

THE CORROSION BEHAVIOUR OF URANIUM AND
OTHER TRANSITION METALS IN RELATION TO
THE PROPERTIES OF THE SURFACE OXIDE FILMS

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ABSTRACT

The effect of hydrogen on the corrosion behaviour of some uranium-rich alloys and titanium has been studied. The impedance and crystal structure of the corrosion films grown on these metals and on vanadium were investigated as a function of the formation potential. Optical absorption and ellipsometric techniques were used for the continuous measurement of film thickness during corrosion, and an impedance bridge was used in measuring the electrode capacitance and conductance. The crystal structure of the corrosion films was examined by electron diffraction.

The results of this investigation emphasise the role of the corrosion product hydrogen in affecting rates of corrosion of these metals by changing the electronic conductivity of the protective, semiconducting oxide film. High values of capacitance and conductance, observed at certain potentials, are considered to arise from a reversible reaction in the oxide involving a valency change of the metal ions. Electron diffraction reveals that the structure of these corrosion films changes with their formation potential.

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CHAPTER ONE

INTRODUCTION

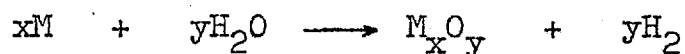
The majority of metals tend to react with oxygen in an aqueous or gaseous environment under normal conditions of temperature and pressure. The formation of an oxide lowers the free energy of the system as is established on the basis of thermodynamics, and this is a reaction which will occur spontaneously.

The good corrosion and oxidation resistance of the useful engineering metals is mainly due to the formation of an adherent film (normally the oxide) which reduces the rate of further attack. It is well known that some of these metals, inspite of a large release of energy on oxidation, show a high resistance to corrosion due to the formation of a very protective film, for example aluminium. In such case the initial rate of reaction of the oxide-free metal may be very rapid, but the oxide film formed will then present a kinetic barrier hindering the diffusion of the reacting (or the product) species. The subsequent corrosion and oxidation behaviour will depend on the physical and electrochemical properties of that oxide layer.

The corrosion of metals and their alloys, employed in nuclear reactor technology, for example, uranium,

zirconium, magnesium, and aluminium is generally characterised by the initial growth of a protective film, during which the rate decreases with time. This is followed by a non-protective regime when the oxide thickness increases linearly with time. The corrosion rate is found to increase with temperature, and a transition to a faster linear or accelerating rate, generally known as "breakaway", is also observed in some cases⁽¹⁾, after a period at the constant rate, the delay depending on the test temperature.

The aqueous corrosion process of these metals, which proceeds in the absence of oxygen, may be represented generally as follows:



However, whether or not the oxide will form a protective film will depend on its physical nature, and the manner in which it grows. An adherent and non-porous film will reduce the rate of further attack, on the other hand a non-adherent or porous oxide will be non-protective. Previous studies have shown that the characteristics of the corrosion product thin films are different from those of the bulk oxides, which adds to

the difficulty of predicting when an oxide will form a protective film.

Corrosion product hydrogen is known to influence the corrosion rate of oxide-covered metals. The importance of hydrogen in the corrosion process has been established by high temperature testing in autoclaves^(1,2) and by polarising test specimens in electrolytic cells^(2,3). The increase in corrosion rate usually associated with the presence of hydrogen has been interpreted as resulting from the mechanical effects on the oxide⁽⁴⁾ or from a change of electrical properties⁽⁵⁾. In specific cases, evidence both for and against the two theories has been given. For example, the corrosion behaviour of aluminium and zirconium has been shown to illustrate the two alternative mechanisms⁽⁶⁾, the effects of hydrogen on the oxide formed on aluminium appear to be primarily mechanical, while those on the oxide formed on zirconium are interpreted as being basically electrical.

The behaviour of hydrogen in these thin protective oxides is important not only for its effect on the corrosion and oxidation rates, but because of the process by which hydrogen accumulates in the underlying

metal. Hydrogen entry into the oxide lattice may cause hydrogen embrittlement (loss of ductility), or may give rise to high internal stresses sufficient to cause spontaneous cracking (hydrogen cracking). The limitations of the use of zirconium and its alloys lie more in the weakening of the metal as a result of hydrogen pick-up than in the reduction in the strength due to the loss of cross section by corrosion.

In the absence of oxygen which depolarises the corrosion product, the factors influencing the movement of hydrogen through the oxide film are not understood. However, these factors must include effects associated with the absorption by, and the diffusion in the oxide of the hydrogen generated by the corrosion process.

The present investigation is directed particularly towards understanding the relation between several different phenomena occurring in oxide films which had previously been observed and associated with the presence of hydrogen.

CHAPTER TWO

PREVIOUS WORK

PART ONE: ELECTRODE PROCESSES1-(a)-Introduction

In electrically conducting media (electrolytes) it is now established that metals corrode by an electrochemical mechanism. The overall reaction of the metal with the environment takes place by two complementary processes, namely anodic and cathodic.

The position of a metal in the electrochemical series is determined by its electrode potential which is an appropriate measure of its thermodynamics instability relative to its ions, but is not a measure of the corrosion rate. The rate at which the corrosion proceeds will depend on the kinetics of the anodic and cathodic processes. These kinetics can be influenced by the formation of a film on the metal which hinders diffusion of the reacting species, by the removal of the reaction products, or by a change in the overpotential of the electrode process.

The electrode potential of a metal in a specific electrolyte is determined by the equilibrium between the metal and its ions in the solution and is measured with respect to a reversible reference electrode in contact

with the electrolyte. The electrode potentials are generally referred to the standard hydrogen electrode, whose potential is taken arbitrarily as zero.

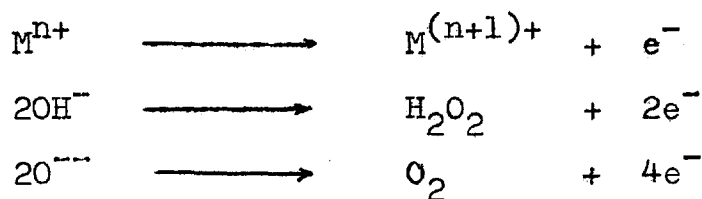
It has been suggested⁽⁷⁾ that the direction of change of electrode potential indicates whether corrosion or passivation is occurring. Change of potential in a positive "noble" direction indicates a tendency to passivity while change in the opposite direction indicates that corrosion is taking place.

1-(b)-Anodic and Cathodic Processes

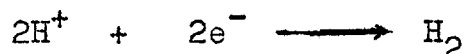
An anodic process is an oxidation reaction i.e. a loss of electrons. The simplest anodic process would be the dissolution of metal according to the equation:



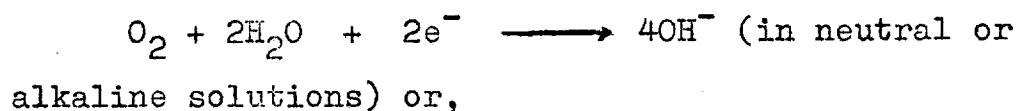
Other anodic reactions may involve cationic oxidation or peroxide formation:



In a cathodic process, a reduction is performed i.e. a gain of electrons. The two most common reactions can be depicted as:



or oxygen consumption, which can be represented by the following equations:



The metal dissolution (anodic) reaction is only controlled by an activation energy in case of a bare metal surface, but this is not the case with an oxide-covered electrode. Anodic and cathodic reactions in this case are separated by an oxide film barrier, the anodic reactions taking place at the metal-oxide interface while the cathodic reactions take place at the oxide-electrolyte interface. A potential gradient develops across the oxide due to the accumulation of excess negative charges at the metal-oxide interface, and of excess positive charges at the oxide-environment interface. The potential gradient acts in opposition to an ionic activity gradient and this may eventually

limit the ionic migration and corrosion would be stifled. The reaction may continue, however, if the conductivity of the film is sufficiently high to allow the charges to flow and neutralise.

Draley and Ruther⁽⁴⁾ have suggested a model describing the anodic and cathodic processes, fig. (1). In this model the growth of an oxide can proceed by the inward diffusion of anions or the outward diffusion of cations under the effect of the concentration gradient. These ionic movements represent electric currents of the same sign. In order to maintain electro-neutrality current must flow in the other direction. Two types of migration have been visualised, diffusion of electrons outwards through the oxide and inward diffusion of protons; both are facilitated by the potential and activity gradients. Draley and Ruther consider it unlikely that hydrogen may be transported through the oxide film as atoms or as hydroxyl ions, and they suggest that protons may migrate via interstitial positions and also in combination with oxygen ions in the lattice, migration then taking place by a series of transfers.

Waber⁽⁸⁾ has suggested an alternative model for uranium. The formation and migration of O^- and OH^- ions is considered more likely than the formation and migration of H^+ and O_2^- . The formation of these species (O^- and OH^-) is thought to result from the absorption of water and oxygen ions on the oxide-electrolyte interface.

1-(c)-Hydrogen Overvoltage

The hydrogen overvoltage of an electrode is a measure of the difficulty of hydrogen evolution, and is defined as the difference between the potential of an electrode when it carries a current density 'i' and the equilibrium potential (at zero imposed current). Evolution of hydrogen at a cathode is opposed by an energy barrier. The rate at which the evolution reaction occurs, defined by the current density, is a function of the activation overvoltage. The latter is related to the energy requirements of the lowest step in the hydrogen evolution reaction.

Tafel⁽⁹⁾ has derived the following relationship between the activation overvoltage and the current

density

$$\eta = a + b \log i$$

where η is the overpotential at a current density i , a is a constant characteristic of the electrode material and its surface state, and b is the Tafel slope, which is one of the parameters indicating the mechanism of hydrogen evolution.

It is generally accepted that the observed overvoltage is due to polarisation caused by activation energy requirements, concentration and resistance effects. The Tafel equation is derived purely by considering the activation process, which assumes that a cation moves away from the metal-solution interface as soon as it dissolved. This is generally not the case. The removal of the anodic products does not increase in the same proportion as the current density and the concentration of these products will increase and cause a back e.m.f. The potential change resulting from concentration polarisation is called concentration overpotential. Polarisation measurements also include ohmic overpotential which arises from an IR drop through a portion of the electrolyte surrounding the

surface of the cathode or through the oxide film that might be formed on the surface or both.

Investigations on the polarisation characteristics of metals have been concerned with the phenomenon of corrosion and passivity. It has been suggested^(10,11) that the corrosion rate of metals can be predicted from polarisation data. Observed rates of corrosion of iron have been found to agree reasonably with rates calculated from polarisation data. The tendency of a metal to passivate has been shown to increase by introducing alloying elements of low hydrogen overpotential. This has been shown for chromium-nickel steels⁽¹³⁾, titanium and its alloys^(14,16), uranium⁽¹⁾ and aluminium⁽³⁾.

Attention has been drawn to the effect of the entry of hydrogen itself, into the metal or oxide film, on the polarisation characteristics of the metal and the mechanism of hydrogen evolution. The overpotential-current relationship of gamma phase uranium, which has a higher hydrogen absorption capacity, is different⁽⁵⁾ from that of the alpha phase. A substantial increase in the potential (in the noble direction) has been observed⁽⁶⁾ when hydrogen is evolved, at a constant current density, from aluminium and zirconium cathodes.

Investigations^(5,17-19) on uranium, titanium, zirconium, niobium, aluminium, and tantalum have shown that after cathodic polarisation, the current density was large at any given potential. Impedance measurements^(3,17,19) have shown a similar hysteresis in the potential-conductivity curves, and one interpretation suggests that the entry of hydrogen into the oxide film increases its conductivity, which would raise the potential in the noble direction.

PART TWO: CORROSION BEHAVIOUR

2-(a)-Protective Oxide Films

The kinetics of oxidation or corrosion are usually described in terms of a mathematical relationship between the oxide thickness and time. This relationship may be of several forms e.g. linear, parabolic, logarithmic, etc., depending on factors such as temperature, stresses developing within the oxide and the existence of an electric field across the oxide.

Pilling and Bedworth⁽²⁰⁾ have introduced the concept of the oxide volume ratio to predict whether the oxide film formed during corrosion will be

protective or not. An oxide film will be protective if the Pilling-Bedworth Ratio, which is the volume per metal atom of the oxide divided by the atomic volume of the metal, is greater than unity. Metals having volume ratios less than unity will not form protective oxides. It has been pointed out by Pilling and Bedworth that the rate controlling step, which is the slowest step, may be the transport of ions through the oxide. Since the oxide is thickening with time, the rate of transport, and consequently the corrosion rate will decrease with time. Assuming that the diffusion process itself does not change with time and is the same throughout the oxide film, then the rate of transport ($\frac{dm}{dt}$) is **inversely** proportional to the oxide film thickness

$$\frac{dm}{dt} = k \frac{1}{x}$$

$$\text{and as } x = \text{const. } m.$$

$$\text{then } \frac{dx}{dt} = \frac{\text{const.}}{x}$$

$$\text{or } x^2 = k_p t + k_o$$

where k_p and k_o are the reaction constants.

It has been reported that there are several exceptions to the Pilling-Bedworth principle^(21,22). For example, although the volume ratio of magnesium

is less than unity, the oxide can be protective under certain conditions. Films formed on some metals with ratios greater than unity have been shown to break down giving rise to various types of irregular cracks. It should be emphasized, however, when mentioning the Pilling-Bedworth Principle, that material transport can take place by diffusion through a protective film, and the overall reaction may still be linear if one of the interface reactions is rate controlling.

The growth of a protective oxide layer with a time-dependent corrosion rate is generally followed by non-protective kinetics. However, the rate may abruptly accelerate after a definite period of time, in which case the transition is often termed "break-away". The transition from protective to non-protective kinetics can be explained in the light of the Pilling-Bedworth theory. If the specific volume of the oxide is greater than that of the metal, and assuming that the reaction takes place by the inward diffusion of anions, a compressive stress will develop within the oxide, and will increase with increasing oxide thickness, until fracture takes place in the oxide layer. The corrosion rate will then be linear, as it will be

determined by the diffusion through the uncracked oxide layer, assumed to have a statistically constant thickness (averaged over the oxide surface). The change from protective to non-protective kinetics is termed "transition". Transition has also been explained in terms of strain-induced recrystallization⁽²³⁾, or loss of ductility of the oxide⁽²⁴⁾ on changing from a non-stoichiometric to a stoichiometric condition.

Previous studies have shown that the corrosion^(3,8,25,26) and high temperature oxidation⁽²⁷⁻³⁴⁾ of metals like uranium, aluminium, zirconium, titanium and niobium follows protective kinetics but after a certain time transition to non-protective kinetics takes place. However, the absence of the parabolic kinetics during the first few seconds of oxidation of uranium at 250°C has been observed by Evans⁽³⁵⁾ and suggested to represent the lateral growth of the oxide on the specimen surface.

The protective ability of the oxide film depends on the thickness to which the film can grow before failure and the rate of diffusion of the reacting species. The first parameter is influenced by the stresses developing throughout, and the plasticity and strength of, the oxide film. In the case of

corrosion of uranium and zirconium, the duration of the protective regime depends on alloying conditions⁽³⁶⁻³⁸⁾, pH of the bath⁽¹⁷⁾ and the potential applied to the corroding specimen⁽³⁹⁾. Diffusion processes are influenced by concentration gradients through, and composition⁽²⁵⁾ and structure⁽⁴⁰⁾ of the oxide film.

2-(b)-Role of the Corrosion Product Hydrogen

(1) The effect of Hydrogen on Corrosion Rate

Earlier attempts to develop corrosion resistant uranium alloys under operational conditions in nuclear reactors have lead to studying the effects of the corrosion product hydrogen. It has been established for the case of uranium⁽¹⁾, aluminium⁽²⁾, and zirconium⁽²⁵⁾ and their alloys that an increase in the corrosion is associated with the presence of hydrogen.

The amount of hydrogen evolved from a corroding specimen of uranium was observed to be less than the theoretical quantity from the uranium-water reaction. This has been established in cases of aqueous corrosion⁽⁴¹⁾ and humid oxidation⁽⁴²⁾. The work of Isaacs and Wanklyn⁽⁴³⁾ and Breen⁽⁴⁴⁾ has also shown that an appreciable amount of hydrogen can be absorbed by

anodic zirconia films on cathodic polarisation.

High temperature testing has shown that the corrosion rate of aluminium is reduced by making it the anode in an electrolytic cell or by alloying with metals of low over-potential such as iron or nickel⁽²⁾. Similar observations were made on titanium⁽⁴⁵⁾ whose corrosion rate is dramatically reduced by applying a small positive potential. Uranium corrosion in a crevice or other confined space in which hydrogen can accumulate, is more severe⁽⁴⁶⁾ than in free exposure to water. More recent work has shown that the corrosion rate of uranium, zirconium and their alloys depends on the hydrogen activity^(3,37). A breakaway has been noticed, after a certain period of time, when zirconium is exposed to steam, and this ~~was~~ thought to be associated with the hydrogen pick-up of the metal. Similar observations have been noted on the effect of steam or humidity on oxidation rates of titanium⁽³¹⁾, mild and low-alloy steels⁽⁴⁷⁾ and plutonium⁽⁴⁸⁾.

