)



(b)

Fig. 36. AUGER sputtering profile for (a) sample A and (b) sample B.

#### 4.4.5. Properties

Having discussed the rate of growth of the oxide film and its dependence on various experimental conditions, as well as the results of optical and spectroscopic studies on such films, we shall now proceed to discuss the behaviour of the various current peaks that appear in the  $i$  vs  $V$  profile of states M, MB and B; that is, how do the current peaks develop with cycling, what is their dependence on sweep-rate and what special features do they exhibit?. This will help them to be assigned to the appropriate electrochemical processes in the film.

As a reference for further discussion, typical  $i$  vs  $V$  profiles for the M state in 0.5 M  $H_2SO_4$ ,  $5 \times 10^{-3}$  M  $H_2SO_4$ , 1 M  $HClO_4$  and 0.5 M  $Na_2CO_3$  are shown in Figs. 37-40, respectively.

As shown, e.g, in Fig. 37 and discussed in section 4.3.1.5, the following regions of the  $i$  vs  $V$  profile for thick Ir oxide films can be distinguished:

(a) A region of H deposition/ionization, almost identical to that of the bare metal, although the total H charge decreases by about 15-20% as the oxide grows. Some redistribution of the adsorbed species (H) occurs amongst the various peaks with cycling.

On the cathodic current side, the H deposition region overlaps with that for irreversible reduction of oxide species which takes place with large hysteresis;

(b) A region of double-layer charging that appears to remain constant, regardless of oxide thickness. This region extends to 0.6 V,  $E_H$  where the onset of current for redox processes in the film obscures the double-layer charging currents. On the cathodic side, larger currents indicate a reduction component again likely to be due to the reduction of irreversibly formed

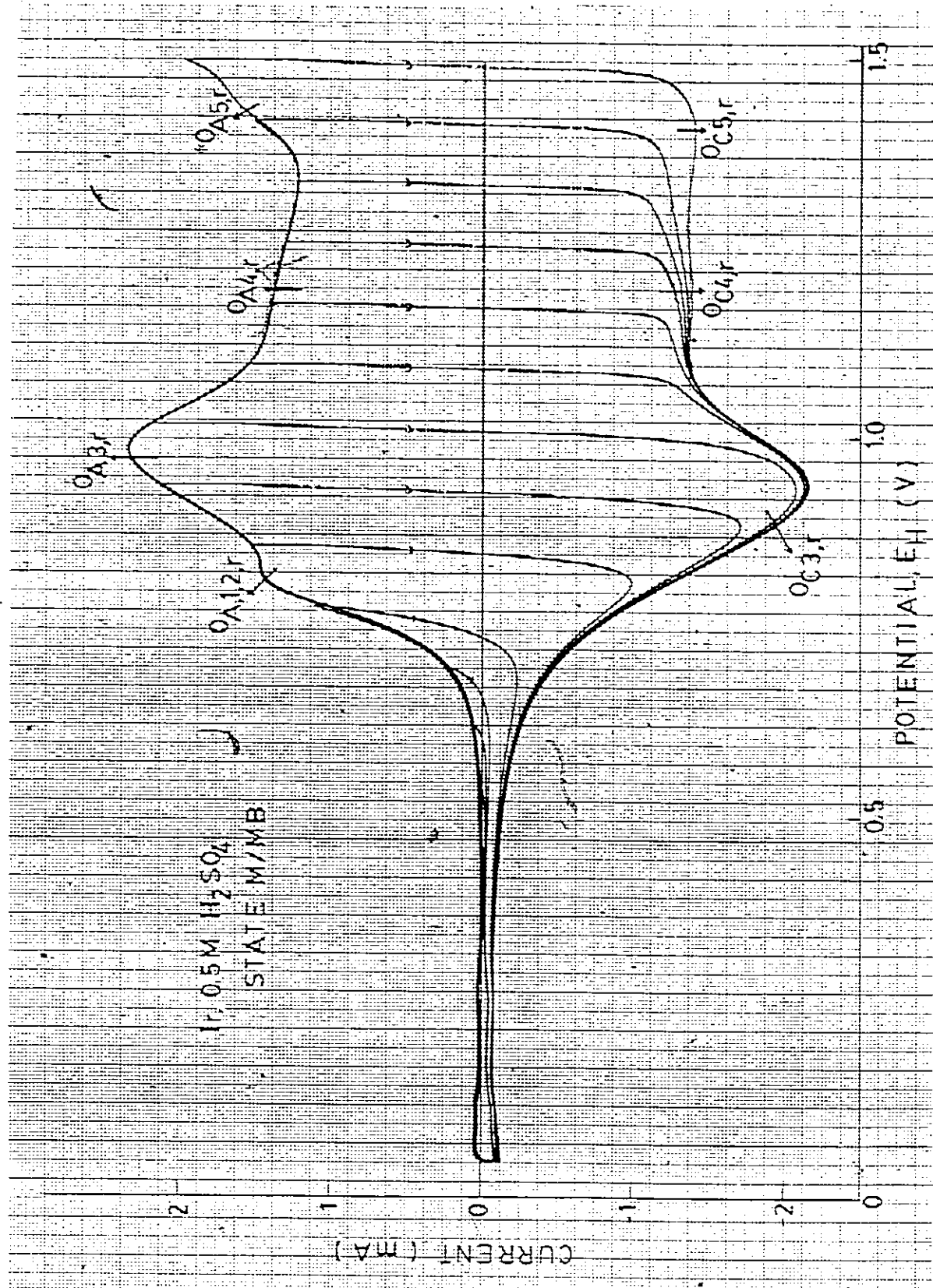


Fig. 37. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir electrode in state M/MB in 0.5 M H<sub>2</sub>SO<sub>4</sub>, at 0.100 V s<sup>-1</sup> at 298 K.

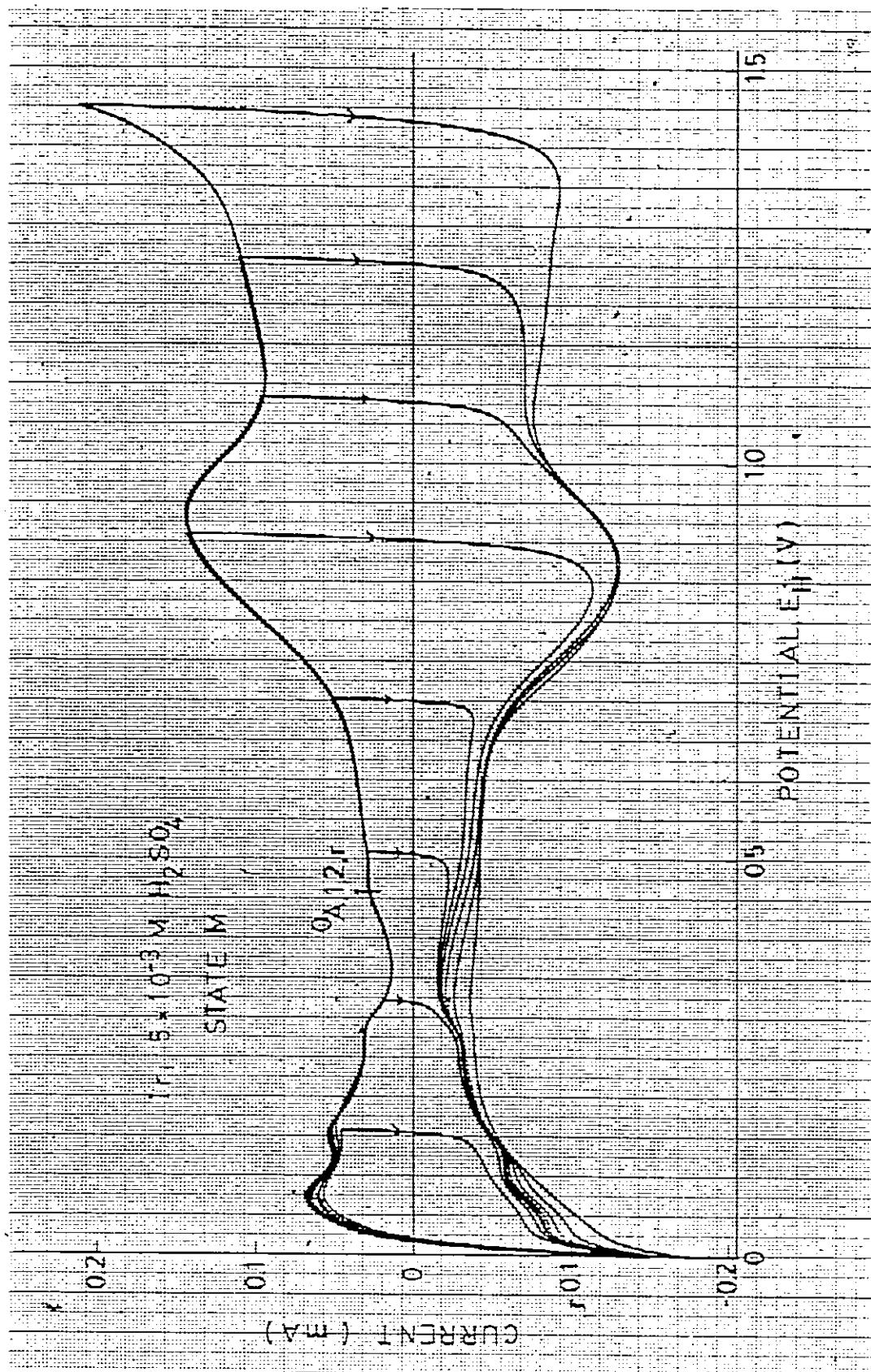


Fig. 38. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir electrode in state M in  $5 \times 10^{-3} \text{ M H}_2\text{SO}_4$  at  $0.100 \text{ V s}^{-1}$ ,  $298 \text{ K}$ .

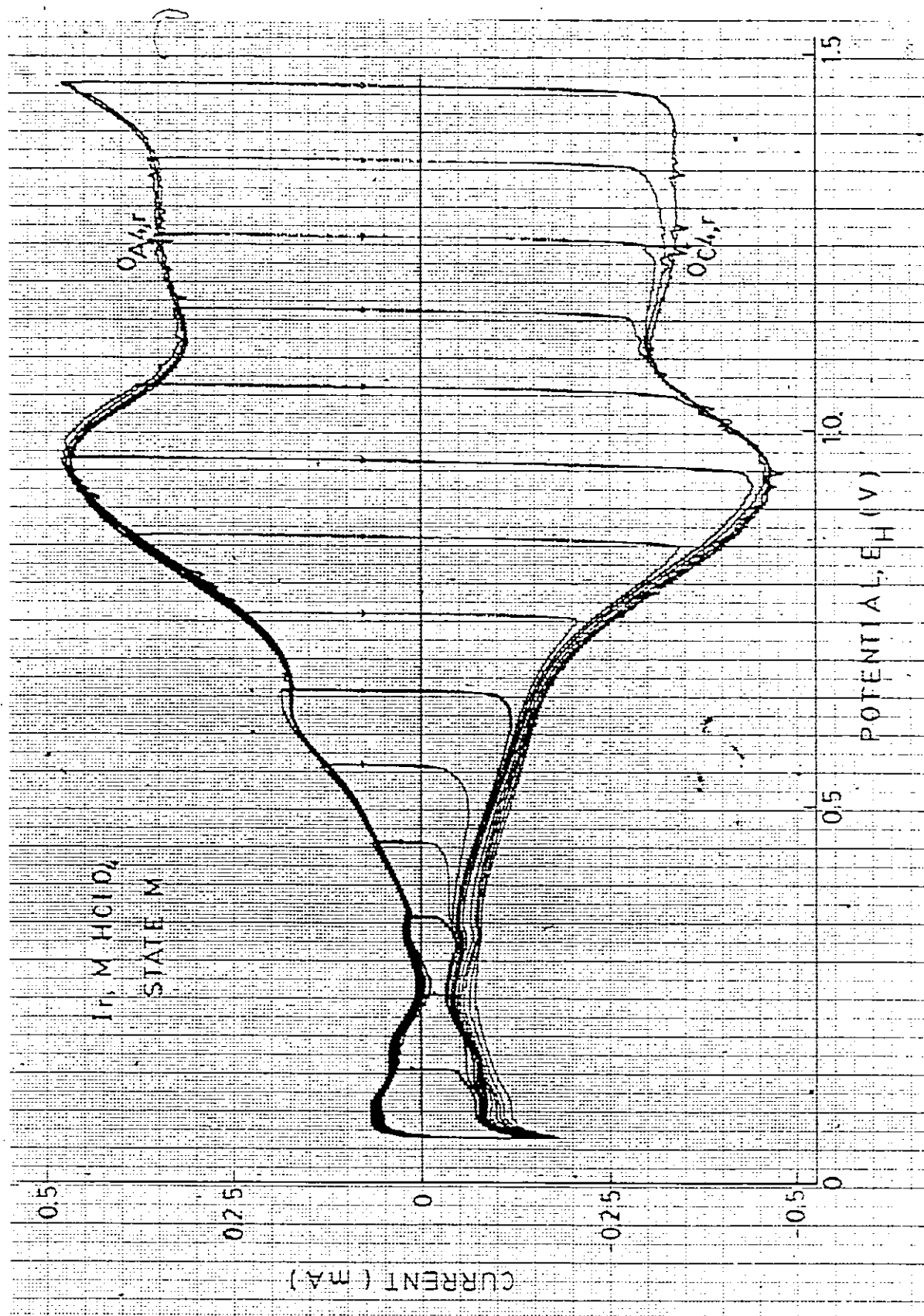


Fig. 39. Cyclic-voltammetry  $i$  vs  $V$  profile for Ir electrode in state M in 1.0 M HClO<sub>4</sub> at 0.100 V s<sup>-1</sup>,

298 K.

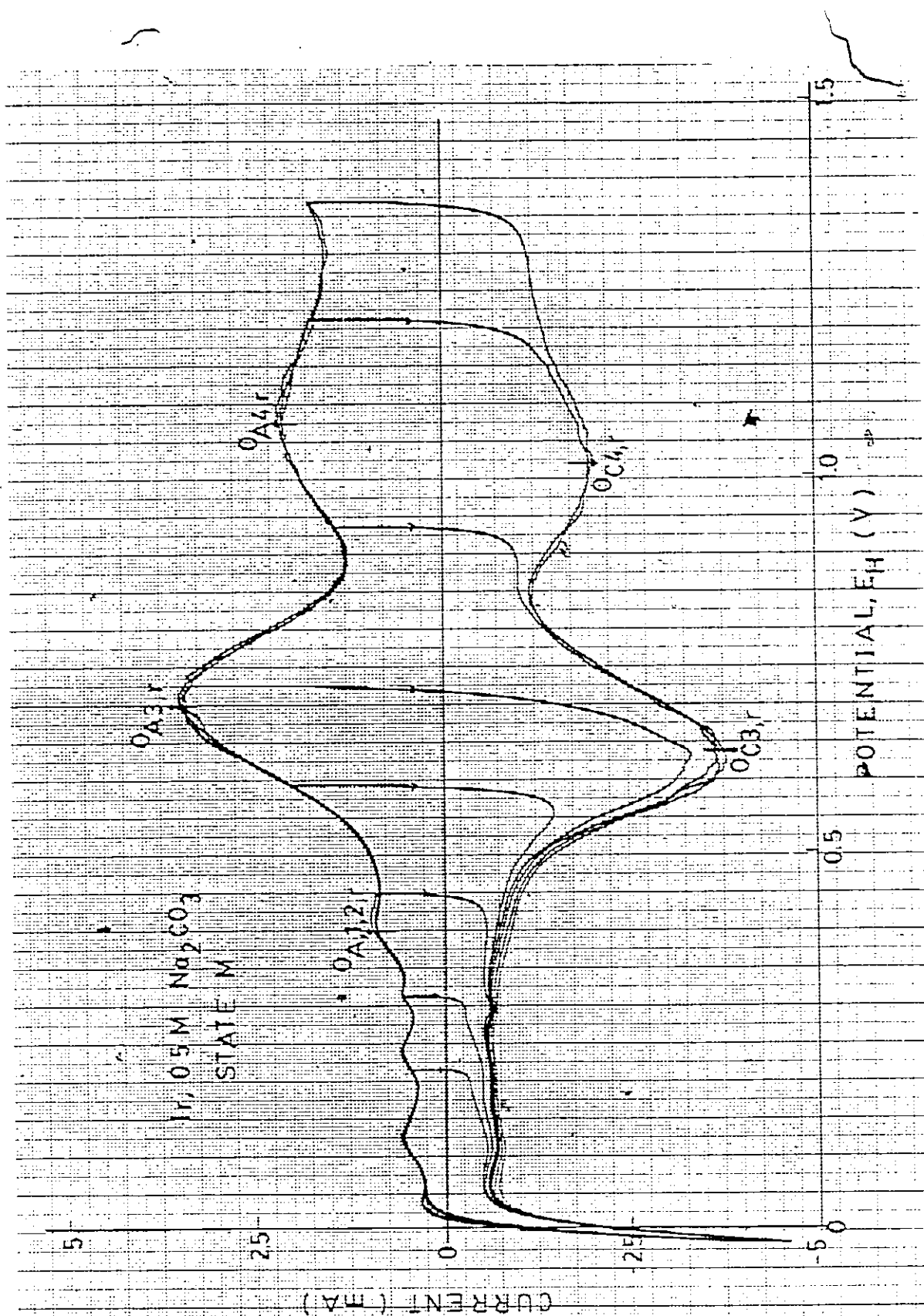


Fig. 40. Cyclic-voltammometry  $i$  vs  $V$  profile for Ir electrode in state M in 0.5 M Na<sub>2</sub>CO<sub>3</sub> at 0.100 V s<sup>-1</sup>,

298 K.

oxide species or to the completion of a solid-state redox process in the film, the potentials for which are continuously displaced in the negative direction due to slowness of pH equilibration.

(c) At around 0.6 V,  $E_H$  the first electrochemical process involving the thick oxide appears, manifested by an anodic peak, and a corresponding cathodic one which appears as a very broad region without any well defined shape. The anodic peak is labelled  $0_{A,1,2,r}$ , as discussed previously, since in some instances it can be clearly seen that it consists of two components. The cathodic region is correspondingly labelled as  $0_{C,1,2,r}$ .

The potential of the anodic peak shifts in the anodic direction as the film thickens until it becomes merged with the next peak,  $0_{A3,r}$ . Its charge also increases with cycling but, because of extensive overlap with its large neighbor, it is difficult to evaluate the charge increase quantitatively. This latter problem also makes it difficult to determine the relation between  $i$  and  $s$  but, after allowance for overlap with  $0_{A3,r}$ , this peak appears to be associated with a surface process (i.e.  $i$  is linear in  $s$ ). However, the peak is very irreversible, as indicated by the variation of its peak potential with  $\log s$ , even at  $s$  as low as  $0.0005 \text{ V s}^{-1}$ . This large degree of irreversibility makes it impossible to determine the kinetic parameter,  $s_0$ , since as shown in Fig. 41, no range of  $s$  where  $E_p$  was independent of  $\log s$  could be reached. The  $dE_p/d(\log s)$  for this peak was  $\approx 0.070 - 0.090 \text{ V decade}^{-1}$ , as indicated in Fig. 41.

As the sweep-rate is decreased in the range  $0.0005 < s < 0.050 \text{ V s}^{-1}$ , the  $i$  vs  $V$  profile is shifted in the cathodic direction, i.e. below the zero current line, probably due to an increase in the charge of the reduction component which is controlled by  $H^+$  diffusion to a certain extent. Also a limiting current after the anodic peak maximum is clearly distinguishable

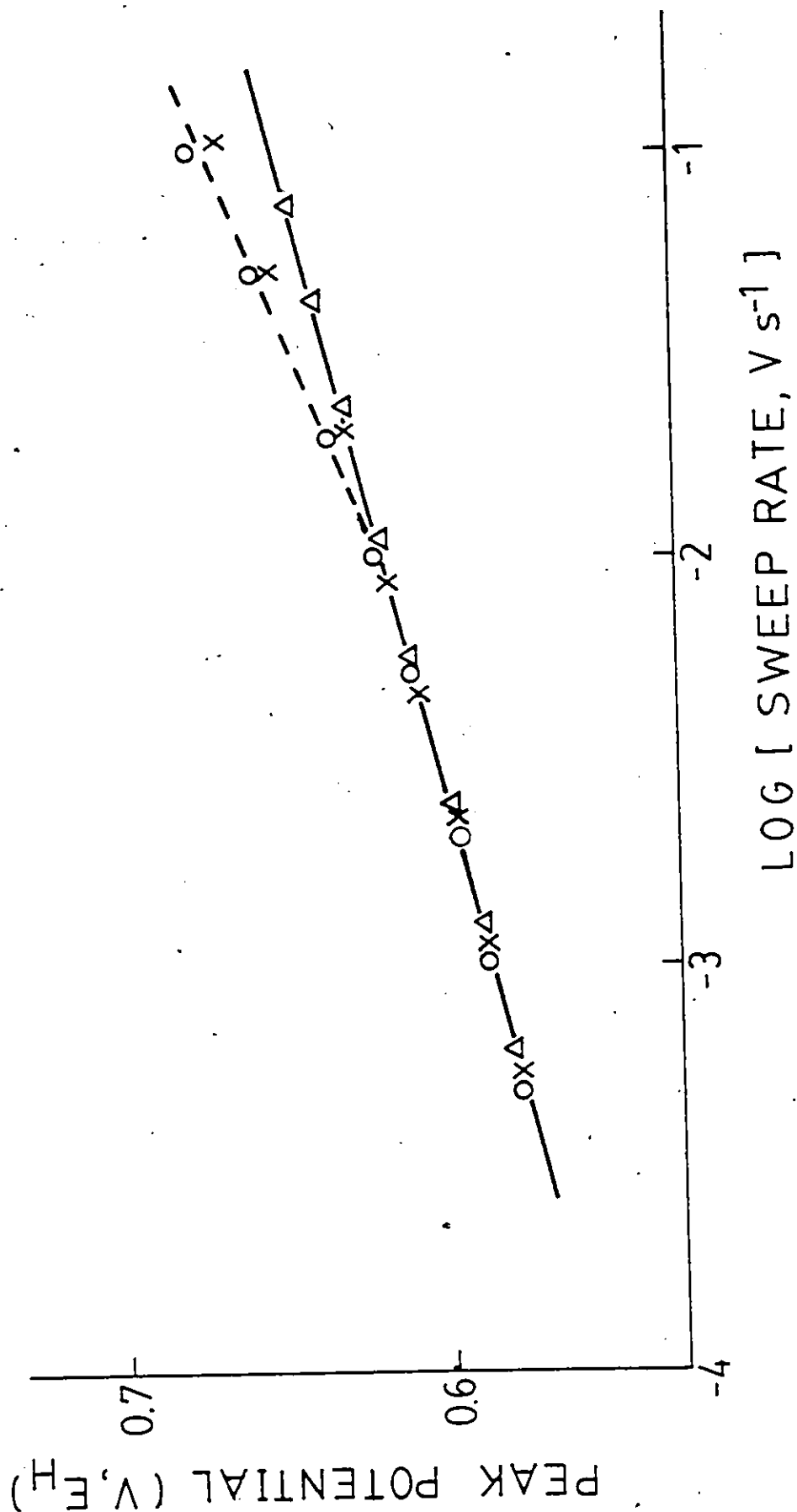
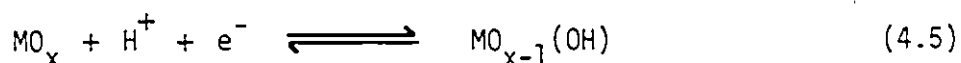


Fig. 41. Dependence of peak potential on  $\log s$  for  $O_{A,1,2,r}$  on Ir in 0.5 M  $H_2SO_4$ , 298 K. Solid and dashed lines represent limiting slopes obtained due to strong overlap of this peak with the  $O_{A3,r}$  region.

as can be appreciated in Figs. 42a,b,c. Such a limiting current could indicate a diffusion-controlled process, following an electrochemical reaction.

The shape, location and resolution of this anodic peak are greatly influenced by ions of the solution; thus, in 0.5 M  $\text{H}_2\text{SO}_4$  the peak,  $O_{A,1,2,r}$ , is sharper than in  $\text{HClO}_4$  and cannot be detected at all in 1 M  $\text{H}_3\text{PO}_4$ . On the other hand, in 0.5 M  $\text{Na}_2\text{CO}_3$  solutions, it is not distinguishable until the film is quite thick. These observations could also indicate that the ions affect this peak indirectly by determining the solid-state characteristics of the oxide film as the latter is grown in the different electrolytes.

When the cathodic counterpart of this peak is analyzed by plotting the current at the capacitance maxima,  $i_p$ , vs  $s^{1/2}$ , a straight line is found, indicating the reduction to be diffusion-controlled. This agrees with the observed featureless shape of this peak which can be related to the fact that on reducing an oxide species protons are consumed, as in the general electrochemical equation



Thus if the reaction responsible for this cathodic shoulder occurs near the Metal/Oxide interface, the supply of protons for the reaction could become rate-controlling (diffusion-limited), especially if this reduction stage occurs after the reduction process corresponding to the main peak,  $O_{C3,r}$ , takes place, and which consumes protons too.

That  $O_{A,1,2,r}$  is not associated with a reaction of the metal substrate itself was clearly demonstrated by Beni and Shay (263) in their study of the electrochromic properties of an iridium oxide film formed by oxidizing 50 nm of Ir metal sputtered on  $\text{SnO}_2$ -glass: when all the metal had been converted to oxide, the  $O_{A,1,2,r}$  peak was still clearly distinguishable indicating that it is due to a process within the film itself and not on

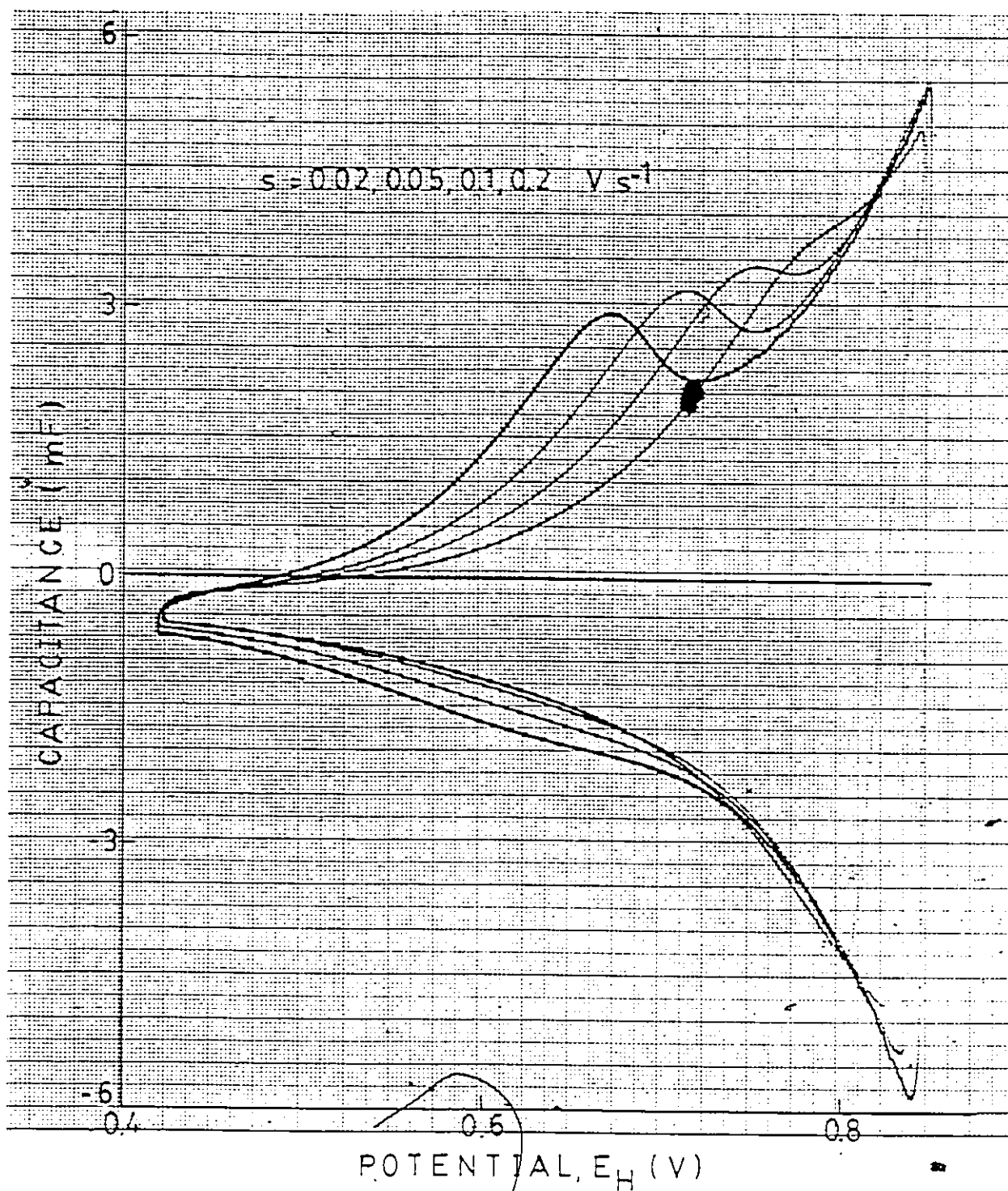


Fig. 42a. Series of cyclic voltammetry  $C$  vs  $V$  profiles for the  $O_{A,1,2,r}/O_{C,1,2,r}$  region on Ir in  $0.5\text{ M H}_2\text{SO}_4$  at sweep rates as noted in the figure.

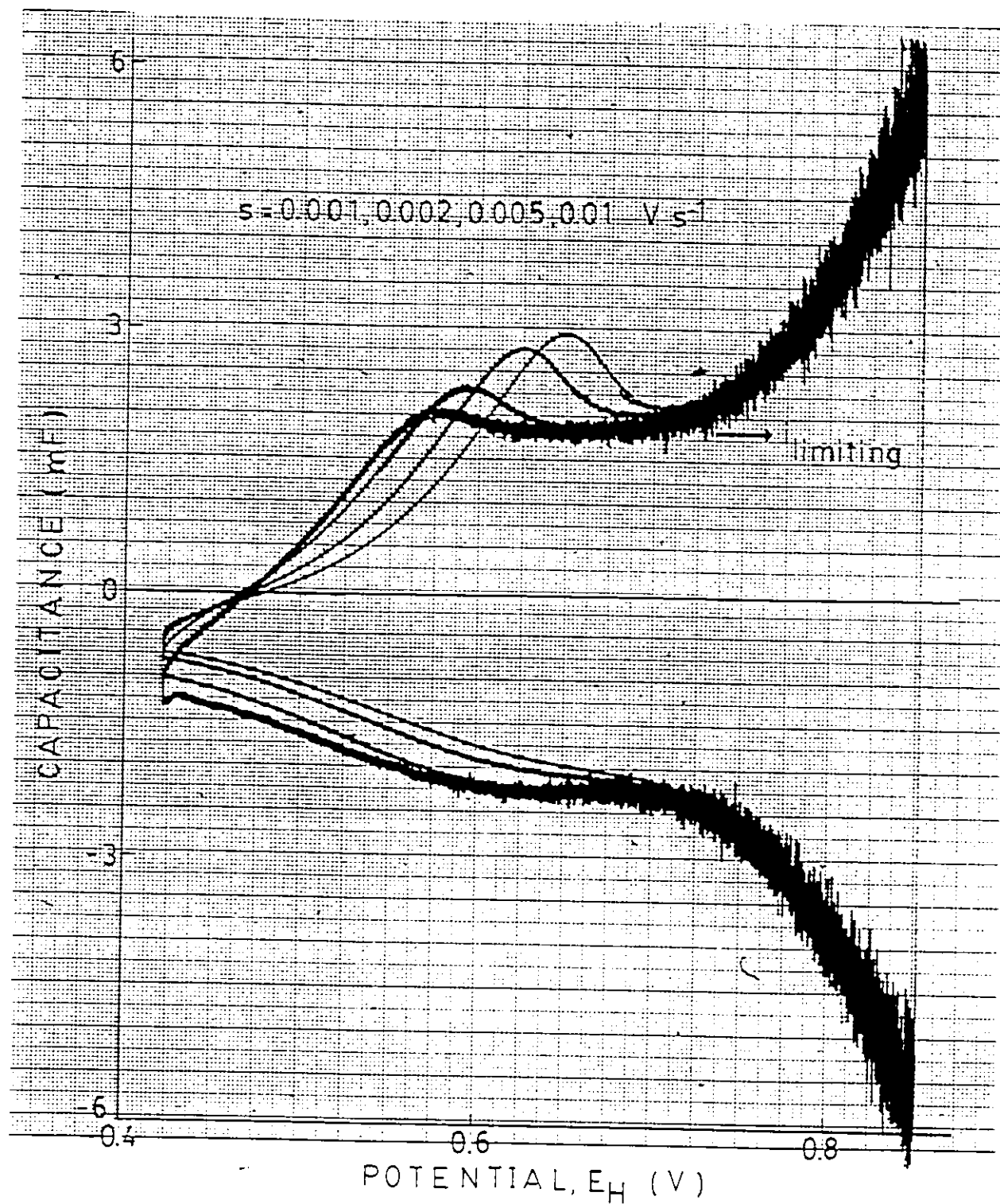


Fig. 42b. As Fig. 42a. Notice the presence of an  $i_{\text{limiting}}$  as  $s$  is decreased.

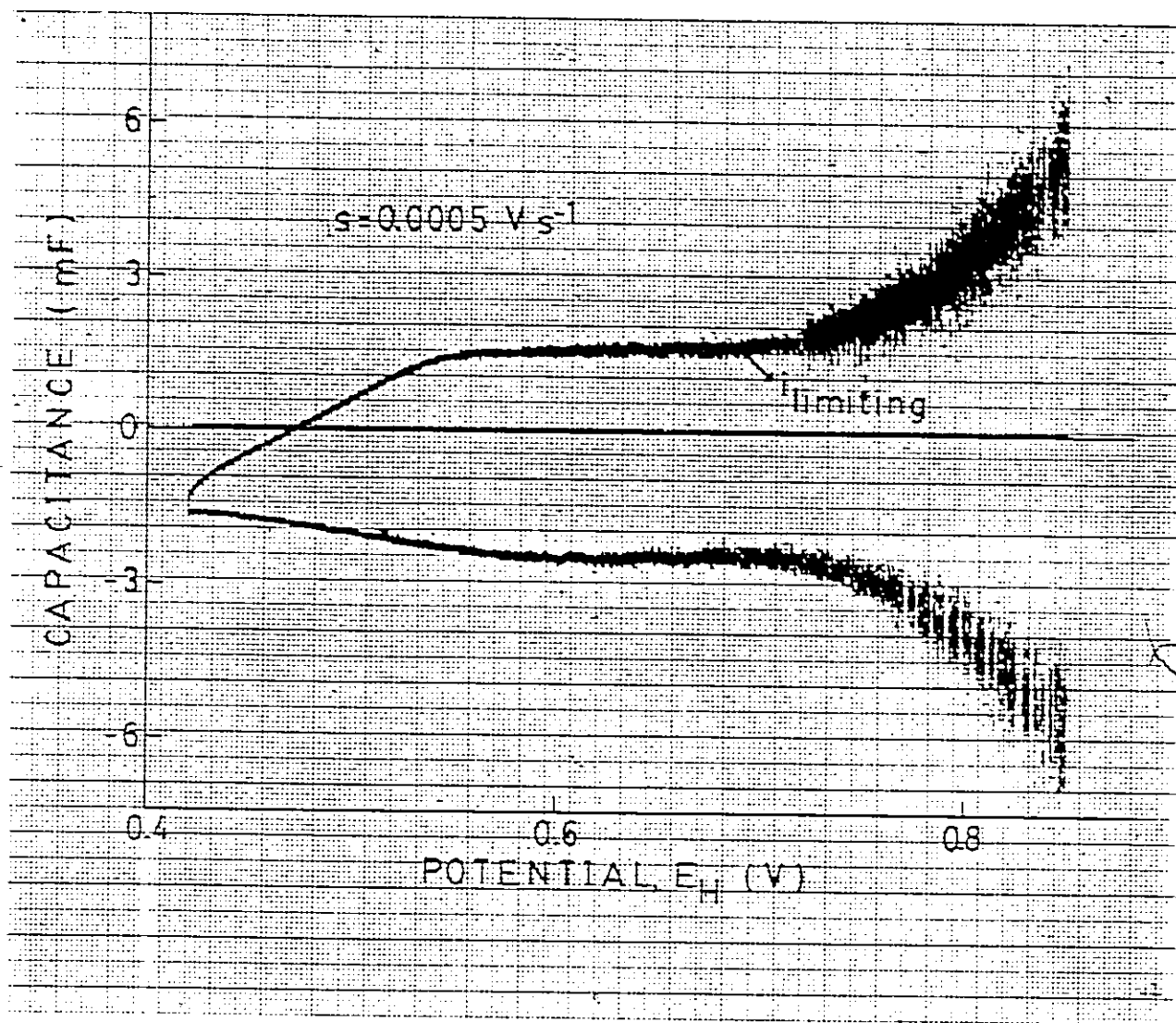


Fig. 42c. As in Figs. 42a, 42b. Notice the presence of  $i_{\text{limiting}}$ , after the capacitance maximum.

the metal. However, because of the conductivity properties of the Ir-oxide system, which will be discussed later, this current peak is probably associated with reaction in oxide layers close to the underlying metal.