Attempts have been made to explain the hydrogen induced damage in the corrosion process. The possibility of reduction of the oxide film by hydrogen is generally excluded due to the great chemical stability of such oxides under the conditions of corrosion. Two

fundamental theories have been proposed to explain the deleterious effect of hydrogen. The first is by Draley⁽⁴⁾ who suggests that hydrogen may accumulate beneath the oxide and cause the mechanical rupture of the film and may react with the metal forming a hydride. The latter is thought to spoil the adherence of the film or cause its crystallisation. For the case of uranium, Draley and others^(4,42,49) suggest that the hydride formed acts as a catalyst in increasing the corrosion rate by its reaction with water giving UO_2 and the further liberation of hydrogen. Waber⁽⁵⁰⁾, however, suggests that UH_3 is more stable than generally thought and thus it can not act as a catalyst, but he considers more likely that UH_3 inclusions may influence the rate of corrosion by increasing the local breakdown of the oxide film.

The other theory has been proposed by Leach⁽⁵⁾, who observed higher rates of corrosion of uranium⁽⁵⁾, manganese⁽⁵¹⁾, and zirconium⁽²⁵⁾, not associated with any mechanical breakdown of the oxide film. This theory suggests that the effect of hydrogen on the protective oxide is primarily of an electrical nature. The mechanism is based on the dissolution of hydrogen in the semiconducting oxide, which by acting as a donor

impurity, changes the electronic conductivity, and this influences the rates of ionic diffusion. The increase in electronic conductivity could accelerate the movement of ions as a result of the space charge created by the movement of the excess electrons as proposed by Wagner⁽⁵²⁾.

(ii)-Effect of pH and Potential

The corrosion behaviour of uranium and zirconium and their alloys have been examined in acidic and alkaline solutions^(3,25,37,39). It has been noticed that rates of corrosion are generally higher in alkaline than in acidic solutions at the same hydrogen activity. Similar effects of pH have been shown for other metals⁽⁵³⁾. The inability to detect the parabolic kinetics in the earlier stages of uranium corrosion in alkaline solutions was attributed to the high speed with which the reaction proceeds, and Nehru⁽¹⁷⁾ concludes that higher rates may be related to a change in the oxide film character.

Rates of corrosion generally increase with cathodic polarisation^(1-3,25,37,128) Studies on uranium, however have shown that the pH of the corrosion environment has an influence on the rate-potential relationship. In acidic solutions, corrosion rate increases parabolically with hydrogen activity, while

in alkaline solutions a complex relationship was obtained, where in a limited region the rate decreases with increasing potential. This led to the suggestion that oxides formed may differ in composition and structure from those formed under acidic conditions, and this was supported by electron diffraction results⁽²⁵⁾.

There is evidence in the literature that the oxides of uranium^(54,55) and other transition metals like manganese⁽³³⁾ and titanium⁽⁵⁶⁾ exhibit a change in their semiconductive nature caused by deviation from stoichiometry. Leach and Nehru explained the reversals in the rate-potential relationship of uranium in terms of the dissolution of protons in an n- or p- type oxide. The entry of a proton into a p-type oxide, accompanied by an electron from the metal to maintain electrical neutrality, will reduce the electronic conductivity, and hence rates of ionic diffusion will be reduced. Hydrogen entry will have an opposite effect on an n-type oxide. Similar observations on the effect of hydrogen on semiconductive oxides have been noted by Hecklesberg⁽⁵⁷⁾. Therefore, it was suggested, that, in regions where corrosion rate decreases with potential, the oxide formed is a p-type semiconductor, and an n-type oxide

is proposed to form in regions where the corrosion rate increases with potential. A modification of the Pourbaix diagram (Fig. 2) of the system uranium-water was proposed (Fig. 3) as a result of these investigations.

(iii)-Effect of Alloying

The good corrosion resistance of gamma phase uranium is attributed to⁽¹⁾ its high capacity for hydrogen absorption (20 p.p.m.) compared with the alpha phase (0.34 ppm)⁽²⁾. Manganese also shows similar characteristics⁽⁵¹⁾. The reasons for alloying uranium with molybdenum lies in the latter's function as a gamma stabiliser⁽¹⁾. Alloying with elements such as niobium and zirconium provides separate phases⁽¹⁾ which act as sinks for hydrogen. Wanklyn also reports⁽⁴⁶⁾ that the Zircaloy-2 can, bonded to uranium, acts as a sink for hydrogen and reduces the rate of attack. Alloying aluminium with metals like platinum, nickel, and iron, or even the existence of such ions as soluble species in the corrosion bath, increases its corrosion resistance by providing sites for the easy discharge of hydrogen⁽²⁾. Alloying zirconium with 0.15 - 1.5% by wt. niobium and small quantities of iron restricts⁽⁵⁸⁾ the

absorption of hydrogen during corrosion.

Alloying can thus influence the removal of corrosion product hydrogen by either stabilising a metal phase in which it is soluble, or by providing sites for its evolution as a gas.

(iv)-Effect of Dissolved Oxygen

The presence of hydrogen depolarisers such as oxygen or H_2O_2 have been observed to lower the initial rates of corrosion of uranium⁽⁵⁹⁻⁶¹⁾. Recently Orman⁽⁶²⁾ has observed that the addition of oxygen to water vapour caused a substantial decrease in the corrosion rate, but the retardation was for a limited period of time depending on the initial gas pressure and the test temperature.

Nehru⁽¹⁷⁾ on the other hand has observed that the presence of excess dissolved oxygen causes an increase in the initial rate of corrosion and the film formed consisted mainly of a non-adherent oxide. Draley⁽⁶³⁾ also reports an increase in the corrosion rate of zirconium alloys in the presence of excess dissolved oxygen. The discrepancy in these results have been attributed⁽¹⁷⁾ to such factors as the amount of dissolved oxygen (as has been demonstrated for steel⁽⁶⁴⁾), the duration of the test and the

electrochemical conditions.

Mechanisms have been proposed explaining the effect of dissolved oxygen on the corrosion rate. Hoar⁽⁶⁵⁾ proposes, in the case of zinc and iron, that dissolved oxygen may "arrest" cations as they emerge from the original air-formed film, thus thickening the oxide and preventing corrosion. For uranium, it has been suggested^(59,66) that a more protective film is formed in the presence of oxygen, which depolarises the corrosion product hydrogen. Radiotracer studies⁽⁶⁶⁾ have confirmed this, by showing that dissolved oxygen does not react directly with the metal during the corrosion process, but is mainly consumed to react with hydrogen.

2-(c)-Temperature Dependence of Corrosion Rate

Studies on the temperature dependence of corrosion rate have shown that the corrosion of uranium is under anodic control i.e. the process is controlled by the diffusion of oxygen ions. Values of the Arrhenius activation energy vary^(67,68) between 22 to 24 k. cal./gm. mole for dry oxidation at temperatures up to 650°C, and those for humid or aqueous corrosion⁽⁶⁹⁾ lie between 6 and 16 k. cal./gm. mole. The higher of these values is in a fair agreement with those

calculated for the self diffusion of oxygen in UO_2 (29.7 k. cal./gm. mole), and far below those for the self diffusion of uranium in UO_2 ^(71,72) (88 - 108 k. cal./gm. mole). Experimental values of the activation energy of oxidation of manganese below 1000°C ⁽⁷³⁾, and of titanium below 700°C ^(30,31) also indicate that oxygen diffusion is the rate controlling step.

It has been noticed that the rates of oxidation of uranium^(74,75) and plutonium⁽⁷⁶⁾ are sometimes lower at a higher temperature, and this was interpreted in terms of a change of the oxide character. The oxide formed on uranium between 900 and 1000°C in a CO_2 atmosphere⁽⁷⁵⁾, where the oxidation rate is low, is thought to be more plastic and can grow to a greater thickness before failure. A more protective film is proposed to form⁽⁷⁶⁾ on plutonium at 410°C compared to that at 50°C .

Experimental values of activation energy for aqueous corrosion or humid oxidation of zirconium⁽³⁷⁾, uranium^(7,49,69), magnesium⁽⁷⁷⁾ and iron⁽⁵³⁾ are lower than for dry oxidation. A further decrease in the activation energy ^{corrosion of} for uranium⁽³⁶⁾ and zirconium⁽³⁷⁾ by alloying and cathodic polarisation has been observed. An explanation was offered by Gregg and Jepson⁽⁷⁷⁾,

to account for the lowering of the activation energy due to the presence of moisture. This model suggests that cation vacancies are created as a result of the entry of protons, and their combination with the oxygen ions in the lattice forming OH^- ions. However, it is difficult to apply this model to metals like uranium where oxidation takes place by the interstitial oxygen diffusion, and in which the existence of cation vacancies is highly improbable⁽⁷⁸⁾.

PART THREE: PROPERTIES OF PROTECTIVE OXIDE FILMS

3-(a)-Mechanical Properties

Stresses are developed within oxide films during their formation due to volume changes. The volume of the oxide is greater than that of the metal by about 100% for UO_2 and 50% for ZrO_2 . Plastic deformation of oxide films and to a lesser extent their strength are regarded as responsible for their survival. Previous work has shown that^(75,79-84) factors which influence the plasticity of oxide films have a marked effect on the corrosion behaviour of metals. These factors include corrosion temperature, gas pressure (in gaseous oxidation), alloying, deviation from stoichiometry and growth current.

Temperature-induced plasticity of oxides formed on uranium between 900 and 1008°C in CO₂ atmospheres is thought to encourage the formation of an uncracked film⁽⁷⁵⁾, thus explaining the decreasing oxidation rate with increasing temperature in this range. Similar observations have been made on the lower oxidation rates of uranium at 20 atmospheres CO₂ compared with that 1 atmosphere. Alloying uranium⁽³⁶⁾ and zirconium^(37,38) increases the thickness to which the oxide grows before failure, possibly due to an increase in oxide plasticity. Deviation from stoichiometry also increases the plasticity of UO₂⁽⁸⁰⁾ and ZrO₂⁽⁸¹⁾. However, the findings of Ashbee and Smallman⁽⁸²⁾, who observed that TiO₂ is hardened when made non-stoichiometric, are apparently not consistent with this generally accepted phenomenon. However, a full explanation must consider deformation rates relative to temperature and the type of lattice defect which accommodates the non-stoichiometry.

Anodic oxides on aluminium show enhanced plasticity during film growth. Neufeld⁽⁸⁴⁾ suggested that this "diffusional plasticity" occurs even at very low current densities and concludes that

this phenomenon can be applied to corrosion films.

Corrosion product hydrogen is known to cause mechanical damage to oxides^(2,6). However, Wanklyn points out that⁽⁴⁰⁾ the difference between the corrosion rate of zirconium in steam and in dry oxygen might be attributed to the influence of H_2O rather than hydrogen, on the oxide failure. Recently Breen⁽⁴⁴⁾ has observed that compressive stresses can arise in anodic oxides of aluminium due to hydration. Dehydration, which can occur by replacing three protons with an aluminium ion, results in tensile stress.

3-(b)-Crystal Structure

Previous work has shown that oxide films in general, and especially those formed on transition metals, have a complex structure. In some cases, diffraction patterns obtained from surfaces of zirconium⁽⁸⁵⁾ and titanium⁽⁸⁶⁾ oxides could not be identified as any of their known oxides. This difficulty has been attributed to the presence of two or more oxides on the metal surface, and the variation of lattice parameter of the oxide with oxygen content. Oxide film structure is influenced by several factors e.g. temperature, environment, growth current "for anodic films", duration of oxidation and method of

surface preparation of the metal.

Only UO_2 is detected on uranium when oxidised in air below 300°C , U_4O_9 and U_3O_7 are formed at temperatures around 400°C and from 500 to 600°C the UO_2 structure is observed⁽⁸⁷⁾. The change of the oxide structure near 400°C was found to coincide with a change in the oxidation rate⁽⁸⁸⁾ roughly at the same temperature, and these phenomena are thought to be related. For the case of titanium only the rutile modification forms at temperatures up to 750°C ^(30,89). However, Koizumi⁽⁹⁰⁾ has observed that both rutile and anatase are formed if a metal specimen is heated at 500°C and quenched in water, while only rutile is formed if it is quenched in oil.

Oxides formed on uranium in alkaline solutions differ in structure from those formed in acidic environments.⁽²⁵⁾ Hart has observed that the oxide formed in water is predominantly UO_2 ⁽⁸⁵⁾ for the first 25 hours, and after longer periods additional phases begin to form, presumably $\text{UO}(\text{OH})_2$ or $\text{UO}_2 \cdot 2\text{H}_2\text{O}$. Anodic oxides formed on uranium in non-aqueous conditions consist mainly of UO_2 ⁽⁹¹⁾, while those formed in aqueous conditions are different⁽⁸⁵⁾. Shorter exposures in H_2SO_4 resulted in the formation

of UO_2 , while U_3O_8 was formed when the specimen was anodised for more than 10 seconds.

The structure of the oxides of titanium formed in dry conditions seem to be different from those formed in aqueous environments. Rutile is the only modification detected in cases of atmospheric^(30,86) or low pressure⁽⁹²⁾ oxidation, although in many cases diffraction data did not correspond to any of the known oxides. In aqueous conditions, the initial film has been thought to be⁽⁹⁰⁾ a layer of anatase. With long exposure, a layer of rutile starts to grow between the metal and the anatase layer.

Data on the anodic oxides of titanium in aqueous systems is rather conflicting, but the structure seems to depend on the growth current density. Anatase and rutile have been detected by some workers⁽⁹⁰⁾ and only anatase by others⁽⁹³⁾. However, at very low current densities (50 uA/cm^2) brookite was identified⁽⁹⁴⁾.

Hart⁽⁸⁵⁾ has shown that the method of surface preparation may affect the oxide structure. While only UO_2 was detected on mechanically polished uranium, U_2O_5 and U_3O_8 were formed on the electro-polished specimens.

3-(c)-Composition

Variations of stoichiometry occur across the thickness of the oxide layer for many metals. This has been shown for tantalum⁽⁹⁵⁾ and aluminium⁽⁹⁶⁾. Wanklyn⁽⁴⁰⁾ suggests that some of the optical and electrical properties of zirconia films may arise from variations of stoichiometry in a layered sequence. The formation of non-stoichiometric oxides on uranium under certain conditions has been proposed to explain⁽²⁵⁾ the corrosion behaviour of the metal.

Electron diffraction studies⁽⁹⁷⁾ have revealed that, at very low pressures, oxides formed on uranium were in the sequence U/UO/UO₂, with the possibility of a high degree of non-stoichiometry at the phase boundaries. Non-stoichiometry in single phase UO₂ films has also been confirmed by diffraction experiments⁽⁹⁸⁾, which showed the UO₂ structure with a slightly reduced lattice parameter attributed to excess oxygen content in the lattice. The formation of non-stoichiometric oxides and layered structures has been shown also for oxides of titanium⁽⁹⁹⁾ and manganese^(33,34).

3-(d)-Semiconduction

Transition metal oxides are predominantly electronic conductors. Due to their departure from

stoichiometry, these oxides exhibit semiconduction properties. Both p-type and n-type conduction has been observed in oxides of uranium⁽⁵⁴⁾, titanium⁽⁵⁶⁾, and manganese⁽³³⁾. For zirconium, although it generally forms an n-type oxide⁽¹⁰⁰⁾, there are some circumstances where a p-type ZrO_2 is suggested to form⁽⁴⁰⁾.

Impedance measurements have shown that the resistance and capacitance of oxide films are frequency dependent^(6,96). This has been interpreted in terms of a layer structure of the oxide. Under conditions of cathodic polarisation⁽⁶⁾, the inhomogeneity of the oxide and the variation of hydrogen concentration throughout the film are thought to be the cause of resistance and capacitance variation across the oxide thickness.

The conductance of oxide films have been found to increase with cathodic polarisation, and this was attributed either to a reduction in the oxide thickness or to a decrease in its resistance⁽⁶⁾. Aluminium, under specific conditions gives an example of the first phenomenon, where the change in the surface conductance has been shown, by metallographic examination, to arise from mechanical damage to the

film which is thought to be due to the accumulation of hydrogen. The increase in conductance of ZrO_2 films has been attributed to the dissolution of hydrogen in the oxide⁽⁶⁾. Similar observations have been noted for uranium⁽⁵⁾ and tantalum⁽¹⁶¹⁾.

The increase of oxide conductance due to hydrogen can be discussed in terms of dissolution of a donor impurity in an n-type oxide. The entry of a proton, whether into an interstitial position in the lattice or to combine with oxygen and form OH^- ions, is accompanied by the entry of an electron from the metal to maintain electrical neutrality. This leads to increased electronic conductivity. By a mechanism similar to that proposed by Wagner⁽⁵²⁾, for the system $\text{Ag-Ag}_2\text{S-S}$ this enhanced electronic conduction may lead to increased ionic diffusion.

3-(e)-Capacity

The oxide film formed on valve metals may be considered as the dielectric of a parallel plate condenser in which the metal represents one plate and the electrolyte the other. The impedance of such oxides is not primarily capacitative and it has been represented by a capacitor and a resistor in parallel⁽¹⁰⁰⁾

or by several such RC elements connected in series^(6,96).

The reciprocal of the capacitance of an oxide film has been taken as proportional to its thickness, since this follows from the equation for the capacity of a parallel plate condenser. A linear relation was found between $\frac{1}{C}$ and the formation voltage of some anodic films demonstrating the validity of this approach. However, the case is different when the oxide is cracked or when water or hydrogen may enter into the oxide. Wanklyn⁽¹⁰²⁾ has found that the protective film on zirconium show higher capacities and attributed this to the penetration of the electrolyte into the cracks in the film. The protective character (or degree of cracking) of films formed on different alloys has been expressed by the term $\frac{1}{CW}$ where W is the weight of the oxide. The term $\frac{1}{CW}$ was found to have a high value and remain nearly constant with time for highly resistive alloys. A low $\frac{1}{CW}$ value, which decreases with time, was obtained for less resistive alloys.

The frequency dependance of the impedance of oxide films has been interpreted in terms of a multi-layer oxide, in which each layer is represented by a

parallel RC element. The capacitance of an oxide film is influenced by changes in its conductance. If the resistance of the oxide is decreased, for example due to cathodic polarisation⁽¹⁹⁾ or as happens by high temperature annealing⁽¹⁰³⁾, the capacitance value would be larger. This increase has been discussed in terms of shorting out one or more the capacitors of the RC elements due to the reduction in resistance. The opposite is true when the oxide resistance is increased⁽⁹⁵⁾.

High values of capacitance, greatly in excess of that of the double layer was observed at certain potentials for titanium, uranium, vanadium and niobium⁽¹⁹⁾. Reversals in the capacitance-potential and conductance-potential relationship were also observed for these metals. This phenomenon was discussed in terms of a Faradaic capacity resulting from a reversible reaction involving a change of valency of the metal ions in the oxide. This would allow the oxide to absorb charge without a change in the potential, and the following reaction ~~reaction~~ was suggested the most probable.



which only involves the movement of protons and electrons.

3-(f)-Effect of Alloying on Oxide Film Properties

The Wagner-Hauffe theory explained the effect of the valency of the alloying element on the defect structure of an oxide⁽¹⁰⁵⁾. The application of this mechanism to ionic and semiconducting oxides has been summarised by Stringer⁽¹⁰⁶⁾. However, this theory is limited to cases where the alloying element dissolves into the oxide lattice, while little is known about the mechanism of oxidation when more than one oxide is formed due to the varying electrical and defect properties of multi-component oxides.

Previous investigations have shown that alloying may change the mechanical, electrical, or structural properties of oxide films. Corrosion rate changes of uranium-zirconium alloys have been explained in terms of an increased oxide plasticity⁽¹⁷⁾ allowing the film to grow to a greater thickness before failure. Douglass⁽²⁴⁾ has found that alloying additions improve the corrosion resistance of zirconium and increases the oxide plasticity. Alloying additions enhance the diffusion rates in the oxide, as has been observed for the system $\text{UO}_2 - \text{ZrO}_2$. This has been attributed to disorder in the UO_2 lattice due to the presence of zirconium ions.⁽¹⁷⁾ Wanklyn⁽⁴⁰⁾ reports also that

alloying zirconium raises the conductivity of the corrosion film. The lattice parameter of the oxide, and hence the degree of misfit at the metal-oxide interface can be affected by alloying. Draley⁽¹⁰⁷⁾ attributed the improved corrosion resistance of uranium-zirconium alloys to the incorporation of ZrO_2 in the lattice, which has been shown to reduce the lattice parameter of the UO_2 cell⁽¹⁰⁴⁾, and hence to influence the migration process.

PART FOUR: METHODS OF MEASUREMENT

4-(a)-Corrosion Rate Measurement

(i)-Optical Methods

The optical techniques are generally simple, accurate and non-destructive. Their main advantage in addition to this is that the film thickness can be measured "in situ". Their main limitation is that errors might arise due to the inaccuracy of the data about the optical constants of thin films. The optical constants normally used are those of the bulk oxides. Interference, absorption, and ellipsometric methods will be described here.

(1)-Interference

If a monochromatic light falls on a film some

light is reflected at the film-air interface and the remainder is refracted by the film and reflected at the metal-oxide interface. Destructive (minimum reflection) and constructive (maximum reflection) interference occurs when:

$$2nt \cos. \phi + f(\lambda) = \left(\frac{2m-1}{2} \right) \lambda$$

or

$$2nt \cos \phi + f(\lambda) = m\lambda$$

respectively; where t is the oxide film thickness, n is the refractive index of the oxide, ϕ is the angle of refraction (normally very small), $f(\lambda)$ is a constant allowing for the phase change produced by the two reflections, and m is an integer corresponding to the order of reflection.

This technique can be used to follow the continuous film formation, or to measure the overall film thickness by the use of spectrophotometers where the wave length of interference minimum or maximum can be determined. However, it does not apply to very thin films, i.e. in regions before the first interference minimum is reached. This technique has been successfully applied to anodic films^(108,109); and Wilkins⁽¹⁰⁹⁾ points out that the high accuracy of measuring thicknesses of anodic oxides compared with that of thermal films might be due to the

unevenness of growth of the latter.

(2)-Absorption

When white light falls on an optically absorbing film on a reflecting surface the change in the intensity of the reflected beam as the film thickens is assumed to be the light absorbed by the film. This is expressed by the Lambert's Law:

$$I = I_0 e^{-2\theta x}$$

where I and I_0 are the intensity of reflected beam for a finite value of x when $x = 0$ respectively, θ is the absorption coefficient of the film, and x is the film thickness. Assuming that θ does not change with time and that losses by processes other than absorption are constant and independent of x , then the value $\log \frac{I_0}{I}$ can be taken as proportional to film thickness.

The technique is simple and has been described elsewhere⁽³⁾. It has been used to study the corrosion kinetics of several metals^(3,25,37), its advantage being that it enables the continuous measurement of corrosion rates, and the estimation of film thickness at early stages of corrosion long before the first interference minimum is reached. The main limitation is that a measurement of the absolute thickness

necessitates a knowledge of the absorption coefficient of the oxide. However, the calculation of absolute thickness is not always necessary in kinetics studies.

(3)-Ellipsometry

When a beam of plane polarised light falls on a bare metal surface, or one with a film on it, it becomes elliptically polarised. The ellipticity depends on the angle of incidence, the thickness of the film, and the optical constants of the metal, the film, and the environment. The ellipticity is defined in terms of two parameters, ρ and Δ . ρ is the ratio of the magnitude of the reflection coefficient for light polarised parallel and perpendicular to the plane of incidence, and Δ is the relative phase difference of the two polarisations. The two parameters describe a vector (called the ellipticity vector $\bar{Z}$) whose magnitude is ρ and direction is Δ . As the film thickness increases this vector changes, and the curve traced by its end on an "Argand diagram", normally called a polar curve, is related to the optical constants of the metal, the film and the thickness of the latter by

complex equations. In practice, the film thickness and optical constants are obtained by fitting theoretically computed curves to the one obtained experimentally.

The basic function of the optics of the ellipsometer is to determine the relative amplitude reduction ρ and the relative phase retardation Δ . This needs a monochromatic polarised beams to pass through a system composed of a polariser, the reflecting surface to be examined and an analyser with a quarter wave plate in a diagonal azimuth fixed either before or after the reflection. A detailed description of various types of ellipsometers, and the recent developments such as the use of photoelectric polarimeters, has been given by Winterbottom⁽¹¹⁰⁾.

The technique is very sensitive, and furthermore, the accuracy of measuring the state of polarisation of light has been increased tremendously by the use of photoelectric devices. A mean film thickness of $10^{\circ}\text{\AA}$ could accurately be measured by Kruger⁽¹¹¹⁾. The usefulness of this technique has also been demonstrated⁽¹¹⁰⁾ in detecting the formation of new phases during film growth and distinguishing between absorbed oxygen and an oxide

film.

(ii)-Electrometric Methods

This method depends on the fact that an oxide film existing on a metal surface can be reduced at a definite potential by making the specimen the cathode in an electrolytic cell. From the quantity of electricity needed to complete the reduction process, the film thickness in angstroms can be calculated from the equation:

$$x = \frac{ItM}{2\rho A} \times \frac{10^5}{96500}$$

where I is the d.c. current in mA (normally very small), t is the time in seconds, M and ρ are the equivalent weight in grams and the density in gms/cm.³ of the oxide and A is the specimen area.

The technique is quite simple. A small d.c. current is applied and the potential difference between the specimen and a reversible electrode is recorded as a function of time. An abrupt change in potential indicates the completion of reduction. Closed deaerated cells are normally used. A description of the cell and the electric circuit has been given elsewhere^(112,113).

This method has been used for measuring the film

thickness of oxides and sulphides. Hoar points out⁽¹¹³⁾ that while it is quite accurate for thin sulphide films it is less so with thick ones. The limitations of the this method are:

- 1- It can not be used for continuous rate measurements.
- 2- It applies only for reducible oxides.
- 3- It is invalid if hydrogen evolution accompanies the reduction process.

(iii)-Gravimetric Methods

This technique has been long in use for the study of high temperature oxidation and corrosion kinetics. The weight gain or weight loss (after mechanically removing the oxide film) of a metal can be taken as a measure of the rate of corrosion. Highly sensitive microbalances have been developed, and that designed by Gulbransen⁽¹¹⁴⁾ is reported to have a sensitivity of $0.3\mu\text{m.}$ for an oxidising sample of a total weight of 0.684 gms. This technique can be used for the continuous determination of corrosion rate in case of dry oxidation, but for aqueous corrosion only intermittent measurements are possible. It has also limitations when oxides are soluble in aqueous media.

(iv)-Volumetric and Manometric Methods

The basic principle of these two techniques is the detection of the decrease in volume or in pressure of the reacting gas during the oxidation process. Neither method is recommended when the reacting gas consists of a mixture of different gases due to the variation in the rate of attack of each gas. While the first technique (constant pressure) has been used successfully for the determination of the rate of growth of oxides layers between 50 and 10,000 °A, the constant volume method has been used only for measurement of greater layer thicknesses⁽¹¹⁵⁾. Apparatus has been described in the literature^(115,116) and both techniques have been recently used⁽⁸⁸⁾ for the kinetic studies of uranium oxidation between 300 and 625°C.

(v)-Other techniques

Several other methods of estimating corrosion rate have been used before. These include electrical methods (capacitance and conductance), radio-active tracer techniques, interferometric techniques, but in the present work were not considered applicable.

4-(b)-Oxide Film Properties

(i)-A.C. Impedance Techniques

This technique enables the determination of oxide film impedance by examining the voltage response of the oxide-covered electrode on which a sine or a square wave current is applied. The voltage response, normally very small, is amplified and examined in different ways. The electrical behaviour of the electrode can be compared with that of an analogue circuit consisting of a capacitor and a resistor in parallel or the voltage response of the electrode may be recorded and analysed as a function of time.

The a.c. impedance bridge designed by Denholm, has the advantage of compensating for the anode impedance and the electrolyte resistance and has been used^(3,19) to examine several metals. A detailed description of the circuit of this bridge has been given by Leach and Isaacs⁽¹⁹⁾. The impedance of metal electrodes have been examined "in situ" during the corrosion process using this technique.

(ii)-Other Techniques

Several other specialised techniques have been used, for example the one designed by Hogarth has been used⁽⁸³⁾ to determine the thermoelectric power

of oxide films. A redox printing technique has been developed by Klein⁽¹¹⁸⁾ to study the electronic conductivity of anodic oxides.

4-(c)-Structure and Composition

(i)-Electron and X-ray Diffraction

Electron diffraction is widely used to identify and examine the structure of oxide films on metals. It is particularly suitable for examining thin oxide layers as the beam penetration is small. Reflection diffraction is used to examine **oxide** layers on massive samples while transmission diffraction is used to examine stripped oxide films, up to a few hundred angstroms in thickness. Information on film orientation and grain size of the oxide can be derived from diffraction results. X-ray diffraction has also been used for oxide film examination but it is mainly limited to thick scales.

(ii)-Electron Probe Micro-analysis

This technique has been extensively used in examining the composition and pore structure of oxide layers. The main limitation is that it can not be used in examining layers in the submicron range of thickness. It can not thus be utilised in case of

corrosion protective films which are normally very thin.

PART FIVE: CONCLUSIONS FROM THE PREVIOUS WORK

It is clear from the literature that understanding the properties of the protective oxide films is of fundamental importance in the study of the corrosion behaviour of metals. Ionic diffusion processes, and the thickness of the uncracked part of the oxide, through which diffusion takes place, are influenced by the electrical, mechanical, and crystallographic properties of the protective oxide. For example, the reversals in the corrosion rate potential relationship in case of uranium are attributed to changes in, electrical properties of the oxide, and the reduction in the corrosion rate of some alloys is explained in terms of the formation of a more plastic oxide.

An attempt has been made, in this project, to study the corrosion behaviour of some uranium alloys and other transition metals and investigate the electrical properties and crystal structure of the oxides and to try to correlate the results of such study.

The metals that have been chosen are uranium 5wt.%

zirconium, uranium-12wt.% molybdenum, manganese-2.0wt.% iron, titanium and vanadium. These metals were chosen for the following reasons:

- 1- They all display a change in valency and form semiconductive oxides, a property to which the changes in corrosion rate and impedance with potential are attributed.
- 2- They are known to form protective oxides.
- 3- The oxides formed are light-absorbing, and thus the optical techniques can be used in film thickness measurements.

The techniques used in this study were chosen so that the properties of the protective thin oxide films can be examined and the thickness of these films can be continuously measured while the metal is being corroded. Both white light absorption and elipsometric techniques were used for the continuous measurement of corrosion rate as both are sufficiently sensitive, accurate and non-destructive. The A.C. impedance technique was used to measure the oxide capacity and conductivity "in situ", and this method has been successfully applied before for the study of thin corrosion and anodic films. The crystal structure of the corrosion films was examined by means of

electron diffraction, where the depth of beam penetration is known to be very small compared with film thickness, and furthermore it can be controlled to some extent by varying the accelerating potential.

CHAPTER THREE

EXPERIMENTAL TECHNIQUES

The section on experimental techniques is divided into three parts. The optical techniques used to measure the film thickness are described and the experimental procedure is given. In the second and third parts an account is given of the A.C. impedance and electron diffraction techniques used for the examination of thin films formed under conditions similar to those used in rate measurements.

PART ONE: CORROSION RATE MEASUREMENTS

A method which fulfils the following conditions can be satisfactorily used for rate determination in the early stages of corrosion:

- 1- It does not involve the removal of the specimen from the corrosion environment.
- 2- It permits the continuous measurement of corrosion rate.
- 3- It can detect the growth of very thin films.
- 4- It does not interfere with the film growth mechanism.

Two optical techniques, namely the white light "absorption" and polarised light "ellipsometry" were selected as the most appropriate for corrosion rate measurement.

1. (a)-The Absorption Method

The operating principle of this technique involves the measurement of the intensity of light reflected from the surface of a metal specimen corroding in an aqueous environment and calculation of the "relative" film thickness by comparison with the intensity from a clean surface. The thickness of the film can be given by Lambert's Equation:

$$I = I_0 e^{-2\theta x} \text{ (previously explained in Chapter Two, Part Four.)}$$

and plot of $(\log I_0 - \log I)$ versus t gives the relative film thickness as a function of time.

The optical equipment is shown diagrammatically in fig. (8). It is similar to that used by Leach and Nehru⁽³⁾, with a modification involving the use of a different light source of greater stability and intensity. Light from an Iodine Quartz Lamp (Atlas TIB/250/30) is focused by a condensing lens on a ~~mirror~~ M mounted inside a tube A at an angle of 45° . The reflected light falls on a plano-convex lens L mounted in the front of the test cell at a distance from the mirror M equal to its focal length. The beam is thus rendered parallel before reflection from the specimen which is positioned immediately behind the lens. After passage through the tube, the

intensity of the reflected light is measured by the photocell P_1 . Any photocurrents produced by light reflected from surfaces other than that of the specimen are cancelled out by the reference photocell P_2 which is connected in opposition to P_1 and also acts as a standard for the light intensity. Power to the light source comes through a 150 watt stabiliser (Advance Components Ltd. M.T. 140 A).

The measuring circuit is shown in fig.(9). The equipment was standardised using a heavily corroded specimen (standard) placed in the optimum position in the cell. The potentiometer R_2 was used before every experiment, to adjust the zero setting of the recorder (that is the 0.1 mV reading on the 1 mV scale) to correspond to the amount of light reflected by the standard specimen. The potentiometer R_1 is used to give a full scale deflection on the 0-1 mV scale of the recorder (Cambridge Electronic Recorder Model D.E.). During the test the decrease in the light intensity was automatically recorded.

The corrosion cell used was constructed from a plastic (polypropylene) capable of withstanding temperatures up to 125°C . The cell fig.(7) is equipped with an immersion heater, a temperature

controlling thermometer, a reflux condenser. The heater was prepared to fit the bottom of the cell by bending a silica tube which contained a heating coil and powdered alumina. Power was supplied through a variac and was increased steadily during the operation up to approximately 100 watts. The thermometer, (Ether), was positioned nearer to the specimen and could be set to control at any temperature between 0 and 100°C. A relay activated by the thermometer, (Ether Type No. 2138), switched the heater circuit.

All the corrosion rate tests were made potentiostatically and most of them at negative potentials. The potentiostat used was the Harwell type (A.E.R.E. Type 1465 A). The voltage was measured by means of a valve voltmeter, with an input impedance of 10^{13} ohms, (E.I.L. pH Meter Type 23 A) with respect to a calomel half cell. A potentiostatic technique was employed since it permitted the quantitative estimation of the effect of hydrogen activity on corrosion rate.

The rate measurements were made for the following materials:

- U- 12 wt.% Mo: Supplied by the A.E.R.E., Harwell and certified as 99.95% pure.
- U- 5 wt.% Zr: Supplied by the U.K.A.E.A. and was

prepared from high purity uranium and low Hf 99.9% pure zirconium. Before testing both uranium alloys were vacuum annealed at 1000°C for 7 days and then quenched in water.