The potential of  $O_{A,1,2,r}$  is seen to shift in the cathodic direction when the electrode is left on open-circuit immersed in solution overnight but, after a few cycles, the system returns to its previous behaviour. This indicates the importance of having an equilibrium concentration of both protons and anions at the Metal/Oxide interface. The pore system becomes depleted to a certain extent during the cycling experiments but ion concentrations are reestablished overnight. As a result of the potential shift of this peak, the cathodic shoulder,  $O_{C,1,2,r}$ , appears narrower and better defined as a peak, which stresses again its dependence on availability of protons.

The peak potential shift towards less positive potential values is also observed when the anodic end potential of the sweep is extended into the  $O_2$  evolution region,  $E_a > 1.6 \text{ V}, E_H$ , especially for the case of  $HClO_4$ . As the rate of growth in the latter electrolyte is low, a less porous, more compact film is expected so that when the film is disturbed by application of high anodic potentials, which lead to its dissolution together with evolution of  $O_2$  gas (which electrochemically involves the film itself), the structure "opens" making it easier for protons and anions to reach the Metal/Oxide interface. Thus the reaction at  $O_{A,1,2,r}$  is facilitated. This idea of "opening" of the structure is supported by the observed increase in double-layer charging currents, consistent with more roughened metal being exposed to the electrolyte.

(d) Next, a peak system labelled  $O_{A3,r}/O_{C3,r}$  is seen in the profile, centered about  $1.0 \text{ V}, E_H$ . This peak system has the largest pseudocapacitance

of the whole profile. Its charge increases continuously with cycling and its peak potential remains relatively constant with respect to increasing sweep-rate, although the  $s_0$  for this peak appears to depend on the oxide thickness, as shown in Fig. 43. Thus, it is found that, as the oxide thickness increases, i.e. in going from state M to MB to B, the lower is the  $s_0$  value, i.e. the process(es) involved become irreversible at lower sweep-rates with increasing film thickness. Fig. 43 also indicates another interesting property of the system; thus, while the variation of the cathodic peak potential with  $\log s$  has a slope of  $0.060 - 0.070 \text{ V decade}^{-1}$  of  $s$ , regardless of film thickness, the behaviour of the anodic peak is rather complex, since  $dE_p/d(\log s)$  seems to change from  $0.050$  to  $0.280 \text{ V decade}^{-1}$  (Fig. 43) as the CEF increases.

This anomalous behaviour can be understood on the basis of the changes that take place in the  $i$  vs  $V$  profiles of the iridium oxide films at the sweep-rates for which the unusually high slopes are observed. As can be seen in Fig. 44, where the  $C = i/s$  vs  $V$  profile is shown for an Ir oxide film in state B for various sweep-rates in the range  $0.005 < s < 0.100 \text{ V s}^{-1}$ , there seem to be two processes, labelled  $O_{A3a,r}$  and  $O_{A3b,r}$ , associated with  $O_{A3,r}$ , while  $O_{C3,r}$  appears to be related only to  $O_{A3a,r}$ .

Thus, in the anodic sweep, the complex behaviour of  $dE_p/d(\log s)$  for the anodic peak is due to the fact that the ratio of the charges for the two processes depends on the film thickness and on the sweep-rate, with  $O_{A3b,r}$ , being favored at higher thicknesses and sweep-rates. Once  $O_{A3b,r}$  becomes predominant, high slopes are observed > ca.  $0.150 \text{ V decade}^{-1}$  because of diffusion related limitations associated with this process.

Then, if the system is carefully analyzed in terms of evaluating  $dE_p/d(\log s)$  only at the early stages of film growth when  $O_{A3a,r}$  is the predominant process\* (Fig. 45), it can be shown (Fig. 46) that  $dE_p/d(\log s)$

---

\* This is relatively easy to distinguish since once  $O_{A3b,r}$  starts to take over, the currents in  $O_{C3,r}$  decrease well below the  $O_{A3b,r}$  expected values.

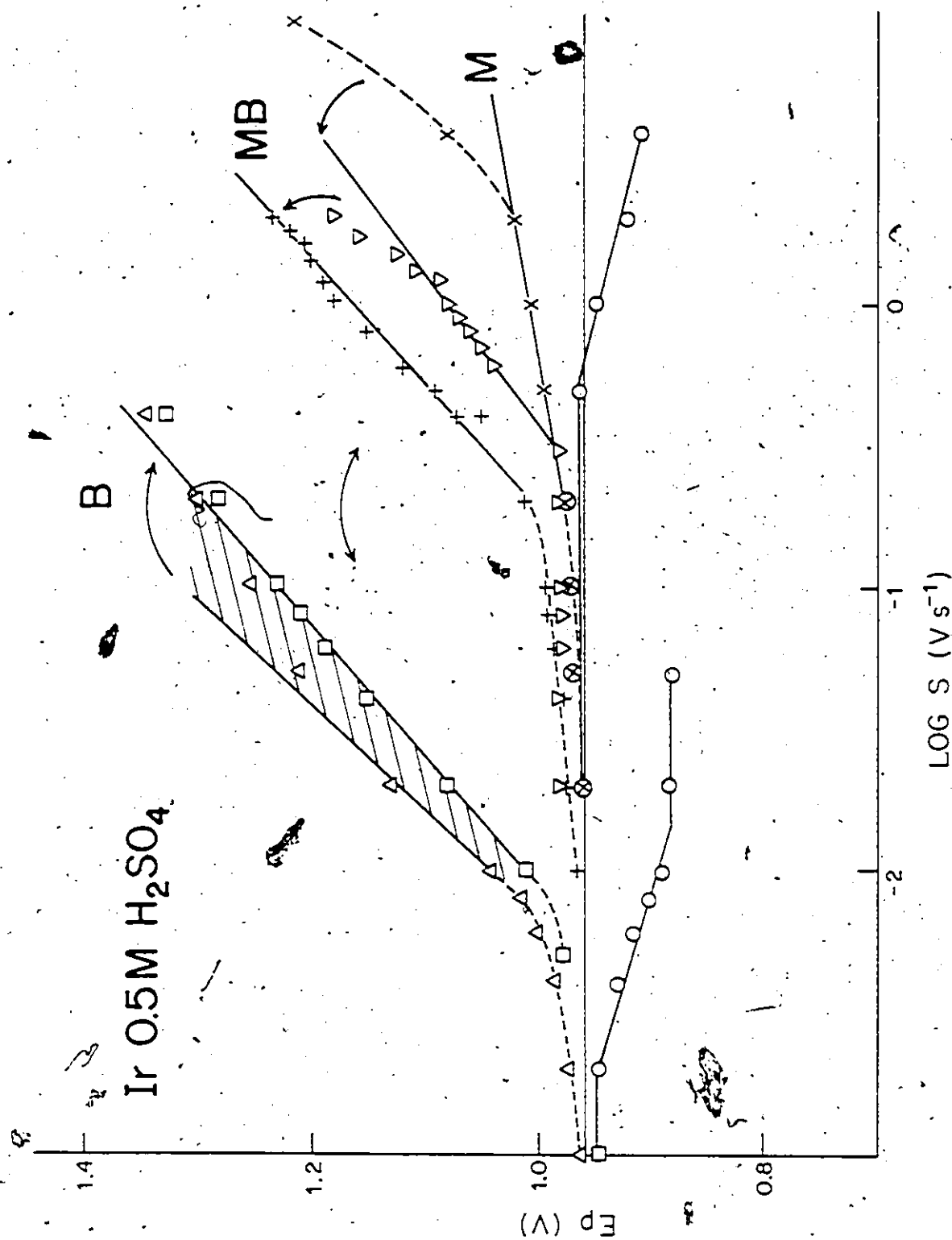


Fig. 43. Dependence of the peak potential for  $O_{A3,r}$  and  $O_{C3,r}$  regions as a function of  $\log s$  and of the electrode thickness. Notice  $dE_p/d(\log s)$  increasing as electrodes go through the  $M \rightarrow MB \rightarrow B$  transitions for  $O_{A3,r}$ , while it remains constant for  $O_{C3,r}$ .

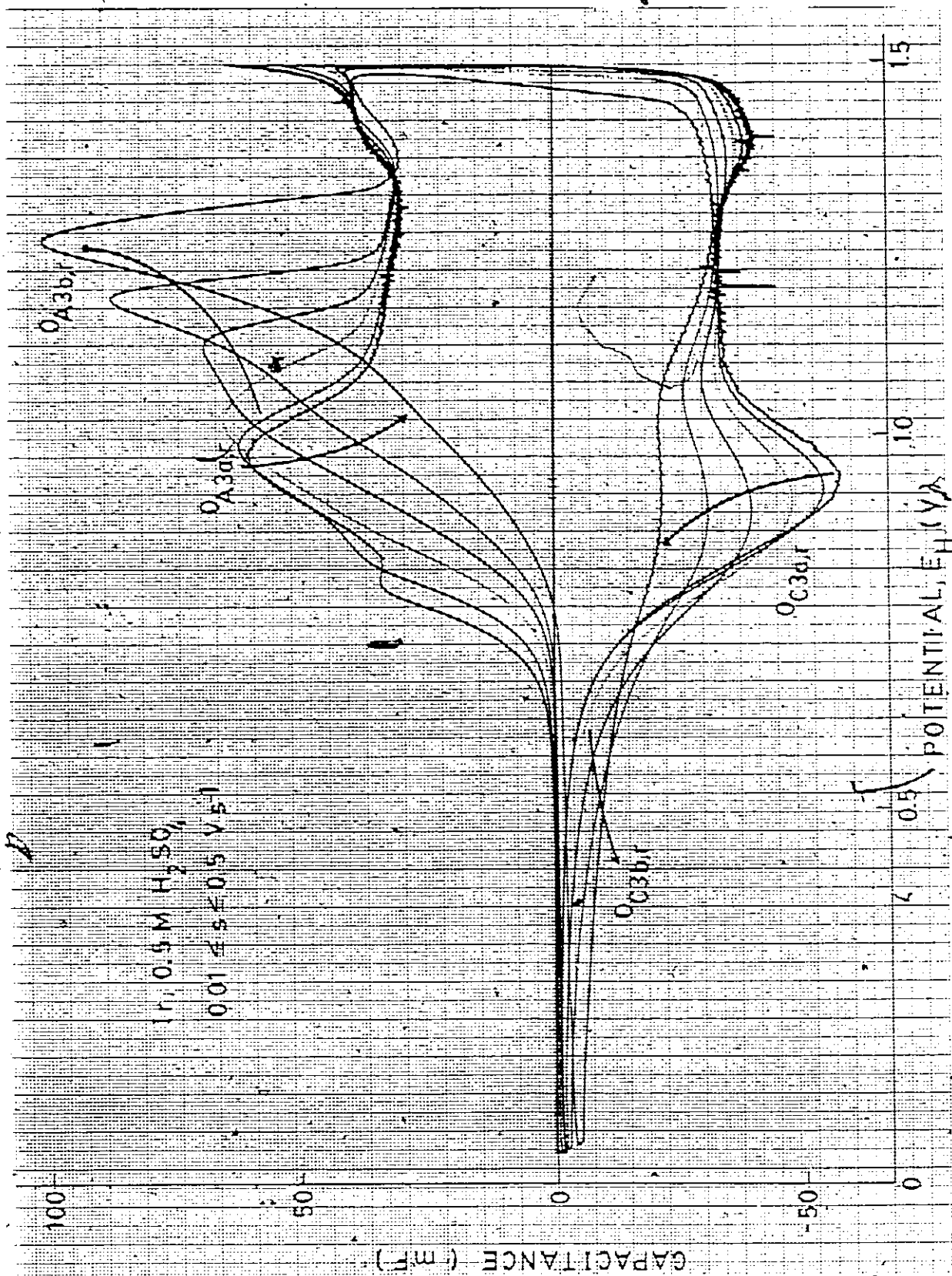


Fig. 44. Series of cyclic-voltammetry C vs. V profiles for Ir in 0.5 M  $H_2SO_4$  at sweep-rates as indicated in the figure, at 298K, showing the disappearance of  $O_{A3a,r}$  and  $O_{C3a,r}$  peak regions, together with the emergence of  $O_{A3b,r}$  and  $O_{C3b,r}$  peaks as  $s$  is increased.

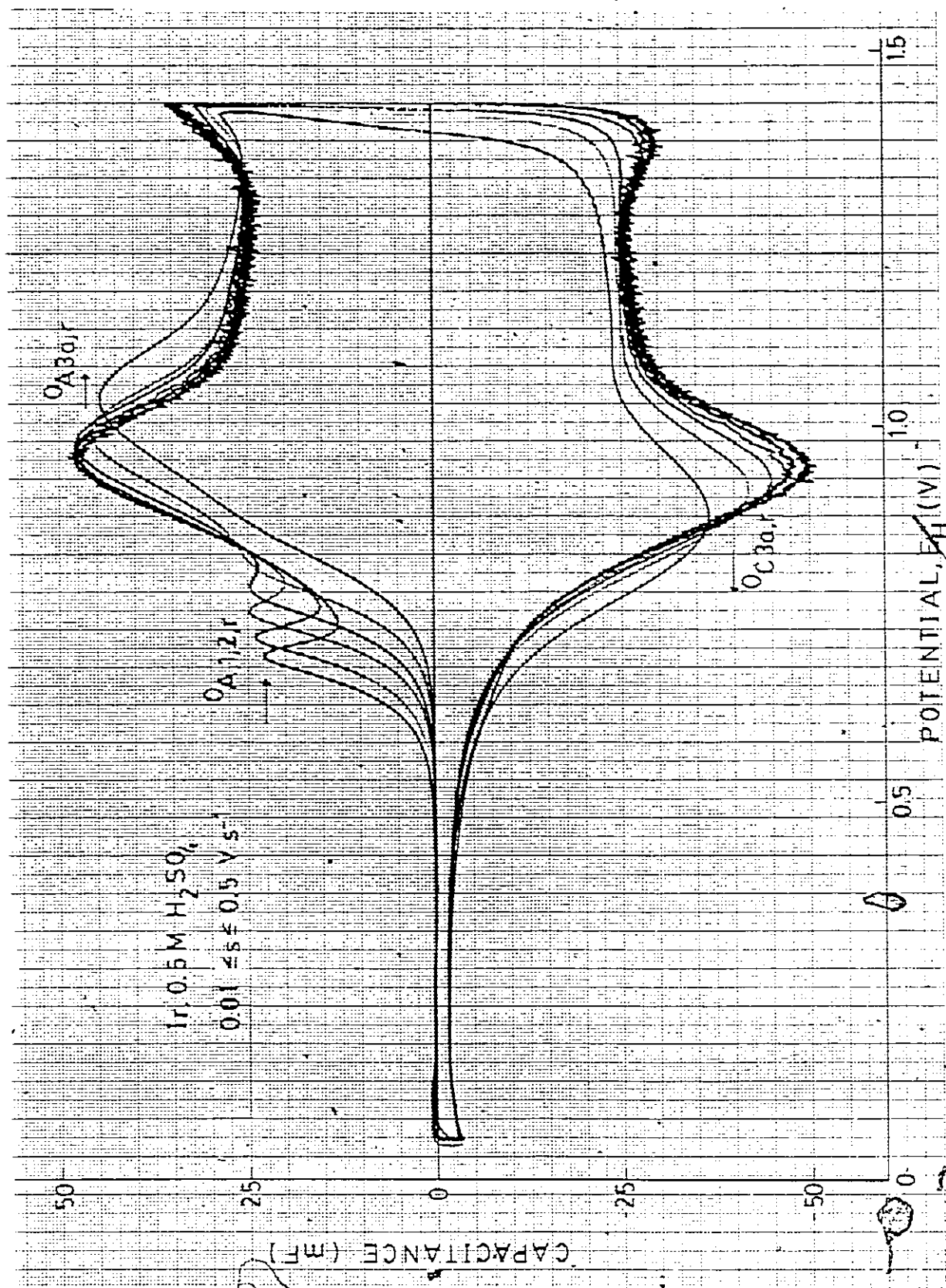


Fig. 45. Series of cyclic-voltammetry C vs V profiles at 298 K for Ir in 0.5 M  $\text{H}_2\text{SO}_4$  at sweep-rates as indicated in the figure. This profile is to be compared to that of Fig. 44.

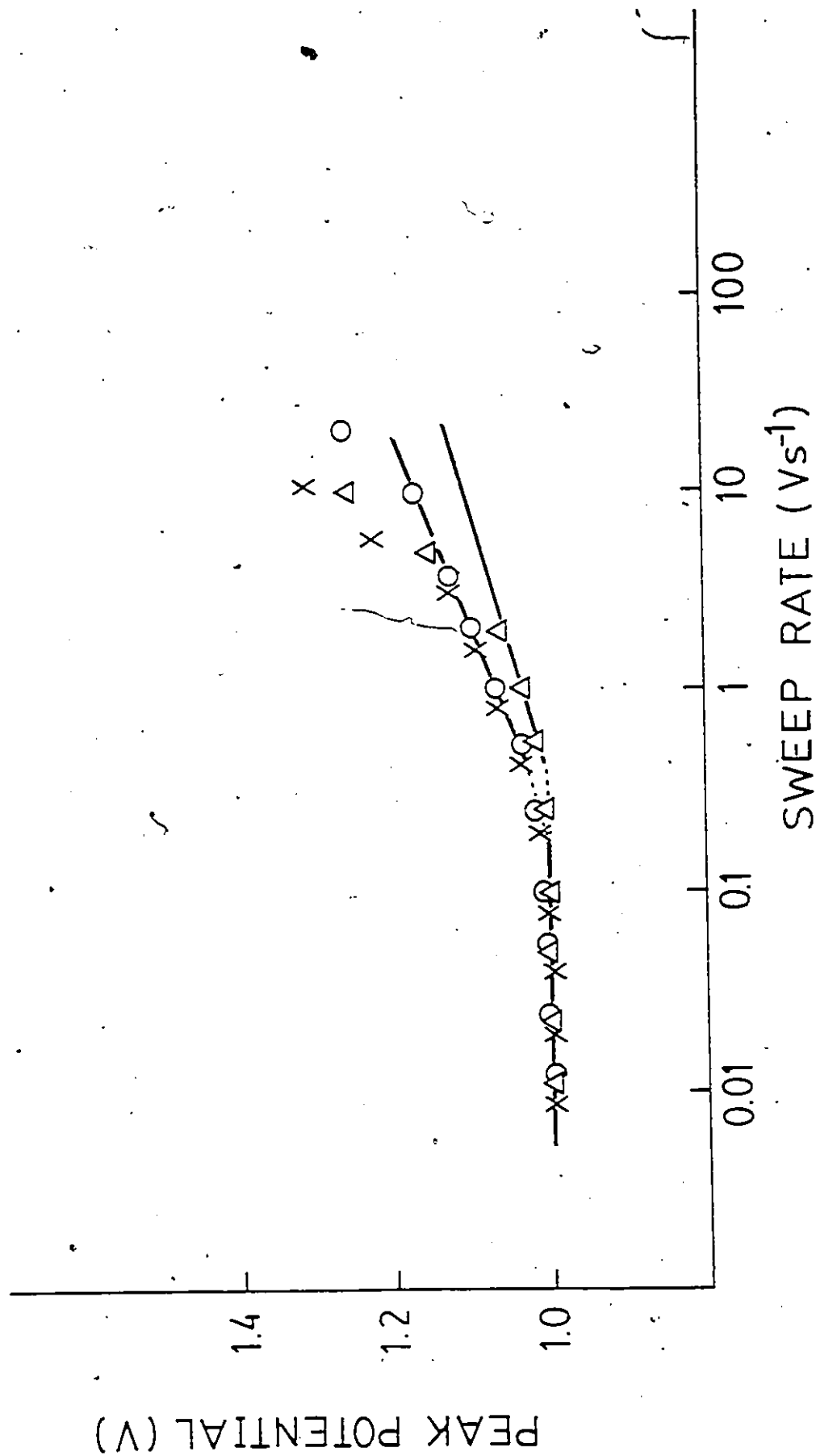
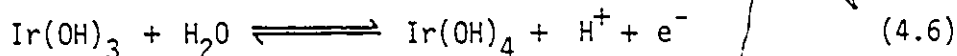


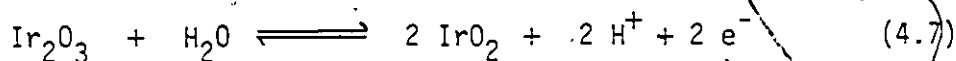
Fig. 46. Dependence of the peak potential for  $0.13a,r$  region on  $\log s$ . Deviations at high  $s$  are due to the problems exemplified in Fig. 44.

for  $O_{A3a,r}$  is about  $0.070 - 0.100 \text{ V decade}^{-1}$ , while that of  $O_{A3b,r}$  can be as high as  $0.300 \text{ V decade}^{-1}$ , as shown in Fig. 43. This clearly indicates that other factors, besides kinetic irreversibility, are involved in determining the behaviour of  $O_{A3b,r}$  as a function of sweep-rate, since such a high slope would be difficult to interpret according to conventional treatments (218,219).

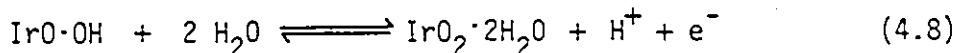
This peak system,  $O_{A3,r}/O_{C3,r}$ , is assumed to correspond to the main redox process occurring in the oxide film. Since that process has been shown to correspond to a  $1 e^-$  change (257), and because the main species in the film, according to ESCA (276, section 4.4.4), appears to be  $\text{IrO}_2$  (which is also consistent with the color of the electrode at anodic potentials  $> 1.0 \text{ V}, E_H$ ), the reaction responsible for this current peak is thought to be



which can also be written as



or



depending on the degree of hydration that is attributed to the oxide species.

The peak potential for the  $O_{A3,r}$  process appears to have a pH-dependence different from  $0.059 \text{ V pH}^{-1}$ , and close to  $0.080 \text{ V pH}^{-1}$ . It is believed that the latter value arises because the peak potential measured is an apparent value due to the overlap of the two components under the envelope. As one of the components,  $O_{A3b,r}$ , has been shown to predominate under conditions where proton supply is becoming diffusion-controlled, it is reasonable to expect that the charge ratio of  $O_{A3a,r}$  and  $O_{A3b,r}$  will be a function of pH and thus that the apparent peak potential could vary in an

unusual manner with pH.

These problems of proton availability and equilibration can be better appreciated if a model calculation is made reflecting the events taking place during oxidation (coloration) and reduction (bleaching) processes in the film. Thus, for a film with a charge of  $10 \text{ mC cm}^{-2}$ , an increase in the oxidation state of the film of one involves the ejection of ca. $10^{-7}$  Faradays of  $e^-$  and of  $10^{-7}$  moles of protons per  $\text{cm}^{-2}$ . Assuming that 50% of the volume of the film consists of electrolyte-filled pores, and taking the film thickness as  $300 \text{ nm}$  (in agreement with SEM estimates, see section 4.4.3), the local pH in pores in a  $0.5 \text{ M H}_2\text{SO}_4$  solution will be changed from 1 to -1.9. On the other hand, during bleaching, studies of the reflectivity transients (259) indicate that there are two processes, a fast one and a slower one. Since, in this case, the reaction requires protons, the fast one is associated with the use of the protons available at the oxide/electrolyte interface or provided by the bound water at the oxide surface. The slower process is related to the diffusion-controlled arrival of protons from the bulk of the electrolyte to sites undergoing reduction.

As can be appreciated, the bleaching process will be more sensitive to pH changes (local pH in the pores can go from 1 to 11 due to the use of the available protons by the fast component) than is the coloration.

Thus, studies performed at variable  $s$  in unbuffered solutions or at constant  $s$  in solutions of variable buffer capacity indicate (259) that, while the anodic peak is simply displaced towards more positive potentials at high  $s$  or low buffer capacity (due to the local decrease in pH), the cathodic peak becomes, under the same extreme conditions, a featureless broad region extending into the H deposition region. This is because of the continuous shift of the equilibrium potential of the cathodic reaction due

to a non-equilibrium situation, such as described above.

(e) After the peak system  $O_{A3,r}/O_{C3,r}$  is crossed in the anodic direction, a flat region of the profile obscures a peak labelled  $O_{A4,r}/O_{C4,r}$ , distinguishable in 0.5 M  $Na_2CO_3$  (Fig. 40, page 136). This is due to the fact that the pH dependence of this peak is different from that of  $O_{A3,r}/O_{C3,r}$  (i.e. 0.054 and 0.080 V  $pH^{-1}$ , respectively). It is also more evident in  $HClO_4$  than in  $H_2SO_4$  (compare Figs. 37 and 39), indicating again the role of the anion in the processes that occur in the film, or on the characteristics of the latter depending on the growth rate and media.

Although the peak appears to be associated with quite a large charge, the fact that the currents in this potential region appear always reversible (even though in  $Na_2CO_3$  at high  $s$  it is apparent that the  $O_{A4,r}/O_{C4,r}$  peak starts to become irreversible) indicates that there is probably another process taking place at the same time. This is a process which has a large capacitance and which behaves very reversibly.

It is proposed that this very reversible process is, in fact, the charging of the real double-layer capacitance of the porous oxide material. This capacitance now truly corresponds to the increased area of the oxidized electrode and can be completely charged due to the conductivity of the oxide at these potential. Relating the increase in area to the CEF value on a 1.:1 basis (as a first approximation which does not take into account increased roughness), about 70% of the charge in that region of  $O_{A4,r}/O_{C4,r}$  can be accounted for as a result of real double-layer charging. The reversibility of this region has also been tested at high frequencies in a.c. impedance measurements (268) and the results show that it is unlikely that the fast response observed could be due to an electrochemical surface process.

Also, when an oxide film is destroyed by means of  $O_2$  evolution, the

charge associated with this potential region decreases less than that associated with the  $O_{A3,r}/O_{C3,r}$  region, as expected, since the loss of material is somewhat balanced by the opening of the oxide structure, thus diminishing the loss of area, while the loss of charge due to redox processes in the film is irreversible and uncompensated for.

The process that takes place over  $O_{A4,r}/O_{C4,r}$  is probably related to oxidation of part of the film to a higher valence state, but with the process being restricted to the outer layer of the oxide.

(f) Finally, before  $O_2$  evolution commences at a measurable rate, a shoulder on the  $i$  vs  $V$  profile around 1.5 V,  $E_H$  indicates the formation of a higher oxide species. This peak is labelled  $O_{A5,r}$ . This state of the oxide is partly reduced in a cathodic peak counterpart,  $O_{C5,r}$ , which is somewhat overlapped by the reduction of adsorbed  $O_2$  evolved in the previous anodic scan.

(g) Beyond region  $O_{A5,r}/O_{C5,r}$  strong oxygen evolution, coupled with film corrosion, probably as  $IrO_4^{-2}$  soluble species, is observed together with the development of a purple solution.

To facilitate the comparison of the various peaks, their properties and the possible processes to which they correspond, a table listing all these features for the peaks described in this section is presented on the next page (see Table VII).

#### 4.5. MODEL OF OXIDE FILMS AT IRIDIUM

In discussing a model for the thick oxide films of Ir, there are two factors that must be considered:

- (a) The mechanism of oxide growth; and
- (b) The explanation of the observed properties of the oxide films.

These two factors are, of course, related since the reason why the

TABLE VII

CHARACTERISTICS OF PEAKS DEVELOPED IN THE  $i$  vs  $V$  PROFILE FOR THICK OXIDE FILMS ON IRIIDIUM ANODES

| PEAK          | POTENTIAL REGION   | CHARACTERISTICS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|---------------|--------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $O_{A,1,2,r}$ | $E_a > 0.6 V, E_H$ | <ul style="list-style-type: none"><li>- charge increases on cycling;</li><li>- <math>E_p</math> becomes more positive, until this peak dissappears into <math>O_{A3,r}</math> on cycling;</li><li>- <math>dE_p/d(\log s) \approx 0.070 - 0.090 V decade^{-1}</math>;</li><li>- <math>i_o</math> not observable, since <math>E_p</math> is not constant even at <math>0.0005 V s^{-1}</math>;</li><li>- an <math>i_{limiting}</math> is observed after the capacitance maximum, as <math>s</math> is lowered;</li><li>- under some conditions it can be seen to consist of two components;</li><li>- associated with oxidation of IrO species to <math>Ir_2O_3</math> at the oxide layers close to the metal surface;</li><li>- strongly affected by ions and by the characteristics of the oxide films;</li><li>- shifts towards less positive potentials after the electrode is left on open circuit immersed in the solution overnight;</li></ul> |

TABLE VII (cont.)

| <u>PEAK</u>         | <u>POTENTIAL REGION</u>     | <u>CHARACTERISTICS</u>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|---------------------|-----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $O_{C,1,2,r}$       | $E_c < 0.85 \text{ V}, E_H$ | <ul style="list-style-type: none"> <li>- the cathodic component is not a clear peak, but a featureless shoulder;</li> <li>- as <math>s</math> is increased, the cathodic peak appears to become diffusion-controlled, i.e. <math>i_p</math> is linear in <math>s^{1/2}</math>;</li> <li>- associated with reduction of some <math>\text{Ir}_2\text{O}_3</math> species to <math>\text{IrO}</math> at oxide layers close to the metal;</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                          |
| $O_{A3,r}/O_{C3,r}$ | <u>ca.</u> 1.0 V, $E_H$     | <ul style="list-style-type: none"> <li>- main peak system in the <math>i</math> vs <math>V</math> profile;</li> <li>- charge increases on cycling;</li> <li>- <math>E_p</math> remains quite constant until appreciable thicknesses, <u>ca.</u> CEF &gt; 100, are attained;</li> <li>- <math>dE_p/d(\log s)</math> for <math>O_{A3a,r}</math> is <u>ca.</u> 0.070 - 0.100 V decade<sup>-1</sup>; that for <math>O_{A3b,r}</math> is &gt; 0.150 V decade<sup>-1</sup> indicating that diffusion-controlled processes play a role;</li> <li>- <math>s_o</math> depends on oxide thickness;</li> <li>- associated with <math>\text{Ir}_2\text{O}_3/\text{IrO}_2</math> redox process which is also, responsible for the electrochromic (EC) effect;</li> <li>- <math>O_{C3,r}</math> appears to be associated mainly with <math>O_{A3a,r}</math>;</li> </ul> |

TABLE VII (cont.)

| PEAK                | POTENTIAL REGION  | CHARACTERISTICS                                                                                                                                                                                                                                                                                                                                                                                                                          |
|---------------------|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $O_{A4,r}/O_{C4,r}$ | ca. 1.25 V, $E_H$ | <ul style="list-style-type: none"><li>- charge increases on cycling;</li><li>- very reversible system even at high thicknesses and sweep-rates;</li><li>- probably consists of two superimposed processes:<ul style="list-style-type: none"><li>(a) charging of a "real" increased double-layer capacitance; and</li><li>(b) oxidation of the outer layers of the oxide film to oxidation states higher than Ir(IV).</li></ul></li></ul> |
| $O_{A5,r}/O_{C5,r}$ | ca. 1.45 V, $E_H$ | <ul style="list-style-type: none"><li>- similar to <math>O_{A4,r}/O_{C4,r}</math>. It is also superimposed on the charging of a real double-layer capacitance;</li><li>- due to further oxidation of the outer oxide layers to a higher oxidation state;</li><li>- cathodic component has superimposed on it a reduction component due to adsorbed <math>O_2</math> evolved in the anodic cycle;</li></ul>                               |

oxide grows according to a certain mechanism will be expected to be related to the observed (electrochemical) properties of the film.

One of the main difficulties encountered with earlier models (93, 249, 252), has been to account for the constancy of currents in the H and double-layer charging regions up to 0.7 V,  $E_H$ , regardless of the oxide thickness. These observations appeared to indicate that no area change has taken place while, on the other hand SEM observations and  $Cl_2$  evolution kinetic studies (see Chapter 5) clearly indicate an appreciable thickness of the oxide and indirectly, therefore, an increase in the real area of the electrode.

On the basis of the experimental evidence presented in this work, together with the results of a.c impedance measurements presented by Glarum and Marshall (268), and with the help of Goodenough's model for describing the electronic structure of the oxide, an electrical and structural model will now be described for the oxide, based on the change of conductivity of the oxide film as a function of the oxidation state of the species in the film, i.e. as a function of potential.

This model will lead to a qualitative explanation of the observed properties of the oxide films and will also shed some light as to the growth mechanism.

As discussed by Glarum et al. (268) in their study of thick Ir oxide films under a.c. conditions, the conductivity of the oxide is found to change from  $G_{a.c} < 10^{-2} \Omega^{-1} \text{ cm}^{-2}$  (units as reported in ref. 268) for the bleached form of the oxide, to  $G_{a.c} > 10^2 \Omega^{-1} \text{ cm}^{-2}$  for the colored, oxidized, form. Also the  $C_\infty$  value, i.e. double-layer capacitance since at infinite frequency, double-layer charging is the only process that can follow the a.c. perturbation, was found to be  $60\text{-}70 \mu\text{F cm}^{-2}$  at 0.4 V,  $E_H$  and  $> 800 \mu\text{F cm}^{-2}$  at 1.1 V,  $E_H$ .

This experimental evidence lead us to formulate a model based on a high-area, porous, rough oxide film which lies on top of the Ir metal substrate exposing about 70% of the substrate surface to the electrolyte through the pore system. Due to the potential-dependent change in conductivity, the oxide can be "turned on" or "turned off" in the electrochemical sense, i.e. it undergoes redox processes in the film and is able to support electron transfer reactions at its surface only at potentials higher than 0.8 V,  $E_H$ , i.e. when it becomes colored and conducting ("turned on"). In its bleached state, the oxide is essentially a very poor conductor. However, because of the large amount of electrolyte available through the pore system at the metal/oxide interface, the latter (actually a metal/"electrolyte" interface) can undergo charging processes (H and double-layer capacitance). In the reduced state, the oxide behaves as an insulator, i.e. "grains of sand" on top of the metal surface, and the oxide simply exerts some blocking effect at the surface similar to that produced by a neutral, non-reactive molecule. Thus, under these conditions, the oxide is "turned off".

It can then be understood how the applied potential difference is distributed across the metal/oxide/electrolyte interphasial system:

At the cathodic end of a potential sweep (insulating region) the applied potential difference will be located mainly at the metal/oxide interface, as shown in Fig. 47a. It also probably affects the first few layers of oxide close to the metal ( $O_{A,1,2,r}/O_{C,1,2,r}$  processes). For these conditions, H deposition takes place on bare metal sites and the amount of surface blocked by the oxide is approximately 20-30%, as determined by the experimentally observed decrease in H ionization charge. At the same time, the double-layer charging currents appear to remain constant, regardless of oxide thickness due to the fact that only the metal/oxide double-layer

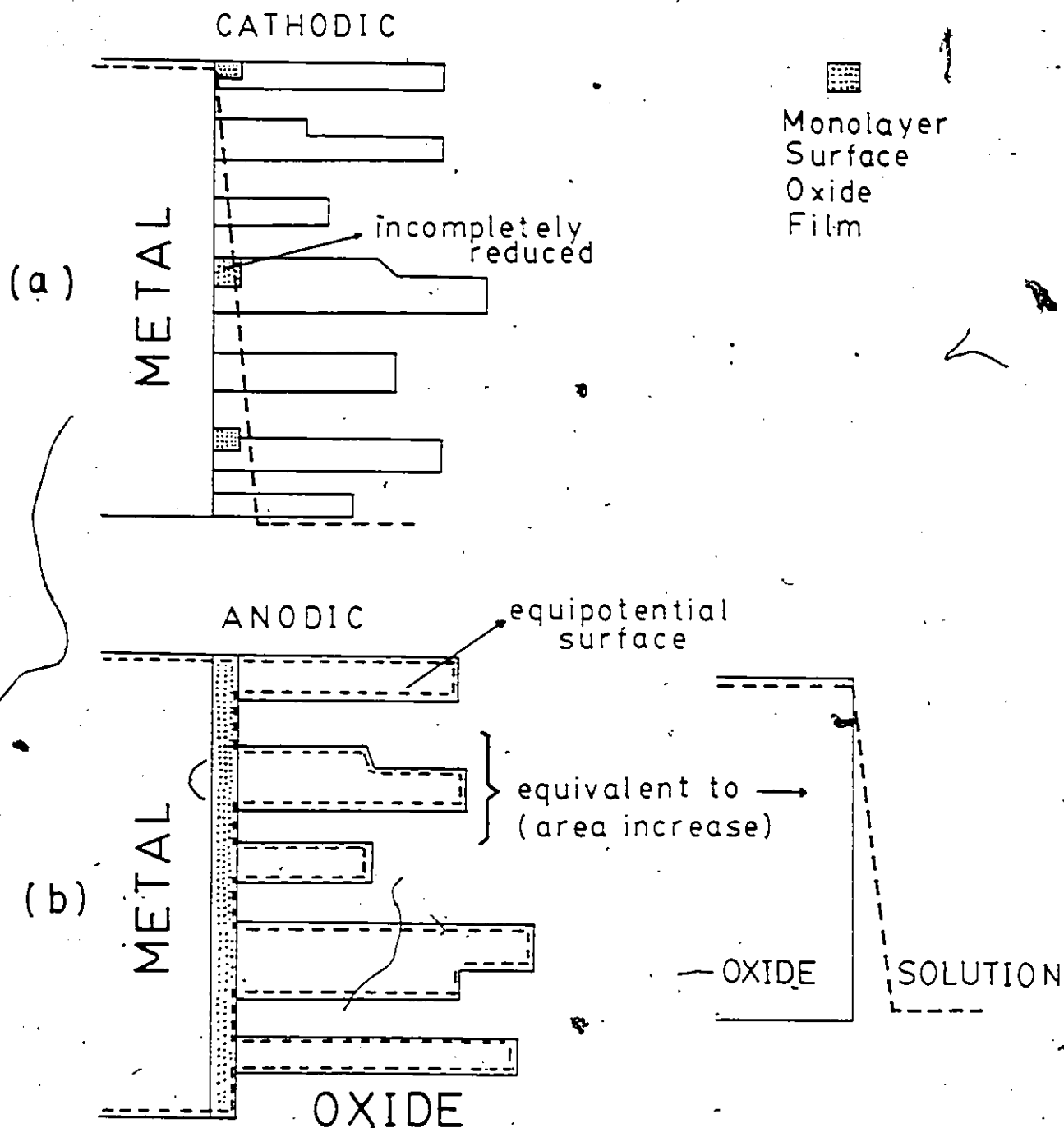


Fig. 47. Schematic model of the thick Ir oxide films:

(a) at cathodic potentials, where the applied potential difference is located at the metal/oxide interface.