Mn- 10 wt.% Fe: Prepared in this laboratory by the
and induction melting of electrolytic
Mn- 20 wt% Fe manganese with mild steel.

The manganese chips were previously baked at 500°C for half an hour to get rid of the hydrogen in a method similar to that recommended by Potter et. al. (118)

Titanium : I.C.I. 130 grade. All specimens were vacuum annealed at 800°C for an hour and air cooled.

The test electrodes were prepared by mounting the specimen in a cold-setting resin (Ciba Araldite) at the end of a glass tube of a previously determined length. Care was taken to ensure that the tube when inserted in the cell would position the specimen directly

behind and parallel to the lens. Electrical contacts were made at the back of the specimen and were so protected that the corrosion environment was allowed access only to the face of the specimen. The uranium-zirconium specimens used for rate measurements were $\frac{1}{2}$ inch diameter discs while all other materials were $\frac{1}{2}$ inch squares.

Electrolytes

The composition of the electrolytes used is given below:

pH 5.4	0.1 N K_2SO_4
pH 8.4	0.1 N Na_2CO_3 + 0.1 N $NaHCO_3$
pH 9.7	0.2 N Na_2CO_3 + 0.2 N $NaHCO_3$
pH 12.5	0.1 N NaOH adjusted by Na_2CO_3

The solutions were prepared from Analar grade reagents and distilled water.

Specimen Preparation

All materials with the exception of titanium were

prepared by wet polishing to a mirror finish on emery papers down to grade 600 and then washed and dried just before use in the corrosion cell. For titanium, a chemical polishing bath recommended by Hayfield⁽¹¹⁹⁾ was used. **This consists** of a mixture of HF , H_2SO_4 and HNO_3 in the ratio 3:3:4 by volume. The specimen is normally degreased in acetone and dried prior to dipping in the chemical polishing bath, which is at about $70\text{--}80^\circ\text{C}$, then washed thoroughly in distilled water.

Experimental Procedure

1- The cell is filled with the electrolyte and the solution is brought to the test temperature and thermostatically controlled. The cell is flushed with oxygen-free nitrogen for about one hour.

2- The extraneous light is backed off with the potentiometer R_2 . An adjustment is made with this potentiometer to give a 0.1 mV deflection on the 0.1 mV scale of the recorder by the maximum reflection from the surface of a heavily corroded (standard) specimen.

3- The test specimen is polished, washed and dried, and then inserted directly in the cell and adjusted to give maximum reflection of the incident light beam on the photocell P_1 and adjustment is made with the potentiometer R_1 to give a full scale on the 0-1 mV scale of the recorder. This takes about 20 seconds.

4- The potential of the specimen is adjusted to the required value with the potentiostat and the decrease of the reflected light intensity with the growth of the oxide film is recorded.

1-(b)-Ellipsometry

The basic theory of the technique has been given in the previous section. The operating principle involves the analysis of the state of polarisation of light after being reflected from the film surface. When a light beam plane polarised at 45° to the plane of incidence, impinges on the metallic surface, it becomes elliptically polarised.

The state of polarisation is defined by p , the ratio of the magnitudes of components parallel and perpendicular to the plane of incidence ($\frac{R_p}{R_n}$), and their phase shift Δ , ($\phi_p - \phi_n$). (Before reflection the two components R_p and R_n are in phase and equal in magnitude). The ellipticity vector $\bar{Z}$ is related to p and Δ by the equation:

$$\bar{Z} = p e^{i\Delta}$$

The ellipsometer used (I.M.I., Witton, Birmingham) is schematically shown in fig.(10). Monochromatic light is obtained from a mercury vapour lamp used in conjunction with a filter, the green line of mercury, wave length 5461°A being used. The light from the source A is passed through a condenser lens B, an aperture C, a filter D, a collimator lens E and then through the plane polariser F. The light beam then falls on the surface to be examined, G. The reflected light passes in the following order

through a quarter wave plate H, a Tronstad ellipticity half shade I, and an analyser fitted with a half shade. The polariser and analyser settings, which respectively determine relative phase retardations and amplitude reductions are made by observation through a low power microscope K which can be focused on the ellipticity half shade or on the analyser half shade as required. The ellipticity half shade can be displaced out of the system when the final analyser setting is to be made, and then exactly replaced in its original position by a simple toggle mechanism.

The corrosion cell used was made of Pyrex glass fig.(11), and fitted with two optical windows for the passage of incidence and reflected light, an inlet and an outlet for the flow of the electrolyte and a provision for a luggin capillary. The cell is clamped rigidly to avoid any disturbances during the operation.

Materials and Solutions:

Only titanium was examined by this method. The

specimen (I.C.I. 130 in the form of 2 cm.² surface area sheet) was chemically polished prior to examination as mentioned before. The electrolyte (pH 9.7 carbonate-bicarbonate buffer) was slowly circulated through the cell, the temperature being controlled at 70°C.

Experimental Procedure

1- The electrolyte is heated to the required temperature, slowly circulated through the cell and thermostatically controlled.

2- The specimen is degreased in acetone and dried then chemically polished, rinsed with deionised water and dried.

3- The back of the specimen is covered with Lacomite, then mounted on the specimen holder so that the specimen is in a vertical position when put into the corrosion cell, and left to dry for about 10 minutes.

4- The specimen is inserted into the corrosion cell, and connections are made to the potentiostat

(Wittons Electronics) which is already set to the required potential.

5- The optical system is aligned to get maximum reflection from the specimen surface, the angle of incidence being about 75° C. (Care is taken that all optical measurements are made in a dark room as extraneous light can cause errors).

6- The potentiostat is switched on and time is recorded. At regular intervals the state of polarisation of light is measured as follows: the microscope is first focused on the ellipticity half shade, the analyser may be kept in the system without greatly affecting the field of view. The polariser is rotated until the two halves are balanced and the reading on the polariser drum is noted (p). At this stage the emergent light from the quarter wave plate is plane polarised again. For measuring the azimuth of the plane of polarisation, the ellipticity half shade is displaced from the system and the microscope is focused on the analyser half shade, which is rotated until a balance is obtained. The analyser reading is noted (A).

7- Values of ρ and Δ are calculated from standard tables and polar curves are drawn.

PART TWO: IMPEDANCE MEASUREMENTS

The apparatus used was developed by Denholm, and described in detail elsewhere⁽¹⁹⁾. A schematic diagram of the equipment is shown in fig.(13). An A.C. (square wave) signal is applied across two networks, the first consists of a high resistance in series with the cell containing the test electrode, the second consists of a high resistance in series with a comparison network or analogue consisting of a resistor and a capacitor in parallel. The two voltage responses (about 10 mV) are applied respectively to the X- and Y plates of an oscilloscope after being amplified. A correct balance is indicated by a straight line at 45°.

The use of the square wave excitation makes it possible to separate the series and parallel components of the resistance. The voltage across the series resistance is in phase with the current applied and produces, with a square current wave, a voltage step. The voltage across the parallel resistance has the form

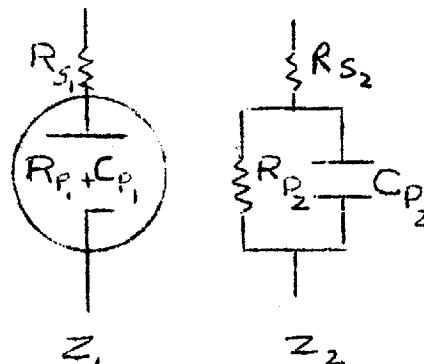
$$V = IR(1 - e^{-t/RC}) \quad \text{i.e. it is exponential}$$

when the RC values of the electrode and the analogue are the same, putting the signals on the Y and X-

plates of the **oscilloscope** respectively produces a straight line or two parallel straight lines if the cell has a series component of resistance. If in addition, the values of Z ($\frac{1}{R^2} + \omega^2 C^2 = \frac{1}{Z^2}$) for each cell is in the ratio of the large series resistances (R_{s1}, R_{s2}) then the line will be at 45° , that is

$$\text{if } \frac{Z_1}{R_{s1} + Z_1} = \frac{Z_2}{R_{s2} + Z_2}$$

$$\text{and } R_{p1} C_{p1} = R_{p2} C_{p2}$$



then we get a balance and a straight line at 45° (fig. 14).

Provisions are made in the bridge used (Wareham Compound R.C. Analysis Bridge Type Co 30) to compensate for the series resistance due to the electrolyte. The equipment used made it possible to measure values of parallel resistance in the range $10^6 - 10^3$ ohms, values of capacitance from few μF to several hundreds, and to potentiostatically control the specimen at any desired potential.

The cell used for impedance measurements is shown in fig.(12). Oxygen-free nitrogen was bubbled into the solution before and during the experiment

to reduce to minimum the oxygen concentration in the solution. The anode consists of a platinum foil, and the potential was measured with respect to a saturated calomel half cell. A silver electrode was used to measure the A.C. voltage of the specimen. Materials examined were prepared in a manner similar to that used for corrosion rate experiments.

Experimental Procedure

Oxygen-free nitrogen is bubbled into the solution for about an hour prior to the test. The surface of the electrode is polished, washed in distilled water, dried and inserted into the cell. The specimen is potentiostatically controlled, then the potential is changed stepwise 100 mV at a time, being kept constant for about a minute at each potential during which measurements of capacity and conductivity are made, and current is noted. Measurements are also made on changing the potential in a positive direction immediately after the cycle of measurements with decreasing potential.

PART THREE: ELECTRON DIFFRACTION

Oxide films, formed under conditions of pH and potential identical to those employed in corrosion rate

measurements, were examined by reflection electron diffraction. This technique enables the identification and structural examination of very thin oxide films. The diffraction camera used in this investigation was the A.E.I. EDC 2 Type. High vacuum could be obtained inside the diffraction chamber after about 15 minutes from placing the specimen. The specimen manipulator is provided with the necessary degrees of freedom i.e. radial, cross traverse, tilting and rotational movements to enable the correct positioning of the specimen. A discharger gun is attached to the camera and is used in case a relatively insulating surface is charged by the electron beam. The camera is provided also with an air lock device so that the plate cassettes can be changed without breaking the main vacuum in the diffraction chamber.

The specimens examined were in the form of $\frac{1}{4}$ inch diameter discs. Surface preparation was similar to that for the corrosion rate experiments. However, additional polishing with two grades of diamond paste (Dialap Compound 6u and 1u), was tried for uranium alloys and titanium but was dispensed with later as the results were similar to those obtained from just

abraded specimens. After polishing the specimen is thoroughly rinsed with distilled water and then corroded for a certain length of time under electrochemical conditions identical to those used in rate experiments. The specimen was held inside a polythene tube at the end of a glass tube.

Electrical contacts were made via a drop of mercury at the back of the specimen in which a brass rod is immersed. After corrosion the specimen was thoroughly washed in a strong jet of tap water, followed by washing with distilled water, immersed in a bath of iso-propyl alcohol (Analar) and quickly transferred into the electron diffraction camera. (In some cases, for example, when specimens were given an additional polish on a diamond paste, they were immersed in iso-propyl alcohol or petroleum ether (~~Analar~~) and shaken in an ultrasonic bath for few minutes to get rid of any embeded particles).

The operating conditions used for the EDC give a resolving power of about $\frac{1}{2000}$ (for a 1 cm. radius diffraction ring). An average of four photographs were taken for each specimen at accelerating voltages ranging from 60 to 100 KV. The exposure time ranges from 5 to 15 seconds

depending on the intensity of the background. The camera length used is 40.5 cm. However, the camera constant (λL) was always calculated by transmission diffraction from a standard specimen of known lattice constant (thallous chloride). This reference specimen was mounted on a specially designed specimen holder on the same horizontal level as the test specimen.

Each of the diffraction plates was measured by using a specially modified travelling microscope. The modification permitted an image of the cross wires of the microscope to be projected onto the plate to be measured, coincidence between this image and the relevant line being determined with the naked eye or by a lens. In this way difficulties associated with measuring diffuse lines at high magnifications were avoided. The radius of the ring was measured in three different directions and the average was taken.

CHAPTER FOUR

RESULTS

PART ONE: CORROSION RATE MEASUREMENTS

a) Uranium-12 wt% Mo

The corrosion behaviour of this alloy, as a function of the applied potential, was examined in pH 5.4 solution at 40°C. The results are recorded in fig.(15) from which the following observations can be made:-

1. Protective kinetics prevail in the initial stages "about 4 hours" followed by linear corrosion.
2. The parabolic growth rate " k_p " and the linear rate " k_l " are both increased by increasing negative potential.
3. The oxide thickness at which transition from protective to linear kinetics takes place increases with cathodic polarisation. However, calculation of the limiting thickness to which the

* k_p is normally calculated by plotting the oxide thickness versus $\sqrt{\text{time}}$, the slope of the straight line, in case of a parabolic process equals $\sqrt{k_p}$.
 k_l is the slope of the oxide thickness-time curve in case of linear kinetics. The values of both k_p and k_l are arbitrary.

oxide normally cracks back from its equilibrium value using the method suggested by Leach and Nehru⁽³⁾, indicates that this value "termed T_{theo} " changes only slightly with potential as can be seen from Table 1.

Table 1

<u>E_{HA} volts</u>	<u>k_p</u>	<u>k_1</u>	<u>T_{theo}</u>
0	9	4.8	0.9
-0.2	14	6.3	1.00
-0.4	30	10.6	1.15

Preliminary corrosion rate measurements were made on U-12 wt% Mo in pH 9.7 at 40°C. The relationship between the rate and applied potential in alkaline solutions appears to be complex and the results were difficult to reproduce. However, it was observed that the corrosion rate tended to decrease with the decreasing potential within the range $E_{HA} = +0.4$ to 0 volts, and then start to increase again. Cathodic polarization at potentials more negative than -0.3 volts caused a high rate of hydrogen evolution at the specimen surface (see for example fig.(21)) and interfered with the measurement, which may be in part the cause

of the irreproducibility.

The effect of temperature on the protective growth of the alloy in pH 5.4 solution is shown in fig.(20). Table (2) shows the variation of k_p with temperature at three different potentials.

Table 2

<u>Temperature °C</u>	<u>k_p</u>		
	<u>+0.2 v</u>	<u>0v</u>	<u>-0.2v</u>
40	-	9	14
45	53	-	18.5
50	9	-	24.8
55	-	20	30
60	17.8	29.5	39
65	47	36	-
75	42.5	62	-
80	54	-	-

The activation energies for the parabolic growth were calculated from the Arrhenius equation and were found to lie between 10.1 k cal/gm. mole "for $E_{HA} = -0.2v$ " and 14.3 k cal/gm. mole " $E_{HA} = +0.2v$ ". Similar observations have been reported⁽²⁵⁾ on the decrease of activation energy with increasing hydrogen activity. It is of interest to note that the decrease in the value of the activation energy E is accompanied by a decrease in the pre-exponential term A of the

Arrhenius equation

$$K = A \exp. -\frac{E}{RT}$$

For example calculations based on these values of activation energy show that at 325°K, k_p should increase by a factor of 14.5 on decreasing the potential from 0 v to -0.2v " E_{HA} " on the assumption that A has the same value in both cases. Experimentally k_p increases only from 18 to 27 i.e. by a factor of 1.5 only, which suggests that the value of A decreases when E decreases.

b) Uranium-5wt.% Zr

Figures (16) and (17) show the corrosion behaviour of this alloy in an alkaline solution at different applied potentials. All measurements were carried out at room temperature in the potential range +0.3 to -1.0v " E_{HA} " with the oxygen content of the bath kept to a minimum. In most cases the corrosion kinetics are parabolic followed by linear. A second faster period of linear growth is also occasionally observed ($E_{HA} = -0.7$ and -0.8 v). The corrosion behaviour of the alloy in alkaline solutions shows a complex variation with potential. Figure (18) shows that $\log k_p$ increases linearly with decreasing potential in the range +0.3 to 0v E_{HA} , decreases with decreasing potential in the range 0 to -0.7 or -0.8v and then starts to

increase again. Annealing the specimens under vacuum at 1000°C for a week, (which homogenises them and extracts any absorbed hydrogen) does not seem to change the type of the rate-potential relationship (fig. 18). Charging the specimen with hydrogen for 24 hours prior to testing changed the values of the rate constant but not the form of the potential dependence. This figure shows that the general trend is always the same and the rate decreases in a limited range of potential, although there is some scatter in the values of K_p . Experiments conducted in pH 8.4 solution gave a similar type of rate-potential relationship (fig. 23).

Observations on this complex relationship has been reported for unalloyed uranium⁽²⁵⁾. It is interesting to notice that while a parabolic relationship is maintained between the hydrogen activity and the increasing corrosion rate of uranium⁽³⁾ and uranium-12wt.% molybdenum (fig. 19) in acidic solutions, a similar relationship exists between the hydrogen activity and the decreasing rate of corrosion (in the region 0 to 0.7v E_{HA}), fig.(19).

c) Titanium

Corrosion rate measurements were carried out in pH 9.7 solutions at 70°C employing two techniques for oxide thickness determination, the optical absorption and the ellipsometric methods. Experiments could not

be conducted at potentials more negative than -1.20 volts ~~when~~ using the white light method due to the high current densities required, and only ellipsometric measurements were made at negative potentials down to -1.55 volts (S.H.E.).