(b) at anodic potentials, indicating the increase in area.

is charged. Hence, under those conditions, the area of the electrode appears to be about the same as that of the initial substrate metal, regardless of the fact that a large area oxide film has been developed on its surface.

As the potential becomes more anodic and the oxide film becomes colored, i.e. it increases its oxidation state, the film becomes an excellent conductor. Then all the available double-layer capacitance can be charged, i.e. that for both the metal/oxide and the oxide/electrolyte interfaces, as indicated in Fig.47b. The latter interface includes the pore system plus the outside surface of the oxide film. This accounts for the observed value of  $C_{\infty}$  being higher at anodic than cathodic potentials, and for the process occurring in the region  $O_{A4,r}/O_{C4,r}$  (Fig. 37) which is partly associated with the charging of a real double-layer on the porous oxide film.

Since the oxide is such a good conductor, the "IR" potential drop across it is quite low, so that electron transfer processes can occur at its interface with the electrolyte. It will be remembered that studies of  $Cl_2$  evolution kinetics on such surfaces (Chapter 5) have proven that an area increase, proportional to the oxide thickness, has almost certainly taken place.

This lack of potential drop across the oxide also explains why the latter does not grow at constant potential, since a field across the oxide is needed to support ionic transport necessary for the growth to occur.

The electrochemical oxidation and reduction of Ir species in the thick films must proceed according to an equation of the type given in Chapter 4, equation 4.6. This implies that (a) electrons and (b) protons are required for the reaction to proceed in either direction. Thus, since the change in conductivity of the oxide film, as a function of potential, appears to involve a change in the oxidation state of the species in the

film, the relation between conductivity properties and the type of oxide in the film, will now be established. The availability of protons as a function of pH in the pore system and in the bulk, will also be mentioned, since protons are required for the processes in the film to occur.

It has been proposed (259) that, at anodic potentials  $> 0.7$  V,  $E_H$ , the species present in the film is mainly  $IrO_2$ , although a mixed system, i.e.  $Ir_2O_3 + IrO_2$ , is impossible to rule out. This identification is based on XPS data (276) and on the color (cf. EC effect) of the oxide film, together with the fact that  $IrO_2$  is the most stable oxide of Ir.

Since the process associated with the electrochromic properties of the film appears to be a  $1 e^-$  transfer, then it is obvious that the bleached form of the oxide, generated at cathodic potentials, is  $Ir_2O_3$  in a hydrated form.

In  $IrO_2$ , Ir has a  $d^5$  electronic configuration which, according to Fig. 4, places the Fermi level inside an allowed band, as shown also by Mattheis (122) in his calculations of the density-of-states function for  $IrO_2$  (Fig. 48). This imparts good electronic conduction properties to the oxide.

On the other hand, when the oxidation state of Ir decreases, as in  $Ir_2O_3$ , the electronic configuration of Ir becomes  $d^6$  and, as can be seen again in Fig. 4, this places the Fermi level in the middle of a band gap. This situation can also be appreciated in Fig. 48 where, if it is assumed that the density-of-states function will not change very much from  $IrO_2$  to  $Ir_2O_3$ , it is clear, from that figure, that adding one  $e^-$  to the system will bring the Fermi level to an energy state above which the density-of-states function has a low value. All this results in the  $Ir_2O_3$  film being a poor conductor.

Thus, the experimentally observed conduction properties of the film

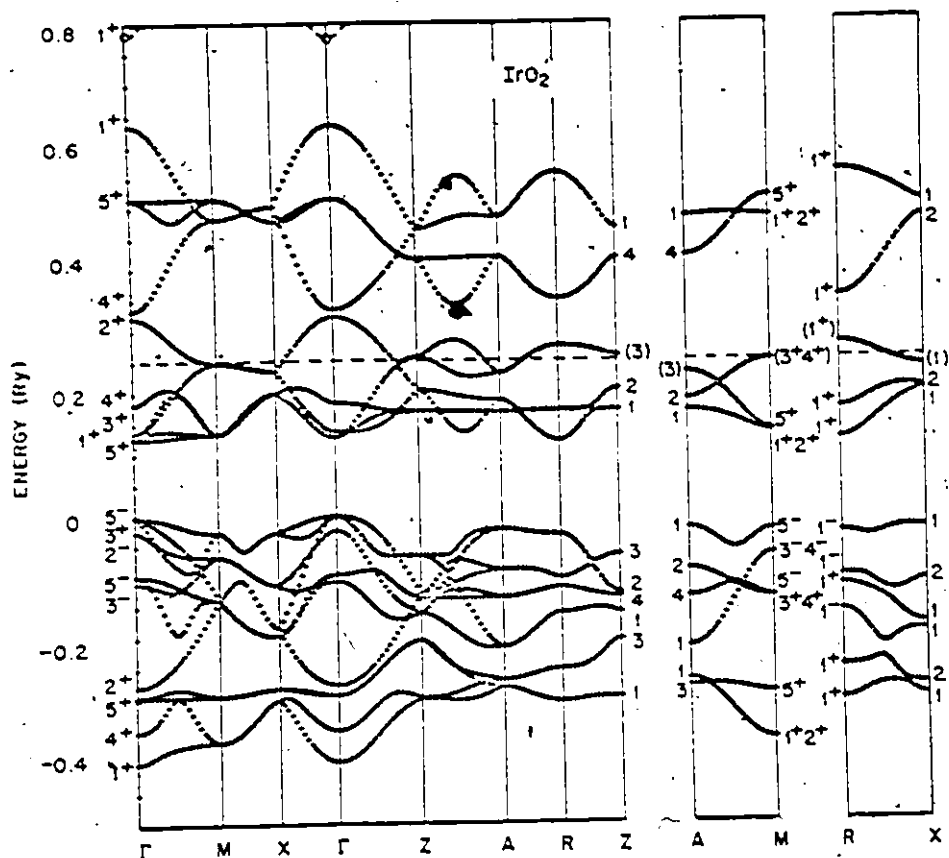


Fig. 48a. APW-LCAO energy bands for  $\text{IrO}_2$  (ref. 122)

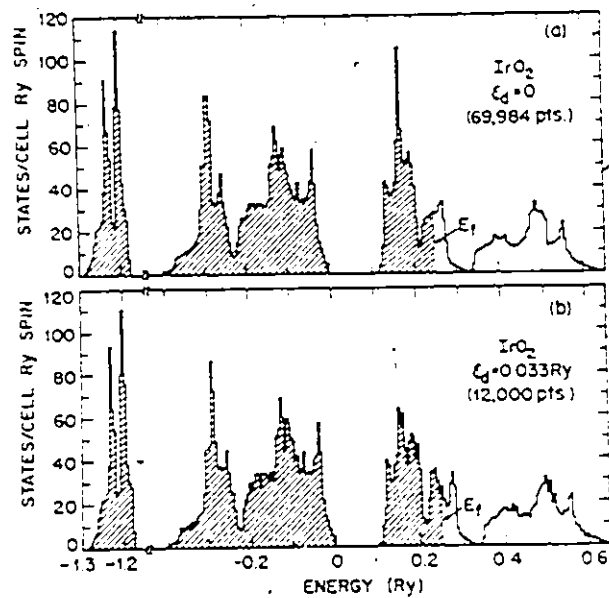


Fig. 48b.  $N(E)$  curves for  $\text{IrO}_2$  with (a)  $\epsilon_{5d} = 0$ ;  
(b)  $\epsilon_{5d} = 0.033$  Ry. (ref. 122)

as a function of potential can be understood on the basis of the dependence of the electronic configuration and band structure of the oxide species involved in the main redox process in the film, on state of oxidation of Ir in the film.

These conductivity characteristics of the film also make the redox process in the film, i.e. the  $\text{Ir}_2\text{O}_3/\text{IrO}_2$  reaction, occur in an interesting fashion. Thus, when the oxide consists of  $\text{Ir}_2\text{O}_3$  species so that it is then a poor conductor, the oxidation proceeds from inside to outside, i.e. it starts near the metal substrate and as successive layers are oxidized, it spreads towards the outside. The reduction process must take place in the opposite direction.

At any time during the redox process, mobile reacting species, i.e. electrons and protons are injected/ejected at two opposite interfaces. On coloration, electrons are injected into the metal at the metal/oxide interface and protons are ejected into the electrolyte at the oxide/electrolyte interface. On bleaching, these processes are reversed.

This model also explains the observation by Gottesfeld (266) on the behaviour of the  $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$  couple at a rotating disc electrode compared to that at a rotating Ir oxide disc. Thus, while both electrodes behaved in a similar manner at anodic potentials, the currents observed at potentials negative to the main oxide peak, i.e. for the bleached state of the oxide, were much smaller for the case of the Ir oxide disk. This observation indicates a decrease in electrochemically available area. The above behaviour is consistent with the applied potential difference being available for reaction at the oxide/electrolyte interface at anodic potentials, but only at the metal/electrolyte interface at cathodic potentials.

The above description, then, is able to provide an explanation for the properties of the oxide film and its behaviour under various conditions.

However, it remains to be understood how the oxide grows from the first layer to the  $> 1\mu\text{m}$  thick films which can be observed under the SEM.

Initially, when the potential of an Ir electrode exceeds 1.3 V,  $E_H$ , (in state A) the coverage of O species reaches a value such that a large degree of turnover of the Ir/O lattice is necessary to establish a more stable two-dimensional lattice. As the potential is made more positive, this reconstructed O/Ir lattice is further oxidized to  $\text{Ir}_2\text{O}_3$ , which presumably would perturb the first 2 or 3 layers of the metal in a three-dimensional way. Owing to the fact that the potential at which these transformation occurs is positive to the equilibrium potential for the  $\text{Ir}_2\text{O}_3/\text{IrO}_2$  couple, some of the  $\text{Ir}_2\text{O}_3$  species will tend to be further oxidized to  $\text{IrO}_2$ .

At the same time, once the anodic potential is more positive than 1.15 V,  $E_H$ , some metal will dissolve, roughening the substrate and, if  $E_a$  exceeds 1.5 - 1.6 V,  $E_H$ , some oxide will also dissolve.

On the next cathodic sweep, the  $\text{IrO}_2$  species present in the perturbed layer are reduced to  $\text{Ir}_2\text{O}_3$  in peaks  $O_{C3}$ ,  $O_{E3,r}$  while the remaining  $\text{Ir}_2\text{O}_3$  species are incompletely reduced back to the bare metal with large hysteresis (266). Because of the large hysteresis in the latter process, not all the oxide species are reduced back to Ir metal and a certain amount, ca. 6% of a monolayer in 0.5 M  $\text{H}_2\text{SO}_4$  at  $0.1\text{ V s}^{-1}$  remains on the perturbed layer, initiating what will become, in subsequent cycles, the thick oxide film.

These processes occurring at the metal/electrolyte interface will continue to take place regardless of film thickness, the latter only influencing the reversibility and availability of protons necessary for the surface monolayer reactions at the metal/oxide interface beneath the film to occur. These monolayer type surface oxidation processes are responsible for the continuous growth of the film on cycling.

Again, the conductivity properties of the oxide must play an important role. Because the oxide in 1 layer, 2 layers or in a thick film, is a good conductor at potentials higher than  $1.0 \text{ V}, E_H$ , the interface of the oxide/solution system becomes almost an equipotential surface. This will allow a potential difference of almost "constant" magnitude to be established, regardless of film thickness, at the oxide/solution interface. Then the above mentioned processes, typical of a monolayer stage and leading to oxide growth by accumulation, can occur.

These considerations lead to the proposal that the  $i$  vs  $V$  profile characteristic of states M, MB and B, reflects exclusively the reactions occurring within the film but these have no influence at all on the film growth processes. The latter continue to take place, as in the monolayer stage, at the metal/oxide interface but are overshadowed by the parallel currents for the film redox processes, because these currents are much larger, in proportion to CEF.

This is confirmed by the effect of sweep-rate on the rate of growth (page 112) where a decrease of rate of growth is observed as the sweep-rate is increased, even for  $s$  values for which the  $i$  vs  $V$  profile remains constant. Thus, the growth processes, which are varying with sweep-rate, are not distinguishable in the  $i$  vs  $V$  profile corresponding to the thick Ir oxide films.

#### 4.6. CONCLUSIONS

We can then conclude that a model of the oxide film, based on the change of conductivity of the film as a function of potential, accounts for the experimentally observed properties of the Ir oxide films and helps to formulate a growth mechanism.

This change in conductivity of the oxide film is understandable on the basis of the electronic configuration and band structure of the two main species in the film, viz.  $\text{Ir}_2\text{O}_3$  and  $\text{IrO}_2$ .

The availability of protons plays an important role since the redox processes taking place in the film, and the growth processes, both consume protons.

Ir metal behaves, at the monolayer stage, like any other noble metal, as discussed by Angerstein-Kozłowska et al. (1) in their comparative study of surface oxidation of Pt, Ir, Ru and Au.

CHAPTER V

ELECTROCATALYTIC EFFECTS OF MODIFIED IRIIDIUM OXIDE ANODES

ON  $\text{Cl}_2$  EVOLUTION KINETICS

5.1. STATEMENT OF OBJECTIVES

As was discussed earlier (Section 1.5) at the potentials at which the  $\text{Cl}_2$  evolution reaction is expected to proceed, the surface of Ir anodes is totally or partially covered by an oxide film. It is therefore this oxide, that is associated with the electrocatalytic properties of the anode, as shown by Conway and Novak (99,100) for the case of Pt in their studies using anhydrous  $\text{CF}_3\text{COOH}$  as a solvent which enabled them to obtain oxide-free surfaces of Pt at which the rates of  $\text{Cl}_2$  evolution could be compared with those of oxide covered surfaces in the aqueous medium.

It was also indicated how the development of the D.S.A.<sup>®</sup> electrodes by De Beer (55-57), revolutionized the chlor-alkali industry. These electrodes are based on  $\text{RuO}_2$  on a Ti substrate and, although they were initially prepared by a thermal decomposition technique, it was shown by various authors (58,59, 90,91,269) that the electrochemically prepared  $\text{RuO}_2$  films are also good electrocatalytic substrates for anodic  $\text{Cl}_2$  evolution.

Similarities between the electrochemical behaviour of Ru and Ir have been noted in terms of their ability to develop thick oxide films showing large reversible oxidation/reduction currents corresponding to electron-transfer processes within the oxide films, coupled with proton ejection/injection. Studies on the nature of the processes in formation of the thick oxide films at Ir (Section 4.4) were carried out in order to provide a basis for investigating the behaviour of modified iridium oxide anodes as electrodes

for the  $\text{Cl}_2$  evolution reaction.

A correlation was sought between the observed oxidation/reduction behaviour of the Ir oxide films and the surface modifications achieved with respect to changes of rates of the  $\text{Cl}_2$  evolution reaction at such surfaces.

The approach through which the D.S.A<sup>®</sup> electrodes were developed, i.e. testing of many electrocatalytic preparations on a trial and error basis, clearly indicates that a better understanding of the electrocatalytic phenomena could lead to improved procedures for the design of better electrodes.

Summarizing the previous work done on  $\text{Cl}_2$  evolution at Ir and  $\text{IrO}_2$  anodes (Section 1.5 ), the following conclusions can be reached:

- (a) There is no agreement between various authors as to the mechanism of the  $\text{Cl}_2$  evolution reaction on Ir and  $\text{IrO}_2$  substrates;
- (b) There is no agreement as to the presence or absence of a linear Tafel region and the quoted values of the Tafel slope vary widely;
- (c) Although our own results and those of all the other workers in the field indicate that high current densities are generated at low overpotentials, most of the available data has not been corrected for IR drop, nor has it been corrected for the influence of the backward reaction which is certainly important at overpotentials,  $\eta$ , < 0.100 V for active electrode surfaces;
- (d) The surfaces at which the kinetic studies were carried out were not in any way characterized prior to or after the experiments; and
- (e) Most of the previous work has been carried out on thermally prepared oxides, which are not as easily and controllably modifiable as the electrochemically prepared ones.

In view of this situation, the purpose of this part of the work was to study the electrocatalytic properties of modified iridium oxide anodes for the  $\text{Cl}_2$  evolution reaction in such a way as to avoid what are considered

as shortcomings in earlier work.

In order to achieve this goal, the present work was performed in the following steps:

- (a) Modification of the anode surfaces by varying the oxide thickness;
- (b) Study of the effect of  $\text{Cl}^-$  ion on the formation, stability, growth and reversibility of the oxide films in the monolayer and multilayer stages;
- (c) Characterization of the surfaces prior to and after the  $\text{Cl}_2$  evolution experiments by cyclic-voltammetry and SEM observations;
- (d) Study of the kinetics of  $\text{Cl}_2$  evolution on the modified anodes by means of steady-state polarization curves corrected for IR drop and the back reaction current component near the reversible potential; and
- (e) Correlation of the observed kinetic effects with the surface modifications achieved.

## 5.2. RESULTS AND DISCUSSION

### 5.2.1. Modification of Iridium Oxide Anodes

The surface properties and characteristics of iridium oxide anodes depend, to a great extent, on the conditions under which the films are developed (93,237,246,248), as is implicit in the material given in Chapter IV.

For the study of the kinetics of the  $\text{Cl}_2$  evolution reaction on oxide surfaces, the Iridium oxide anodes were modified only with respect to the oxide thickness developed, i.e. all the films were grown in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence of  $\text{Cl}^-$  ion by a cyclic potential programme at  $0.100 \text{ V s}^{-1}$ , at 298 K, with the potential limits of the programme being  $E_a = 1.485 \text{ V}, E_H$  and  $E_c = 0.055 \text{ V}, E_H$ .

The growth was continued for variable lengths of time, while the apparent oxide thickness was monitored by measuring the charge corresponding to the area under the  $i$  vs  $V$  profiles, and determining the CEF (charge

enhancement factor, see definition on page 48).

Films were prepared with CEF's ranging from 1 to 200. Such electrodes covered the whole range of states of the Ir oxide anodes discussed previously (Chapter 4.), i.e. states A, M, MB and B (Fig. 49). The main characteristics of such states are:

- (a) State A: the electrode bears a monolayer surface oxide;
- (b) State M: large reversible oxidation/reduction currents are observable and the electrode bears a thicker phase oxide, consisting (88) probably of an Ir(III)/Ir(IV) hydrated mixed-valence oxide;
- (c) State MB: the same as state M, but an EC effect is observable; and
- (d) State B: the electrode appears always black, implying that the film is not 100% efficient with respect to the reduction cycle of the redox processes occurring in it.

Once the state M has been attained (after a few cycles), the type of oxide does not change further except that the thickness and probably the roughness or porosity increases. As greater film thicknesses are achieved (CEF's > 100), the film starts to crack macroscopically (see Fig. 29a-d).

#### 5.2.2. The State of Ir Electrode Surfaces in H<sub>2</sub>O as a Function of Cl<sup>-</sup> Ion Concentration

As mentioned in Section 4.3, in a cyclic-voltammetry experiment, an Ir electrode in state A behaves like most other noble metals (1). In this state, when Cl<sup>-</sup> ion is present, the following effects, shown in Fig. 50, are observed: H deposition is blocked by the competitive adsorption of the Cl<sup>-</sup> ion, so that the charge under the i vs V profile decreases and the peak potentials are shifted to less positive values with increasing Cl<sup>-</sup> concentration. Also, a double-layer charging region becomes better resolved since Cl<sup>-</sup> ion adsorption shifts the onset of upd of OH species towards more positive

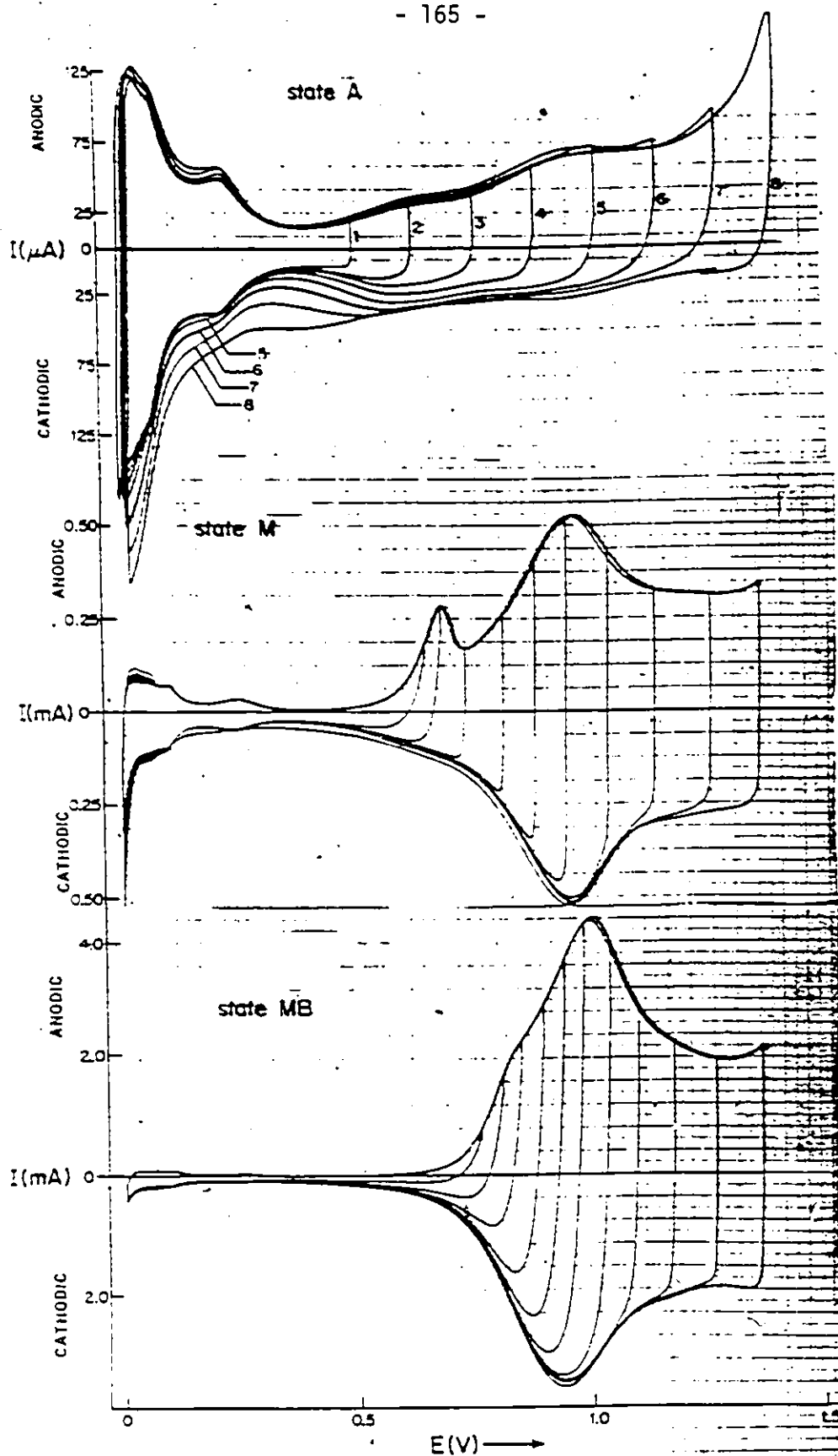


Fig. 49. Cyclic- voltammetry  $i$  vs  $V$  profiles for Ir electrodes at  $0.05 \text{ V s}^{-1}$ , 298 K in  $0.5 \text{ M H}_2\text{SO}_4$ . State A, CEF = 1; State M, CEF = 8; State MB, CEF = 50.

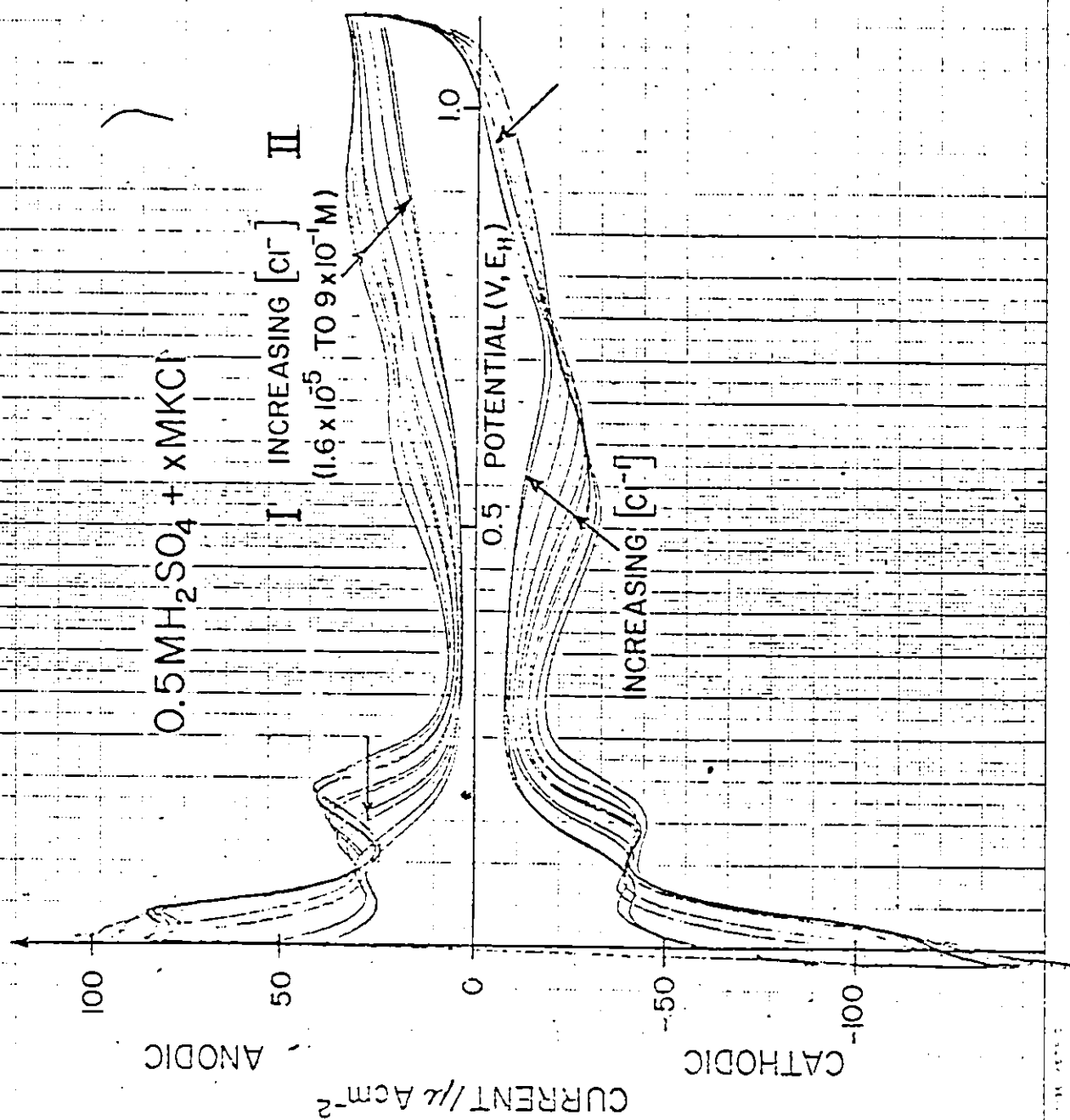


Fig. 50. Series of superimposed cyclic-voltammetry  $i$  vs  $V$  profiles for Ir in 0.5 M  $\text{H}_2\text{SO}_4$ , with successive additions of  $\text{Cl}^-$  from  $1.6 \times 10^{-5}$  to  $9 \times 10^{-1} \text{ mol dm}^{-3}$ . Arrows show direction of change of curves with increasing  $[\text{Cl}^-]$ .

potentials and of H to less positive potentials. This eliminates the overlap between the regions of H ionization and commencement of upd of OH species which otherwise almost obscures the double-layer region at Ir [and at Ru(269)].

Of particular interest here is the displacement of the surface oxidation region at Ir to more positive potentials by blocking on account of strong competitive adsorption of  $\text{Cl}^-$  ion, as also occurs at Pt (99,273) but in a somewhat different manner. This blocking of surface oxide formation is conveniently measured from the diminution of oxide formation charge on each anodic sweep, following successive additions of  $\text{Cl}^-$  ion (cf. ref. 99).

The extent (as %) to which the formation of the monolayer surface oxide is blocked as a function of concentration of  $\text{Cl}^-$  ion is shown in Fig. 51, compared with that observed (99) at Pt under similar conditions. As can be seen, both relations have the same initial slope but, to achieve the same % blocking, the concentration of  $\text{Cl}^-$  ion in the case of Ir must be 10 times larger than that for Pt. This is because surface oxidation of Ir starts already at a potential of 0.45-0.5 V,  $E_H$ , making the metal surface less sensitive, thermodynamically, to competitive adsorption of  $\text{Cl}^-$ .

The charge isotherm for monolayer surface oxide formation as a function of  $\text{Cl}^-$  concentration, measured at various end potentials,  $E_a$ , in anodic sweeps, is shown in Fig. 52, which indicates two regions of influence of  $\text{Cl}^-$  corresponding to the two broad oxidation peaks (Section 4.3, Fig. 15) observed in the absence of  $\text{Cl}^-$  ion.

In the case of Ir anodes on which a thicker oxide has been grown in the absence of  $\text{Cl}^-$  ion, the addition of this ion produces similar effects. in the H region to those observed on the bare metal in that region, as described above.

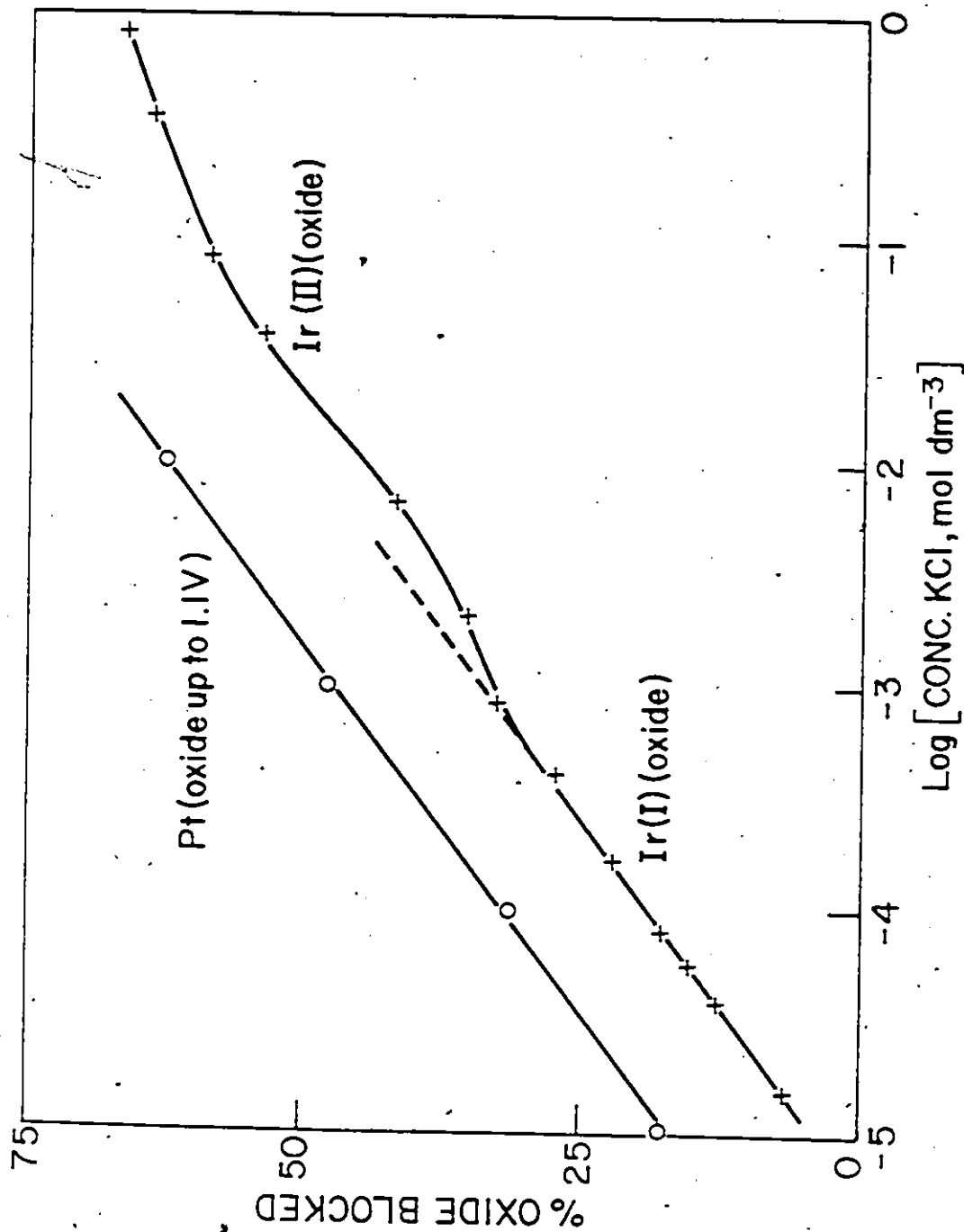


Fig. 51. Percentage of surface oxide, measured as charge for its anodic formation, blocked by  $\text{Cl}^-$  as a function of  $\log [\text{Cl}^-]$  for Ir as compared to Pt (99). Supporting electrolyte is  $0.5 \text{ M H}_2\text{SO}_4$  for Ir and  $0.1 \text{ M H}_2\text{SO}_4$  for Pt. (Region I and II correspond to the two broad peaks indicated in Fig. 50).