It is clear from the results figs.(24, 26) that the rate of corrosion increases with increasing negative potential. For example the time required to build up a 150°A film (fig.26) is about 17 hours at -0.45 volts, and only about 36 minutes at -1.15v. It can also be seen that the parabolic kinetics predominates when the potential is -1.05 or more positive. (Assuming that the rate relationship is of the form $x^n = Kt$, the value of $n = 2$ at all these potentials). From -1.15v downwards the value of n is different (see Table)

Table 3

<u>Potential, E_H</u>	<u>n</u>
-1.15	1.25
-1.25	1.40
-1.35	1.4
-1.45	1.0
-1.55	1.5

Results derived from optical absorption measurements also indicate a similar behaviour (fig.(24)), where the value of n is 1.8 at -0.9v and more positive potentials,

and 1.4 at -1.20 volts. This might mean that the parabolic kinetics prevails only for a very short time and was not detected.

The corrosion rate increases with negative potential down to -1.25v, below which the ~~reaction~~ rate is observed over a limited range to be slower (fig.(27). At a more negative potential (-1.55v) a faster reaction rate is again observed. As the reaction kinetics were not the same throughout the whole potential range, a strict comparison was difficult, and the reciprocal of the time to grow a certain thickness can be taken as proportional to the rate constant "K". Fig.(28) shows a plot of log K versus potential and the reversals in the curve indicate that the corrosion rate decreases with increasing hydrogen activity in a limited range of potential. Similar observations have been reported for uranium⁽²⁵⁾, and the results of the present work (fig.18) records such behaviour for uranium-zirconium.

Figure (25) shows a plot of log K versus potential for the measurements in which the optical absorption method was used. It is interesting to note that in the potential range -0.5 to -1.2v the rate of corrosion increases 10 times over a range of ~ 0.58 volts. This figure is ~ 0.70 volts for the results derived from

ellipsometric data (fig.28) over the same potential range.

The potentiostat current was recorded during corrosion for each potential, Fig.(29). At less negative potentials (for example -1.05, the current is low and decreases slightly with time; at slightly negative potentials e.g. -1.15 volts it decreases for the first 30 minutes and starts to increase again. At very negative potentials the current density is high (80 mA/cm² at -1.55 volts), and an appreciable increase in current with time is observed. Similar results have been obtained in the case of U-5wt% Zr (fig.22), although the magnitude of the current density is much lower, and a hysteresis in the current--overpotential curve for many metals has been reported⁽¹⁰¹⁾.

d) Manganese

Corrosion rate experiments on the alloys Mn-10wt% Fe and Mn-20wt% Fe were attempted in pH 12.5 solution at temperatures from room temperature down to 0°C. (The bath was held at 0°C by circulating refrigerated methanol through a stainless steel tube immersed in the cell). This work has not been successful due to the high corrosion rate of the material. The

rate of oxide formation was too fast to be detected with the optical absorption technique used, and the results were very difficult to reproduce. Experiments were confined to this pH as it is known (fig.6) that manganese oxides are most stable in a narrow range of pH around 12. Preliminary tests in an acid solution (pH 5.4) have shown that no passive film was formed and a dissolution process appears to be taking place.

Figure (32) shows the current-overpotential relationship for manganese-20wt% Fe in pH 12.5 solution at room temperature. The anodic current decreases on decreasing the positive potential down to +0.15 volts after which the current becomes cathodic and increases exponentially with potential. A transition to easy hydrogen evolution kinetics takes place at about -0.6 volts. On decreasing the negative potential the current remains cathodic up to -0.1v where it becomes anodic. A slight hysteresis is exhibited by this curve at potentials below the transition potential. This has been reported for many oxide-covered metal electrodes.

PART TWO: IMPEDANCE MEASUREMENTS

a) Titanium

Fig.(31) shows the results for the variation of conductance and capacitance of titanium with potential,

in a pH 9.7 solution. Two specimens were examined, the first was just abraded, while a thin-thermally formed film was grown onto the other.

With the abraded specimen both the capacitance and the conductance increase with the decreasing potential to a maximum at about -1.15 volts, and then both decrease if the potential is made more negative. As these measurements were carried out at potentials only down to -1.20 volts, only the first capacitance and conductance peak are observed. The magnitude of these are 320 uF/cm^2 and 700 mho/cm^2 respectively, and these are comparable to the values observed by Leach⁽¹²¹⁾ who studied the impedance of titanium over a wider range of potential (fig.30). From Leach's results (fig.30) it is clear that a marked decrease in both capacitance and conductance occurs below -1.16 volts to a minimum, after which both increase again with increasingly negative potential. It is also observed that the conductance shows a minimum at a slightly less positive potential than the capacitance.

For the case of the thermally grown film a similar behaviour of impedance can be observed. At less negative potentials the capacitance is very close to that corresponding to the abraded specimen, and the conductance is similar or slightly higher. However, as the potential is made more negative a marked difference

is noted, for example, the capacitance maximum of the thermal film is $\sim 160 \mu\text{F}/\text{cm}^2$ compared with $\sim 320 \mu\text{F}/\text{cm}^2$ for the abraded specimen, the difference is very comparable to that of conductance, which is shown to be reduced from about 700 to about 260 m Mho/cm².

b) Vanadium

Figures (33, 34) show the variation of the capacitance and conductance of a vanadium electrode with potential at a repeat frequency of 500 c.p.s. All these measurements were made in a pH 9.7 solution with the oxygen content kept to a minimum. On making the potential of the abraded specimen more negative, the capacitance and conductance increase to a maximum at -0.4v and -0.45v respectively, and decrease to a minimum at about -0.8 to 0.85 volts. At potentials below that, the capacitance increases to another maximum at -1.30 volts and then decreases again, while the conductance increases markedly. A marked hysteresis in the curve is observed when increasing the potential in the opposite direction, the magnitude of capacitance and conductance being higher in this latter case. Similar observations have been reported by Leach and Isaacs⁽¹⁹⁾.

The behaviour of the electrode on which a thermal

film has been grown is generally similar to the freshly abraded one (Figs. 33, 34). The values of capacitance and conductance are very near at less negative potentials but the difference is more marked when they reach their peak values.

PART THREE: ELECTRON DIFFRACTION

Electron diffraction measurements were made on samples of U-5wt% Zr, Ti and vanadium, corroded at various applied potentials in the range where they are known, from thermodynamics, to form stable oxides. Values of the d spacings corresponding to the diffraction rings obtained were calculated, the calibration being made against the thallous chloride d_{111} ring. The results were compared with the ASTM data on the relevant oxides.

Difficulties were encountered, however, in making positive identification of these oxides. Three factors contribute to this:

1. The large number of different oxides with complex structures. Titanium, for example, is known to form not less than 17 oxides of slightly different crystallographic structure⁽¹²²⁾.
2. The lattice constants of each oxide phase may

change as a function of composition, and the latter is influenced by the applied potential.

3. Two or more oxide phases may co-exist, in which case the diffraction pattern corresponds to a mixed oxide structure.

However, these results indicate that the structure of these oxide films do change with the corrosion potential, and a detailed discussion of that will appear later.

a) Uranium-5wt% Zr

Fig. (35a) shows graphically the lattice spacings corresponding to the oxide films formed at various electrochemical potentials and the diffraction patterns are shown in fig. (35b). Values of d spacings are given in tables. The following observations are of interest:

1. The main oxide at all the potentials is UO_2 , with a F.C.C. structure, $a_0 = 5.46 \text{ \AA}$.

2. Few additional lines appear at different potentials, for example at +0.6v and +0.2v EHA two additional rings corresponding to d spacings of 2.11 and 1.31 $\text{\AA}$ (tables 7, 8). These two lines are near to the reported values U_2O_5 , which are 2.07 and 1.27 $\text{\AA}$ respectively (ASTM Index Card No. 10-99).

3. Extra lines with different values appear at more

negative potentials. For example, at -0.2v EHA the lines $2.48 \text{ \AA}$ and $1.83 \text{ \AA}$ are very clear (table 9), the latter being very near to the reported value ~~of~~ corresponding to the oxide U_8O_{19} (ASTM 15-3) ($1.89 \text{ \AA}$). It is noted also that the intensity of the line $2.11 \text{ \AA}$ is markedly increased, which might be due to a reflection from a different plane of an additional oxide phase.

4. Few experiments were conducted in pH 13 solutions and it was clear that the oxide structure does not change in this pH range.

5. Oxides grown at high anodic potentials (3 volts anodic film) appear to consist mainly of UO_2 but the lines are more diffuse, suggesting that the oxide is more amorphous.

b) Titanium

Similar diffraction tests were carried out on titanium. These results are graphically shown in fig. (36a) and the patterns are shown in fig. (36b) and (tables 12-16). The identification of these patterns as corresponding to a single phase oxide was very difficult, however, a marked change in the structure with corrosion potential can be observed from these graphs. Comparing for example, the structure of the film grown at -0.5 volts E_H with that at -1.35v , it can be seen that most of the clear lines at the more

positive potential disappear at -1.35 volts. Few lines of this latter correspond reasonably to the reported values of Ti_2O_3 . The diffraction pattern changes again if the potential is lowered to -1.85 volts. (A detailed discussion of all these results will be given later.

It is observed also that the air-formed film does not correspond to any of the known oxides of titanium. This has been reported by others⁽¹²²⁾ It is also reported that there are seven distinct phases between $\text{Ti O}_{1.75}$ and $\text{Ti O}_{1.90}$ ⁽¹²²⁾. An oxide film grown at high temperature was found to consist mainly of rutile (fig.36 and table 13).

c) Vanadium

The results on vanadium are given in figures (37a & b). It shows also that a change in the oxide structure is induced by variation of potential, this is very clear if the results of the films grown at $\text{EH} = 0$ and -0.8 volts are compared. Here also a clear identification in terms of a distinct oxide, hydroxide or a hydrated oxide is very difficult, and each diffraction ring may be treated to get the best fit to the various known oxides of vanadium (20 oxides and hydrous oxides are listed in the ASTM X-ray Data Index). It is interesting to note here also that the thermally grown oxides consists mainly of V_2O_5 (see table 18).

CHAPTER FIVE

DISCUSSION

PART ONE: CORROSION BEHAVIOURa) Introduction

The two optical techniques adopted for the rate measurements enable the continuous measurements of the corrosion rate with a reasonably accuracy. Estimation of the absolute thickness was not possible with the absorption technique but this is not essential in kinetic studies. Previous investigations⁽¹²³⁾ using the monochromatic techniques have shown that for uranium and its alloys at room temperature, the first minimum (using blue light $\lambda = 4340 \text{ \AA}$) occurs after 2.1 hours, and the first maximum after 19 hours, which shows that this technique would not be suitable for rate studies in the very early stages of corrosion.

It could be argued that the continuous illumination of the specimen might lead to enhanced rates of diffusion. Such an effect has been observed by some workers⁽¹²⁴⁾ due to ultraviolet irradiation. It seems unlikely, however, under our experimental conditions using filament lamps, that such an effect would occur due to the marked difference in wave length and intensity. Furthermore, experiments conducted during this work have shown no change in the corrosion current as a result of switching off the light source, indicating

that there is no change in the rate of corrosion due to light irradiation.

It may also be pointed out that the optical properties of the oxide films **formed** at different electrochemical potentials might undergo a change with composition or structure. Recent experiments have shown⁽¹²⁵⁾, however, that the optical reflectivity of uranium oxides is almost identical for all oxide compositions, if the incident light lies in the visible range.

b) Effect of Potential

The dependence on the applied potential of the rate of corrosion of the materials examined in this work can be classified in two main categories. The first includes cases where a simple relationship is maintained between rate and potential, and is illustrated by the behaviour of U-12wt% Mo in pH 5.4 solution (fig.15). In the second category reversals are exhibited in the rate-potential relationship. Examples in such case are the behaviour of U-5wt% Zr and of Ti in alkaline solutions (figs. 18, 25). The results of each category will be discussed separately.

(i) Simple Rate-Potential Relation:

The influence of imposing a negative potential on the corrosion rate of U-12wt% Mo is illustrated in .

fig.15. All these measurements were conducted at 40°C due to the relatively high corrosion resistance of this alloy, which is predominantly a gamma phase uranium. The high hydrogen solubility⁽¹⁾ (19.7 p.p.m.) in this phase had caused non-reproducibility in the results obtained initially. It was only after saturating the specimen with hydrogen, by polarising over long periods, that results became reproducible.

The following points may be of interest in the discussion of the effect of potential:

1. The corrosion kinetics follows a parabolic linear sequence.
2. The thickness at which the partial breakdown of the film and the kinetics transition occur is approximately constant and independent of potential.
3. Both the parabolic and linear rates of corrosion increase with increasing negative potential.

Most of the metals having a Pilling-Bedworth ratio greater than unity form a protective oxide film in the initial stages of corrosion. The transition from parabolic to linear kinetics has been reported by many workers^(3,8), and has generally been discussed in terms of the formation of a highly stressed oxide, which cracks at a certain critical stress. Waber⁽⁸⁾ has estimated the thickness of the protective part of the oxide under mild conditions of temperature as

750 Å. Leach and Nehru have observed and commented⁽³⁾ on the parabolic linear sequence in the growth of oxides on uranium. They suggested that the thickness of the barrier part of the oxide is not represented by the point where the transition in kinetics occur, but is believed to be lower. The difference between the non-equilibrium thickness (represented by the transition point), and the steady state barrier thickness (referred to as T_{theo}) was discussed in terms of supersaturation of stresses within the oxide. These stresses lead to cracking of the film leaving an undamaged **layer of thickness T_{theo}** . The value of T_{theo} was found⁽³⁾ to remain constant irrespective of the applied potential, although a marked increase in the rate of oxidation was observed.

The increase in corrosion rate with potential observed here has also been reported earlier for uranium⁽³⁾ in acidic solutions and for zirconium^(3,37) in acidic and alkaline media and has been mainly attributed to the presence of hydrogen. An increase in rate under our experimental conditions, where the reaction is a diffusion controlled process may be argued to arise from:

1. A physical reduction in the thickness of the barrier film through which diffusion takes place, or
2. an increase in the diffusion constants.

It is worth noting that in these systems there is little possibility of a chemical reduction of the oxides, due to their great chemical stability. In addition experiments under extremely cathodic conditions on uranium⁽²⁵⁾ have shown that a film build up is proceeding. An electron diffraction investigation, part of the present work proves the existence of an oxide at these potentials.

The physical breakdown of the film due to hydrogen accumulation was considered by Draley⁽⁴⁾ who suggested three alternative mechanisms for hydrogen induced film damage:

1. Hydrogen diffusion into metal until supersaturation occurs, and then blistering of the surface.
2. The formation of molecular hydrogen at the metal-oxide interface, which might lead to rupture of the oxide films.
3. The formation of a metal hydride leading to reduction of film adhesion and possible recrystallization of the oxide.

Mechanisms of the type proposed in Draley's theory suggest a reduction in the barrier **film** thickness as a result of increased hydrogen activity. This, however, is not observed in our results, which show (table 1) that the protective film thickness remains approximately

constant with increasing negative potential. Hydride formation as proposed by Draley⁽⁴⁾ and Waber⁽⁸⁾, as a possible cause for enhanced corrosion, was not observed during the present work. Under severe cathodic conditions, the electron diffraction investigation has shown no evidence of hydride formation.

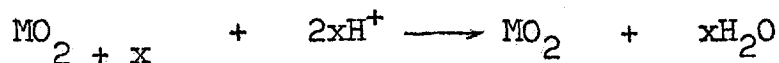
The role of hydrogen, as responsible for enhancing the ionic diffusion through the protective oxide film, was proposed by Leach⁽⁵⁾. This theory was developed on the basis of observations on enhanced rates of corrosion of metals in the presence of hydrogen without any reduction in the protective film thickness. It was also substantiated by evidence of increase in conductivity of the metal-oxide electrode system under the same conditions. Leach suggested that the presence of protons, which can act as a donor impurity, in an essentially semiconducting oxide film, would tend to change its electronic conductivity. The latter would increase if the oxide is an n-type semiconductor and decrease for a p-type oxide. Enhanced rates of ionic diffusion due to increase in electronic conductivity have been reported in the literature. Wagner⁽⁵²⁾, who studied the rates of diffusion of Ag in Ag_2S , has shown that the interdiffusion coefficient of Ag can be increased by a factor of 2.8×10^3 if Ag_2S

contains an excess of 2×10^{-3} gm. atoms. silver per gm. mole Ag_2S . An increase in the electronic conductivity, due to the excess silver ions, is suggested as the cause of the observed increase in ionic diffusion rates.

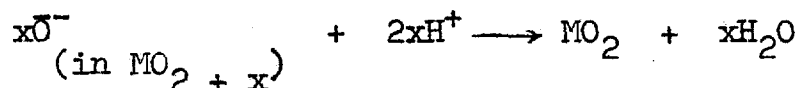
Our results may thus be discussed in terms of the semiconduction theory, as the models suggesting a mechanical damage fail to account for our observations. It can be suggested that the oxide formed on U-12wt% Mo behaves as an n-type semiconductor in the range 0 - -0.4v (EHA). A proton dissolved into this oxide, which would occupy an interstitial position in the lattice requires an electron to maintain electrical neutrality. This electron, which might come from the metal, would increase the electronic conductivity and consequently the diffusion rate.

It can be pointed out that as the activity of hydrogen increases at the oxide-electrolyte interface, due to increasing cathodic potential so would the concentration in the oxide of dissolved hydrogen. This follows from considering the oxide as solid electrolyte "solvent". In addition hydrogen and oxygen solubilities may be considered as related by a simple solubility product. So as the potential of the metal-oxide electrode is made more negative, the activity of hydrogen within the oxide increases partly because

of a higher activity at the oxide-electrolyte interface, and partly because of a lower oxygen activity within the nonstoichiometric oxide. This can be illustrated from the hypothetical equation:



or



in which case, the solubility product K would be

$$K = \frac{[\text{A}_{\text{H}^+}]^{2x} [\text{A}_{\text{O}^{2-}(\text{in MO}_2 + x)}]^x}{\text{constant}}$$

as the activity of MO_2 is constant.