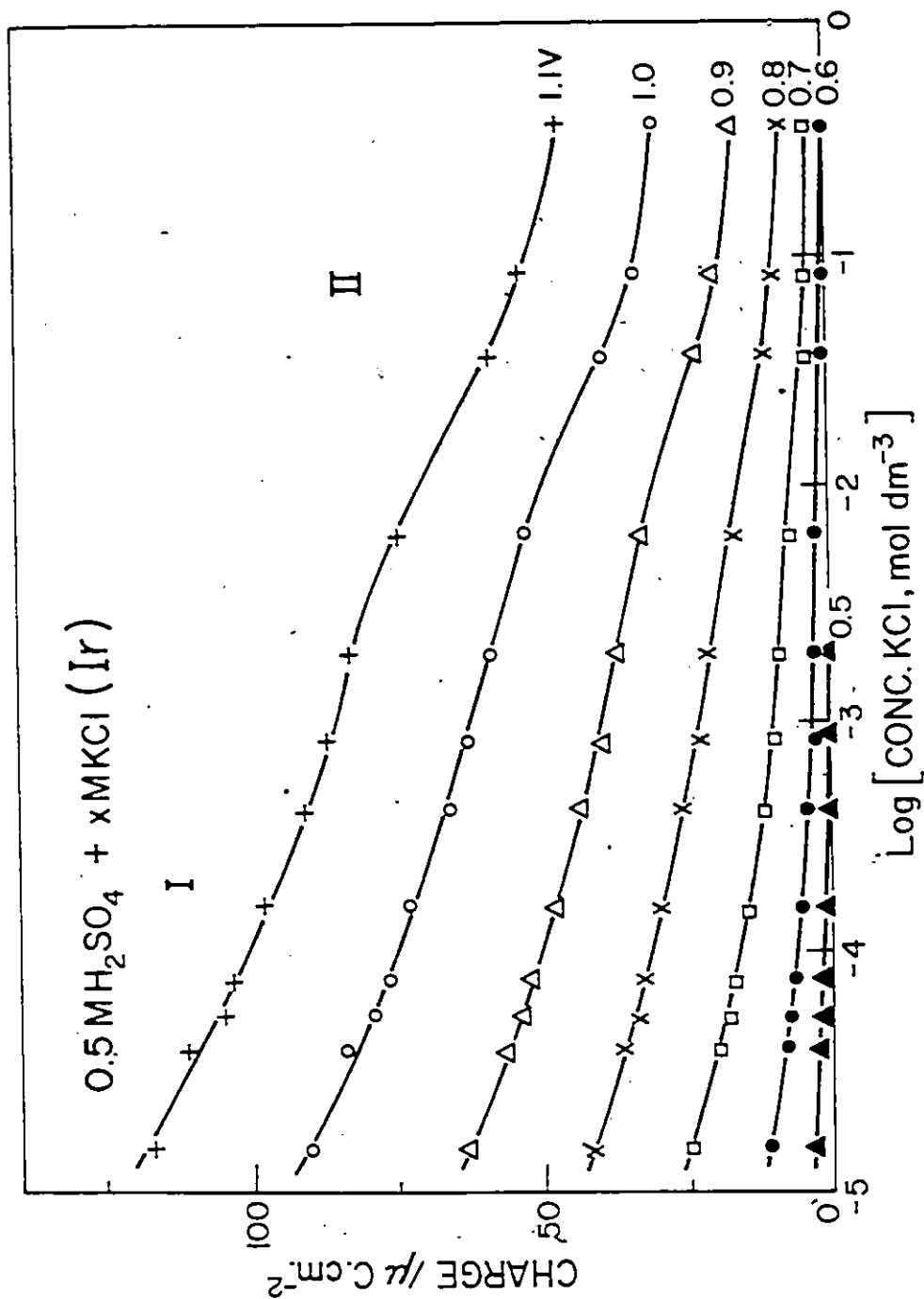


Fig. 52. Surface oxide coverages, as charge, at Ir electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  + x M KCl solutions, as a function of  $\log [\text{Cl}^-]$ , evaluated for different end potentials of anodic sweeps. (Regions I and II, as in Fig. 50).

These two situations are compared in Fig. 53; with the thicker oxide (curve 1), it is experimentally observed that H deposition is diminished to some extent by the presence of the oxide, so the % blocking of the H region at low  $\text{Cl}^-$  concentrations is higher than that (curve 2) for  $\text{Cl}^-$  adsorption effects at the "bare" metal since the blocking effect is calculated as a % of the H charge measured at the "bare" (oxide free) metal. As the  $\text{Cl}^-$  concentration increases, the behaviour of both types of surfaces referred to above is remarkably similar. This indicates, as discussed in Section 4.5 where a model for the oxide structure was proposed, that the film is porous enough to allow  $\text{Cl}^-$  ions to reach "bare" metal sites beneath the oxide film. No time effects are experimentally observed in the  $\text{Cl}^-$  ion blocking effect, so that diffusion-controlled movement of  $\text{Cl}^-$  ion through the pore system does not seem to be involved significantly.

However, in the oxide region, the  $\text{Cl}^-$  ion seems to have no effect whatsoever. This is as expected, since the oxide has already been deposited (see Section 4.4) and does not get reduced to bare metal in every cycle (248), as does an oxide film at Pt (19). For these conditions, therefore,  $\text{Cl}^-$  ion can have no effect on the behaviour of oxide films already formed at Ir. Continuous cycling of a previously oxidized Ir electrode in  $\text{Cl}^-$  causes only a slight decrease in the CEF, probably due to some dissolution of the oxide. On the other hand, attempts to continue growing the thick oxide film, exhibiting reversible redox processes, in the  $\text{Cl}^-$  solution, were unsuccessful; this may be for various reasons, e.g. enhanced rate of dissolution of Ir and/or (more likely) interference of adsorbed  $\text{Cl}^-$  ions with the growth mechanism either by blocking H deposition that could be needed indirectly for the growth (since a minimum potential in the cathodic sweep of ca. 0.2 V,  $E_H$

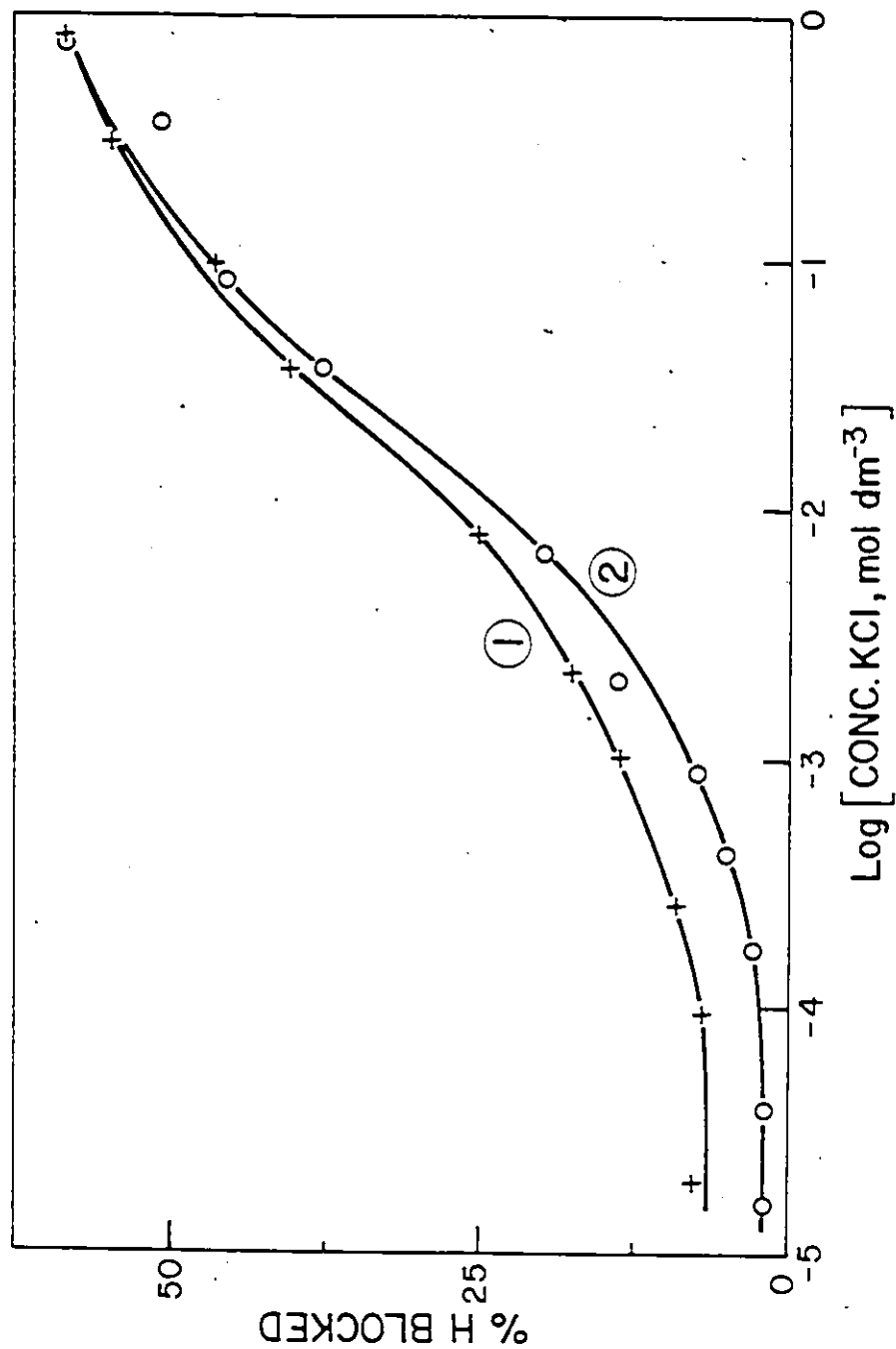


Fig. 53. Percentage of H deposited, measured with respect to initial monolayer H coverage at Ir in state A, which is blocked by  $\text{Cl}^-$  as a function of  $\log [\text{Cl}^-]$  for Ir electrodes. Curve 1: Ir in state M; curve 2: Ir in state A. Supporting electrolyte is 0.5 M  $\text{H}_2\text{SO}_4$ .

is required for oxide growth to be maintained in the cyclic regime) or by inhibiting the underlying metal surface from participating in the film growth reaction. Such inhibition is most likely to be responsible for the observed effect of  $\text{Cl}^-$  ion in preventing continued oxide film growth at Ir, since continuous oxidation/reduction of the underlying metal surface is essential for the growth of the thick oxide film, as discussed in section 4.5.

### 5.2.3. $\text{Cl}_2$ Evolution Kinetics on the Conditioned Ir Oxide Films

In order to study the kinetics of the  $\text{Cl}_2$  evolution reaction on the modified iridium oxide anodes, steady-state  $i$  vs  $V$  relations were obtained potentiostatically. As all the surfaces studied were very "active", i.e. large current densities were observed at relatively small overpotentials, < ca. 0.200 V, the data were corrected for IR drop effects, the latter being measured by a current interruption technique (183,184).

The IR drop-corrected  $\log$  (current-density) vs  $\eta$  curves for  $\text{Cl}_2$  evolution on the oxide films at Ir, prepared to various extents of thickness (CEF), are shown in Fig. 54. As can be seen, the apparent electrocatalytic effectiveness of the surfaces of these electrodes increases steadily with increasing CEF up to a limit, after which the  $\text{Cl}_2$  evolution currents become independent of the CEF. The relation between  $i$  at a given overpotential and CEF can be represented by a linear  $\log$ - $\log$  plot (up to the limit mentioned above), as shown in Fig. 55. This line has a slope close to 1. A similar slope was obtained by Trasatti et al. (90) for  $\text{O}_2$  evolution on  $\text{RuO}_2$ , and was attributed to increasing concentration of "defects" in the film, although in their case (90) no limiting region was found.

As the overpotential values are quite small, viz. < 0.150 V from the reversible potential, it is important to eliminate the influence of the back reaction in the polarization plots of Fig. 54.

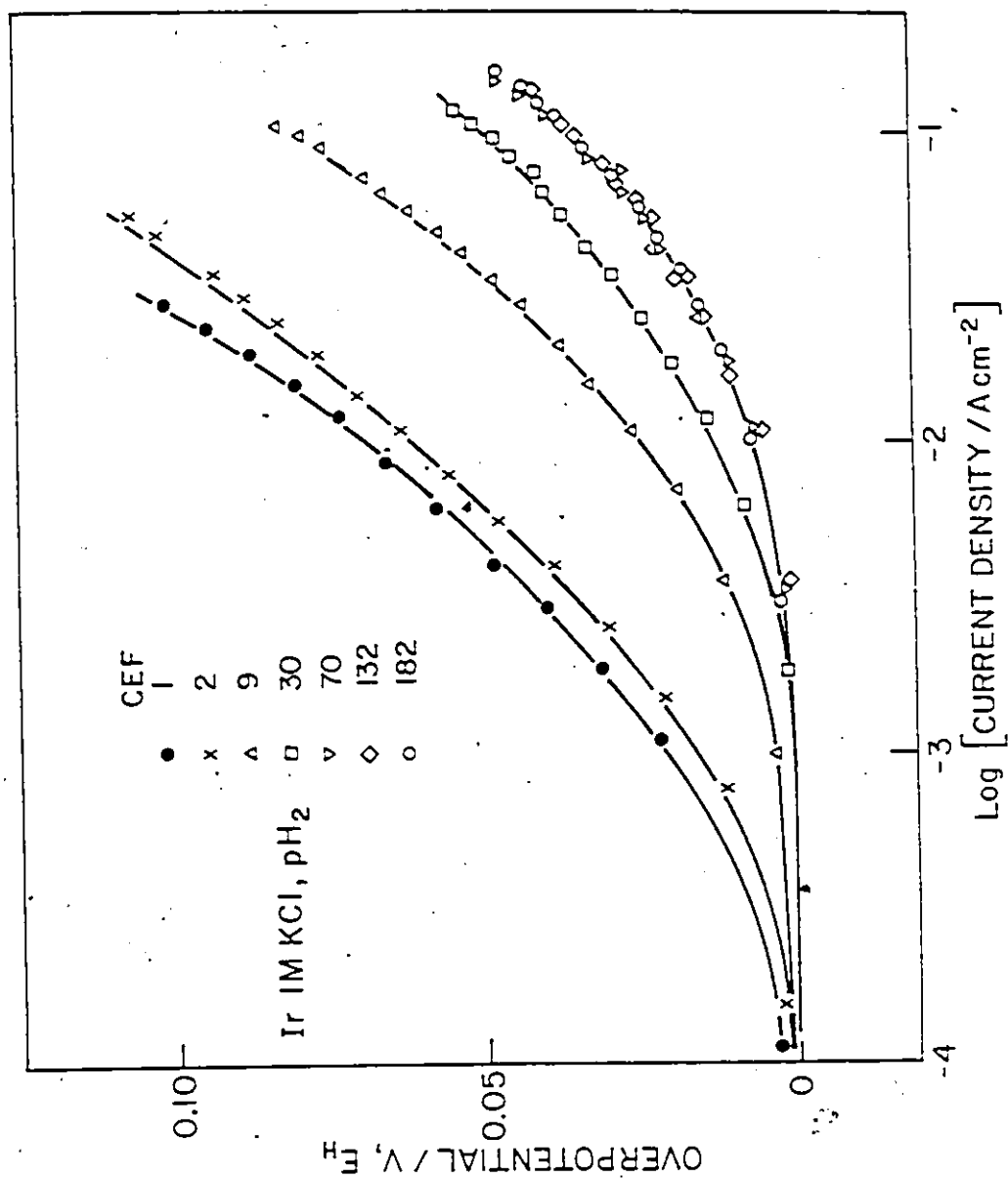


Fig. 54. Steady-state log (current density) vs overpotential relations for anodic  $Cl_2$  evolution on Ir at 298 K in aq. KCl + HCl to pH 2; CEF values as shown.

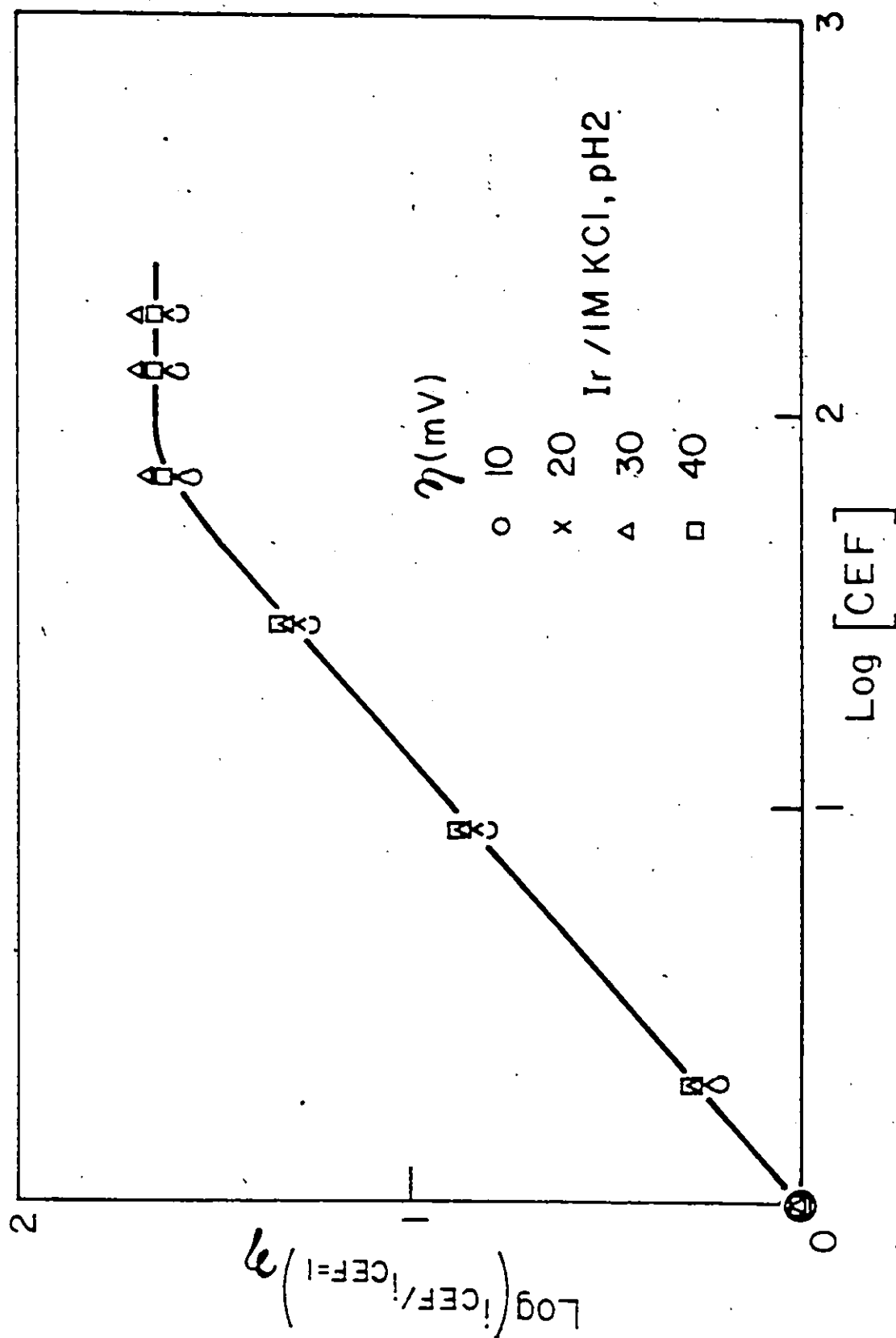


Fig. 55. Plots of  $\text{Cl}_2$  evolution rates at various indicated constant overpotentials as a function of CEF, expressed relative to currents for  $\text{CEF} = 1$ , for Ir anodes at 298 K in 1 M KCl + HCl to pH 2.

Thus, according to the Butler-Volmer equation, the current for an electrochemical reaction will be given by

$$\frac{I}{A} = i_a - i_c = i_o \{ \exp (\alpha n F / RT) - \exp -[(1-\alpha) n F / RT] \} \quad (5.1)$$

or, if the back reaction is neglected, the normal exponential Tafel relation is obtained

$$\frac{I}{A} = i_a = i_o \exp (\alpha n F / RT) \quad (5.2)$$

taking logarithms

$$\log \frac{I}{A} = \log i_o + \frac{\alpha n F}{RT} 2.303 \quad (5.3)$$

which is the standard Tafel relation, used in Fig. 54.

However, if the back reaction cannot be neglected, then rearranging eqn.(5.1) gives

$$\frac{I}{A} = i_o \exp (\alpha n F / RT) \{ 1 - \exp -(\eta F / RT) \} \quad (5.4)$$

so that by plotting

$$\ln \frac{I}{A \{ 1 - \exp -(\eta F / RT) \}} \quad \text{vs} \quad n \quad (5.5)$$

the current component due to the back reaction can be taken into account.

When this is done, as in Fig. 56, the data become represented by straight lines the slopes of which are  $\alpha F / RT$  and the intercepts of which represent  $\ln i_o$ . For all of the Ir oxide electrode surfaces, the value of  $\alpha F / RT$  was  $34 \pm 4 \text{ V}^{-1}$ , which corresponds to a value of  $\alpha = 1$  ( or a Tafel slope of  $RT/F$ ) for the  $\text{Cl}_2$  evolution reaction at these surfaces.

That the slope remains constant over all the range of CEF values is rather important since such behaviour indicates that the mechanism is the same for all surfaces developed. This allows us to speculate on the reason for the observed apparent enhancement of  $\text{Cl}_2$  electrocatalysis on a common basis for each of the CEF values and corresponding states of the oxide films.

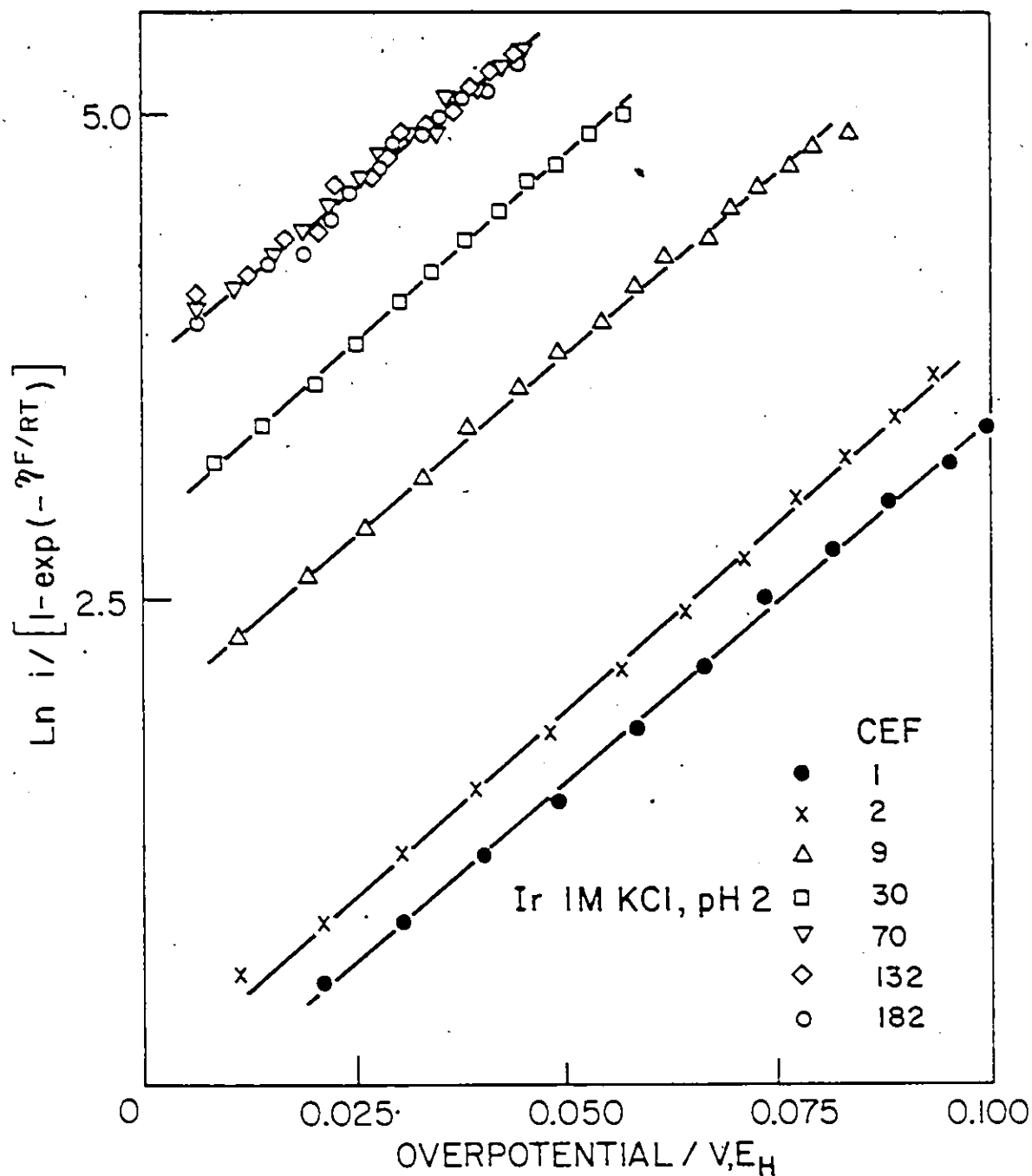


Fig. 56. Steady-state log (current density) vs overpotential plots for anodic  $\text{Cl}_2$  evolution at Ir, as in Fig. 54, corrected for back-reaction current component. ( $T = 298 \text{ K}$ ).

The well-defined Tafel slope of  $RT/F$  is an unusual value in electrode kinetics but three types of explanations for such a value have been proposed for other observed examples:

- (a) The rate is controlled by an heterogeneous chemical recombination step in which "activated" chemisorption of the  $Cl^*$  intermediate applies (277);
- (b) The  $Cl^-$  discharge is followed by rate-controlling quasi-chemical surface-diffusion step (to sites where  $Cl^*$  is desorbed) (278); or
- (c) Barrierless discharge (279) applies.

We shall not attempt to argue a preference for applicability of one or other of these mechanisms to the present results except that (c) is unlikely since a transition to a Tafel slope of ca.  $2RT/F$  ( $\beta$  changing from 1. to 0.5) is not found with increasing  $n$  (Fig. 56). This then implies that the discharge step is not rate-controlling. Also it should be mentioned that Kuhn and Mortimer (111) found Tafel slopes from  $RT/2F$  to  $2RT/F$  for  $Cl_2$  evolution on  $RuO_2$ , Sbr and Mraz (280) the same range for  $MnO_2$  and Morita et al. (281), the value of  $RT/F$  for  $MnO_2$  doped with Ir or Ru, so that the slope of  $RT/F$  for  $Cl_2$  evolution has been encountered previously in other systems. By contrast, at Pt, a value of  $RT/2F$  is convincingly found.

#### 5.2.4. Stability of the Ir Oxide Films

From a practical point of view, it is important to note that the anodes with larger CEF were more stable with respect to their activity as a function of time. Thus, an electrode with a CEF of 123, when held at  $n \approx 0.120$  V (apparent current density  $0.10 \text{ A cm}^{-2}$ ) for 2 hours, lost only 7% of its activity, measured as  $Cl_2$  evolution current, at a given  $n$ . Afterwards a potentiostatic polarization for 60 s at  $0.0 \text{ V}, E_H$ , restored the activity to within 1% of the original value. In contrast, electrodes with intermediate

degrees of oxide formation were less stable.

Electrodes having a CEF higher than 50 were visibly black when polarized anodically [known EC effect (259)]. This served as a secondary feature enabling flaking of the film, which occurs under certain conditions, to be observed. This phenomenon is quite evident during  $O_2$  evolution in the absence of  $Cl^-$  ion, indicating that this reaction is in some way more intimately connected with the state of the oxide film. For  $Cl_2$  evolution experiments at comparable rates, however, no flaking is observed and mechanical intactness is preserved.

Cyclic-voltammograms of the anodes taken in 0.5 M  $H_2SO_4$  after prolonged  $Cl_2$  evolution indicate that the electrochemical redox behaviour of the various anodes remained essentially unchanged, as expected, since  $IrO_2$  does not grow on anodic potential holding (77). However, electrodes with intermediate CEF values lost some of their charge (as much as 60%) during the  $Cl_2$  evolution, while electrodes with CEF's > 50, suffered no appreciable change in the  $i$  vs  $V$  profile under the same conditions. This explains the time effects observed in the activity of the electrodes studied as being due to mechanical or electrochemical reasons.

#### 5.2.5. SEM Examination of the Oxide Films

Our own SEM studies on Ir oxide films grown in 0.5 M  $H_2SO_4$  (Section 4.4) show that as the CEF increases, an apparently macroporous, initially relatively uncracked film (Fig. 29a), develops wide cracks in between oxide patches (Fig. 29b,c,d).

The oxide structure appears to remain unchanged in going from a cycling regime in  $H_2SO_4$  to one in  $Cl^-$  solutions. Thus, it appears that  $Cl^-$  ion does not chemically attack or modify the film, although it probably enhances metal and film dissolution rates by facilitating the formation of

$[\text{Ir}_x\text{Cl}_y]^{-2}$  soluble complexes.

However, after the  $\text{Cl}_2$  evolution experiments, SEM observations of the morphology of the oxide film showed that substantial changes had occurred. The film had developed widespread cracking, as shown in Fig 57a for an oxide film whose surface appearance was comparable to that in Fig. 29a before the evolution of  $\text{Cl}_2$  took place. Under high magnification (Fig. 57b) some porosity was still observable. Also the surface was quite homogeneous in terms of its cracked appearance and no oxide fragments had fallen off due to mechanical failure. On the other hand, if  $\text{O}_2$  evolution had taken place under similar conditions on the same electrode preparation, pieces of oxide film could be seen to have become detached from the surface. The underlying roughened metal is then exposed and the remaining oxide patches appear rough and spongy (Fig. 57c). This observation corroborates the idea that  $\text{O}_2$  evolution involves, in an intimate way, the O species of the oxide film itself.

#### 5.2.6. Electrocatalysis in the $\text{Cl}_2$ Evolution Reaction at Ir Oxide Anodes

In discussing the electrode kinetics of a reaction at an oxide electrocatalyst substrate which is being modified in some way, two factors must be taken into account:

- (a) The possible change of real area (of technological importance); and
- (b) Changes of intrinsic electrocatalytic activity (of fundamental and technological interest).

Factor (b) may be due to changes of energy of adsorption of intermediates, changes of transition state of the reaction, modifications of electronic band structure of the material due to changes of valence states of metal ions in the oxide structure, etc. (see Section 1.6.2).

$\text{Cl}_2$  evolution appears to proceed by either the Volmer-Tafel or Volmer-Heyrovsky type of mechanism (98,103,145). (see page 28). The fact

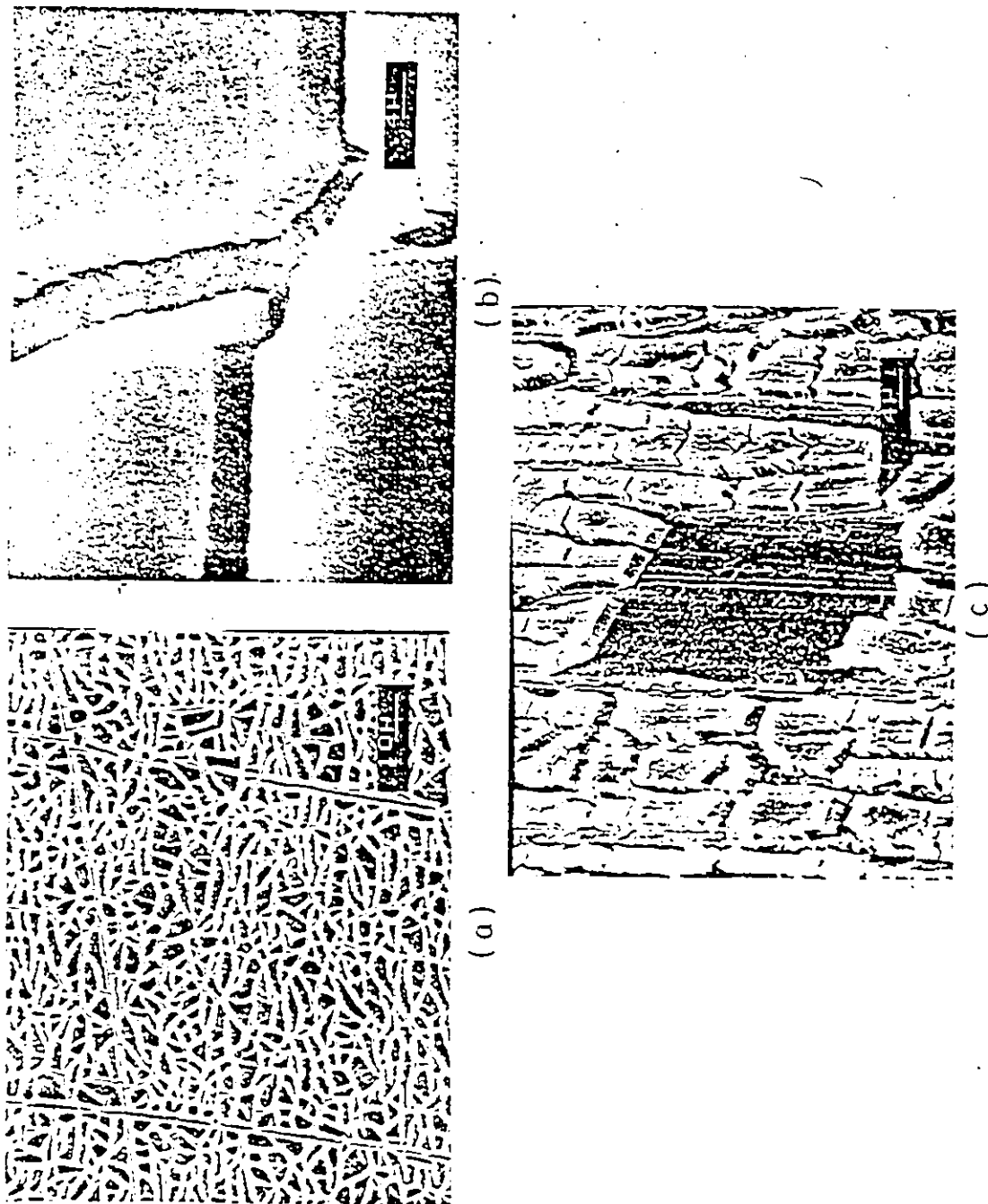


Fig. 57. SEM micrographs of an Ir oxide film. (a) surface similar to that of Fig. 29a, after being used as an anode for  $\text{Cl}_2$  evolution for ca. 10 min. at a c.d. of ca.  $0.05 \text{ A cm}^{-2}$  showing widespread cracking. (b) higher magnification of surface shown in (a). (c) thick oxide film after being used as an anode for  $\text{O}_2$  evolution, conditions as in (a), showing oxide peeled and peeling off from the surface, and also roughness of the film.

that the observed Tafel slopes clearly remain unchanged (Fig. 56) with radically changed thickness of the surface film, means that the mechanism remains unchanged. Although the value of  $RT/F$  for the Tafel slope cannot be unambiguously interpreted (see above) in terms of mechanism, it is reasonable to suppose that the surface modification (at least in going from state A to thicker oxides, in which a monolayer surface oxide becomes replaced by a thick, phase oxide film) could affect the binding energy of  $Cl^{\cdot}$  intermediates in the reaction.

However, the observed changes of rate of the  $Cl_2$  evolution reaction must first be considered in terms of possible changes of real area of the substrate, as the relation between current at a given overpotential and CEF (Fig. 55) seems to indicate is the case.

The fact that the H and double-layer charging regions remain relatively constant regardless of the oxide thickness, has been interpreted by some authors (89,248,249,252) as indicating that no area change takes place when the thick oxide film is developed on an Ir substrate. However, the SEM appearance of the film, porous and rough, and various other observations discussed in section 4.4, indicate that the oxide film has a much greater area than the metal substrate.

For an electron-transfer process to occur at a certain point on the oxide surface, it is necessary that a potential difference across the oxide/electrolyte interface exists at that point. Thus, the important parameter that relates the observed currents to an area factor is the distribution of the applied potential difference across the metal/oxide/electrolyte system, as a function of thickness and oxidation state of the film.

As discussed in Section 4.5, where a model for the oxide film

was proposed, the evidence available indicates that the film is not a very good conductor at low anodic potentials; for the latter conditions, it can be assumed that the applied potential difference is located mainly at the metal/oxide interface. This explanation accounts for the observed constancy of the currents over the H deposition/ionization and double-layer charging potential regions, since the system behaves as Ir metal in contact with electrolyte. The latter would be available at the metal/oxide interface on account of the porous nature of the overlying oxide film, (Fig. 47a).

In order to account for the observed results for  $\text{Cl}_2$  evolution rates, we utilize other features of the proposed model, which indicate that, as the potential increases in the anodic direction, the conductance of the film increases (268) and the oxide becomes a metallic conductor. Thus, the oxide film as a whole assumes a potential difference with respect to the electrolyte as a result of the applied potential difference, (Fig. 47b). Microscopically, of course in a porous structure, such a situation would require a distribution of oxide-to-solution interfacial potential drops throughout the thick film when it is in the conducting state. The real equivalent circuit for such a situation is then quite complex but elements of it will be like the circuit for a low resistance transmission line.

Some potential difference remains, of course, at the metal/oxide interface (actually, the metal and the oxide become an almost equipotential surface with respect to the electrolyte) and a fraction of the applied potential is lost across the film, due to residual IR drop, this amount being presumably a linear function of the film thickness.

Thus,  $\text{Cl}_2$  evolution, which occurs at high anodic potentials, takes place under conditions where, in principle, the whole surface of the oxide, i.e. the outer surface + interface of the pore structure, is available

for electron transfer. In the case of iridium oxide films, the change in conductivity of the oxide on varying the oxidation state of the film, acts as a switch with respect to the area of the system, "turning" the area "on" at high anodic potentials and "turning it off" for the corresponding cathodic ones.

The changes in the distribution of the applied potential difference across the interphasial system discussed above are illustrated in Fig. 47, page 153.