This equation may be written:

$$[\text{A}_{\text{H}^+}]^2 [\text{A}_{\text{O}^{2-}}] = \text{constant}$$

i.e. the proton concentration in a nonstoichiometric oxide would be inversely proportional to the oxygen activity.

It is interesting to note that a parabolic relationship is maintained between the rate constant "Kp" and the hydrogen activity (fig.19). A similar relationship has been reported before⁽³⁾ in the case of corrosion of uranium and U-5wt% Zr. Although it seems difficult at this stage to account for this phenomenon, it may be related to the simple fact that

two hydrogen molecules are produced per UO_2 molecule in the reaction:



and as hydrogen is known to activate the diffusion processes in the manner discussed before, it might seem that such a relationship between the activity of hydrogen and the diffusion constants is not unreasonable.

(ii) Reversals in Rate-Potential Relationship

(1) Uranium-5wt% Zirconium

Rate results of U-5wt% Zr in a pH 9.7 solution illustrated in figs. 16,17 show that although a similar sequence of kinetics to that observed in acidic conditions⁽³⁾ appears, the relation between the rate and the applied potential is different (fig.18). This figure shows that the parabolic rate constant " K_p " increases with negative potential in the range +0.3 to 0v (E_{HA}), decreases in the range 0 - -0.7v, and then increases below this potential. A nearly similar trend is shown for the corrosion of the same alloy in pH 8.4 solution (fig.23) where the first reversal takes place at -0.1v. Comparision of the magnitudes of the rate constants in both solutions show that, while they are nearly similar in the range around 0v, rates are slightly higher in pH 8.4 solutions

at lower potentials.

The existing theories⁽⁴⁾ which attribute changes in the corrosion behaviour of metals to a mechanical damage caused by hydrogen do not seem to explain the rate-hydrogen activity phenomenon. Such mechanisms would imply a reduction in the barrier film thickness with increased hydrogen activity, whereas a ten-fold reduction in the rate of corrosion is shown to take place (fig.19) on increasing the hydrogen activity five times.

An interpretation of **this** phenomenon may be given on the basis of the semiconduction theory⁽⁵⁾. The incorporation of foreign ions mainly H^+ or OH^- ions, has been recently suggested⁽¹²⁶⁾ to increase dramatically the conductivity of amorphous oxide films, which are normally much more insulating than corrosion films, which adds substantial evidence to the semiconduction theory. Uranium is known to form a series of oxides each of which can exhibit nonstoichiometry such as UO_2 or U_4O_9 , and the dissolution of protons in any of these oxides would cause changes in the electronic conductivity depending on whether the oxide is p- or n-type. The dissolution of the proton in the oxide would be encouraged by the existence of a high hydrogen activity on the oxide electrolyte

interface due to polarisation, and to a hydrogen saturated metal on the other interface.

It is suggested that⁽⁵⁾ hydrogen migrates through the oxide film as protons rather than as atoms for two reasons. The first is that the ionic radius is smaller, and hence migration is easier, the second is that it seems unlikely that a neutral species would be attracted towards or exist within an essentially charged medium. The mechanism by which protons migrate is not yet fully understood. It has, however, been suggested⁽⁵⁾ that, for the particular case of oxides like UO_2 , protons would occupy interstitial sites. In such a case, they would be expected to decrease the electronic conductivity of a p-type oxide and increase that of an n-type oxide.

The mechanism by which changes in the electronic conductivity of an oxide changes the rate of ionic diffusion has been discussed earlier. Take for example changes in stoichiometry of an oxide such as UO_2 , formed within its domain of thermodynamic stability in an aqueous solution^(25,127)(fig.3). It would be expected that oxides formed at the positive end of the potential domain would be oxygen-excess (p-type), while oxygen-deficit oxides (n-type) would be most likely at the negative end. The intrinsic phase would lie in the middle. The entry of a proton

into an oxide would require the incorporation of an extra electron to maintain electrical neutrality. In a p-type oxide, where the conduction is mainly by holes, this would result in the decrease in the number of effective charge carriers and consequently in the electronic and ionic conductivity conversely in an n-type oxide, enhanced rates of diffusion would be expected.

Considering figure 18 it may be suggested from changes in the rate, believed to be associated with changes in the conductivity, that the oxide formed in the potential range +0.3 to 0v E_{HA} is an n-type semiconductor, and the oxide formed in the range 0 to -0.7v is p-type. Below this potential an n-type oxide is again formed. Comparison of the present results with the earlier observations for corrosion of pure uranium⁽²⁵⁾ shows that alloying with zirconium extends to more negative potentials the range in which the oxide formed is believed to be a p-type semiconductor. The potential at which transition from the p-type to the n-type oxide occurs is -0.7v as compared to -0.5v in the case of uranium. Similar observations have been reported for the corrosion of U-10wt% Zr⁽¹⁷⁾.

The results of the present work indicate that one type of oxide species might be formed in the potential

range 0 to -0.9v , where it is a p-type semiconductor above -0.7v and n-type below that. Considering the modified version of the Pourbaix diagram⁽²⁵⁾ (fig.3) for pure uranium, the domains of thermodynamics stability of U_4O_9 lies between -0.1 and -0.7v . This discrepancy might be attributed, as previously suggested, to the effect of alloying, where the free energies of formation of mixed oxides formed in case of corrosion of U-5wt% Zr would be different from those of pure uranium.

Comparing the results in pH 9.7 and 8.4 solutions (figures 18, 23) shows that although reversals in the rate-potential relationship are shown in both cases, the rates are higher in pH 8.4 solution especially with observations reported earlier⁽¹⁷⁾, however, this may be discussed in terms of some recent observations⁽⁴²⁾ on the effect of pH where the corrosion rate maximum occurs at around pH 7. It could also be pointed out that the corrosion rate, in the case of uranium which forms a semiconductive oxide would be a function of the degree of nonstoichiometry of the oxide, which may be influenced by pH.

(2) Titanium

The main observations which may be relevant to the discussion are:

1. The reversals in the rate-potential relationship. The rate increases markedly with potential down to $-1.25\text{v } E_H$, decreases in the range -1.25 to -1.35v , then faster rates are again observed at more negative potentials.

2. Protective kinetics predominate throughout the whole duration of the test when potentials are more positive to -1.0 volts. Below that linear or paralinear kinetics are found.

The reversals in the rate-potential relationship observed for titanium (fig.28) may be interpreted in terms similar to the case of uranium corrosion in alkaline solutions. Both uranium and titanium are known to form protective oxides in a variety of aqueous media and both are multi-valent. It should be pointed out here that the titanium rate measurements, which show the rate-potential reversals, were done ellipsometrically, while those on uranium were done using the optical absorption technique. The fact that these reversals are shown in both cases, suggests that this is a genuine phenomenon, and adds weight to the accuracy of the absorption technique.

A mechanical model⁽⁴⁾ for hydrogen damage would certainly fail to account for the marked increase (of

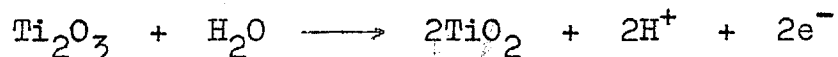
the order of 10 times over a potential range of about 0.7 volts) in rate (figs. 25, 28), followed by more than two fold decrease at some more negative potential. Changes in the refractive index of the oxide are unlikely to be as large as this. These arguments suggest that a model based on the effects of proton dissolution on changing the electronic conductivity of the oxide film can be applied to titanium oxides. Such a contribution to conductivity, may be very appreciable in the nonstoichiometric oxides of titanium, as opposed to the case of aluminium where hydrogen influences the corrosion rate by inducing mechanical damage to the oxide film. Some indications as to the reasons of these different types of behaviour can be obtained from the comparison of the electronic properties of the two oxides. Thus rutile has an energy gap ranging from 3.05 eV⁽¹³⁰⁾ to 0.4 eV⁽¹²⁹⁾ depending on its composition, and a dielectric constant of 100⁽¹⁰⁰⁾, while for Al₂O₃ the band gap is 10 eV⁽¹³⁰⁾, and the dielectric constant is 10⁽¹⁰⁰⁾. The energy required for the ionization of a hydrogen atom, once it is incorporated into an oxide, is inversely proportional to the square of the dielectric constant of the oxide, which would suggest that the tendency of hydrogen to ionize in case of a TiO₂ film would be much greater than in case of

an alumina film. Moreover, by the virtue of the small band gap of TiO_2 , the donation of the electron to its conduction band would be much easier, than in case of Al_2O_3 , where it would be opposed by an energy barrier of 10 ev. This argument suggests, then, that while the incorporation of hydrogen into a TiO_2 film would change its electronic conductivity, no such effect would be expected in case of aluminium.

Thus, from figure 28 it may be suggested that the oxide formed at potentials above $-1.25\text{v } E_H$ behaves as an n-type semiconductor (probably of the composition TiO_{2-x}), and in the potential range -1.25 to -1.55v , a different oxide species is formed, presumably Ti_2O_3 , which would be an oxygen-rich "p-type" at potentials positive to -1.35v , and an oxygen-deficit n-type oxide at potentials negative to -1.35v . Extrapolating to the next region another reversible reaction (Ti_2O_3 to TiO) should occur⁽¹³¹⁾ at -1.70 volts, where TiO would behave as a p-type semiconductor in the positive region of its domain of thermodynamic stability and as n-type in the negative region.

It is interesting to compare the potential at which the first reversal in the rate of corrosion occurs, and which is believed to be associated with a valency change, with the potential calculated by Pourbaix⁽¹³¹⁾

for the reaction:



The reversible reaction potential is given by the equation:

$$E = -0.556 - 0.059 \text{ pH}$$

and thus for pH 9.7 E would be -1.14 volts, which is lower than that corresponding to the observed rate reversal (-1.25v). However, since the corrosion experiments were conducted at 70°C and Pourbaix calculations are all based on 25°C thermodynamic data, this difference can be attributed to the difference in temperature. The effect of temperature on the electrode potential for a constant hydrogen activity can be derived from the equation:

$$E_H = E_o - \frac{2.303 RT}{F} \text{ pH}$$

the $\frac{2.303 RT}{F}$ term is 0.059 at 25°C and 0.068 at 70°C, and at 70°C a 90 mV negative shift of the transition potential would take place. Room temperature experiments on the capacitance dependence of electrode potential have shown⁽¹²¹⁾ a transition potential of -1.16 volts. Thus, the potential at which corrosion rate reverses is in good agreement with the potential at which capacity maximum occurs and also with the potentials reported by Pourbaix⁽¹³¹⁾.

It is difficult at this stage to account for the

apparent change in kinetics of corrosion of titanium at potentials below -1.0 volts as shown in figures 24, 27. and tables 3 and 4. However, the fact that this is shown by results obtained by two independent techniques, and that it has been reported earlier for the corrosion of uranium in a similar environment,⁽¹⁷⁾ suggests that this may be a real change. This, however, does not mean the absence of a diffusion-controlled process, but it is possible that the period during which a barrier film grows is too short to be detected by the instruments used.

(c) Current Measurements

Measurements were made of the potentiostat current during corrosion tests and an attempt was made to relate this parameter to the corrosion behaviour. Figures 22 and 29 show that the current increases appreciably with time for titanium at most potentials, while for uranium this increase was only observed at very cathodic potentials. It is interesting to note that with uranium (fig. 22) the rate of current increase in the initial stages, where protective kinetics prevail is much lower than that during linear growth. This is also apparent in the case of titanium, where at some less negative potentials, the current decreases with time in the first few minutes before it starts to increase.

An increase in current with time may be interpreted as due to an increase in oxide conductivity as a result of dissolution of protons. A hysteresis in the current overpotential curve has been shown before for many metals⁽¹⁰¹⁾, and figure 21 illustrates a similar phenomenon for both alpha and gamma phase uranium. It is interesting here to note a bigger hysteresis for the alpha-phase uranium which can be attributed to a higher hydrogen concentration in this oxide than in that formed on the gamma phase alloy. This may result from the lower capacity for hydrogen dissolution of the alpha phase uranium.

(d) Effect of Temperature

Fig. 20 illustrates the temperature dependence of the parabolic corrosion of U-12wt% Mo in pH 5.4 solution. The following points may be of interest in discussing the activation energy results:

1. The experimental values of the activation energy are generally lower than those reported^(67,68), for dry oxidation, and comparable (slightly higher) with those previously reported⁽⁶⁹⁾ for the aqueous corrosion of unalloyed uranium.

2. The activation energy decreases with increasing cathodic potential, and this is also accompanied by a decrease in the pre-exponential term A of the

Arrhenius equation.

The values derived here (10.1 - 14.3 kcal/gm. mole) are generally lower by a factor of 2-2.5 than those reported for the dry oxidation of uranium⁽⁶⁷⁻⁶⁸⁾. The effect of humidity on decreasing the values of activation energy has been established^(8,49) and has generally been interpreted⁽⁷⁷⁾ in terms of hydrogen incorporation into the protective film (the mechanism will be discussed later). The values of activation energy derived in this investigation for U-12wt% Mo are high compared with values calculated for uranium and U-5wt% Zr corroded in a similar environment. For example at 0v E_{HA} the value given by Leach and Nehru⁽⁶⁹⁾ for pure uranium is 10.3 kcal/gm mole and 6.2 kcal/gm mole for U-5wt% Zr, whereas the results (fig.20) show a value of 11.8 kcal/gm mole at the same potential. The slightly higher values of activation energy derived here may, however, be discussed in terms of the properties of the oxide film formed on the alloy U-12wt% Mo, which might be different from those formed on uranium and U-Zr alloys.

Explanations to the marked reduction in activation energy with humidity have been given⁽⁷⁷⁾. One suggested⁽⁷⁷⁾, for the particular case of magnesium oxidation, that hydrogen, incorporated into the oxide

lattice, combines with oxygen forming OH^- ions. This necessitates the introduction of cationic vacancies, which leads to enhanced rates of cation diffusion. Such a model does not seem to explain satisfactorily the corrosion of uranium, where anionic diffusion is believed to be the rate-controlling step. Other experiments suggest that⁽⁶⁹⁾ a change of the electronic properties of the oxide, due to the dissolution of protons may influence the activation energy for ionic conduction. Such an argument has been substantiated by observations⁽⁶⁹⁾ on change in corrosion rate and in activation energy, at potentials where changes in the type of semiconductivity occur. For example values as low as 7 kcal/gm mole for the activation energy of corrosion were obtained at potentials where the oxide formed is believed to be a p-type semiconductor. Higher values, very close to those reported⁽⁵⁴⁾ for electronic conductivity in n-type oxides were obtained at potentials where a change in the type of semiconductivity is believed to occur.

The decrease in the pre-exponential term A of the Arrhenius equation:

$$K = A e^{-E/RT}$$

has also been found and commented on by other

workers^(37,69,77). This effect is very marked in the present results, as the value of A decreases about 10 times for a decrease of about 1.2 times in the activation energy between 0 and -0.2 volts E_{HA} . Gregg and Jepson⁽⁷⁷⁾ attributed this change to the distortion of the lattice resulting from hydrogen dissolution, which would reduce the entropy of activation. On the other hand Ubbelohde⁽¹³²⁾ has suggested that both the reduction of E and A may be attributed to the migration of ions through selective routes ~~due to~~ the presence of ions of different electrovalency accompanied by holes which would permit a different migration mechanism.

PART TWO: EFFECT OF POTENTIAL ON IMPEDANCE

Two points may be relevant to the discussion of impedance results;

1. Reversals occur in the capacitance-potential and conductance-potential dependence.
2. The values of the capacitance and conductance maxima are lower for a thermally formed film than for a corrosion film.

Consider, for example, figure 31, where on making the titanium electrode potential more negative both the capacitance and parallel conductance increase to

a maximum at -1.15 volts then start to decrease at lower potentials. Two other maxima appear at more negative potentials⁽¹²¹⁾ (fig.30). A similar effect is clear with vanadium, where two capacitance maxima are found at -0.4 and -1.3 volts respectively. Titanium, and other metals which can show a change in valency and also form protective oxide films have been observed⁽¹⁹⁾ to show a similar behaviour. The behaviour of this group of metals differs markedly from that of valve metals like aluminium and zirconium⁽⁶⁾.

Although aluminium and zirconium show an increase in the capacitance on decreasing the electrode potential, the capacitance value is never ~~greater~~ than the double layer capacity, and the increase is generally attributed to the effect of hydrogen on the dielectric behaviour of the oxides. A mechanical effect has been reported in the case of aluminium⁽⁶⁾, whereby hydrogen causes a reduction in the effective thickness of the dielectric film while for a zirconium electrode the effect is believed to be electrical. This is attributed⁽⁶⁾ to the proton dissolution in the oxide, which would lead to short-circuiting parts of the resistive paths, and thus contributes to a higher measured capacitance.

It seems difficult to apply models which consider the oxide merely as the dielectric of a parallel plate

condenser to the results illustrated in this work. Consider for example the capacitance value of 300 uF/cm^2 shown by titanium, where the thickness of the oxide film would be $\sim 3 \text{ \AA}^0$, if this is a dielectric behaviour. This value corresponds only to one layer of TiO_2 and is much lower than the thickness of films under consideration. The formation of an orientated oxide film where the dielectric constant may be different in different crystallographic directions is also unlikely as the diffraction investigations show that these corrosion films are polycrystalline.