As the thickness of the film increases, an increasing IR drop, coupled with mass-transport limitations at the bottom of the pores, restricts the real area available for the reaction.

Furthermore, the change of location of the applied potential difference with change of conductance of the film has been confirmed in this part of the work by carrying out H<sub>2</sub> evolution studies on the same modified oxide film covered Ir electrodes.

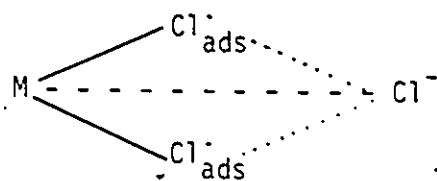
According to the proposed model, at cathodic potentials the applied potential difference is located mainly at the metal/oxide interface; thus, any increase in real area of the oxide film with increasing CEF is irrelevant for a reaction, such as H<sub>2</sub> evolution, which occurs at cathodic potentials, since the oxide cannot support electron transfer at the interfaces of its pore structure if it is essentially non-conducting.

Experimental results indicate that, as expected, the polarization curves for the H<sub>2</sub> evolution reaction remain essentially constant, regardless of the CEF, and exhibit a Tafel slope of  $2RT/F$ . The small observed variations in the polarization curves for various CEF's, in the range CEF = 1 - 160, can be attributed to roughening of the underlying substrate with continuous oxidation and to the change of metal area available for the H<sub>2</sub> reaction on

account of some mechanical failure of the overlying oxide film. However, it is clear that even with an increase of CEF > 100, no corresponding increase in  $H_2$  evolution currents is observed.

Related work from this laboratory, to be published elsewhere (112), on the electrocatalytic behaviour of oxidized Ru electrodes for  $Cl_2$  evolution showed that a changed state of monolayer surface oxidation could be induced by cycling at that metal over a restricted potential range; the observed  $Cl_2$  evolution rates were then enhanced some 30 x, independently of any area change, which was unambiguously less than 5%. On the other hand, at the thickened oxide films that can be formed at Ru in a similar way to those at Ir (54),  $Cl_2$  evolution rates were found, in the present work, not to increase with increasing CEF of the Ru oxide film. This is due to the different, impervious character of the oxide film at Ru in comparison with that at Ir, as can be observed microscopically, and stresses the importance of the open-porous structure of Ir oxide films, that allows the internal area of the pore structure to enter the reaction as a catalytic substrate surface.

The enhanced  $Cl_2$  evolution rates found with the conditioned monolayer at Ru leads to the conclusion that possibly, also at Ir, the d-electron configuration of the oxide may play a role. This was already stressed by Arriado et al. (103) who suggested that, in the case of  $Cl_2$  evolution at  $IrO_2$  anodes, this oxide which has a  $(t_{2g})^5$  electronic configuration showed an activation energy for the  $Cl_2$  evolution reaction of  $29.7 \text{ kJ mol}^{-1}$ . Theoretical calculations for the activation energy of the reaction, based on a square pyramidal or pentagonal bipyramidal geometry of the activated complex, gave values of  $14.2$  and  $28.4 \text{ kJ mol}^{-1}$ , respectively. Thus, these data suggested (103) a transition state having a bipyramidal geometry of the form:



From that configuration a mixed mechanism could arise where the adsorbed  $\text{Cl}^-$ 's either recombine or react with  $\text{Cl}^-$ , depending on  $n$ , the geometry of the site, etc.

The rather sharp limit in activity enhancement which is eventually reached with increasing CEF (Fig. 55), could be explained in terms of two factors: First, an increasing IR drop within the film (which would not be included in the experimentally measured IR drop in the solution due to "RC" coupling in the equivalent circuit of the film itself) with increasing thickness. This would account for fall-off of the rate of activity increase with CEF, but hardly as sharp an inflexion as observed (Fig. 55); and second,  $\text{Cl}^-$  mass-transport limitations that render the innermost regions of the film inactive because of the ultimate diffusion-control in  $\text{Cl}^-$  migration into the pores. The redox processes occurring in the film itself are affected in a similar way as shown by the fact that at high CEF, > ca. 150, the film appears always black (B state) indicating that the EC reaction is not 100% efficient any more in terms of amount of oxide involved in it.

Attempts to model the situation for the case of  $\text{Cl}_2$  evolution encounter the following problem: consider that at  $t = 0$  a potential step is applied to the system which depletes the surface of adsorbed  $\text{Cl}^-$ , and  $\text{Cl}^-$  ion is allowed to migrate to the surface from the bulk under the influence of a concentration gradient and/or a field. The diffusion problem in this situation is one that could be solved if the electrode was a planar surface but, in the real case, when  $\text{Cl}^-$  enters the top of the pore system it can be electrolyzed at that point. Thus, the diffusion towards the lower parts of the structure, i.e.

those closer to the metal, is diminished and the differential equations relating concentration to distance down pores as a function of time become almost impossible to solve.

### 5.3. CONCLUSIONS

It can be concluded, then, that the apparent large enhancement of electrocatalysis of the modified iridium oxide films for  $\text{Cl}_2$  evolution is due mainly to an increase in real, microscopic surface area with increasing CEF. Also, that IR drop across the film, coupled with diffusion limitations, accounts for the leveling off of the activity at CEF's  $> 100$ . By comparison with the behaviour of  $\text{RuO}_2$  films, it is apparent that the d-electron configuration of the Ir oxide films could play some role in the electrocatalytic activity, although compared to the area factor in this case, it is a minor one. A Tafel slope of  $RT/F$  is observed for the  $\text{Cl}_2$  evolution reaction on the modified oxide films and could arise on account of a mixed mechanism, due to the geometry of the transition state or, more likely, to a quasi-chemical rate-determining step, following  $\text{Cl}^-$  ion discharge. The experimental results have been accounted for in terms of a model for the interphasial potential distribution across the metal/oxide/electrolyte system, discussed in Section 4.5 and based on a conducting state of a micro-porous, hydrated thick film of Ir oxide in the  $\text{IrO}_2$  state.

## CHAPTER VI

### EFFECT OF $\text{Cl}^-$ ON SURFACE OXIDE FORMATION AT Pt

#### 6.1. INTRODUCTION

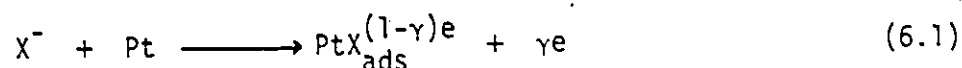
As discussed previously (section 1.4), ions of the solution electrolyte (especially anions) have a marked effect on the formation of surface oxides at noble metals, and on the reversible characteristics of their reduction. The work described in previous chapters has referred to Ir.

In the case of Pt, early work by Breiter (273,282) and by Bagotzky et al. (283), indicated that the halide ions, except  $\text{F}^-$ , specifically adsorb on that metal, even at low concentrations, i.e. about  $10^{-6}$  M, in the order of strength:  $\text{F}^- \ll \text{Cl}^- < \text{Br}^- < \text{I}^-$ . The main effects of the adsorption were:

(a) Compression of the potential range for hydrogen adsorption, i.e. blocking of H deposition, and shifting of the H adsorption region to less positive potentials (3,284,285,286); and

(b) Blocking of the initial stage of Pt surface oxidation with an associated tendency to increase the irreversibility of that process (34,273,287,288).

These effects were studied at room temperature by various authors (273,282,283) and more recently by Conway and Novak in a more quantitative way (99,100,289). The latter authors showed that the effect of  $\text{Cl}^-$  ion was different from that of  $\text{Br}^-$  and  $\text{I}^-$ , in presenting a linear dependence of the % oxide blocking on the  $\log [\text{Cl}^-]$ , i.e. linear dependence in chemical potential of  $\text{Cl}^-$ . This difference in behaviour was attributed to a difference in the electrosorption valency (290) of  $\text{Cl}^-$  and  $\text{Br}^-$  or  $\text{I}^-$ , which is a measure of the actual charge that the adsorbed ion retains in the adsorbed state,



It was concluded that the value of  $\gamma$  was close to zero for  $Cl^-$  and near to one for  $Br^-$  and  $I^-$ , indicating that the latter ions are adsorbed as almost neutral atoms. Lane and Hubbard (291) and Bagotzky et al. (283) had previously reached similar conclusions with respect to the effects of  $H_2$  adsorption on H deposition on Pt.

Another interesting observation reported by Conway and Novak (289) was that  $Cl^-$  ion appears to block selectively the OH monolayer which is completed at Pt, in the absence of  $Cl^-$  ion, at about 1.1 V,  $E_H$ , and that the linear logarithmic dependence of blocking arises after about 50% of the OH monolayer has been selectively blocked.

On account of these interesting features of the effect of  $Cl^-$  ion on the surface oxide formation at Pt, it was decided to extend the previous work (289) of  $Cl^-$  adsorption to studies at low temperatures, i.e. 213 K since, under such conditions, it is known that at high sweep-rates it is possible to distinguish the reversible, early stage of oxide formation (19) from the later, irreversible one. Thus it would be possible to determine the effect of  $Cl^-$  ion on the reversibility of the distinguishable states of Pt surface oxidation and compare the effects with those at Ir (Fig. 50).

At the same time, it was also considered of interest to study the growth of Pt oxide at constant potential as a function of  $Cl^-$  ion concentration in order to observe any effects in the growth kinetics resulting from competition between  $Cl^-$  adsorption and continuing OH and O deposition.

Preliminary work in this area had been carried out by Gilroy et al. (29,30) and also by Vetter and Schultze (18,27) in the absence of  $Cl^-$  ion. Both these groups of authors concluded that the growth of Pt oxide at constant potential obeys a direct logarithmic law in time as a result of a place-exchange

growth mechanism.

## 6.2. EXPERIMENTAL

From the experimental point of view, the study of the effect of  $\text{Cl}^-$  ion on the growth of Pt oxide at constant potential, presents important difficulties, some of which cannot be overcome, as discussed below. Thus, a special potential-time programme had to be devised to ensure the accuracy and reproducibility of the results.

### 6.2.1. Potential-Time Programme for the Study of Pt Oxide Growth in $\text{Cl}^-$

#### Solutions

When studying the growth of oxide at a noble metal surface at constant potential by the potentiodynamic method, i.e. using cyclic-voltammetry, it is important to realize that the time spent,  $\tau_s$ , in the sweep to reach the required growth potential can influence the results if it is of comparable magnitude to the growth time, i.e. the holding time,  $\tau_h$ . In order to minimize  $\tau_s$  in relation to  $\tau_h$  for short  $\tau_h$ , a potential-stepping programme is recommended to reach the holding or growth potential.

After the programmed growth time,  $\tau_h$ , the oxide is reduced in a corresponding cathodic sweep, and integration of the  $i$  vs  $V$  profile allows the amount of oxide formed during the growth time to be calculated. However, the cathodic sweep should be fast enough to avoid problems of continued oxidation on the initial part of the cathodic sweep after the latter is initiated. Effects of this kind can occur if the oxide reduction presents a large hysteresis, which results in continuation of net anodic currents during the early stages of the cathodic sweep. This behaviour is found at Au and in some cases at Pt (1,19).

It should also be noted that it is necessary to scan the H ionization region at the same sweep-rate as that at which the oxide was reduced and H deposited,

in order to avoid erroneous measurements which arise from H ionization taking place during the growth time, if the step to the growth potential is initiated from 0.0 V,  $E_H$ .

While all the above effects can be minimized in a controlled way, the last experimental difficulty proves to be the limiting one in terms of applicability of the technique. A problem also arises in terms of the potential-dependence of the  $Cl^-$  ion coverage, especially because in the anodic direction, which spans the range 0.0 - 1.4 V,  $E_H$ , the p.z.c. of Pt is crossed in the potential step. Thus, if a step is applied to reach the growth potential immediately after the H species are ionized (i.e. about 0.45 V,  $E_H$ ), the coverage of adsorbed  $Cl^-$  will be quite low and for short holding times  $\tau_h < 10^{-2}$  s and/or for low  $Cl^-$  concentrations  $< 10^{-4}$  M, the equilibrium coverage cannot be established. This can result in a much lower degree of  $Cl^-$  blocking than expected, as is seen experimentally.

In order to circumvent this problem to a certain extent, and the others mentioned above, the potential-time programme shown in Fig. 58 was used. It can be described as follows:

- (a) Formation of oxide at a given anodic potential,  $E_a$ , for programmed periods of time,  $\tau_h$ ;
- (b) Reduction of the oxide and deposition of H at  $20 \text{ V s}^{-1}$ ;
- (c) Ionization of H at the same sweep rate, viz.  $20 \text{ V s}^{-1}$ , followed by continued potential sweeping at that sweep-rate, up to 0.75 V,  $E_H$ , since no Pt oxide is formed up to that potential during the cyclic programme;
- (d) A holding period of 10 s at 0.75 V,  $E_H$  to allow  $Cl^-$  to establish an equilibrium coverage at that potential; and
- (e) A step, at  $s > 200 \text{ V s}^{-1}$  from 0.75 V,  $E_H$  to the desired oxide growth potential,  $E_a$ .

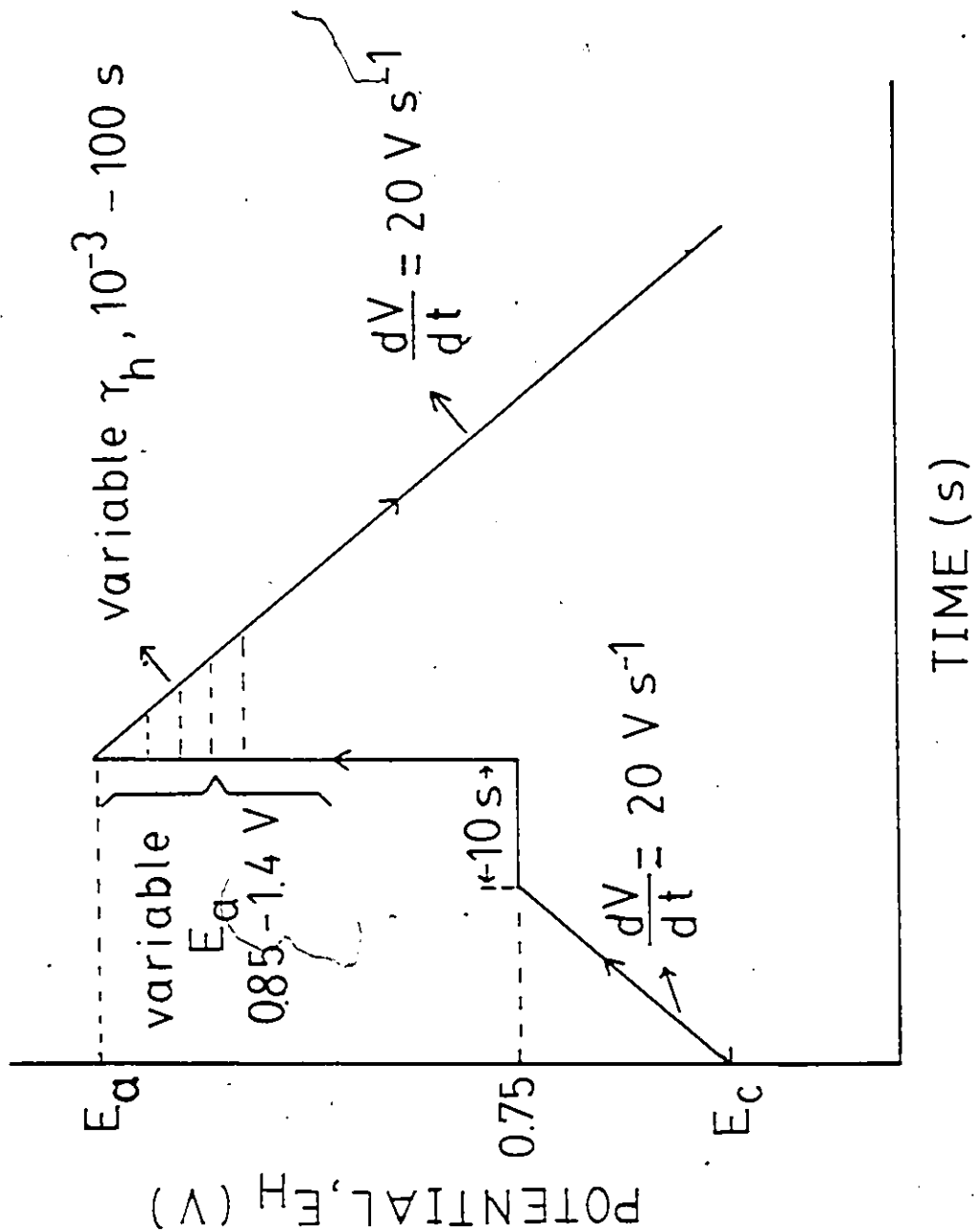


Fig. 58. Potential-time programme for the study of  $\text{Cl}^-$  effects on the kinetics of growth of Pt oxide at constant potential,  $E_a$ , for programmed periods of time,  $\tau_h$ .

It should be mentioned that when (c) was eliminated from the programme, the results deteriorated to the point that it was impossible to extract any information from the experiments. Although an equilibrium coverage of  $\text{Cl}^-$  ion can be established at the potential of 0.75 V,  $E_H$ , this does not guarantee that equilibrium coverage will be reestablished at the  $E_a$  potential chosen for oxide growth, but this procedure does appear to help minimize that problem, i.e. it extends the lower limit of the range of  $\tau_h$  and of  $\text{Cl}^-$  ion concentrations that can be accurately studied.

In conclusion, we can say that of the various programmes that were tested and whose results were analyzed in terms of the above mentioned difficulties, the programme described above proved to be the best. The experimental limitations were evident for results obtained at  $\tau_h < 10^{-2}$  s and  $[\text{Cl}^-] < 10^{-4}$  M and the extent of the limitation depended on  $E_a$ . However, under most other conditions the results appeared quite satisfactory and the deviations observed for conditions below the above limits, agreed with the trends discussed above. For  $\tau_h > 10^{-2}$  s, there are no serious problems.

### 6.3. RESULTS AND DISCUSSION

The results obtained will be dealt with in two parts: first, the  $\text{Cl}^-$  ion effects at low temperatures and second, the growth of Pt oxide in the presence of this type of ion.

#### 6.3.1. Effect of $\text{Cl}^-$ Ion on the Pt Surface Oxide Formation at Low Temperatures

The effects of  $\text{Cl}^-$  ion on the surface oxide formation at Pt have been recently studied at 298 K by Conway and Novak (289) in 0.1 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$ . In order to be able to carry out the experiments at the temperature of interest, viz. 213 K (acetone-dry ice bath), it was necessary to increase the acid concentration to 6 M in  $\text{H}_2\text{SO}_4$ , since more dilute solutions freeze at these low temperatures.

This increase in acid concentration, however, brings about, as discussed previously (292), an unavoidable increase in the blocking of surface oxide formation at Pt due to the adsorption of  $\text{HSO}_4^-$  ions. Normally  $\text{HSO}_4^-$  adsorption is much weaker than that of  $\text{Cl}^-$  ion but becomes substantial at the high, 6 M, concentrations. This "extra" blocking by the  $\text{HSO}_4^-$  ion appears to be similar in behaviour to the effect of  $\text{Cl}^-$  ion at low concentrations, viz.  $10^{-6}$  -  $10^{-5}$ . Thus, it blocks and displaces the H peaks and selectively blocks the initial stages of surface oxide formation at Pt, indicating that its electrosorption valency (290,293) is, as with  $\text{Cl}^-$ , close to zero.

The effect of  $\text{Cl}^-$  ion was first determined at a sweep-rate of  $0.100 \text{ V s}^{-1}$ , with a growth potential,  $E_a$ , fixed at  $1.4 \text{ V}, E_H$ . The amount of oxide deposited in the anodic sweep was measured by integration of the  $i$  vs  $V$  profile of the cathodic sweep, i.e. over the oxide reduction peak, in the usual way.

The results shown in Fig. 59 were, in principle, similar to those observed by Conway and Novak under the same potentiodynamic conditions but at 298 K, as shown in Fig. 60 and Fig. 59 (curve b).

The first competitive effects of  $\text{Cl}^-$  adsorption on the surface oxidation of Pt at 213 K become discerned at ca.  $10^{-5} \text{ M}$  compared to  $2 \times 10^{-6} \text{ M}$  at 298 K. The difference can be understood on the basis of blocking by  $\text{HSO}_4^-$  adsorption which already competes with  $\text{Cl}^-$  ion adsorption at low concentrations of the latter ion, since the % blocking is measured relative to the amount of oxide formed at a given  $E_a$  in the absence of  $\text{Cl}^-$  ion (in this case in the presence of  $\text{HSO}_4^-$ ).

Once the blocking effect at 213 K becomes measurable at  $[\text{Cl}^-] > 10^{-5}$ , the relation between % oxide blocked and  $\log [\text{Cl}^-]$  is found to be a linear one for the range  $10^{-5}$  -  $10^{-3} \text{ M}$ , as seen in Fig. 59. As  $[\text{Cl}^-] > 10^{-3} \text{ M}$ , the

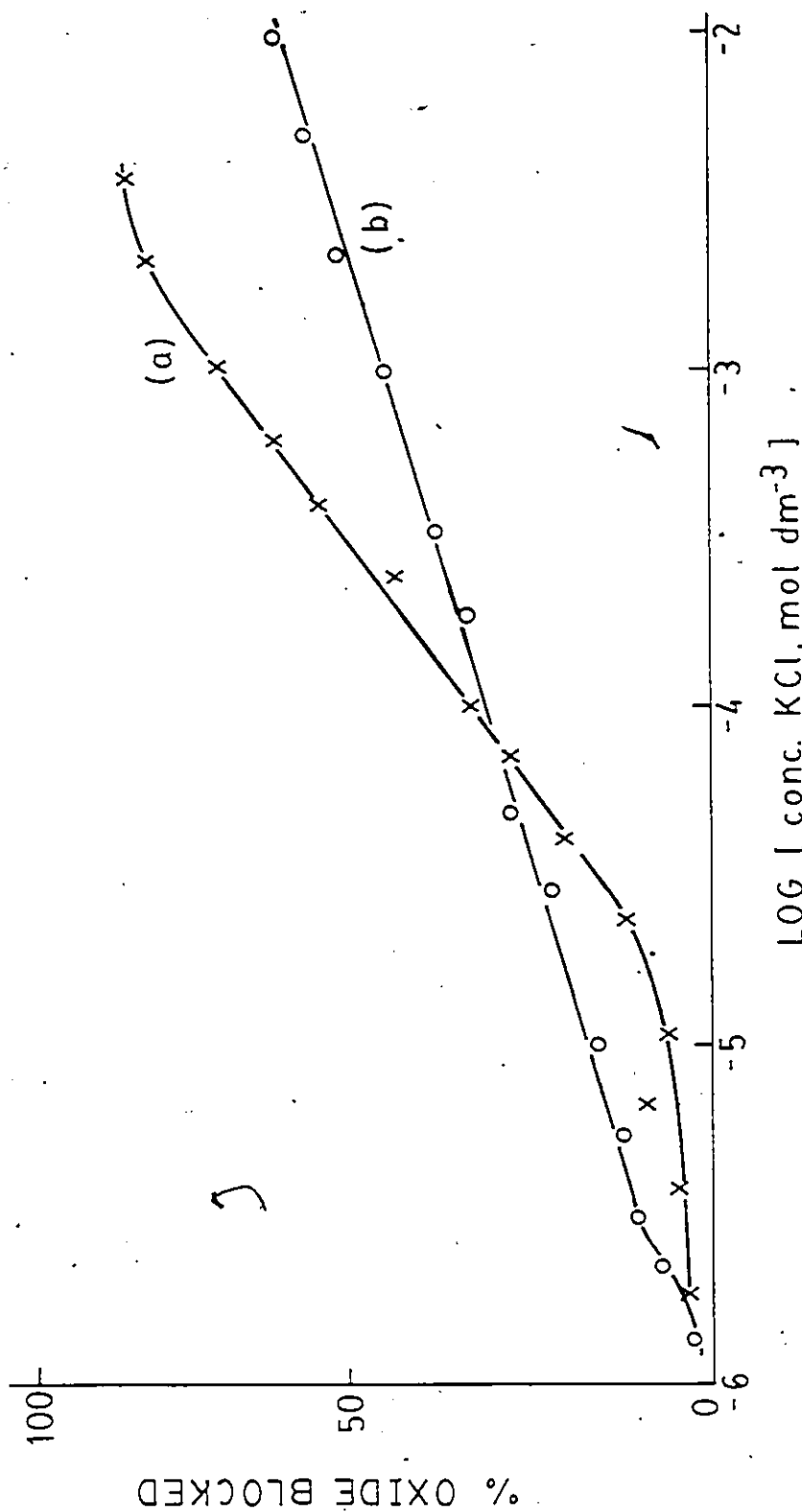


Fig. 59. Percentage of surface oxide blocked by  $\text{Cl}^-$  ion as a function of  $\log [\text{Cl}^-]$  at : (a) Ir in 6 M  $\text{H}_2\text{SO}_4$  in potential sweeps taken to 1.4 V,  $E_H$  at  $0.10 \text{ V s}^{-1}$  at 213 K and (b) Pt in 0.1 M  $\text{H}_2\text{SO}_4$  in potential sweeps taken to 1.4 V,  $E_H$  at  $0.10 \text{ V s}^{-1}$  at 298 K (ref. 289).

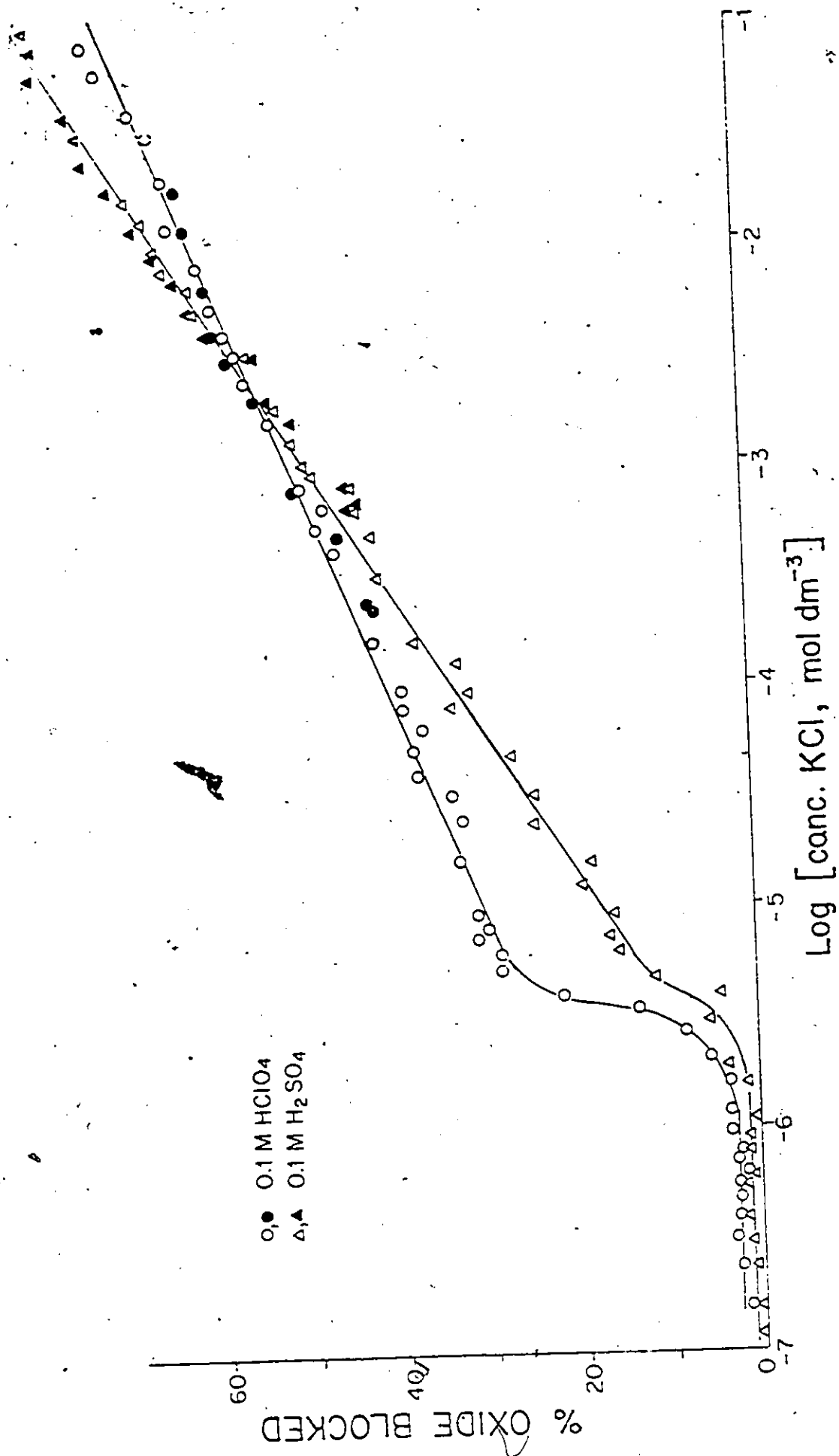


Fig. 60. Percentage of surface oxide blocked by  $\text{Cl}^-$  ions as a function of  $\log [\text{Cl}^-]$  in potential sweeps taken to 1.4 V,  $E_H$  at  $0.10 \text{ V s}^{-1}$  at 298 K. Supporting electrolyte as indicated in the figure.

blocking is already greater than 80% and tends to approach a 100% limit (note that determination of such small amounts of oxide, as 100% blocking is approached, becomes unavoidably rather inaccurate). Thus, the behaviour compares to that observed at 298 K, Fig. 60, where a linear dependence was found in the range  $10^{-5}$  -  $10^{-1}$  M  $\text{Cl}^-$ , with the % blocking being close to 75% at the higher concentrations.

The smaller range of linearity of % blocking with  $\log [\text{Cl}^-]$  at low temperatures, as well as the higher slope of the relation in Fig. 59, viz. 37% oxide blocked per decade of  $[\text{Cl}^-]$  at 213 K compared to 17% at 298 K (Fig. 60), can be accounted for in terms of the smaller coverage by oxide in the low temperature experiments, which makes the surface oxide formation more sensitive to blocking effects. Thus, in the absence of  $\text{Cl}^-$  ion, it is evident that in going from 298 K to 213 K the amount of oxide formed at a given  $E_a$  is substantially less at the lower T, e.g. there is 40% less oxide formed at 213 K for  $E_a = 1.4$  V,  $E_H$  with  $\tau_h = 0$  s. The latter effect is related to slowdown of the oxidation processes involved. Then, even though the  $E_a$  was the same for each of the series of experiments at 213 and 298 K, the total oxide deposited at a given  $E_a$  is not comparable. For this reason, as will be shown below, the results at 298 K for  $E_a = 1.4$  V,  $E_H$  are more comparable to those obtained at 213 K for  $E_a = 1.6$  V,  $E_H$ , at which potential the oxide coverage becomes similar to that at 1.4 V,  $E_H$  for a temperature of 298 K.

The most important difference between the two results (Figs. 59,60) is at low  $[\text{Cl}^-]$  where the blocking effects commence significantly. Thus, while at 298 K an S-shaped region is seen before the linear region becomes predominant, and was attributed to selective blocking of the early stages of OH monolayer formation, this S-shaped region is absent in the results at 213 K. However, comparison of the results at 298 K (Fig. 60) for  $\text{H}_2\text{SO}_4$  and

HClO<sub>4</sub> clearly shows that with increasing anion adsorption from the supporting electrolyte, the S-shaped region becomes less evident. Since the low T experiments have to be performed at high concentrations of H<sub>2</sub>SO<sub>4</sub>, which results in some initial blocking of the OH monolayer, it is reasonable that the S-shaped region is found to be absent in such solutions at 213 K.

The study of Cl<sup>-</sup> ion adsorption effects was extended to higher sweep-rates and higher oxide formation potentials, E<sub>a</sub>. Thus, for the case of  $s = 10 \text{ V s}^{-1}$  and E<sub>a</sub> = 1.6 V, E<sub>H</sub> the effect of Cl<sup>-</sup> ion on surface oxide formation at Pt is shown in Fig. 61, curve a. As can be seen, the linear dependence of % blocking on log [Cl<sup>-</sup>] is observed from 10<sup>-5</sup> - 10<sup>-1</sup> M, as at 298 K, with no limiting region being detectable. The % blocking at 10<sup>-1</sup> M was about 70%, compared to 75% at 298 K, and the slopes for both temperatures were similar, viz. 19% blocking decade<sup>-1</sup> of [Cl<sup>-</sup>] at 213 K, compared to 15% at 298 K. However, as mentioned earlier, the S-shaped region at low [Cl<sup>-</sup>] was absent at 213 K, as expected.

It was proposed earlier that the difference between the extent of the linear dependence of oxide blocking in log [Cl<sup>-</sup>] at 213 K and 298 K (integrated up to E<sub>a</sub> = 1.4 V, E<sub>H</sub>) was due to the smaller oxide coverage obtained at a given E<sub>a</sub> at low T. The results of Fig. 61, curve a, obtained by integration up to 1.6 V, E<sub>H</sub>, confirm this conclusion, since under the latter conditions the oxide coverage is increased and the behaviour becomes closer to that observed at 298 K for a similar oxide coverage. This stresses the importance of comparing results on the basis of total oxide coverage initially present at the surface.

The study of Cl<sup>-</sup> ion adsorption effects at higher sweep-rates, ca. 10 V s<sup>-1</sup> was also carried out in order to determine the influence of this ion on the reversibility of the early stages of Pt surface oxide formation.

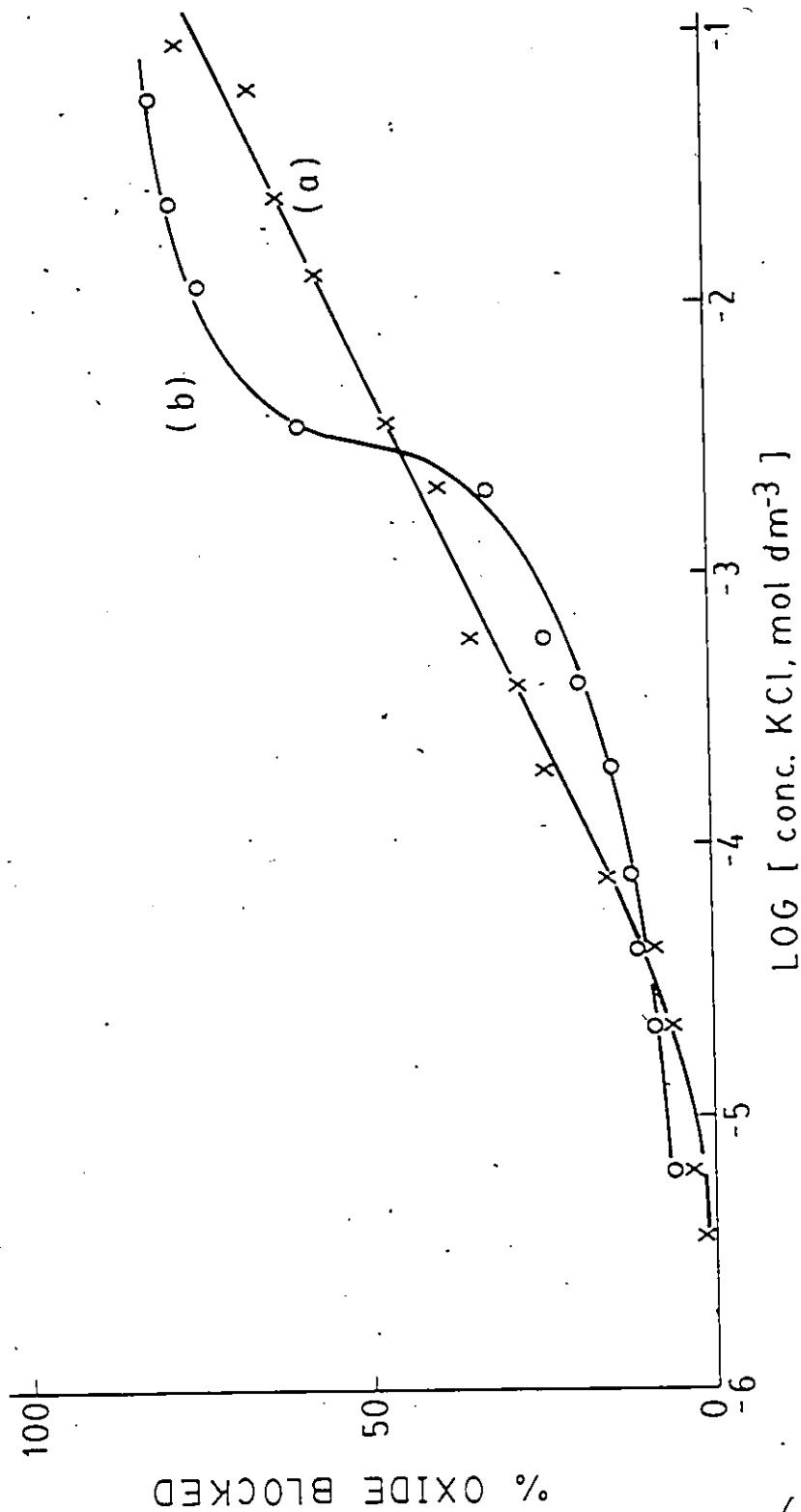


Fig. 61. Percentage of surface oxide blocked by  $\text{Cl}^-$  ions as a function of  $\log [\text{Cl}^-]$  at Ir in 5 M  $\text{H}_2\text{SO}_4$  in potential sweeps taken to 1.6 V,  $E_H$  at  $10 \text{ V s}^{-1}$  at 213 K: (a) total oxide charge measured up to 1.6 V,  $E_H$ ; (b) reversible reduction component charge.

As discussed in Chapter 1 (page 10), the early stages of monolayer oxide formation and reduction at Pt, viz.  $\theta_{OH} < 15\%$ , are almost reversible as was shown by Angerstein-Kozłowska et al. (19) in experiments performed at low T and high s, and also by Conway et al. (293) by means of reflectance measurements.

By increasing the sweep-rate to  $10 \text{ V s}^{-1}$ , it was possible to distinguish clearly the reversible component of reduction of the early stages of surface oxide formation at 213 K, as shown in Fig. 62a-e. As the concentration of  $\text{Cl}^-$  ion was increased, the blocking effect of surface oxide formation, discussed above (Fig. 61) becomes apparent. However, the effect of  $\text{Cl}^-$  ion on the reversible component of oxide reduction (Fig. 62a-e) is rather surprising, since it was expected that  $\text{Cl}^-$  ion would tend to block this process already at low  $[\text{Cl}^-]$  by favoring the formation of the irreversible component through increased rate of turnover.

However, as can be seen in Figs. 62a-e, and as analyzed quantitatively in Fig. 61, curve b,  $\text{Cl}^-$  ion appears to have only a small effect on the reversible component up to  $[\text{Cl}^-] = 10^{-3} \text{ M}$ ; at somewhat higher concentrations, this reversible component becomes blocked over a relatively small range of increased concentration. This leads to the conclusion that, at 213 K, the rate of turnover is slow enough not to be influenced drastically by the presence of adsorbed  $\text{Cl}^-$  ions.

Attempts were also made to study the reversibility of the early stage of oxidation in  $\text{HClO}_4$ , since  $\text{ClO}_4^{2-}$  adsorbs much less strongly than  $\text{HSO}_4^-$  and thus should allow us to observe the reversible component much better. While this is the case (Fig. 63a-c), 6 M  $\text{HClO}_4$  solutions tend to freeze at 213 K, making it impossible to carry out experiments over a long period of time. Nevertheless it was possible to observe the reversible reduction of

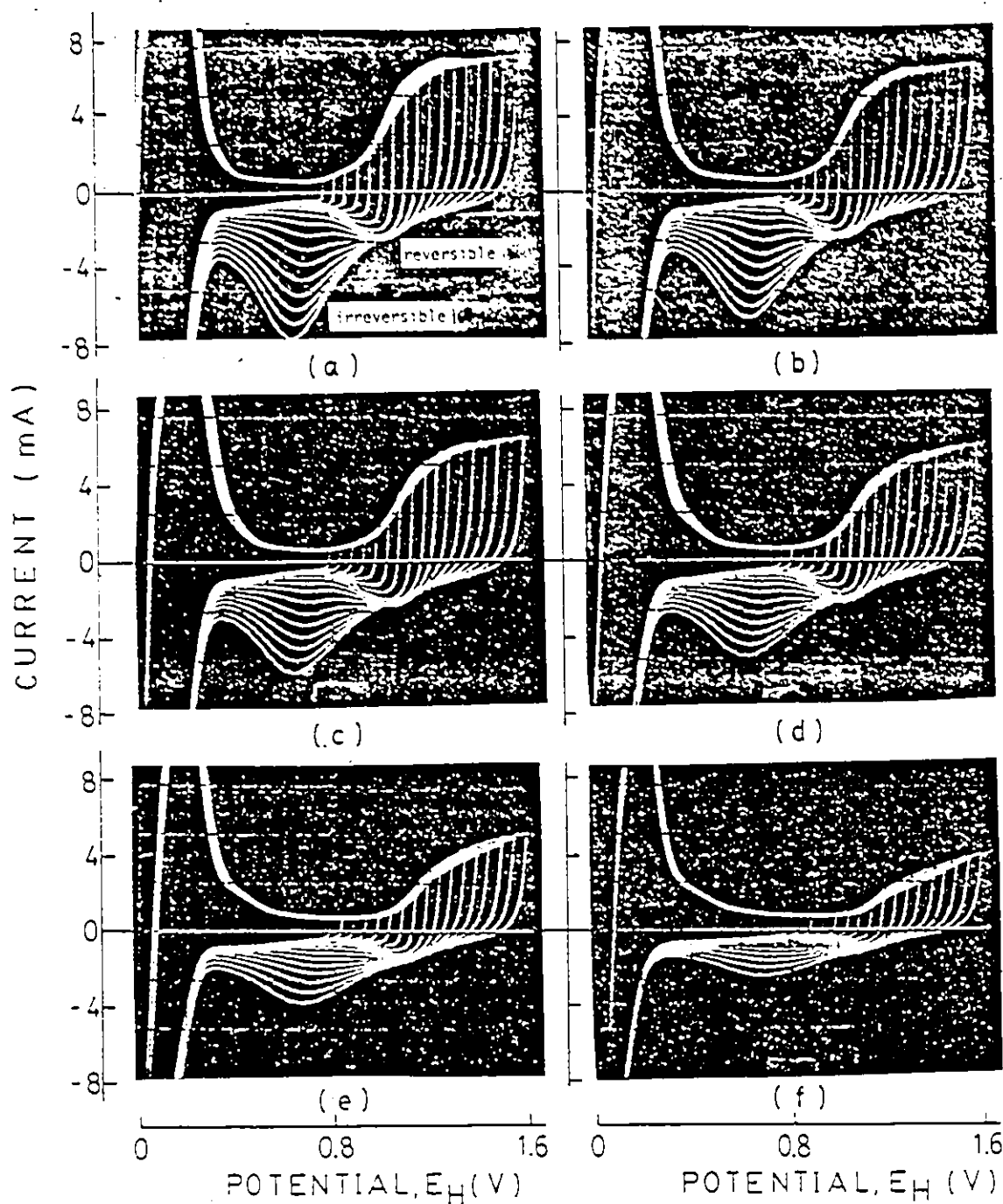


Fig. 62. Series of cyclic-voltammetry  $i$  vs  $V$  profiles for Ir in 5 M H<sub>2</sub>SO<sub>4</sub> +  $x$  KCl at 10 V s<sup>-1</sup> at 213 K: (a) 0; (b)  $4 \times 10^{-5}$ ; (c)  $8 \times 10^{-5}$ ; (d)  $4 \times 10^{-4}$ ; (e)  $4 \times 10^{-3}$  and (f)  $6 \times 10^{-2}$  M KCl.

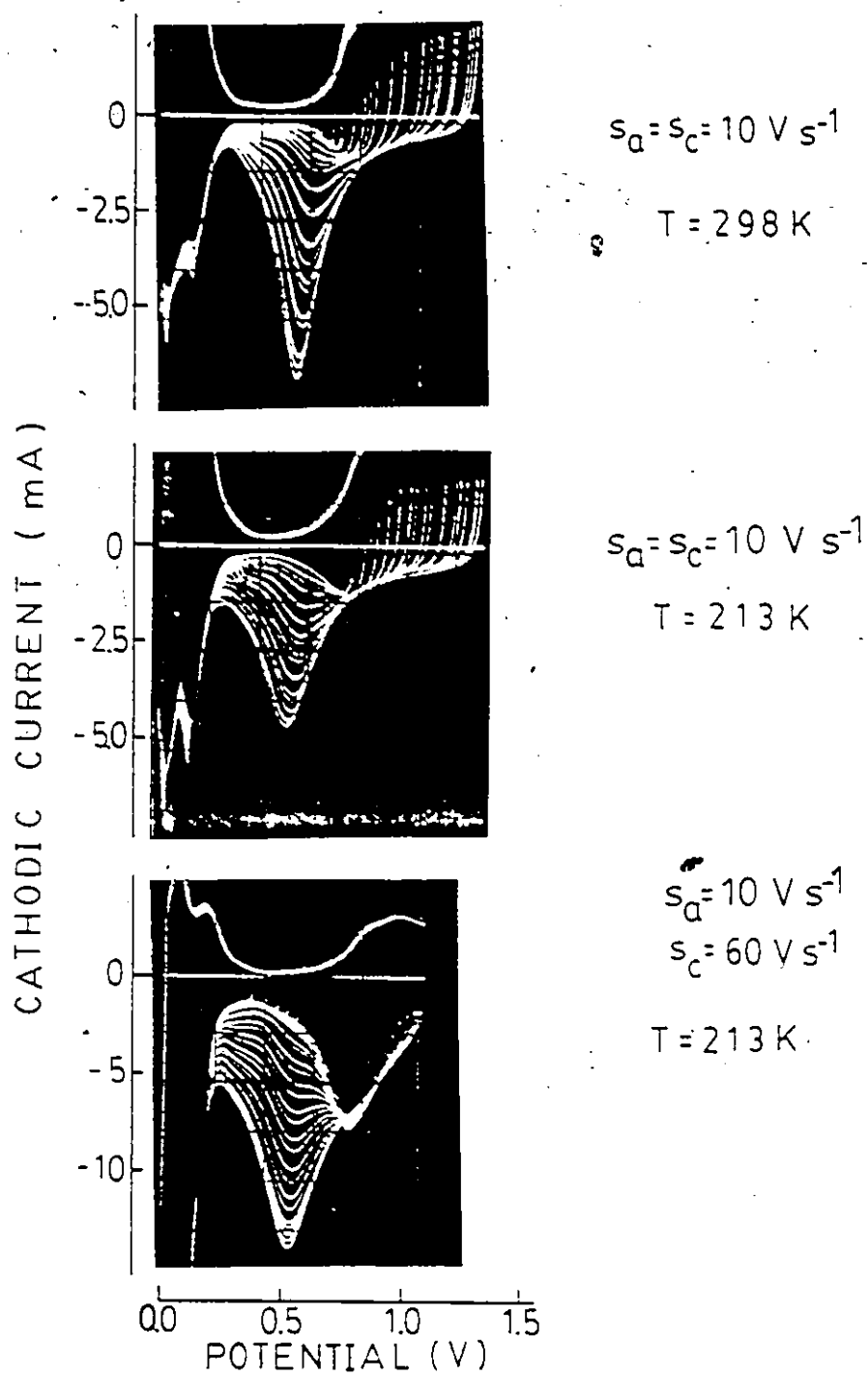


Fig. 63. Cyclic-voltammetry  $i$  vs  $V$  profiles for Pt in 6 M HClO<sub>4</sub>, conditions as described in the figure.

oxide species at low coverages in experiments carried out before the solution froze extensively.

Figs. 63a,b compare the  $i$  vs  $V$  profiles in 5 M  $\text{HClO}_4$  at 298 K and 213 K, at  $10 \text{ V s}^{-1}$ . As can be seen, there is less oxide at 213 K, but the reversible component is more evident at the latter temperatures. By increasing the cathodic sweep-rate to  $60 \text{ V s}^{-1}$ , while keeping the anodic sweep-rate constant, the main (irreversible) oxide reduction peak could be seen, Fig. 63c, to consist of two components, as also found for the case of Au (1). In the latter Fig., the  $E_a$  was made less positive so as to increase the relative amount of reversible oxide and thus to make it more easily distinguishable.

#### 6.3.1.1. Calculation of the Interaction Parameter, $g$

The blocking effect of  $\text{Cl}^-$  ion and of halide ions in general, was treated in a quantitative way by Conway and Novak (289) in terms of competitive adsorption isotherms modified by interaction effects.

From their treatment of this problem, a general equation for the calculation of the interaction parameter,  $g$ , was obtained.

By using an isotherm of the form:

$$\frac{\theta}{1-\theta} = K \exp (VF/RT) \exp (-g\theta) \cdot C \quad (6.2)$$

and relating two halide ion ( $X^-$ ) coverages through (6.2), such as  $C_{X^-} = 0.75$  and  $C_{X^-} = 0.25$ , the equation

$$g = 2 \ln \frac{C_{X^-,0.75}}{C_{X^-,0.25}} - 2 \ln 9 \quad (6.3)$$

was obtained which allows the interaction parameter,  $g$ , to be calculated if  $C_{X^-}$  is known for both coverages.

Referring back to Figs. 59 and 60, it can be assumed, as a first approximation, that the coverage of  $X^-$  is equal to the % oxide blocked and, as the relation is linear in that % blocking range, the fact that  $\text{HSO}_4^-$  is

also adsorbed does not interfere with the results.

On applying such a treatment to the present results and to those of the above authors, the following results are obtained:

| T (K) | $E_a$ (V, $E_H$ ) | g     | $gRT_{298\text{ K}}$ (KJ mol <sup>-1</sup> ) | $gRT_{213\text{ K}}$ | $\gamma$ |
|-------|-------------------|-------|----------------------------------------------|----------------------|----------|
| 298   | 1.4               | 10.41 | 26                                           | 18                   | = 0      |
| 213   | 1.4               | 1.97  | 5                                            | 3.5                  | ?        |
| 213   | 1.6               | 7.61  | 19                                           | 13.5                 | = 0      |

Again, as described previously, it is seen that the results at 298 K for  $E_a = 1.4\text{ V}, E_H$  are more similar to those at 213 K derived for  $E_a = 1.6\text{ V}, E_H$  than to those obtained at 213 K for  $E_a = 1.4\text{ V}, E_H$ . The latter results are qualitatively more similar to those obtained for  $\text{Br}^-$  and  $\text{I}^-$  at 298 K. This similarity can also be seen in the shape of the relation between % blocking and  $\log [\text{Cl}^-]$ , where, while the % blocking vs  $\log [\text{Cl}^-]$  relation at low T for  $E_a = 1.6\text{ V}, E_H$  is almost like that at 298 K, corresponding behaviour at 213 K with  $E_a = 1.4\text{ V}, E_H$  tends to be similar to the S-shaped curves observed at 298 K for  $\text{Br}^-$  and  $\text{I}^-$  surface-oxide blocking at Pt, which do not present linear regions and indicate the attainment of 'ca. 100% coverage.

#### 6.3.2. Growth of Pt oxide at Constant Potential in the Presence of $\text{Cl}^-$ Ion

Measurements of the growth of surface oxide layers at constant potential normally yield interesting information on the growth mechanism and on the "ageing" processes in the film, i.e. with regard to transition between reversible and irreversible behaviour.

In the case of Pt, as is now well known (19), the early stages ( $\theta_{\text{OH}} < 15\%$ ) of surface oxide formation behave almost reversibly in terms of reduction of the deposited OH species. As  $\theta_{\text{OH}}$  increases, a place-exchange process is assumed to be responsible for the cooperative turnover of the Pt/OH layer which leads to irreversibility in the subsequent reduction of

the restructured oxide film.

When the oxide is formed at constant potential, the turnover process, which is relatively slow, has more time to take place. As shown by Conway et al. (19), as the growth time increases, the amount of surface oxide which is irreversibly reduced becomes larger.

Since one of the effects of adsorbed anions on surface oxide formation at Pt is to assist the turnover process, presumably by introducing a lateral repulsive interaction between the adsorbed anion and neighboring OH surface dipoles, it was considered to be of interest to evaluate the effects of  $\text{Cl}^-$  ion on the kinetics of growth of Pt oxide at constant potential as a function of the  $\text{Cl}^-$  ion concentration. First, however, we shall describe the kinetics of Pt surface oxide growth in the absence of  $\text{Cl}^-$  ion.

As described in section 6.2, a special potential-time programme was devised for this work (Fig. 58).

#### 6.3.2.1. Kinetics of Pt Oxide Growth in the Absence of $\text{Cl}^-$ Ion

The growth of Pt oxide at constant potential in 0.5 M  $\text{H}_2\text{SO}_4$ , in the absence of  $\text{Cl}^-$  ion, obeys a direct logarithmic law in growth time,  $\tau_h$ , as shown in Fig. 64a,b for the range  $\tau_h = 10^{-3}$  to 100 s, for various anodic growth potentials,  $E_a$ . The relation can be expressed by an equation of the form

$$q_t = A \log t + q_{t=0} \quad (6.4)$$

where  $q_{t=0}$  is the charge in a multisweep experiment at high  $s$  and  $A$  is a constant. Both  $A$  and  $q_{t=0}$  depend on  $E_a$ , so that as  $E_a$  increases,  $A$  and  $q_{t=0}$  also increase. The dependence of  $A$  on  $E_a$  will be examined in more detail below.

It can also be observed in a qualitative way (Fig. 65a) that, as the growth time increases when  $E_a$  is low (ca. 0.9 V), it is the relative

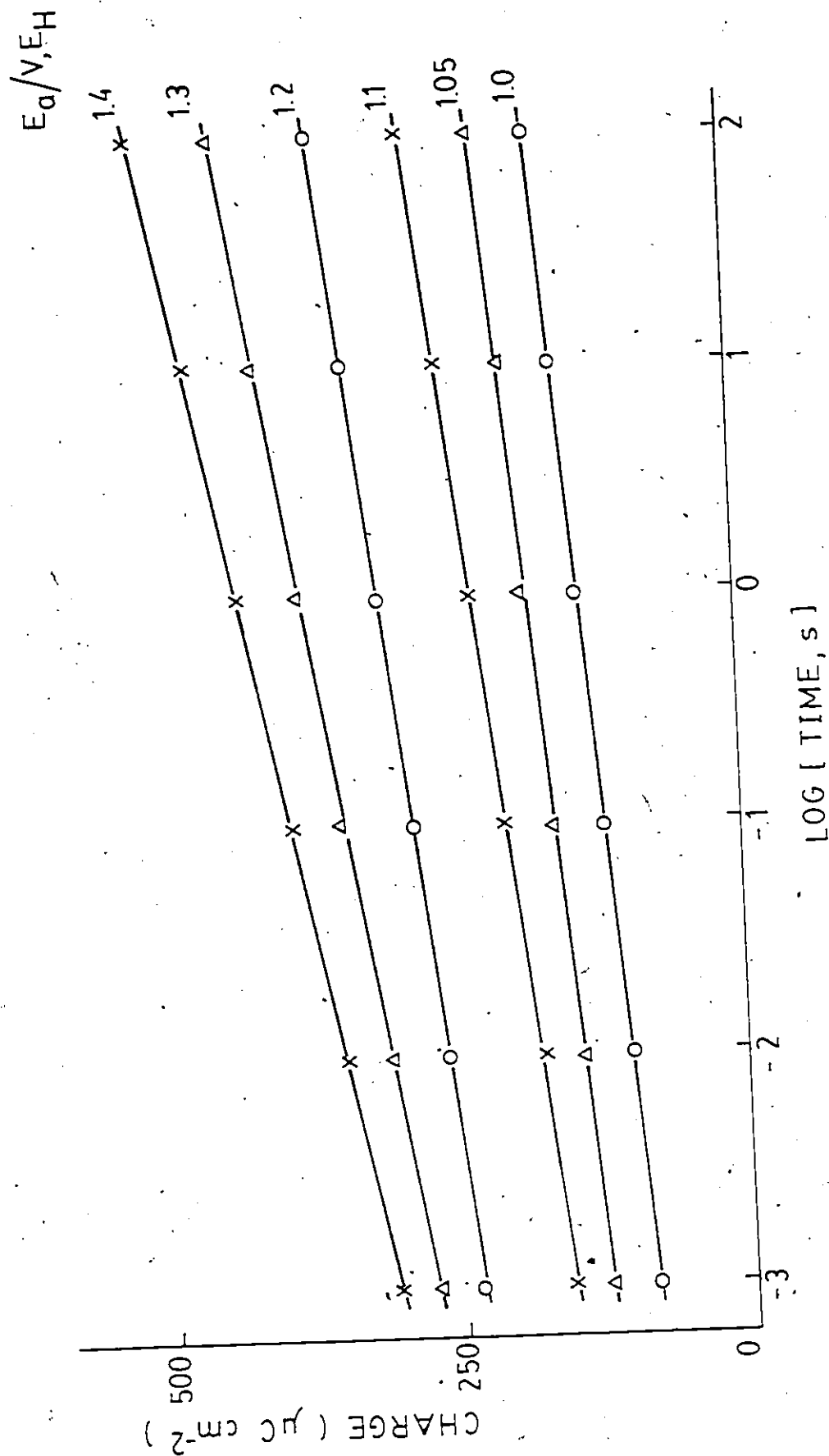


Fig. 64a. Oxide charge as a function of log (time) for growth of Pt oxide at constant potential,  $E_a$ , as indicated in the figure.

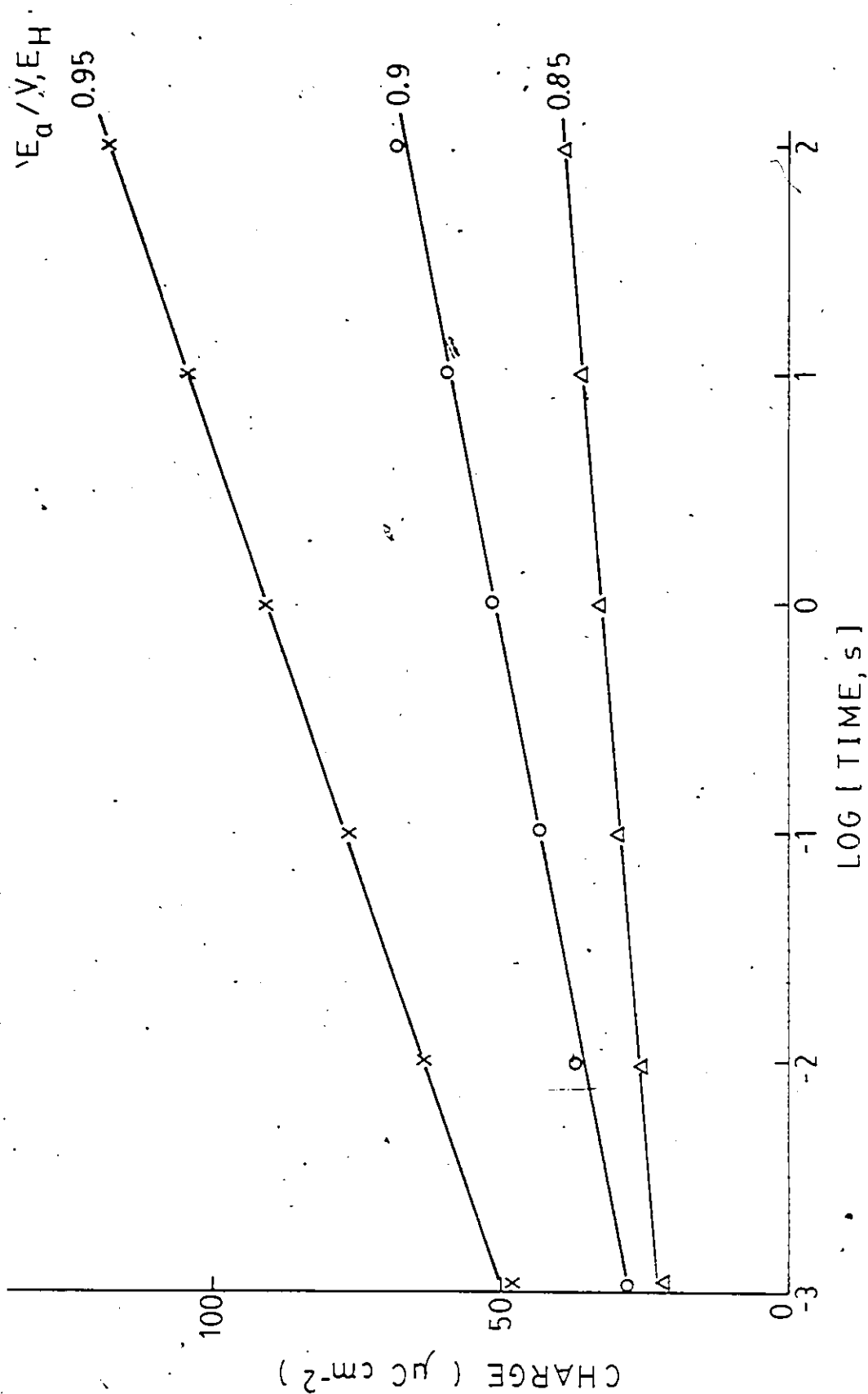


Fig. 64b. Oxide charge as a function of log (time) for growth of Pt oxide at constant potential,  $E_a$ , as indicated in the figure.

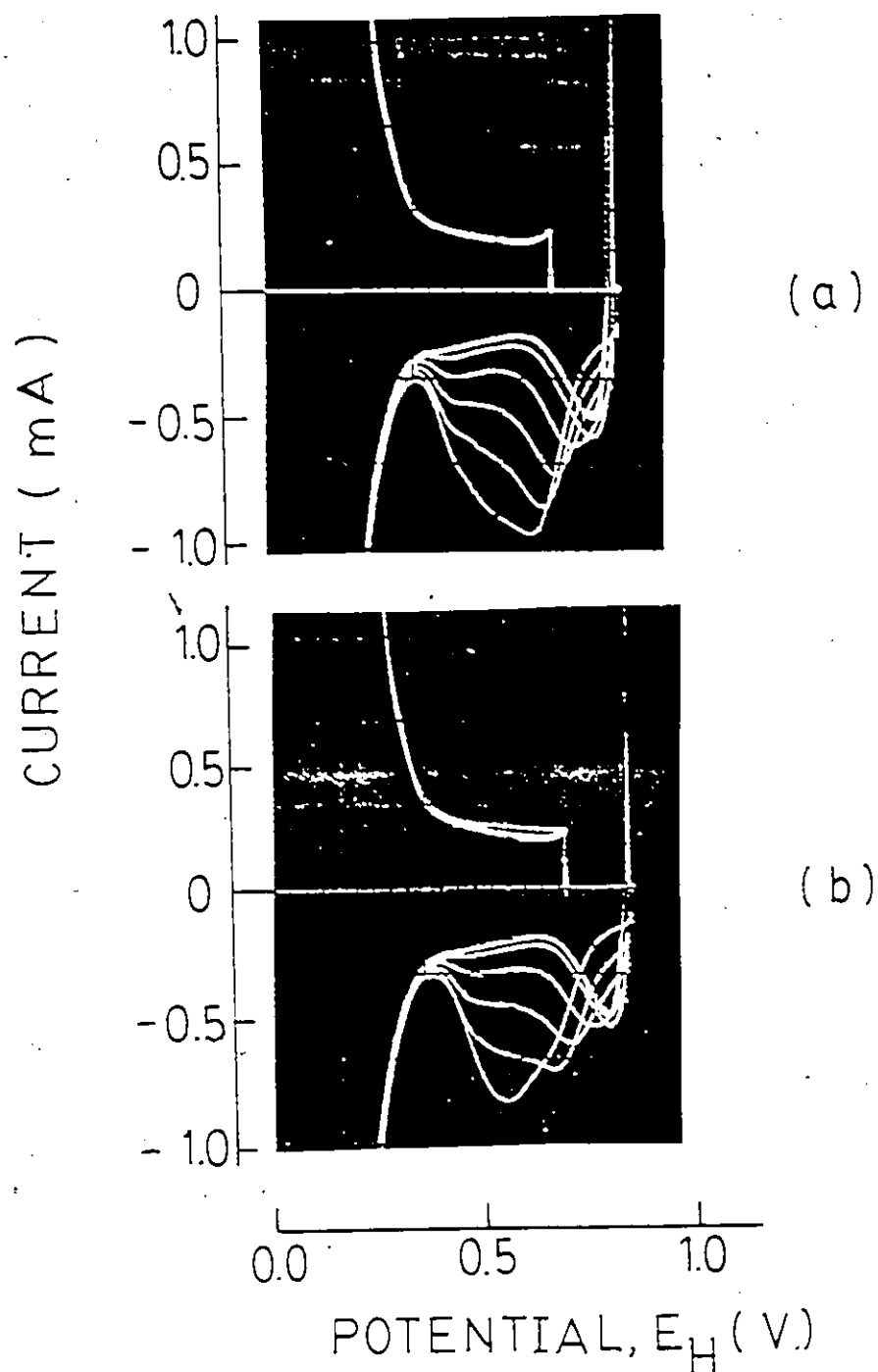


Fig. 65. Cyclic-voltammetry  $i$  vs  $V$  profiles for Pt in 0.5 M  $H_2SO_4$ , 298 K, after various  $\tau_h$ : 0,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$ , 1, 10 and 100 s, at  $E_a = 0.9$  V,  $E_H$ ; (a) 0.5 M  $H_2SO_4$ ; (b) 0.5 M  $H_2SO_4$  +  $1 \times 10^{-6}$  M KCl.

amount of the more irreversibly reduced component that increases with time. This observation is in agreement with previously published results by various authors (18,19,27,29,30) on this point.

#### 6.3.2.2. Kinetics of Pt Oxide Growth in the Presence of $\text{Cl}^-$ Ion

When  $\text{Cl}^-$  ion is added to the supporting electrolyte, i.e. 0.5 M  $\text{H}_2\text{SO}_4$ , there are two immediately apparent effects, as described previously: H deposition is blocked and shifted towards less positive potentials and surface oxide formation is also blocked by the competitive adsorption of  $\text{Cl}^-$  ion.

In addition, however, as the oxide grows at constant potential in the presence of  $\text{Cl}^-$  ion, it becomes qualitatively apparent (Fig. 65b) that  $\text{Cl}^-$  adsorption leads to preferential formation of the more irreversibly reduced component(s) (compare Figs. 65a and 65b), i.e.  $\text{Cl}^-$  increases the extent or rate of turnover of the deposited OH/O species.

Fig. 66 shows a series of  $i$  vs  $V$  profiles for various increasing  $\text{Cl}^-$  ion concentrations (0 to  $10^{-1}$  M), for oxide growth at  $E_a = 1.1$  V,  $E_H$  for various  $\tau_h$  ( $10^{-3}$  to 100 s), which clearly demonstrate the progressively increasing blocking of oxide formation as the  $\text{Cl}^-$  concentration increases, together with favored growth of the irreversible component. Thus, the apparent peak potential,  $E_p$ , determined at the capacitance maximum for oxide reduction is displaced in the negative direction as shown below for  $\tau_h = 100$  s;

| $[\text{Cl}^-]$ M | $E_p$ (V, $E_H$ ) | $\theta_{\text{OH}}$ |
|-------------------|-------------------|----------------------|
| 0                 | 0.750             | 1.3                  |
| $10^{-5}$         | 0.750             | 0.93                 |
| $10^{-4}$         | 0.741             | 0.79                 |
| $10^{-3}$         | 0.733             | 0.50                 |
| $10^{-2}$         | 0.672             | 0.19                 |
| $10^{-1}$         | 0.568             | 0.08                 |

together with the oxide coverage evaluated with respect to an  $\theta_{\text{OH}}$  for monolayer

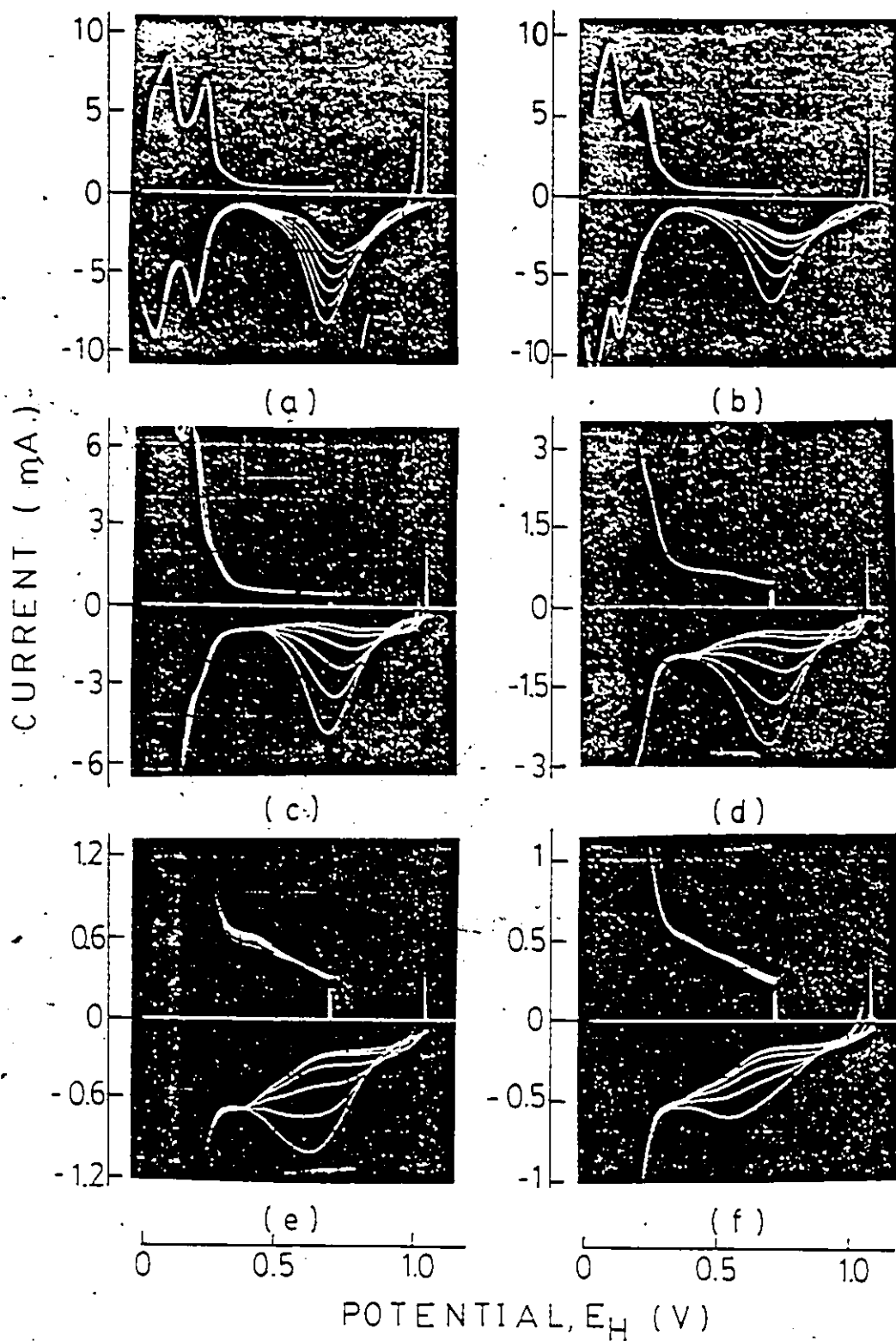


Fig. 66. Series of cyclic-voltammetry  $i$  vs  $V$  profiles for Pt in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 298 K, for various  $\tau_h$ : 0, 10<sup>-3</sup>, 10<sup>-2</sup>, 10<sup>-1</sup>, 1, 10 and 100 s at  $E_a = 1.1$  V,  $E_H$ , for various Cl<sup>-</sup> concentrations: (a) 0; (b) 10<sup>-5</sup>; (c) 10<sup>-4</sup>; (d) 10<sup>-3</sup>; (e) 10<sup>-2</sup> and (f) 10<sup>-1</sup> M.

charge taken as  $210 \mu\text{C cm}^{-2}$ .

This effect of  $E_p$  becoming less positive with diminishing  $\theta_{\text{OH}}$  due to  $\text{Cl}^-$  adsorption is even more striking if it is noted that as the concentration of  $\text{Cl}^-$  ion increases, the coverage of OH species becomes substantially decreased. Contrarily, in the absence of  $\text{Cl}^-$ , as discussed by Angerstein-Kozłowska et al. (19), the  $E_p$  normally appears at more positive potentials with decreasing surface oxide coverage, i.e. as reduction becomes less irreversible.

The presence of  $\text{Cl}^-$  ion does not seem, however, to change the direct logarithmic dependence of extent of growth on time, as is shown in Fig. 67, where it can be observed that as the concentration of  $\text{Cl}^-$  ion increases the slopes of the lines decrease. Notice that for low  $\text{Cl}^-$  concentrations and small  $\tau_h$ 's the charge readings appear to be too high; this is for experimental reasons as discussed in section 6.2.

However, when this graphical approach is applied to the data obtained at all the  $E_a$  studied, viz. in the range 0.85 - 1.4 V,  $E_H$ , the slopes of the charge vs  $\log [\text{Cl}^-]$  lines behave in a rather interesting way as illustrated in Fig. 68. Thus, two types of behaviour are observed: first, for  $[\text{Cl}^-] = 0, 10^{-6}, 10^{-2}$  and  $10^{-1}$  M, the values of the slopes increase with increasing  $E_a$  but after a narrow S-shaped transition region, the relation becomes linear. The curves for  $[\text{Cl}^-] = 10^{-2}$  and  $10^{-1}$  M in Fig. 68 are obviously displaced towards higher potentials due to the strong blocking effect of  $\text{Cl}^-$  at these two high concentrations for which the onset of oxide formation has been displaced to 1.0 and 1.05 V,  $E_H$ , respectively.