A model has been offered⁽¹⁹⁾, which discussed the high values of capacitance and conductance in terms of a reversible reaction involving valency change of metals ions in the oxide, and this model seems to offer the most acceptable explanation to the present results. A general reaction such as



has been suggested⁽¹⁹⁾. For this reaction to proceed, electrons and protons are the only mobile species necessary. Large capacities are measured since electric charge can be absorbed without a change in the potential. A comparison of the potentials at which the capacitance maxima occur with potentials at which

the reversible reaction occur (calculated by Pourbaix^(131,133) from thermodynamic data), shows good agreement (table 4). This table also indicates, for the case of titanium, that a reversal in the corrosion rate occurs at a potential very close to that at which a peak in capacitance occurs.

Table 4

Reaction	Potential, volts		
	calculated (131,133)	Observed from capacity measure- ments	Observed from rate measure- ments
$\text{Ti}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{TiO}_2 + 2\text{H} + 2\text{e}$	-1.14	-1.15	-1.16*
$\text{V}_2\text{O}_2 + \text{H}_2\text{O} = \text{V}_2\text{O}_3 + 2\text{H} + 2\text{e}$	-1.39	-1.30	-
$\text{V}_2\text{O}_3 + \text{H}_2\text{O} = \text{V}_2\text{O}_4 + 2\text{H} + 2\text{e}$	-0.36	-0.40	-

Titanium shows also two more capacity maxima⁽¹²¹⁾ (figure 30) and these correspond to reversible reactions $\text{Ti}^{+3}/\text{Ti}^{+2}$ and Ti^{+2}/Ti respectively. No large capacities of the order shown here are exhibited by metals like aluminium and zirconium⁽⁶⁾ which do not exhibit a change in valency.

* The reversal occurs at -1.25v at 70°C and would occur at -1.16 volts at 25°C.

The degree of reversibility of the reaction could depend partly upon the hydrogen concentration in, and at the surface of the oxide. This may explain the marked increase in capacity values if the potential is reversed after being made extremely negative. Such a hysteresis in the capacitance-potential relationship has been observed for uranium, vanadium and titanium^(17,101,121). This may also account for the time dependence of the capacitance, which has been shown earlier⁽¹⁹⁾, and would suggest that the reversible reaction is not only a surface phenomenon but may involve the bulk of the oxide.

The potential at which the reversible reaction occurs is pH dependent as shown:

$$E = E_0 - 0.059 \text{ pH}$$

where E_0 is the equilibrium potential of the reaction at pH = 0. The potential of the capacity maximum should also be pH dependent and this has been shown by recent work⁽¹²¹⁾. Earlier experiments⁽¹⁹⁾ in which the maximum appeared to be independent of pH (up to pH 11) were made in unbuffered solutions and can be interpreted in terms of local changes in concentration of OH^- ions in the vicinity of the electrode.

The parallel conductance is a maximum at the same potential as the capacitance (figures 30,31,33,34),

although the peak is not as marked. At very negative potentials, where the current densities are higher the conductance increases independently of the capacitance (fig.34). This phenomenon was observed before for tin and titanium⁽¹³⁴⁾, and it has been suggested that at low current densities, the parallel conductance ($\frac{1}{R_p}$) is proportional to the capacitance (C_p) and related by the equation:

$$\frac{C_p}{R_p} = \omega^{\frac{1}{2}}$$

where ω is the angular frequency of the applied current wave, whereas at more negative potentials, the changes in conductance (G) are related to the polarization current by the equation

$$G = \frac{2.3 I}{b}$$

where I is the current density and b is the Tafel slope.

The marked reduction in capacitance and conductance maxima measured for thermally-formed films in aqueous solutions is difficult to explain at this stage. Interpretations in terms of a difference in the thickness or the dielectric properties of the two oxides are not convincing, as these high capacitance values are believed to be related to a valency change reversible

reaction, and not to a dielectric behaviour. The diffusion properties of the two oxides are also probably similar, which adds to the difficulty of interpretation of these results.

PART THREE: OXIDE FILM STRUCTURE

It is established that changes occur in the oxide structure as a function of the growth potential. However, there have been difficulties associated with the interpretation of electron diffraction patterns obtained in terms of metal oxides of known structures. These changes are most marked in the cases of titanium and vanadium.

Consider titanium for example. None of the diffraction patterns, with the exception of those corresponding to a thermally formed oxide, could be indexed as a distinct oxide phase, e.g. TiO_2 or TiO etc. Similar difficulties have been encountered in the identification of oxides grown on titanium carbide single crystals⁽⁸⁶⁾ and in case of those grown on titanium under a high vacuum⁽⁹²⁾. Several reasons may be suggested to account for the difficulty in indexing the diffraction patterns:

1. The large number of titanium oxides with complex crystal structures. TiO_2 for example has 3

polymorphic modifications, rutile, anatase and brookite. There are also numerous oxides⁽¹²²⁾ less rich in oxygen. For example in addition to the known Ti_2O , TiO , Ti_2O_3 and Ti_3O_5 structures, no fewer than seven distinct phases exist⁽¹²²⁾ in the range $\text{TiO}_{1.75}$ to $\text{TiO}_{1.90}$. In this range the metal apparently forms a series of oxides (Magneli shear structures) $\text{Ti}_n\text{O}_{2n-1}$ where n ranges from 4 to 10, with a behaviour similar to that of molybdenum, vanadium and tungsten.

2. The variation in the lattice constant as a function of composition in each individual phase. Previous observations have shown⁽¹³⁵⁾ for example that the increase in O/U ratio in uranium oxides cause a slight reduction in the lattice parameter.

3. More than one oxide phase may co-exist in a structure.

4. The possible formation of hydrated oxides and/or hydroxides with **different** crystal structure. It is clear from the Pourbaix diagram⁽¹³¹⁾ of the system titanium-water, that the stable oxides of titanium form below the hydrogen evolution line, in which case the dissolution of hydrogen in the oxides with the possible formation of hydroxides is not unlikely.

A few diffraction lines could be identified in

some cases. For example, the titanium oxide grown at $-0.5 E_H$ shows three lines, $d = 2.96, 2.54, 2.28 \text{ \AA}^\circ$, which are in a nearly constant proportion to the known brookite lines $2.90, 2.476$ and $2.24 \text{ \AA}^\circ$. The following table shows a comparison between the indexed lines for an oxide grown at -1.35 volts and those reported (ASTM X-ray Data Index) for a Ti_2O_3 structure

Table 5

d values in $\text{\AA}^\circ$

<u>Experimental</u>	<u>Ring Intensity</u>	<u>ASTM</u>	<u>I/I₀</u>
2.51	medium	2.572	60
2.06	strong	2.116	11
1.46	medium	1.480	45
1.18	strong	1.215	7

This shows, despite the fact that the strongest lines for brookite and Ti_2O_3 are not shown, and the relative ring intensities are not similar, that the structures may be related to those of oxides expected to form from thermodynamic considerations. Furthermore, some recent work⁽¹³⁶⁾ has shown that a brookite type oxide is formed on titanium corroded in H_2SO_4 , and it was argued that high energy structure such as brookite would be more likely to form a protective film

than the more stable rutile for example.

Other workers⁽¹³⁷⁾ have observed hydride formation after titanium specimens were cathodically polarized for several weeks in a chloride bath at a current density of 200 mA/cm^2 . A direct comparison with the present results, where no hydride formation is observed even at potentials as low as -1.85v (fig.36) is difficult, but it may be relevant to consider the difference in the length of time of cathodic charging and the type of anion present.

The diffraction results on U-5wt.% Zr show that in the potential range $+0.8$ to -0.8v (E_{HA}) the oxide film structure is identical with that of UO_2 (a F.C.C. fluorite type, $a_0 = 5.46 \text{ \AA}$). The extra lines which appear at different potentials may be attributed to the presence of other uranium oxide phases. Although this is not yet conclusively established there exists a similarity between some of these lines and those reported for oxide phases like U_2O_5 , U_4O_9 . For example the lines $d = 2.11 \text{ \AA}$ and $d = 1.31 \text{ \AA}$ which are detected at the potentials $E_{\text{HA}} = +0.6$ and $+0.2\text{v}$ (Fig.35a & tables 7,8) are close in value to the U_2O_5 lines $d = 2.07$ and $d = 1.27 \text{ \AA}$ respectively. Furthermore the ring $d = 1.83 \text{ \AA}$ which is shown for oxides grown at -0.2v can be comparable to the line $d = 1.89$ for

a modified U_4O_9 structure.

From thermodynamic considerations, increase in the oxygen to uranium ratio should occur with increasing positive potential. Although diffraction measurements show F.C.C. patterns for the oxides formed at all potentials, it is possible that the oxidation of UO_2 to a higher phase can occur without a significant change in the structure. UO_2 possesses a fluorite-type F.C.C. structure, where the anions occupy the tetrahedral interstices. Extra oxygen ions can occupy the octahedral interstices without causing an appreciable change in the cation sublattice arrangements. It has been shown⁽¹³⁵⁾ that the lattice parameter of a UO_2 unit cell can only be reduced from 5.458 to 5.430 Å by an increase in oxygen content to form U_4O_9 . A single phase has also been reported⁽¹³⁸⁾ to extend from $UO_{1.75}$ to $UO_{2.30}$ with a reduction in the lattice parameter from 5.477 Å to 5.430 Å. It seems quite possible then, from the present results, that the oxide formed may be U_4O_9 in the potential range 0 to -0.8v E_{HA} , with an oxygen-rich phase at more positive potentials and UO_2 or $U(OH)_4$ ⁽²⁵⁾ at more negative potentials. A change of lattice parameter of less than 1% would not be detected by an electron diffraction investigation. Furthermore, the percentage of oxide

which undergoes a reversible valency change reaction is probably very small⁽¹⁹⁾, so that while changes in the impedance behaviour of the electrode can be measured, these would not necessarily be accompanied by detectable changes in oxide structure.

It has been suggested that the extra diffraction rings obtained might be associated with the presence of unknown uranium oxide phases. It could also be argued that they might correspond to the presence of a ZrO_2 second phase (the alloy examined is U-5wt% Zr). However, the strongest lines corresponding to the three known modifications of ZrO_2 were not detected. Furthermore, previous investigations⁽¹⁰⁴⁾ have shown that the oxidation of urania-zirconia can proceed to a composition of $\text{U}_{0.9} \text{Zr}_{0.1} \text{O}_{2.10}$ before any other phases appear, the lattice parameter being reduced to $5.42 \text{ \AA}$.

It is concluded that, although the actual structures can not be clearly identified, the oxides of titanium, vanadium and uranium do undergo a change in structure with formation potential. This is much more marked for the first two. For example with titanium, the oxide detected within the thermodynamic domain of stability of TiO_2 differs in structure from that formed in the range -1.16 to -1.70 volts, where Ti_2O_3 should form. A third modification of structure is found in the potential range where TiO should be stable.

Similar changes can be observed with vanadium (figs. 37 & tables 17-21) where V_2O_4 , V_2O_3 and V_2O_2 are known to form⁽¹³³⁾ in the potential ranges; positive to -0.36v, and between -0.36 and -1.39v and below -1.39v respectively. The difficulty in establishing change in the structures of UO_2 might be attributed to the changes in the lattice parameter with increasing oxygen content being too small to measure precisely with electron diffraction.

PART FOUR: GENERAL DISCUSSION

The similarity in the dependence relation of rates of diffusion through, impedance and crystal structure of the corrosion films on formation potential may be attributed to a common factor. As has been pointed out earlier, a valency change reaction, which is thermodynamically very likely for transition metals like titanium, uranium and vanadium, is thought to be the cause. Consider for example titanium which is known to form a wide variety of semiconductive oxides. A reversible reaction involving Ti^{+4}/Ti^{+3} ions would occur at -1.14v⁽¹³¹⁾, from purely thermodynamic considerations. Experimental observations show a capacitance maximum at -1.15 volts (fig.31), and a reversal in the corrosion rate dependence on potential

occurs at -1.16 volts (E_H). The oxide film formed at potentials positive to that of the reversible reaction would be an oxygen-deficit n-type oxide of composition TiO_{2-x} , which explains the observed increase in the rate of corrosion with increasing hydrogen activity. In the potential range between these potentials corresponding to the Ti^{+4}/Ti^{+3} and Ti^{+3}/Ti^{+2} reactions, the composition of the film should correspond to Ti_2O_3 , and diffraction investigations have indicated a change to a different structure in this potential range, although this could not be established as Ti_2O_3 . However, the formation of an oxide species which behaves as p-type oxide in the positive half of this potential range and as n-type in the lower part is indicated by corrosion rate results, fig.38 and the occurrence of the reversible reaction Ti^{+3}/Ti^{+2} is shown by the capacitance results (fig.30).

For the case of U-5wt% Zr, although the corrosion rate behaviour indicates the occurrence of valency change reactions (fig. 18) a clear capacitance maximum⁽¹⁷⁾ was not very clearly shown. The discrepancy between the behaviour of titanium and uranium might be attributed factors such as the degree of reversibility of the reaction, the structure of, and the solubility of hydrogen in such oxides.

CHAPTER SIX

SUMMARY AND CONCLUSIONS

The results obtained may be summarized as follows:

1. The corrosion of U-12wt% Mo in acidic solutions follows a parabolic-linear sequence of kinetics. The rate of corrosion increases as a function of the square of the hydrogen activity.
2. The corrosion behaviour of U-5wt% Zr in alkaline solutions is different from that in an acidic environment. In pH 9.7 solutions, the rate increases with negative potential in the range +0.3 to 0v (E_{HA}), decreases in the range 0 to 0.7v and again increases below this potential. A parabolic relationship is maintained between the rate of corrosion and cathodic potential in the range 0 to 0.7v.
3. The corrosion of titanium in an alkaline environment (pH 9.7) follows protective kinetics in the early stages of corrosion at potentials above -1.0v E_H . Below this potential the kinetic are linear or para-linear. The rate increases with hydrogen activity in the range -0.5 to -1.25v (E_H), decreases to a minimum at -1.35v and increase again at more negative potentials.
4. The activation energy of the corrosion of U-12wt% Mo is a function of the hydrogen activity. The

experimental values of activation energy are reduced with increasing negative potential.

5. The impedance properties of titanium are potential dependent. The capacitance and conductance increases to a maximum at -1.15v then starts to decrease. The capacitance and conductance maxima are lower by an order of magnitude for the thermally-grown films.

6. Capacitance maxima for a vanadium electrode occur at -0.40v and -1.30v respectively. The conductance shows a maximum at -0.45v , decreases to a minimum at -0.8v and increases at more negative potentials. A slight reduction in the capacitance and conductance maxima is observed in case of thermally-grown oxides.

7. The electron diffraction investigation shows that the oxide formed on U-5wt% Zr at various potentials has an F.C.C. lattice corresponding to a UO_2 structure. A few additional rings, which though, difficult to identify appear at potentials where a change in structure would be expected.

8. The change with potential of the crystal structure of films grown on vanadium and titanium is shown by electron diffraction. However, it is difficult to identify these oxides.

The following conclusions can be made from the

results obtained during the present work:

1. The change in corrosion behaviour of uranium and titanium with hydrogen activity is basically due to the influence of the latter on the electrical properties of the oxide film.

2. The oxide film formed on U-12wt% Mo in an acidic environment behaves as an n-type semiconductor. The dissolution of protons in such an oxide would lead to an increase in its electronic conductivity⁽⁵⁾, which enhances the rates of ionic diffusion in a manner similar to that proposed by Wagner⁽⁵²⁾ for the system Ag-Ag₂S-S.

3. Oxides formed on U-5wt% Zr and titanium in an alkaline environment display a change in the type of semiconductivity depending on the formation potential. Increased rates of corrosion in a given potential range are attributed to the influence of proton dissolution in an n-type oxide. Reduction in rate can be attributed to the effect of hydrogen on a p-type oxide.

4. The change in electronic properties of the protective oxide films caused by proton dissolution are thought to be related to the observed decrease in the activation energy values with increasing activity of hydrogen. An increase in the conductivity is also

thought to be responsible for the hysteresis in the current-potential curve.

5. The high values of capacitance and conductance observed for titanium and vanadium at certain electrode potentials are thought to result from a valency change reaction taking place within the oxide.

6. A change in the oxide film structure and composition seems to be taking place with formation potential.

Proposals for Future Work:

1. The dependence on electrode potential of the corrosion rate of vanadium, to attempt a correlation between the observed impedance and structural changes and corrosion behaviour.

2. Investigation of the corrosion behaviour, film structure and impedance of titanium electrodes in an acidic environment.

3. The temperature dependence of the rate of corrosion of titanium in both acidic and alkaline environments and the relation of that to its corrosion behaviour.

4. An investigation of the semiconductive properties of transition metal oxides as a function of oxygen to metal ratio and of proton concentration.

5. An investigation by electron microscopy and electron diffraction of stripped oxide films (if possible) previously grown at various potentials.