Second, although it should be expected that the results for  $[\text{Cl}^-] = 10^{-5}, 10^{-4}$  and  $10^{-3}$  should fill the gap between the two extreme types of behaviour mentioned above and behave in a similar way with respect to.

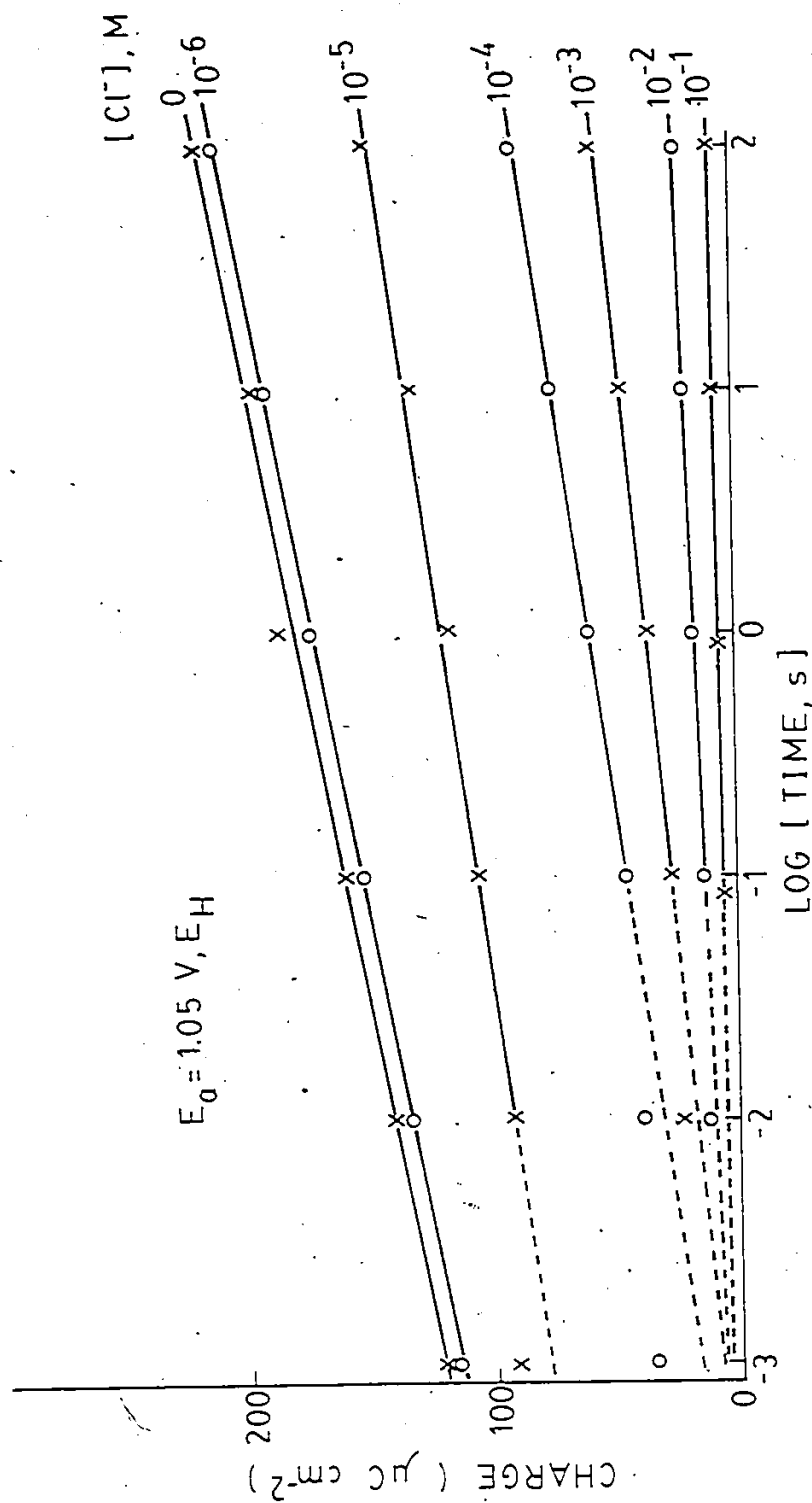


Fig. 67. Oxide charge as a function of log (time) for growth of Pt oxide at constant potential,  $E_0$ , for various  $\text{Cl}^-$  concentrations, as indicated in the figure.

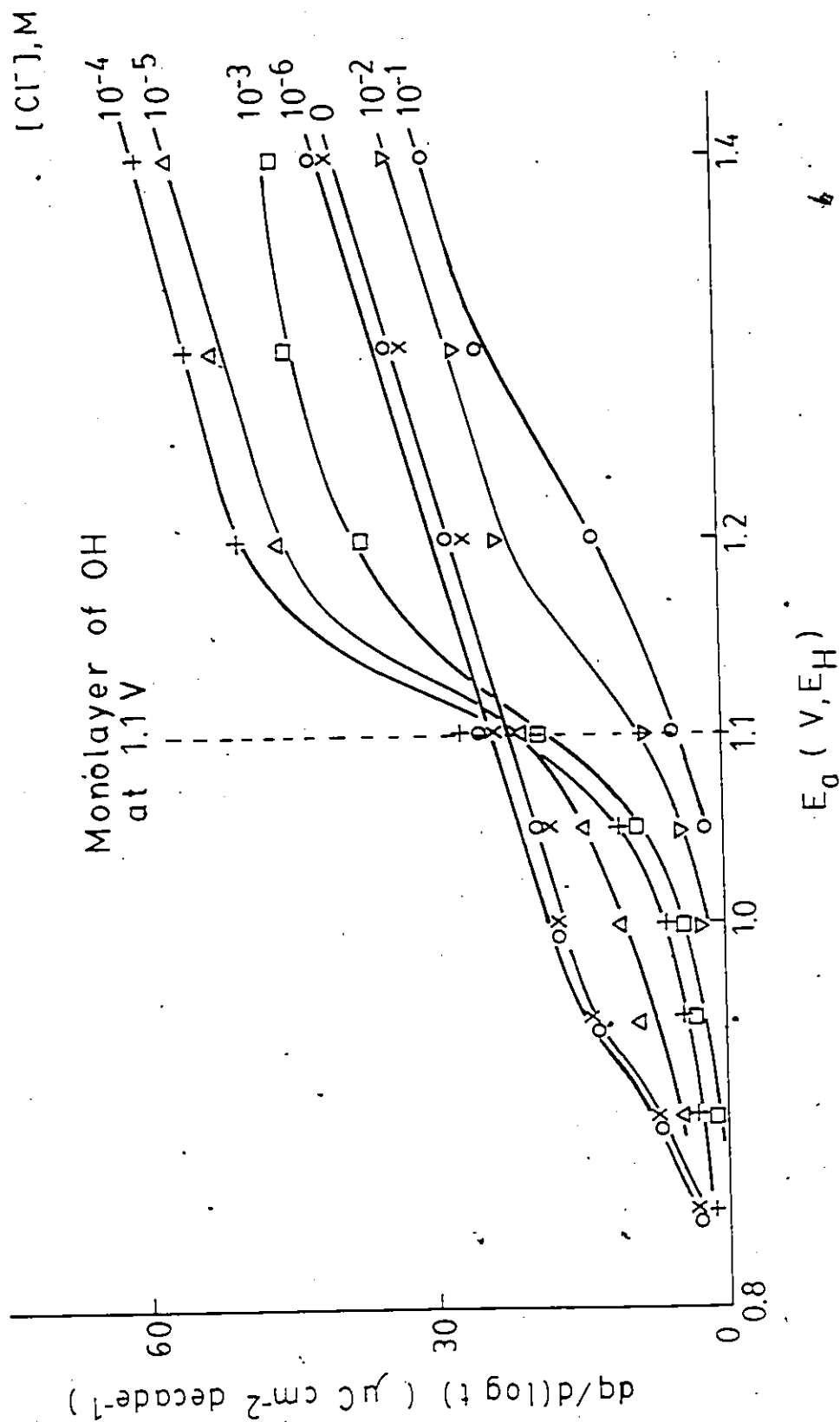


Fig. 68.  $dq/d(\log t)$  as a function of the growth potential,  $E_a$ , for various  $\text{Cl}^-$  concentrations, as indicated in the figure.

increasing  $E_a$ , this is only observed, to a certain extent, up to potentials  $E_a \leq 1.05 \text{ V}, E_H$ , quite close to the potential at which the monolayer of OH species is completed at Pt in the absence of  $\text{Cl}^-$ . At  $E_a > 1.05 \text{ V}, E_H$ , however, the value of  $dq/d(\log t)$  appears to be higher than expected, although the S-shaped region, followed by the linear region, is still maintained.

It is our opinion that the abnormally high slopes observed when  $E_a > 1.05 \text{ V}, E_H$  and  $[\text{Cl}^-] = 10^{-3}, 10^{-4}$  and  $10^{-5} \text{ M}$  are due to competition between oxide growth and oxide blocking by means of  $\text{Cl}^-$  ion adsorption. Thus, at low  $\text{Cl}^-$  concentrations, viz.  $10^{-5} - 10^{-3} \text{ M}$  and with  $E_a < 1.05 \text{ V}, E_H$ , the  $\text{Cl}^-$  ion blocks the oxide formation in the expected way. However, when  $E_a > 1.1 \text{ V}, E_H$ , then the oxide formed on the surface competes actively with the adsorbed  $\text{Cl}^-$  ion, probably reducing the coverage of the latter and thus increasing the growth rate, i.e. the  $dq/d(\log t)$  value. It is evident from the charge vs  $\log t$  plots that at longer  $\tau_h$  and high  $E_a > \text{ca. } 1.1 \text{ V}, E_H$ , the lines corresponding to the above  $\text{Cl}^-$  concentrations tend to join with the one corresponding to the absence of  $\text{Cl}^-$  ion.

On the other hand, for high  $\text{Cl}^-$  concentrations, viz.  $10^{-2} - 10^{-1} \text{ M}$ , the effect of  $\text{Cl}^-$  ion is strong enough that the electrodeposition of oxide cannot compete successfully (at least at the maximum  $E_a$  attained, viz.  $1.4 \text{ V}, E_H$ ) with the  $\text{Cl}^-$  blocking effect and hence the curves behave as expected.

The change in behaviour around  $1.1 \text{ V}, E_H$  was anticipated, in a sense, since the previous work had indicated that  $\text{Cl}^-$  ion blocks selectively the formation of the OH monolayer before starting to block the formation of oxide in a higher state of oxidation. The transition is even more evident when the % oxide blocked is plotted as a function of  $\log [\text{Cl}^-]$ , for various  $E_a$  and for two  $\tau_h$  values, as shown in Figs. 69 and 70.

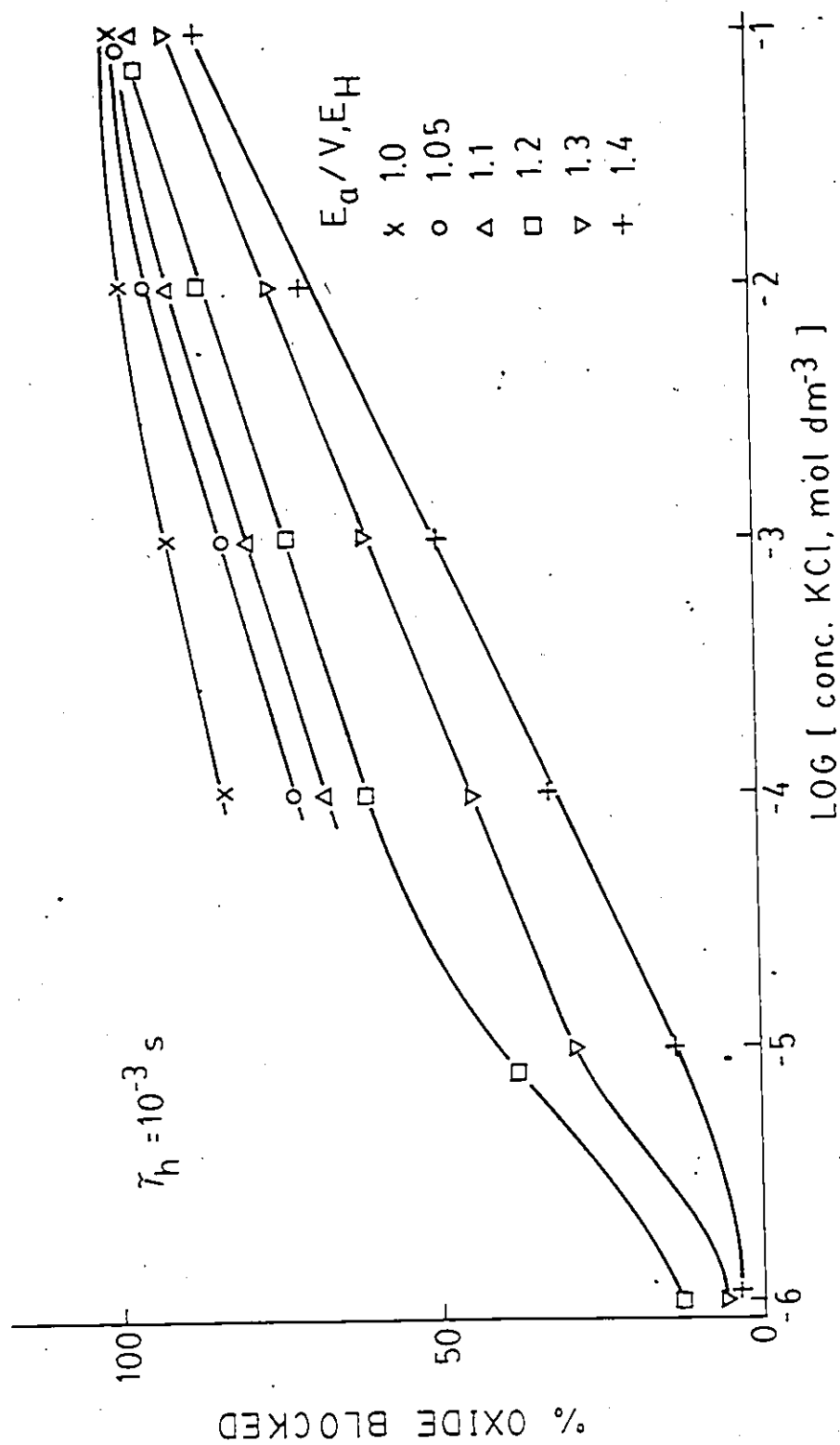


Fig. 69. Percentage of surface oxide blocked by  $\text{Cl}^-$  ions as a function of  $\log [\text{Cl}^-]$  for a growth time,  $\tau_h$ , of  $10^{-3}$  s, for various growth potentials,  $E_a$ , as indicated in the figure.

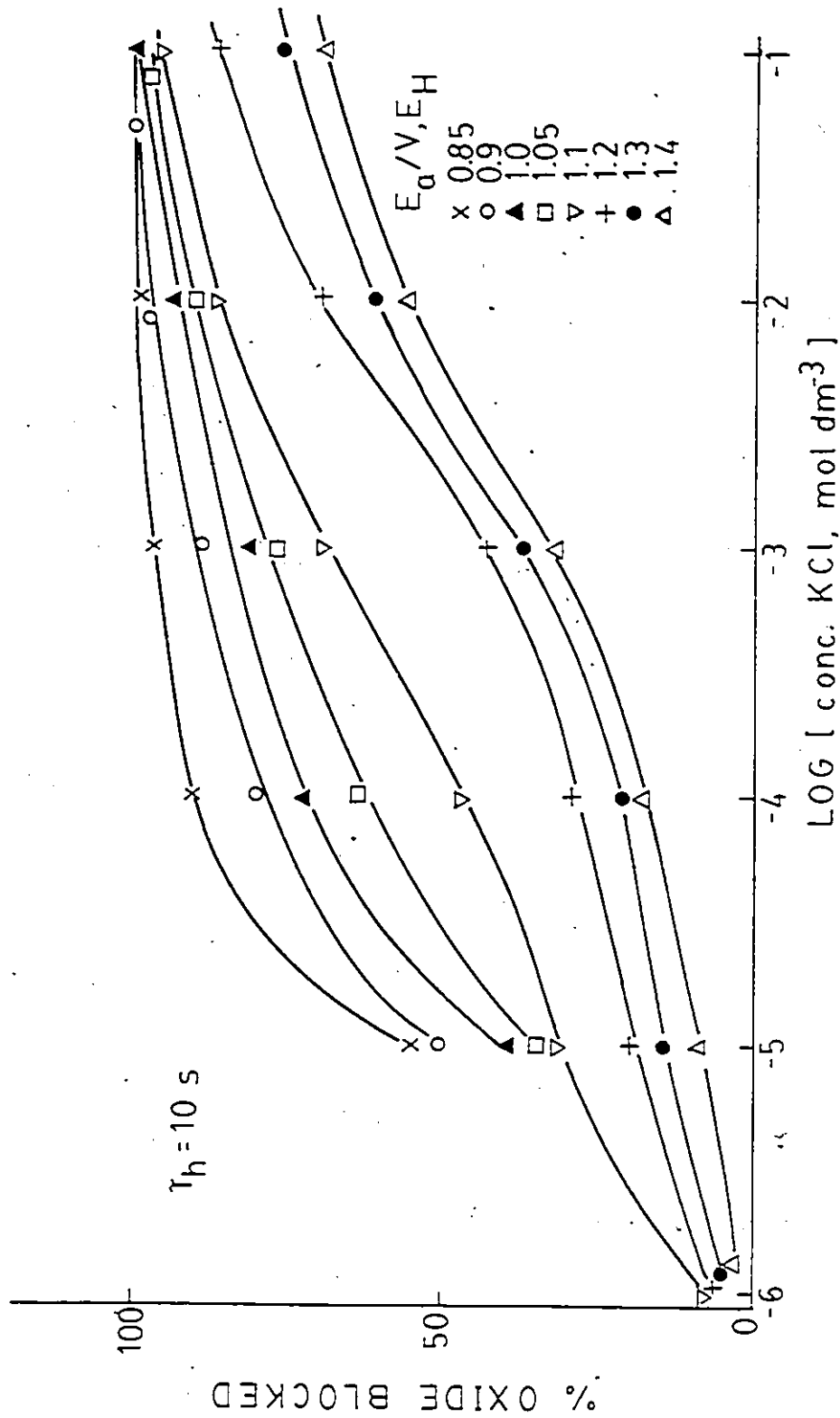


Fig. 70. Percentage of surface oxide blocked by  $\text{Cl}^-$  ions as a function of  $\log \text{Cl}^-$  for a growth time,  $\tau_h$ , of 10 s, for various growth potentials,  $E_a$ , as indicated in the figure.

The behaviour shown in Fig. 69, is similar to that found in the multisweep studies of Conway and Novak (289) and shows a linear-log region for the blocking effect which starts to curve and reaches close to 100% blocking at high  $[Cl^-]$  for  $E_a$  values  $< 1.1 V, E_H$  (compare with Figs. 59,60).

When the results for a longer growth time are plotted, as in the case of Fig. 70 for  $\tau_h = 10$  s, then the linear region disappears for  $E_a > 1.1 V, E_H$ , indicating again that some other component is entering the picture. Notice that the curves for  $E_a = 1.2, 1.3$  and  $1.4 V, E_H$ , appear to have become bent down in the range  $10^{-5} - 10^{-3}$  M, the same range where the higher  $dq/d(\log t)$  values were found (Fig. 68). This bending effect is consistent with the higher slopes observed in Fig. 68 and thus indicates less blocking than expected on the basis of comparison with the behaviour in the absence of  $Cl^-$  ion (Fig. 64).

#### 6.4. CONCLUSIONS

In conclusion, it can be said that despite certain limitations of the experimental procedure available for study of  $Cl^-$  ion effects on surface oxide growth and reversibility, some clear and interesting new effects have been demonstrated.  $Cl^-$  ion, as expected, blocks the formation of Pt surface oxide and reduces the rate of growth at constant potential, except for conditions such as high anodic potentials and low  $[Cl^-]$ , where it appears that the oxide being formed is able to displace  $Cl^-$  from the surface and thus an unexpectedly high rate of growth is observed. At the same time,  $Cl^-$  ion favours the growth of the irreversible component of surface oxide reduction by probably increasing the rate of turnover.

On the other hand, the effect of  $Cl^-$  ion on surface oxide formation at Pt under cyclic conditions at 213 K is similar to that observed at 298 K in that a linear relation is found between % oxide blocked and  $\log [Cl^-]$ .

However, it is clear that, for comparative purposes, results should be referred to the same initial oxide coverage. At 213 K, the behaviour of  $\text{Cl}^-$  ion at low oxide coverages resembles that of  $\text{Br}^-$  and  $\text{I}^-$  at higher oxide coverages at 298 K. Using the treatment by Conway and Novak (289), it is possible to calculate a value for the interaction parameter,  $g$ , based on the adsorption isotherms.

The reversible component of surface oxide formation at Pt is clearly distinguishable at 213 K in 6 M  $\text{H}_2\text{SO}_4$  and even more in 6 M  $\text{HClO}_4$ . Investigation of the effect of  $\text{Cl}^-$  on the extent to which this component can be resolved showed smaller than expected effects relative to those on the irreversible component.

APPENDIX I

This appendix contains the listings for some of the computer programs and subroutines that were used in the present work for:

- (a) data acquisition and storage from a cyclic-voltammetry experiment;
- (b) output of stored data onto an X-Y recorder; and
- (c) computer control of steady-state polarization experiments.

The details of the respective programs and subroutines are given in the commentaries that appear in the listing.

PROGRAM: JDCOL. FOR

FORTRAN IV 002.04 PAGE 001

```

C      PROGRAM TO SAMPLE TWO CHANNELS (I-V) THROUGH THE A/D
C      CONVERTER, AT RATES CONTROLLED BY THE CLOCK.
C      INPUT PARAMETERS!
C      L1=FIRST CHANNEL TO BE SAMPLED, IN OCTAL
C      H1=SECOND CHANNEL TO BE SAMPLED, IN OCTAL
C      T1=TIME BETWEEN READINGS IN SECONDS
C      SUBROUTINE TIMER IS CALLED AND CODES
C      FOR THE CLOCK STATUS AND BUFFER ARE PROVIDED
C
C      AFTER THE SAMPLING IS DONE, THE DATA CAN BE DISPLAYED
C      ON THE VT55 SCREEN
C      DISPLAY PARAMETERS!
C      MULT=MULTIPLIER FOR SCALING TO FIT THE SCREEN
C      IFIRS=PARAMETER TO DETERMINE IF I OR V IS TO BE DISPLAYED
C      ICHU=ALLOWS THE USER TO CHANGE THE MULTIPLIER IF THE
C      SCALING WAS NOT APPROPRIATE
C      DECISION PARAMETERS!
C      IFILE=ALLOWS THE USER TO STORE THE ARRAY IN A 4096 ELEMENT INTEGER FILE
C      IRE=TO RUN ANOTHER EXP, UNDER THE SAME OR NEW CONDITIONS.
C
C      USES SUBROUTINE TIMER (NOT IN SYSLIB)
C      USES A MACRO PROGRAM THAT CONTAINS THE GLOBAL RAIN2
C
C      TO RUN IT LINK IT TO TIMER.OBJ AND JDCOL.H.OBJ
C
C      INTEGER DATBUF
C      DIMENSION IPLO(4096)
C      COMMON /DATA/ I,L,M,K,DATBUF(4096)
C
C      ACCEPT INPUT PARAMETERS
C
C      TYPE 876
C      FORMAT(1X,'INPUT FIRST CHANNEL(I)='*)
C      READ(5,3) L1
C      L=(L1*512/2)+32
C      TYPE 987
C      FORMAT(1X,'INPUT SECOND CHANNEL(V)='*)
C      READ(5,3) H1
C      H=(H1*512/2)+32
C      FORMAT(06)
C      TYPE 543
C      FORMAT(1X,'INPUT TIME BETWEEN READINGS IN SEC='*)
C      READ(5,4) T1
C      FORMAT(F12.7)
C
C      CALCULATE CLOCK AND COUNT PARAMETERS
C
C      CALL TIMER(T1,ICODE,ICOUNT)
C      I=ICODE
C      K=ICOUNT
C
C      ACQUIRE DATA

```

PROGRAM: JDCOL.FOR (cont.)

```

0020 119 C      CALL RAIN2
0021 116 C
0022 964 C      DISPLAY DATA
0023 964 C
0024 116 C      TYPE 964
0025 964 C      FORMAT(IX,' INPUT MULT AND PLOTTING PARA(1 I,2 V)='*)
0026 964 C      ACCEPT*,AHULT,IFIRS
0027 300 DO 300 J=1,4096
0028 300 IFLO(J)=INT((FLODAT(DATREF(J))-2048.)*(10000./4096.))
0029 300 1*AHULT)+118
0030 300 CALL INIT
0031 300 CALL PLOT55(2,1+512+2+4+32+64,*)
0032 300 CALL PLOT55(1,0,*)
0033 300 CALL PLOT55(7,0,0)
0034 300 DO 200 J1=IFIRS,4000,8
0035 300 CALL PLOT55(8,((J1-IFIRS)/8),IFLO(J1))
0036 300 CALL PLOT55(5,0,1)
0037 300 CALL PLOT55(4,1,0)
0038 300 CALL PLOT55(4,1,118)
0039 300 READ(5,2) KR
0040 300 FORMAT(I2)
0041 300 CALL INIT
0042 300 TYPE 115
0043 300 FORMAT(IX,'TO CHANGE MULT INPUT 1='*)
0044 300 ACCEPT*,ICMU
0045 300 IF (ICMU .EQ. 1) GOTO 116
0046 300 C      CREATE DATA FILE
0047 300 C
0048 300 C
0049 111 TYPE 111
0050 111 FORMAT(IX,'TO STORE YOUR RESULTS INPUT 1='*)
0051 111 ACCEPT*,IFILE
0052 111 IF (IFILE .EQ. 1) GOTO 112
0053 111 GOTO 113
0054 111 CALL ASSIGN (2,-1,'NEW',*)
0055 111 DEFINE FILE 2(1,4096,U,NREC)
0056 111 NREC=1
0057 111 WRITE(2,NREC) DATREF
0058 111 CALL CLOSE(2)
0059 111 TYPE 114
0060 114 FORMAT(IX,'TO RUN ANOTHER EXP INPUT 1(DIF COND)
0061 114 1,2(SAME COND)='*)
0062 114 ACCEPT*,IRE
0063 114 IF (IRE .EQ. 1) GOTO 110
0064 114 IF (IRE .EQ. 2) GOTO 111
0065 114 CALL EXIT
0066 114 END

```

# SUBROUTINE: JDCOLM.MAC

.HATR. MACRO V03.02R 0110313B PAGE 1

|    |        |                     |                                      |
|----|--------|---------------------|--------------------------------------|
| 1  | 170400 | ADSTAT=170400       | DEFINITION OF STATUS AND BUFFER      |
| 2  | 170402 | ADRUF=ADRUF+2       | ADDRESSES FOR A/D AND CLOCK          |
| 3  | 170404 | CLSTAT=170404       |                                      |
| 4  | 170406 | CLKRUF=170406       |                                      |
| 5  | 000000 | MOV#2048,R1         | SET UP COUNTER(NUMBER OF DATA PAIRS) |
| 6  | 000004 | MOV#ADRUF,R0        | SET POINTER TO STORAGE BUFFER        |
| 7  | 000010 | MOV K,CLKBUF        | LOAD CLOCK BUFFER                    |
| 8  | 000016 | MOV I,CLSTAT        | LOAD CLOCK STATUS                    |
| 9  | 000024 | MOV L,ADRUF         | SELECT FIRST CHANNEL TO BE SAMPLED   |
| 10 | 000032 | ISR ADRUF           | SAMPLE DONE?                         |
| 11 | 000036 | BFL BLOOP           | LOOP IF NOT                          |
| 12 | 000040 | MOV ADRUF,(R0)+     | MOVE DATA INTO BUFFER                |
| 13 | 000044 | MOV H,ADRUF         | SELECT SECOND CHANNEL TO BE SAMPLED  |
| 14 | 000052 | ISR ADRUF           |                                      |
| 15 | 000056 | BFL BLOOP           |                                      |
| 16 | 000060 | MOV ADRUF,(R0)+     | MOVE DATA INTO BUFFER                |
| 17 | 000064 | MOV L,ADRUF         | RETURN TO SAMPLE CHANNEL ZERO        |
| 18 | 000072 | DEC R1              | DECREMENT COUNTER                    |
| 19 | 000074 | BNE BLOOP           | LOOP IF NOT DONE                     |
| 20 | 000076 | BIC #1,CLSTAT       | STOP CLOCK                           |
| 21 | 000104 | RTS PC              |                                      |
| 22 | 000000 | .FSECT DATA,OBL,DVR |                                      |
| 23 | 000000 | .BLKW 1             | CONTAINS CLOCK STATUS PARAMETER      |
| 24 | 000002 | .BLKW 1             | CHANNEL NUMBER                       |
| 25 | 000004 | .BLKW 1             | CLOCK BUFFER PARAMETER               |
| 26 | 000006 | .BLKW 4096          | LOCATIONS FOR DATA STORAGE           |
| 27 | 000010 | DATRUF:             |                                      |
| 28 | 000001 | .END                |                                      |

SUBROUTINE: JTIMER.FOR

PAGE 001

FORTRAN IV V02.04

```

0001 C
0002 C SUBROUTINE TIMER (TI,ICODE,ICOUNT) ALLOWS THE
0003 C TIMING OF EVENTS BY SELECTION OF THE APPROPRIATE
0004 C CLOCK CODE AND COUNTER DEPENDING ON THE SAMPLING
0005 C RATE REQUIRED.
0006 C
0007 C
0008 C INPUT PARAMETERS:
0009 C
0010 C TI=TIME IN SECONDS PER EVENT TO BE CLOCKED
0011 C
0012 C OUTPUT PARAMETERS:
0013 C
0014 C ICODE=CLOCK CODE TO BE LOADED IN CLOCK STATUS REGISTER
0015 C ICOUNT=CLOCK COUNT TO BE LOADED IN CLOCK COUNTER.
0016 C
0017 C ERROR CONDITIONS:
0018 C
0019 C IF THE TIME/EVENT IS GREATER THAN 500 SEC,THE RETURNED
0020 C ICODE WILL BE 0,THE USER PROGRAM SHOULD TEST FOR
0021 C THIS POSSIBILITY.
0022 C
0023 C SUBROUTINE TIMER(TI,ICODE,ICOUNT)
0024 C IF( TI .LE. 0.3) GOTO 100
0025 C IF( TI .LE. 3.0) GOTO 200
0026 C IF( TI .LE. 30.0) GOTO 300
0027 C IF( TI .LE. 300.0) GOTO 400
0028 C IF( TI .LE. 500.0) GOTO 500
0029 C ICODE=271
0030 C ICOUNT=-(INT(TI/.0167))
0031 C GOTO 1000
0032 C ICODE=261
0033 C ICOUNT=-(INT(TI/.00001))
0034 C GOTO 1000
0035 C ICODE=263
0036 C ICOUNT=-(INT(TI/.0001))
0037 C GOTO 1000
0038 C ICODE=265
0039 C ICOUNT=-(INT(TI/.001))
0040 C GOTO 1000
0041 C ICODE=267
0042 C ICOUNT=-(INT(TI/.01))
0043 C GOTO 1000
0044 C ICODE=0
0045 C RETURN
0046 C END

```

PROGRAM: JLI.FOR

FORTRAN, IV

V02.04

PAGE 001

PROGRAM TO OUTPUT A 2048 INTEGER DATA FILE THROUGH  
THE D/A CONVERTER ONTO THE Y-AXIS OF AN X-Y RECORDER  
WITH CONTROL OVER THE RATE OF TRANSMISSION AND OF  
THE X-AXIS SCALING.

INPUT PARAMETERS:

IBUF=DATA BUFFER TO BE PLOTTED  
J=TIMING DELAY LOOP (OCTAL)  
L=X-AXIS SCALING (OCTAL)

TO USE LINK IT TO JLI1.0BJ

COMMON /DATA/ J,L,IBUF(2048)

CREATE DATA BUFFER TO BE OUTPUT

CALL ASSIGN (2,-1,'OLD',,)  
DEFINE FILE 2(1,2048,0,NREC)  
NREC=1  
READ(2,NREC) IBUF  
CALL CLOSE(2)

INPUT PARAMETERS

TYPE 10  
FORMAT(1X,'INPUT DELAY LOOP='\*)  
READ(5,3) J  
FORMAT(06)  
TYPE 20  
FORMAT(1X,'INPUT SPACING (X-AXIS)=\*')  
READ (5,3) L

OUTPUT DATA BUFFER TO X-Y RECORDER

CALL LHI  
TYPE\*, 'DONE'  
CALL EXIT  
END

0001  
0002  
0003  
0004  
0005  
0006  
0007  
0008 10  
0009  
0010 3  
0011  
0012 20  
0013  
0014  
0015  
0016  
0017





PROGRAM: JPG1.FOR (cont.)

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FORTRAN IV V02.04

```

0019 200 I(I2)=INT((VINIT+(I2-1)*VINC)*(4096./10000.))+2048
0020 I4=-1
0021 DO 300 I3=NP1+1,2*NP1
0022 I4=I4+1
0023 300 I(I3)=INT((VFIN-I4*VINC)*(4096./10000.))+2048
0024 TYPE*, 'GOING'
C
C OUTPUT POTENTIAL-TIME PROGRAMME
C
0025 CALL GEN
0026 TYPE*, 'DONE'
0027 CALL EXIT
0028 END

```

SUBROUTINE JFG1M.MAC

.MAIN. MACRO V03.02B 01105114 PAGE 1

|    |        |               |                                               |
|----|--------|---------------|-----------------------------------------------|
| 1  | 170404 | CLSTAT=170404 | IDEF OF STATUS AND BUFFER ADDRESSES           |
| 2  | 170406 | CLKBUF=170406 | IFOR KW11-K AND A111-K INTERFACES             |
| 3  | 170430 | CLKC00=170430 |                                               |
| 4  | 170416 | D1STAT=170416 |                                               |
| 5  | 170426 | DA3OUT=170426 |                                               |
| 6  | 000000 | GEN11         | ICLEAR DISPLAY STATUS                         |
| 7  | 000004 | HL00F1        | IFSET UP COUNTER FOR NUMBER OF                |
| 8  | 012700 |               | IFPROGRAMS ON A SWEEP                         |
| 9  | 000010 |               | IFR0 POINTS TO CLOCK CODES                    |
| 10 | 000014 |               | IFR1 POINTS TO CLOCK COUNTERS                 |
| 11 | 000020 |               | IFR2 POINTS TO # OF POINTS/PROGRAM            |
| 12 | 000024 |               | IFR3 POINTS TO VOLTAGE RAMP                   |
| 13 | 000030 |               | IFLOAD CLOCK BUFFER                           |
| 14 | 000034 |               | IFLOAD CLOCK STATUS WITH APPROPRIATE RATE     |
| 15 | 000040 |               | IFSET UP COUNTER FOR # OF POINTS              |
| 16 | 000042 |               | IFLOAD Y CHANNEL(DZA)                         |
| 17 | 000046 |               | IFCLEAR DONE FLAG IN CLOCK STATUS(PRECAUTION) |
| 18 | 000054 |               | IFCHECK IF COUNTING FINISHED                  |
| 19 | 000060 |               | IFLOOP IF NOT                                 |
| 20 | 000062 |               | IFDEC COUNTER                                 |
| 21 | 000064 |               | IFLOOP IF NOT DONE                            |
| 22 | 000066 |               | IF***IMPORTANT***                             |
| 23 | 000074 |               | IFSTOP CLOCK BEFORE CHANGING ITS PARAMETERS   |
| 24 | 000076 |               | IFDEC # OF PROGRAMS COUNTER                   |
| 25 | 000100 |               | IFLOOP IF NOT DONE                            |
| 26 | 000102 |               | IFLOOP ALWAYS FOR CONTINUOUS DISPLAY          |
| 27 | 000102 |               |                                               |
| 28 | 000000 |               | IFSECTION FOR PARAMETERS PASSING FROM FORTRAN |
| 29 | 000000 |               | IFNUMBER OF PROGRAMS IN A SWEEP               |
| 30 | 000002 |               | IFCLOCK CODES ARRAY                           |
| 31 | 000146 |               | IFCLOCK COUNTERS ARRAY                        |
| 32 | 000312 |               | IFNUMBER OF POINTS/PROGRAM ARRAY              |
| 33 | 000456 |               | IFPOTENTIAL RAMP ARRAY                        |
| 34 | 000001 |               |                                               |

As mentioned in program JPG1.FOR (page 224), the subroutine JFG1M.MAC (page 225) forms part of a program package developed in our Laboratory, in order to utilize the computer as a programmable function generator.

One of the problems in electrochemical research is the need, in some cases, of sophisticated electronic instrumentation. In the particular case of cyclic-voltammetry, complex potential-time programmes are needed to elucidate the kinetic parameters of some surface processes.

As minicomputers are becoming more and more common in the research laboratory, it is obvious that a computer-based programmable function generator could be a useful tool if only for those occasions in which a complex waveform is required.

The approach used in our Laboratory consisted in building a symmetrical triangular waveform between the required potential limits, in potential steps of width determined by the resolution of the D/A converter utilized (in our case 2.5 mV). This triangular sweep was then output, through the D/A converter, point by point at time intervals determined by software according to the sweep-rate or holding time for that portion of the sweep.

Through software programming, the user indicates at which points in the sweep a change in programme has to take place, whether the new programme is to be sweeping or holding, and indicates the time parameters for either of the latter regimes. The program then calculates the codes for the clock status and buffer.

At this stage a set of arrays has been built:

I: contains the symmetrical waveform;

NP: contains the number of programmes/sweep;

NS: contains the clock codes for every programme;

NC: contains the counter values for the counter buffer of the clock; and

MS: contains the number of points/programme.

By calling the MACRO subroutine JFG1M.MAC, the waveform is available at the Y channel of the D/A converter on a real time basis, in a continuous way.

CONTRIBUTIONS TO ORIGINAL RESEARCH

1. A PDP-11/34 minicomputer based system was adapted for the acquisition and treatment of cyclic-voltammetry data and the necessary software and interfacing procedures developed.
2. The monolayer surface oxidation stage of Ir was studied in detail for the first time, after the necessary precautions to avoid the development of thick oxide films on the electrode surface were taken. It has been found that, at the monolayer level, Ir behaves like any other Pt group metal, but the differences in properties that are observed are a function of the different interaction of Ir with ions in solution and of the strength of the OH and H to metal bonds.
3. The  $s_0$  value for the H state,  $H_{A3}$ , on Iridium in 0.5 M  $H_2SO_4$ , 298 K, has been determined.
4. The influence of a series of experimental conditions on the growth rate of the thick oxide films at Ir has been studied. Of special importance are the results obtained with a rotating Ir disc electrode which ruled out the possibility of a dissolution/redeposition growth mechanism.
5. A detailed study of the oxide films has been performed for the first time in  $Na_2CO_3$  solutions. These results indicated the possibility of growing the oxide in media at basic pH's and showed the anomalous dependence of the peak potential on pH.
6. Studies of the oxide film in dil.  $H_2SO_4$  and  $HClO_4$  solutions have also been performed for the first time.
7. All the current peaks in the  $i$  vs  $V$  profile of the thick oxide films have been annotated and related to processes which are likely to be occurring in

the film over the corresponding potential ranges. The peak properties have also been discussed.

8. It was also found that the main current peak in the thick oxide state,  $Q_{A3,r}$ , appears to consist of two separate peaks, whose relative charges are a function of oxide thickness.

9. A model based on the change of conductivity of the oxide film as a function of applied potential, is proposed and accounts for the experimentally observed properties of Ir oxide films.

10. A growth mechanism, involving continuous monolayer surface oxidation of the underlying substrate, combined with incomplete reduction of the deposited oxide species in the cathodic sweep, is also proposed and is consistent with the oxide model.

11. The apparent electrocatalytic effects of the modified iridium oxide anodes for the  $Cl_2$  evolution reaction, has been proven to be due to a remarkable increase in real area of the electrode as a function of the oxide thickness. The model referred to above has been used successfully to account for the distribution of the applied potential difference across the metal/oxide/solution interphase.  $H_2$  evolution experiments carried out on the same Ir oxide surfaces confirmed the importance of potential-dependent conductivity changes in the oxide.

12.  $Cl^-$  ion was shown to block the monolayer surface oxide at Pt at low temperature, ca. 213 K, in a manner similar to that at room temperature. The importance of comparing results at different temperatures on the basis of equal initial oxide coverages has been demonstrated.

13. A special potential-time programme was developed to study the effect of  $Cl^-$  ion on the growth kinetics of Pt oxide at constant potential. Its advantages and limitations are discussed.

14.  $\text{Cl}^-$  ion lowers the rate of growth of Pt oxide at constant potential; the growth follows a direct logarithmic law in time, favoring at the same time, a relative increase in the most irreversible component. At intermediate  $\text{Cl}^-$  ion concentrations and high anodic potentials, a competition appears to be established between oxide growth and  $\text{Cl}^-$  blocking, with the former being able to offset the latter.

15. The reversibility of the early stages of monolayer surface oxidation of Pt has been studied at low T in 6 M  $\text{H}_2\text{SO}_4$  and 6 M  $\text{HClO}_4$ . The effects of  $\text{Cl}^-$  ion on this process have also been demonstrated and quantitatively evaluated.

REFERENCES

1. H. Angerstein-Kozłowska, B.E. Conway, B. Barnett and J. Mozota, J. Electroanal. Chem., 100(1979)417.
2. F.G. Will and C.A. Knorr, Z. Elektrochem., 64(1960)270.
3. A. Slygin and A.N. Frumkin, Acta Physicochim., U.R.S.S., 3(1935)791
4. J.A.V. Butler and G. Armstrong, Proc. Roy. Soc. London, A317(1932)604.
5. G. Armstrong, F.R. Himsworth and J.A.V. Butler, Proc. Roy. Soc. London, A143(1933)89.
6. B.V. Ershler and M.W. Proskurnin, Acta Physicochim., U.R.S.S., 6(1937)195.
7. S.W. Feldberg, C.C. Enke and C.E. Bricker, J. Electrochem. Soc., 110(1963)826.
8. K.J. Vetter and D. Berndt, Z. Elektrochem., 62(1958)378.
9. H.A. Laitinen and G.C. Enke, J. Electrochem. Soc., 107(1960)773.
10. F.G. Will and C.A. Knorr, Z. Elektrochem., 64(1960)258.
11. J. Mayell and J. Langer, J. Electrochem. Soc., 111(1964)438.
12. S. Gilman, Electrochim. Acta, 9(1964)1025.
13. T. Biegler and R. Woods, J. Electroanal. Chem., 35(1972)209.
14. A.K. Vijh and B.E. Conway, Z. Anal. Chem., 224(1967)160.
15. R. Parsons and W.H.M. Visscher, J. Electroanal. Chem., 36(1972)329.
16. M. Becker and M.W. Breiter, Z. Elektrochem., 60(1950)1080
17. W.H.M. Visscher and M.A.V. Devanathan, J. Electroanal. Chem., 8(1964)127.
18. K.J. Vetter and J.W. Schultze, J. Electroanal. Chem., 34(1972)141.
19. H. Angerstein-Kozłowska, B.E. Conway and W.B.A. Sharp, J. Electroanal. Chem., 43(1973)9.
20. P. Stonehart, H. Angerstein-Kozłowska and B.E. Conway, Proc. Roy. Soc. London, A310(1969)541.

21. B.Y. Tilak, B.E. Conway and H. Angerstein-Kozłowska, J. Electroanal. Chem., 48(1973)1.
22. B.E. Conway, H. Angerstein-Kozłowska, W.B.A. Sharp and E.E. Criddle, Anal. Chem., 45(1973)1331.
23. T. Biegler, D.A.J. Rand and R. Woods, J. Electroanal. Chem., 29(1971)269.
24. G.A. Garwood and A.T. Hubbard, Surf. Sci., 92(1980)617.
25. N. Sato and M. Cohen, J. Electrochem. Soc., 111(1964)512.
26. A.K.N. Reddy, M. Genshaw and J.O'M. Bockris, J. Electroanal. Chem., 8(1964)406.
27. K.J. Vetter and J.W. Schultze, J. Electroanal. Chem., 34(1972)131.
28. S. Shibata, Electrochim. Acta, 22(1977)175.
29. D. Gilroy and B.E. Conway, Can. J. Chem., 46(1968)875.
30. D. Gilroy, J. Electroanal. Chem., 71(1976)257.
31. Yu.M. Tyurin and G.F. Volodin, Elektrokhim., 5(1969)1203.
32. J. Balej and O. Spalek, Collection Czechoslov. Chem. Commun., 37(1972)499.
33. V.S. Bagotskii, W.J. Lukjanytscheva, A.J. Osche and W.J. Tichomirov, Dokl. Akad. Nauk., U.R.S.S., 159(1964)644.
34. B. Ershler, Disc. Faraday Soc., 1(1947)269.
35. S. Shibata, Bull. Chem. Soc. Japan, 36(1963)5.
36. S. Shibata, Bull. Chem. Soc. Japan, 40(1967)696.
37. S. Shibata, J. Electroanal. Chem., 89(1978)37.
38. S. Shibata and M.P. Sumino, J. electroanal. Chem., 99(1979)187.
39. M. Pourbaix, "Atlas d'équilibres électrochimiques à 25° C", Gauthier-Villars, Paris, 1963, p.343.
40. T.N. Stoyanovskaya, G.P. Khomchenko and G.D. Vovschenko, Vestn. Mosk. Univ., Ser. Khim., 18(1963)20.
41. S. Hadzi-Jordanov, H. Angerstein-Kozłowska, M. Vukovic and B.E. Conway, J. Electrochem. Soc., 125(1978)1471.

42. T.N. Stoyanovskaya, G.P. Khomchenko and G.D. Vovschenko, Vestn. Mosk. Univ., Ser. Khim., 2(1963)20.
43. T.N. Stoyanovskaya, G.P. Khomchenko and G.D. Vovschenko, Vestn. Mosk. Univ., Ser. Khim., 5(1962)30.
44. J. Llopis, I.M. Tordesillas and J.M. Alfayate, Electrochim. Acta, 11(1966)623.
45. J. Llopis and M. Vazquez, Electrochim. Acta, 11(1963)633.
46. J. Llopis, J.M. Gamboa and J.M. Alfayate, Electrochim. Acta, 12(1967)57.
47. P. Eighner, Bull. Soc. Chim. Fr., 6(1967)2051.
48. L.D. Burke nad T.O. O'Meara, J. Chem. Soc., Faraday Trans. I, 68(1972)839.
49. S. Trasatti and G. Buzzanca, J. Electroanal. Chem., 29(1971)App. 1.
50. S. Hadzi-Jordanov, H. Angerstein-Kozłowska and B.E. Conway, J. Electroanal. Chem., 60(1975)359.
51. L.D. Burke and J.K. Mulcahy, J. Electroanal. Chem., 73(1976)207.
52. R. Woods, J. Electroanal. Chem., 49(1974)217.
53. J. Mozota and B.E. Conway, J. Electrochem. Soc., (in course of publication)
54. S. Hadzi-Jordanov, H. Angerstein-Kozłowska, M. Vukovic and B.E. Conway, J. Phys. Chem., 81(1977)2271.
55. H.B. Beer, Neth. Pat. Appl., 216,199(1957); U.S. Patent, 3,236,756(1966).
56. H.B. Beer, South African Patent, 680,834(1968).
57. H.B. Beer, U.S. Patents: 3,214,110(1966); 3,632,498(1972); 3,711,385(1973); 3,751,291(1973).
58. S. Trasatti and W. O'Grady. Advan. in Electrochem. and Electrochem. Eng., in press(1980).
59. D. Galizzioli and S. Trasatti, J. Electroanal. Chem., 44(1973)367.
60. M. Inai, C. Iwakura and H. Tamura, Electrochim. Acta, 24(1979)993.
61. C. Iwakura, H. Tada and H. Tamura, Electrochim. Acta, 22(1976)217.

62. T. Arikado, C. Iwakura and H. Tamura, *Electrochim. Acta*, 22(1976)513.
63. T. Yokoyama and N. Enyo, *Electrochim. Acta*, 24(1979)997.
64. D. Michell, D. rand and R. Woods, *J. Electroanal. Chem.*, 89(1978)11.
65. L.D. Burke and D. Whelan, *J. Electroanal. Chem.*, 103((1979)179.
66. G.D. Vovschenko, N.G. Ulko and G.P. Khomchenko, *Elektrokhim.*, 1(1965)659.
67. G.D. Vovschenko, A.A. Sotyagina and I.N. Golianitskaya, *Elektrokhim.*,  
8(1972)908; 12(1976)401.
68. A.J. Appleby, *J. Electrochem. Soc.*, 117(1970)1157.
69. J. Llópez and M.Vazquez, *Electrochim. Acta*, 11(1966)633.
70. F. Colom and J.H. Gonzalez, *J. Electroanal. Chem.*, 73(1976)303.
71. F. Colom, J.H. Gonzalez and J. Peinado, *J. Electroanal. Chem.*, 89(1978)397.
72. F. Colom and J.H. Gonzalez, *J. Electroanal. Chem.*, 107(1980)147.
73. S. Shibata, *Bull. Chem. Soc. Japan*, 38(1965)1330.
74. W. Bold and M.W. Breiter, *Electrochim. Acta*, 5(1961)169.
75. D.A.J. Rand and R. Woods, *J. Electroanal. Chem.*, 35(1972)209.
76. D.A.J. Rand and R. Woods, *J. Electroanal. Chem.*, 31(1971)29.
77. L.D. Burke and E.J.M. O'Sullivan, *J. Electroanal. Chem.*, 93(1978)11.
78. S. Gottesfeld, *J. Electrochem. Soc.*, 127(1980)272.
79. A. Frumkin, *Z. Physik. Chem.*, 164(1933)121; *Trans. Faraday Soc.*, 55(1959)156.
80. Z.A. Iofa, B. Kabanov, E. Kuchinskii and F. Chistyakov, *Acta.*  
*Physicochim.*, U.R.S.S., 10(1939)317.
81. R. Parsons, *J. Electroanal. Chem.*, 21(1969)35.
82. M. Sluyters-Rehbach, *J. Electroanal. Chem.*, 19(1968)85.
83. De Kreuk, *J. Electroanal. Chem.*, 28(1970)391.
84. M.W. Breiter, *J. Amer. Chem. Soc.*, 80(1958)511.
85. G. Florianovich and A. Frumkin, *Zhur. Fiz. Khim.*, 29(1955)1827.
86. J.M. Kolotyrkin, *Trans. Symps. Elec. Processes*, Ed. E. Yeager, New York, 1961.

87. D.N. Buckley and L.D. Burke, J. Chem. Soc., Faraday Trans. I, 72(1976)2431.
88. S. Gottesfeld and S. Srinivasan, J. Electroanal. Chem., 86(1978)89.
89. E.J. Frazer and R. Woods, J. Electroanal. Chem., 102(1979)127.
90. G. Lodi, E. Sivieri, A. De Battisti and S. Trasatti, J. Appl. Electrochem., 8(1978)135.
91. L.D. Burke, O.J. Murphy, J.F. O'Neill and S. Venkatesan, J. Chem. Soc., Faraday Trans. I, 73(1977)1659.
92. L.D. Burke and E.J.M O'Sullivan, J. Electroanal. Chem., 97(1979)123.
93. R. Woods, Israel J. Chem., 18(1979)118.
94. R.H. Stevens, U.S. Patent, 1,007,894(1913).
95. A. Hickling, Trans. Faraday Soc., 41(1945)333.
96. A.N. Frumkin and G. Tedoradze, Z. Elektrochem., 62(1958)251.
97. E.L. Littauer and L.L. Shrier, Electrochim. Acta, 11(1966)127.
98. T. Yokoyama and N. Enyo, Electrochim. Acta, 15(1970)1921.
99. B.E. Conway and D.M. Novak, J. Chem. Soc., Faraday Trans. I, 75(1979)2454.
100. B.E. Conway and D.M. Novak, J. Electroanal. Chem., 99(1979)133.
101. R.G. Erenburg, L.I. Krishtalik and V.I. Byströv, Elektrochim., 8(1972)1240.
102. T. Yokoyama and N. Enyo, Abstract No. A124, The 43rd Annual Meeting of the Electrochem. Soc. Japan, Tokyo(1960).
103. T. Arikado, C. Iwakura and H. Tamura, Electrochim. Acta, 23(1978)9.
104. F.T. Chang and H. Wick, Z. Phys. Chem., 33(1935)129.
105. S. Glasstone and A. Hickling, J. Chem. Soc., 10(1934)253.
106. G.A. Tedoradze, Zhur. Fiz. Khim., U.R.S.S., 33(1959)129.
107. T. Dickinson, R. Greef and Lord Wynne-Jones, Electrochim. Acta, 14(1969)467.
108. G. Faita and G. Fiori, J. Appl. Electrochem., 2(1972)31.
109. T. Yokoyama and N. Enyo, Electrochim. Acta, 13(1968)412.

110. H.G. Erenburg, L.I. Krishtalik and I.P. Yaroshevskaya, *Elektrokhim.*,  
11(1975)1068.
111. A.T. Kuhn and C.J. Mortimer, *J. Electrochem. Soc.*, 120(1973)231.
112. M. Vukovic, H. Angerstein-Kozłowska and B.E. Conway, *J. Appl. Electrochem.*,  
(in course of publication, 1981).
113. A. Damjanovic and A.T. Ward in "Electrochemistry. The Past Thirty and  
the Next Thirty Years", Eds. H. Bloom and F.G. Gutmann, 1977, Chapter 6.
114. A. Sherman and H. Eyring, *J. Amer. Chem. Soc.*, 54(1932)2661.
115. R. Piontelli, L. Peraldo Bicelli and A. La Vecchia, *Rend. Accad. Naz.  
Lincei VIII*, 27(1959)312.
116. J.O'M. Bockris and S. Srinivasan, "Fuel Cells: Their Electrochemistry",  
MacGraw-Hill, New York, 1969, pag. 314.
117. A.K.N. Reddy, M. Paunovic and J.O'M. Bockris, NASA contract (No. NsG325),  
Sept. 30, 1964.
118. B.E. Conway and J.O'M. Bockris, *Electrochim. Acta*, 3(1961)349.
119. D. Drazic and J.O'M. Bockris, *Electrochim. Acta*, 7(1962)293.
120. H. Kita, N. Enyo and J.O'M. Bockris, *Can. J. Chem.*, 39(1961)1670.
121. G.C. Bond, "Catalysis by Metals", Academic Press Inc., New York, 1962.
122. L.F. Mattheis, *Phys. Rev. B*, 13(1976)2433.
123. B.E. Conway and J.O'M. Bockris, *J. Chem. Phys.*, 26(1957)532.
124. H. Gerischer, *Advan. in Electrochem. and Electrochem. Eng.*, 1(1961).
125. See ref. 116, pages 309-312.
126. G. Faita, G. Fiori and N. Nidola, *J. Electrochem. Soc.*, 117(1970)1333;  
120(1973)1702.
127. J.O'M. Bockris and H. Wroblowa, *J. Electroanal. Chem.*, 7(1964)428.
128. A. Damjanovic and V. Brusić, *Electrochim. Acta*, 12(1967)1171.
129. J. B. Warner and S. Schuldiner, *J. Electrochem. Soc.*, 111(1964)992.

130. F. Hine, M. Yasuda and T. Yoshida, J. Electrochem. Soc., 124(1977)500.
131. J.D. Levine and P. Mark, Phys. Rev., 182(1969)926.
132. G.C. Bond, Disc. Faraday Soc., 41(1966)200.
133. C.N.R. Rao and G.V. Subbarao, Phys. Stat. Col. (a), 1(1970)597.
134. E.P. Wigner, "Group Theory", Academic Press, New York, 1959.
135. J.M. Luttinger, Phys. Rev., 119(1960)1153.
136. A.W. Overhauser, Phys. Rev., 128(1962)1437.
137. R.E. Watson and A.J. Freeman, Phys. Rev., 156(1967)1.
138. J.S. Griffith, J. Chem. Phys., 41(1964)516.
139. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, Chapter 20.
140. M.L.B. Rao, A. Damjanovic and J.O'M. Bockris, J. Phys. Chem., 67(1963)2508.
141. L.L. Varizandt and J.M. Honig, Am. Rev. Mat. Sci., 4(1971)191.
142. D. Adler, Rev. Mod. Phys., 40(1968)714; J. Solid State Chem., 12(1975)332.
143. L.M. Falicov and B. Koiller, J. Solid State Chem., 12(1975)349.
144. J.B. Goodenough, in "Progress in Solid State Chemistry", Ed. H. Reiss, Pergamon Press, New York, 1973, Vol. 5, Chapter 4.
145. D.M. Novak, B.V. Tilak and B.E. Conway, "Modern Aspects of Electrochemistry", Eds. J.O'M. Bockris and B.E. Conway, Vol. 14, (in press, 1981).
146. J.B. Goodenough, J. Appl. Phys., 37(1966)1415; 39(1968)403.
147. F. Arntz and Y. Yacoby, Phys. Rev. Letters, 17(1966)847.
148. R. Haul and G. Dumbgen, J. Phys. Chem. Solids, 26(1965)1.
149. P.F. Chester, J. Appl. Phys. Suppl., 32(1961)2233.
150. S. Anderson, Acta Chem. Scand., 14(1960)1161.
151. L. Young, Proc. Roy. Soc. London, A258(1960)496.
152. J.W. Diggle, T.C. Downie and W. Goulding, Chem. Rev., 69(1969)365.
153. R.E. Meyer, J. Electrochem. Soc., 107(1960)847.

154. A.C. Makrides, J. Electrochem. Soc., 113(1966)1158.
155. J.O'M. Bockris, A.K.N. Reddy and B. Rao, J. Electrochem. Soc., 113(1966)1133.
156. K. Huffle and M. Ilscher, Z. Elektrochem., 58(1954)382.
157. A.T. Tromhold and E.L. Cook, J. Chem. Phys., 44(1966)4564.
158. L. Young, "Anodic Oxide Films", Academic Press, New York, 1961.
159. A.C. Makrides, "Symposium on Electrode Processes", The Electrochem. Soc., Cleveland, 1966.
160. A. Damjanovic and A.T. Ward, Int. Rev. of Sci. Phys. Chem., Series Two, Vol. 6, Chapter 3.
161. L.B. Harris and A. Damjanovic, J. Electrochem. Soc., 122(1975)593.
162. J.L. Ord and F.C. Ho, J. Electrochem. Soc., 102(1955)1.
163. J.F. Dewald, J. Electrochem. Soc., 102(1955)1.
164. C.P. Bean, T.C. Fisher and D.A. Vermilyea, Phys. Rev., 101(1956)551.
165. E.J.W. Verwey, Physica, 2(1935)1059.
166. L. Young, Trans. Faraday Soc., 50(1954)159.
167. J.F. Dewald, J. Phys. Chem. Solids, 2(1957)55.
168. N.F. Mott, Trans. Faraday Soc., 43(1947)429.
169. N. Cabrera and N.F. Mott, Repts. Prog. Phys., 12(1949)163.
170. A.K. Vijh, "Electrochemistry of Metals and Semiconductors", Marcel Dekker Inc., New York, 1973.
171. U.R. Evans, "The Corrosion and Oxidation of Metals", St. Martin's, New York, 1960.
172. S. Tajima, M. Soda and T. Mori, Electrochim. Acta, 1(1959)205.
173. G.C. Wood and G.W. Patrick, Trans. Inst. Metal Finishing, 45(1967)174.
174. G.C. Wood and J.P. O'Sullivan, Electrochim. Acta, 15(1970)1865.
175. N. Sato, Electrochim. Acta, 16(1971)1683.
176. R.F. Tylecote and W.K. Appleby, Werkst. und Korrosion, 23(1972)855.

177. "Electronic and Structural Properties of Amorphous semiconductors",  
Eds. P.G. Le Comber and J. Mort, Academic Press, London, 1973.
178. A.K. Vijh, J. Electrochem. Soc., 116(1969)1323.
179. L. Young, Can. J. Chem., 50(1972)574.
180. M.J. Dignam, J. Electrochem. Soc., 112(1965)722.
181. F. Fehlnner and N.F. Mott, Oxidation of Metals, 2(1970)59.
182. B.E. Conway, Proc. Roy. Soc. London, A256(1960)128.
183. D. Britz, J. Electroanal. Chem., 88(1978)309.
184. J.D.E. McIntyre and W.F. Peck, Jr., J. Electrochem. Soc., 117(1970)747.
185. R.A. Osteryoung, Comput. Chem. Instrum., 2(1972)353; and see also W.S.  
Woodward and C.N. Reilley, Pure Appl. Chem., 50(1978)785.
186. J.S. Litter and R.M. Reeves, Chem. in Brit., 14(1978)118.
187. D.M. Kolb, Advan. in Electrochem. and Electrochem. Eng., 11(1978)125;  
see also B.E. Conway, F.C. Ho and H. Angerstein-Kozłowska, J. Vacuum  
Sci. Technol., 14(1977)351.
188. U.v. Alpen, K. Graf and M. Hafendorfer, J. Appl. Electrochem., 8(1978)557.
189. H.B. Sierra-Alcazar, A.N. Fleming and J.A. Harrison, Surf. Technol.,  
6(1977)61.
190. A.M. Bond, R.J. Schwall and D.E. Smith, J. Electroanal. Chem., 85(1977)217.
191. R. Virtanen, Kem. Kemi., 5(1978)460.
192. R.E. Deny, J.V. Vuuren P. and J.A. Titus, Anal. Chem., 46(1974)11.
193. J. Slaïma, F. Bakker, J.J. Moels, J.E. Ordelman and M. Bruyn-Hes,  
Anal. Chim. Acta, 112(1979)45.
194. J.A. Harrison and S. Rangarajan, Faraday Symp., Chem. Soc. London,  
12(1977)70.
195. A. Rahman and F.H. Stillinger, J. Chem. Phys., 55(1972)3336.
196. K. Heinzinger and P.C. Vogel, Z. Naturforsch., 31a(1976)463.

197. J. Klinger, B.E. Conway and H. Angerstein-Kozłowska, *Comp. in Chem.*, 2(1978)117.
198. A. Yamada, Y. Kato, M. Sato, M. Sasaki and N. Tanaka, *Bunseki Kagaku*, 25(1976)69.
199. A.V. Mode, G.C. McMillan and R.D. Carver, *DOE-Symp. Ser.*, 1978
200. W. Butler, G.S. Smith and M.L. Lyndrup, *J. Chem. Educ.*, 56(1979)776.
201. J. Moore, G. Gerhold, G.L. Breneman, S.G. Oven and M. Page, *Chem. Educ.: View Second.-Tertiary Interface.*, Proc. Conf., 1979, Part 1.
202. S.P. Perone and D.O. Jones, "Digital Computers in Scientific Instrumentation; Applications to Chemistry". MacGraw-Hill, New York, 1973.
203. S.P. Perone, *Inf. Chem. Comput. Assisted Chem. Res. Des.*, 51(1973)25.
204. R.A. De Palma and S.P. Perone, *Anal. Chem.*, 51(1979)825.
205. Q.V. Thomas, L. Kryger and S.P. Perone, *Anal. Chem.*, 48(1976)761.
206. J.R. Birk and S.P. Perone, *Anal. Chem.*, 40(1968)496.
207. D. Gosden, M. Hayes, A.T. Kuhn and D. Whitehouse, *J. Appl. Electrochem.*, 8(1978)437.
208. N.A. Hampson and M.J. Willard, *Surf. Technol.*, 7(1978)247.
209. D.M. Mohilner and P.R. Mohilner, *J. Electrochem. Soc.*, 115(1968)261.
210. C.T. Chen, Ph. D. Thesis, Case Western Reserve Univ., 1979.
211. G. Shia and L. Meites, *J. Electroanal. Chem.*, 87(1978)369.
212. K. Bergner, *Anal. Chim. Acta*, 87(1976)1.
213. L. Rames, *Chem. Instrum.*, 6(1975)119.
214. L. Kryger and D. Jagner, *Anal. Chim. Acta*, 78(1975)251.
215. M.W. Breiter, *J. Electrochem. Soc.*, 112(1965)845.
216. K.F. Drake, R.P. Van Duyne and A.M. Bond, *J. Electroanal. Chem.*, 89(1978)231.
217. P.E. Whitson, H.W. Vandenborh and D.H. Evans, *Anal. Chem.*, 45(1973)1298.

218. H. Angerstein-Kozłowska, J. Klinger and B.E. Conway, J. Electroanal. Chem., 75(1977)45; S. Srinivasan and E. Gileadi, Electrochim. Acta, 11(1966)321
219. H. Angerstein-Kozłowska, J. Klinger and B.E. Conway, J. Electroanal. Chem., 75(1977)61.
220. H. Angerstein-Kozłowska, B.E. Conway and J. Klinger, J. Electroanal. Chem., 87(1978)301.
221. H. Angerstein-Kozłowska, B.E. Conway and J. Klinger, J. Electroanal. Chem., 87(1978)321.
222. E. Laviron, J. Electroanal. Chem., 101(1979)19.
223. E. Laviron, J. Electroanal. Chem., 52(1974)355.
224. T. Gueshi, K. Tokuda and H. Matsuda, J. Electroanal. Chem., 101(1979)29.
225. T. Gueshi, K. Tokuda and H. Matsuda, J. Electroanal. Chem., 89(1978)247.
226. B.E. Conway and H. Angerstein-Kozłowska, Acc. Chem. Res., (in press, 1981).
227. F.B. Hildebrand, "Introduction to Numerical Analysis", MacGraw-Hill, New York, 1956, pag. 71.
228. R. Zurmühl, "Praktische Mathematik für Ingenieure und Physiker", Springer, Berlin, 1963, page 214.
229. F.C. Ho, B.E. Conway and H. Angerstein-Kozłowska, Surf. Sci., 81(1979)125.
230. H. Angerstein-Kozłowska and B.E. Conway, J. Electroanal. Chem., 95(1979)1.
231. N.V. Sigwick, "Chemical Elements and their Compounds", Clarendon Press, Oxford, 1950, Vol. II, page 1530.
232. D.A.J. Rand, R. Woods and D. Michell, in "Electrode Materials and Processes for Energy Conversion and Storage", Eds. J.D.E. McIntyre, S. Srinivasan and F.G. Will, Electrochem. Soc., 1977, pag. 217.
233. L.D. Burke, T.A.M. Twomey and D.P. Whelan, J. Electroanal. Chem., 107(1980)201.
234. M.W. Breiter, Z. Phys. Chem. N.F., 52(1967)73.

235. M.W. Breiter, Ann. N. Y. Acad. Sci., 101(1963)709.
236. M.W. Breiter, Electrochim. Acta, 7(1962)25.
237. A. Capon and R. Parsons, J. Electroanal. Chem., 39(1972)275.
238. B.E. Conway and S. Gottesfeld, J. Chem. Soc., Faraday Trans. I, 69(1973)1090.
239. B.D. Kurnikov, A.I. Zhurin and Yu. V. Vasil'ev, Elektrokhim., 8(1972)1603.
240. B.D. Kurnikov and Yu. V. Vasil'ev, Elektrokhim., 10(1974)70.
241. B.D. Kurnikov and Yu. V. Vasil'ev, Elektrokhim., 9(1973)1138.
242. B.D. Kurnikov and Yu.V. Vasil'ev, Elektrokhim., 9(1973)1845.
243. B.I. Polovchenko, N.A. Ephstein and A.N. Frumkin, J. Electroanal. Chem.,  
53(1974)95.
244. A.N. Frumkin and O.A. Petry, Electrochim. Acta, 15(1970)391.
245. C.C. Schubert, C.L. Page and B. Ralph, Electrochim. Acta, 18(1973)33.
246. J.M. Otten and W. Visscher, J. Electroanal. Chem., 55(1974)1.
247. J.M. Otten and W. Visscher, J. Electroanal. Chem., 55(1974)13.
248. D.A.J. Rand and R. Woods, J. Electroanal. Chem., 55(1974)375.
249. D.N. Buckley and L.D. Burke, J. Chem. Soc., Faraday Trans. I, 71(1975)1447.
250. D.N. Buckley, L.D. Burke and J.K. Mulcahy, J. Chem. Soc., Faraday Trans.  
I, 72(1976)1896.
251. D. Michell, D.A.J. Rand and R. Woods, J. Electroanal. Chem., 84(1977)117.
252. J.O. Zerbino, N.R. de Tacconi and A.J. Arvia, J. Electrochem. Soc.,  
125(1978)1266.
253. S. Gottesfeld, J.D.E. McIntyre, G. Beni and J.L. Shay, Appl. Phys.  
Letters, 33(1978)208.
254. G. Beni, S. Gottesfeld, J.D.E. McIntyre and J.L. Shay, U.S. Patent,  
4,191,453(1980).
255. S.K. Deb, Phil. Mag., 27(1973)801.
256. H.R. Zeller and H.U. Beyeler, Appl. Phys., 13(1977)231.

257. J.D.E. McIntyre, W.F. Peck and S. Nakahara, J. Electrochem. Soc., 127(1980)1264.
258. J.D.E. McIntyre, G.A. Pasteur and W.F. Peck, to be published(1981).
259. S. Gottesfeld and J.D.E. McIntyre, J. Electrochem. Soc., 126(1979)742.
260. G.E. Rice, Appl. Phys. Letters, 35(1979)563.
261. J.L. Shay and G. Beni, IEEE Trans. Electron. Devices, 26(1979)1138.
262. L.M. Schiavone, W.C. Dautremont-Smith, G. Beni and J.L. Shay, Appl. Phys. Letters, 35(1979)823.
263. J.L. Shay, G. Beni and L.M. Schiavone, Appl. Phys. Letters, 33(1978)942.
264. C.E. Rice, in "Fast Ion Transport in Solids", Eds. Vashista, Mundy and Sherroy, Elsevier, 1979, pag. 103.
265. G. Beni and J.L. Shay, Appl. Phys. Letters, 33(1978)567.
266. S. Gottesfeld, J. Electrochem. Soc., 127(1980)1922.
267. J.O. Zerbino and A.J. Arvia, J. Electrochem. Soc., 126(1979)93.
268. S.H. Glarum and J.H. Marshall, J. Electrochem. Soc., 127(1980)1467.
269. J. Mozota, M. Vukovic and B.E. Conway, J. Electroanal. Chem., 114(1980)153.
270. I.I. Labovskaya, V.I. Luk'yanycheva and V.S. Bagotzky, Elektrokhim., 1(1965)514.
271. N.A. Balasheva and V.E. Kazarinov, Elektrokhim., 1(1965)612.
272. V.E. Kazarinov and N.A. Balasheva, Dokl. Akad. Nauk., U.R.S.S., 157(1964)1174.
273. M.W. Breiter, Electrochim. Acta, 8(1963)925.
274. B.E. Conway, H. Angerstein-Kozłowska and W.B.A. Sharp, in "Symposium on Electrocatalysis", Ed. M.W. Breiter, The Electrochem. Soc., N.Y., 1974.
275. J.C. Huang, W.E. O'Grady and E. Yeager, J. Electrochem. Soc., 124(1977)1732.
276. K.S. Kim, C.D. Sell and N. Winograd, in "Symposium on Electrocatalysis", Ed. M.W. Breiter, The Electrochem. Soc., N.Y., 1974.
277. J.G.N. Thomas, Trans. Faraday Soc., 57(1961)1603.

278. N. Pentland, J.O'M. Bockris and E. Sheldon, J. Electrochem. Soc., 104(1957)182.
279. L.I. Krishtalik, Elektrokhim., 2(1966)624.
280. V. Srb, R. Mraz and S. Tichy, Scientific Papers of the Institute of Chemical Technology, Prague, B15(1972)93.
281. M. Morita, C. Iwakura and H. Tamura, Electrochim. Acta, 24(1979)639.
282. W. Böld and M.W. Breiter, Electrochim. Acta, 5(1961)145.
283. V.S. Bagotzky, Y.B. Vasil'ev, J. Neber and J.N. Pirtskhaleva, J. Electroanal. Chem., 27(1970)31.
284. A. Slygin, A.N. Frumkin and V.I. Medvedovskii, Acta Physicochim., U.R.S.S., 4(1933)911.
285. A.N. Frumkin and A. Slygin, Acta Physicochim., U.R.S.S., 6(1936)819.
286. P. Dolin and B. Ershler, Acta Physicochim., U.R.S.S., 13(1940)747.
287. B.V. Ershler, B.G. Deborin and A.N. Frumkin, Acta. Physicochim., U.R.S.S., 8(1938)365.
288. V.S. Bagotzky and Yu. V. Vasil'ev, Electrochim. Acta, 9(1964)869.
289. D.M. Novak and B.E. Conway, J. Electrochem. Soc., (in course of publication, 1981).
290. J.W. Schultze, Electrochim. Acta, 21(1977)327.
291. R.F. Lane and A.T. Hubbard, J. Phys. Chem., 79(1975)808.
292. W.B.A. Sharp, Ph.D. Thesis, University of Ottawa, 1976.
293. B.E. Conway and H. Angerstein-Kozłowska, J. Electroanal. Chem., 113(1980)63.
294. B.E. Conway, L.H. Laliberté, S. Gottesfeld and H. Angerstein-Kozłowska, in "Proc. Symp. Oxide-Electrolyte Interfaces", The Electrochemical Soc., 1974.