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TABLES OF d SPACINGS ($\text{\AA}^\circ$) OF OXIDES

GROWN AT VARIOUS POTENTIALS

TABLE 6

U-5wt% Zr Air-formed Film

<u>Ring</u>	<u>Intensity</u>	<u>d $\text{\AA}^\circ$</u>
1	s	3.15
2	m	2.74
3	s	1.94
4	s	1.68
5	w	1.57
6	w	1.38
7	m	1.26
8	w	1.22
9	m	1.07
10	w	1.01
11	w	0.97
12	w	0.93
13	w	0.88
14	w	0.84

TABLE 7

U-5wt% Zr - $E_{FA} = +0.6v$

<u>Ring</u>	<u>Intensity</u>	<u>d $\text{\AA}^\circ$</u>
1	s	3.13
2	m	2.72
3	m	2.11*
4	s	1.93
5	s	1.65
6	w	1.58
7	mw	1.38
8	w	1.31*
9	m	1.28
10	w	1.23
11	m	1.06
12	w	1.01
13	w	0.98
14	w	0.92
15	w	0.85
16	w	0.82

s = strong m = medium w = weak

* Reflections that do not correspond to a UO_2 structure.

TABLE 8U-5wt% Zr E_{HA} = +0.2v

<u>Ring</u>	<u>Intensity</u>	<u>d Å^o</u>
1	s	3.14
2	m	2.73
3	w	2.12*
4	s	1.93
5	s	1.67
6	w	1.58
7	w	1.39
8	w	1.31*
9	m	1.26
10	w	1.21
11	m	1.11
12	w	1.06
13	w	0.97
14	w	0.93
15	w	0.88
16	w	0.84
17	w	0.83

TABLE 9U-5wt% Zr E_{HA} = -0.2v

<u>Ring</u>	<u>Intensity</u>	<u>d Å^o</u>
1	s	3.14
2	m	2.74
3	w	2.48*
4	s	2.11*
5	s	1.93
6	w	1.83*
7	s	1.66
8	w	1.58
9	m	1.38
10	w	1.30*
11	m	1.26
12	m	1.21
13	m	1.12
14	w	1.06
15	w	0.97
16	w	0.93
17	w	0.88
19	w	0.84
20	w	0.83

* Reflections that do not correspond to UO₂ structure.

TABLE 10U-5wt% Zr $E_{HA} = -0.6v$

<u>Ring</u>	<u>Intensity</u>	<u>d Å^o</u>
1	s	3.17
2	m	2.75
3	m	2.12*
4	s	1.93
5	s	1.66
6	w	1.58
7	m	1.37
8	w	1.30*
9	mw	1.25
10	w	1.21
11	m	1.10
12	w	1.05
13	w	0.97
14	w	0.94
15	w	0.92

TABLE 11U-5wt% Zr $E_{HA} = -0.8v$

<u>Ring</u>	<u>Intensity</u>	<u>d Å^o</u>
	s	3.16
2	m	2.73
3	w	2.47*
4	w	2.25*
5	w	2.12*
6	s	1.94
7	s	1.66
8	w	1.58
9	w	1.38
10	w	1.29*
11	m	1.25
12	w	1.21
13	m	1.11
14	w	1.06
15	w	0.97
16	w	0.92

* Reflections that do not correspond to UO_2 structure.

TABLE 12Titanium Air-formed Film

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>
1	w	4.47
2	w	3.47
3	m	2.66
4	m	2.46
5	m	2.13
6	s	2.03
7	s	1.56
8	m	1.42
9	w	1.18

TABLE 13Titanium-Thermally formed
Film

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>	<u>d A°</u> <u>for</u> <u>Rutile</u> <u>(ASTM)</u>
1	s	3.24	3.245
2	m	2.49	2.489
3	m	2.17	2.188
4	s	1.69	1.687
5	w	1.46	1.48
6	m	1.20	1.17
7	w	1.09	1.093
8	w	1.05	1.042

TABLE 14Titanium $E_H = -0.5v$

<u>Ring</u>	<u>Intensity</u>	<u>d Å°</u>
1	w	2.96
2	s	2.54
3	m	2.28
4	s	2.100
5	m	1.85
6	w	1.681
7	m	1.54
8	w	1.41
9	s	1.30
10	s	1.10
11	w	1.05
12	w	0.99
13	w	0.95
14	m	0.84
15	m	0.71
16	w	0.77
17	w	0.70

TABLE 15Titanium $E_H = -1.35v$

<u>Ring</u>	<u>Intensity</u>	<u>d Å°</u>
1	m	2.51
2	s	2.06
3	m	1.46
4	s	1.18
5	m	1.02
6	m	0.93
7	m	0.84
8	m	0.78
9	w	0.69
10	w	0.65
11	w	0.63

TABLE 16Titanium $E_H = -1.85v$

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>
1	m	2.57
2	s	2.36
3	w	1.94
4	s	1.50
5	w	1.13
6	w	0.98
7	w	0.96
8	w	0.91

TABLE 17Vanadium Air-formedFilm

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>
1	s	2.23
2	m	1.52
3	s	1.23
4	m	1.07
5	w	0.96
6	m	0.81
7	w	0.61

TABLE 18

Vanadium Thermally-formed
Film

<u>Ring</u>	<u>Intensity</u>	<u>d Å°</u>
1	s	3.70
2	w	3.02
3	w	2.69
4	w	2.43
5	w	2.02
6	m	1.91
7	s	1.80
8	m	1.70
9	m	1.62
10	s	1.55
11	w	1.46
12	w	1.41
13	w	1.32

TABLE 19

Vanadium E_H = 0v

<u>Ring</u>	<u>Intensity</u>	<u>d Å°</u>
1	m	4.67
2	s	2.23
3	s	1.56
4	s	1.27
5	s	0.98
6	s	0.83
7	s	0.73
8	m	0.69
9	s	0.61

TABLE 20Vanadium $E_H = -0.8v$

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>
1	m	3.05
2	m	2.51
3	s	2.20
4	m	1.96
5	w	1.48
6	m	1.32
7	m	1.20
8	w	0.98
9	w	0.82

TABLE 21Vanadium $E_H = -1.5v$

<u>Ring</u>	<u>Intensity</u>	<u>d A°</u>
1	s	2.23
2	m	1.97
3	m	1.53
4	s	1.29
5	s	1.13
6	m	0.99
7	m	0.84

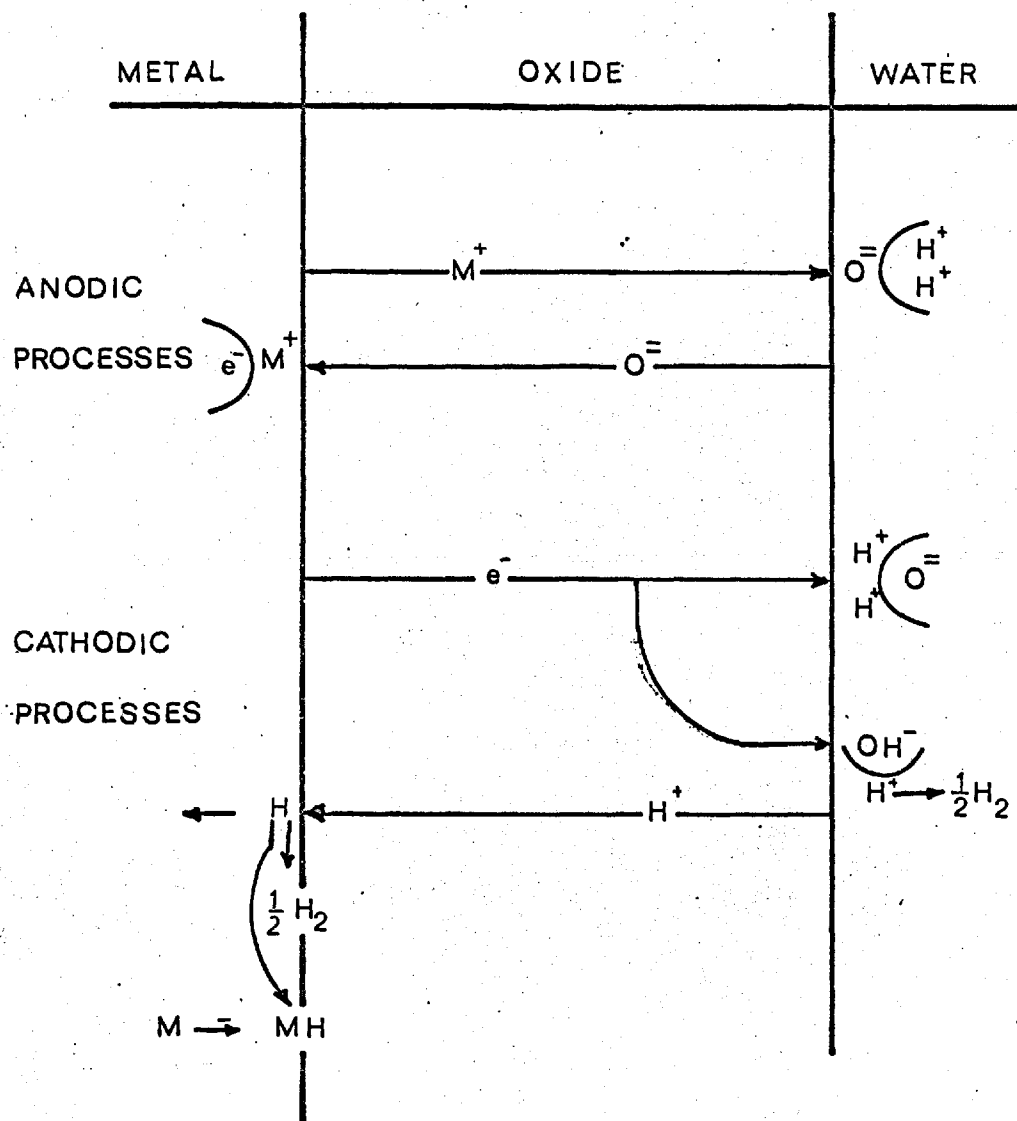
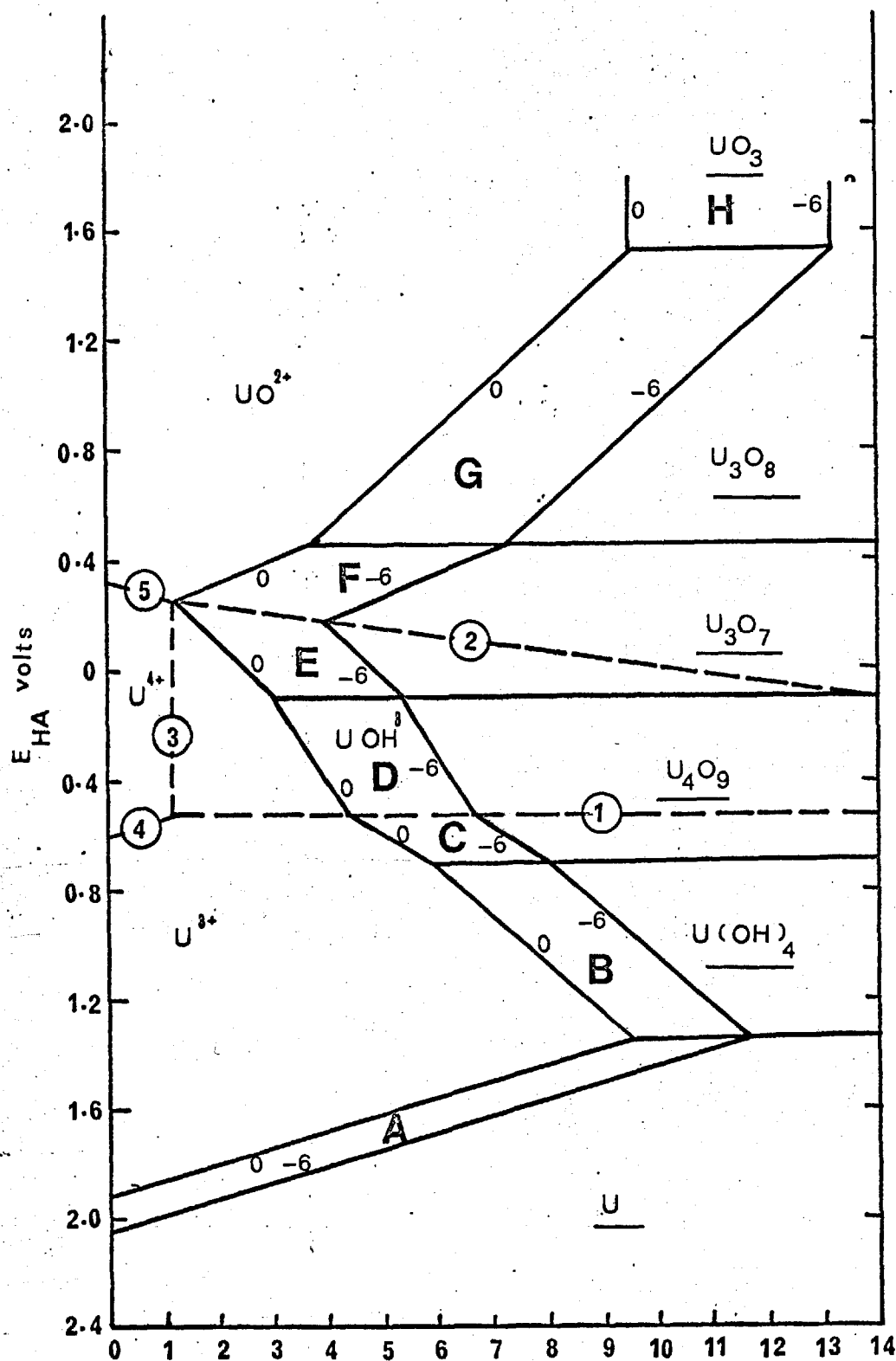


FIG.1 SCHEMATIC DIAGRAM OF CORROSION
PROCESSES⁽⁴⁾



pH-POTENTIAL DIAGRAM FOR U-H₂O
SYSTEM (MODIFIED BY NEHRU)

FIG.2

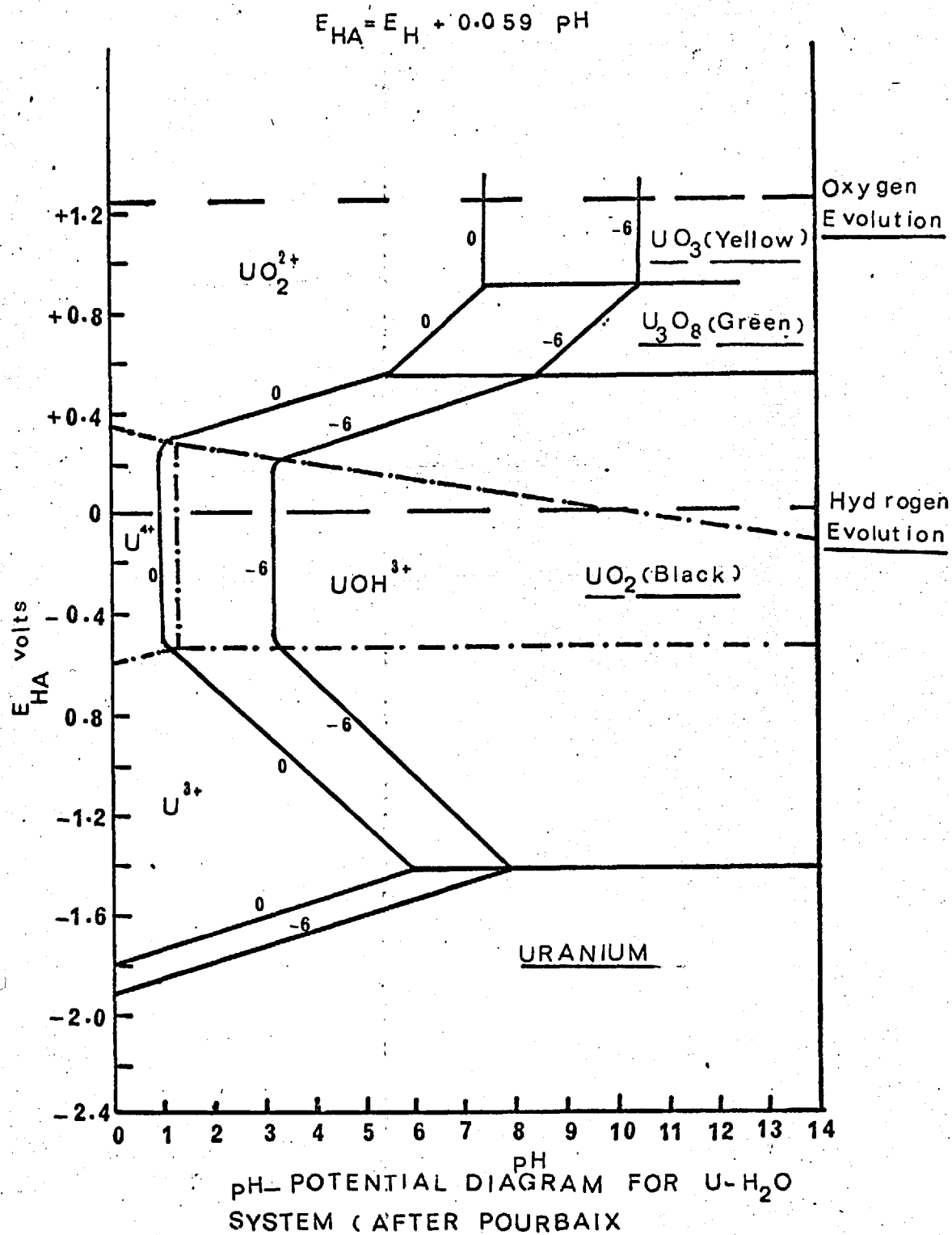


FIG.3

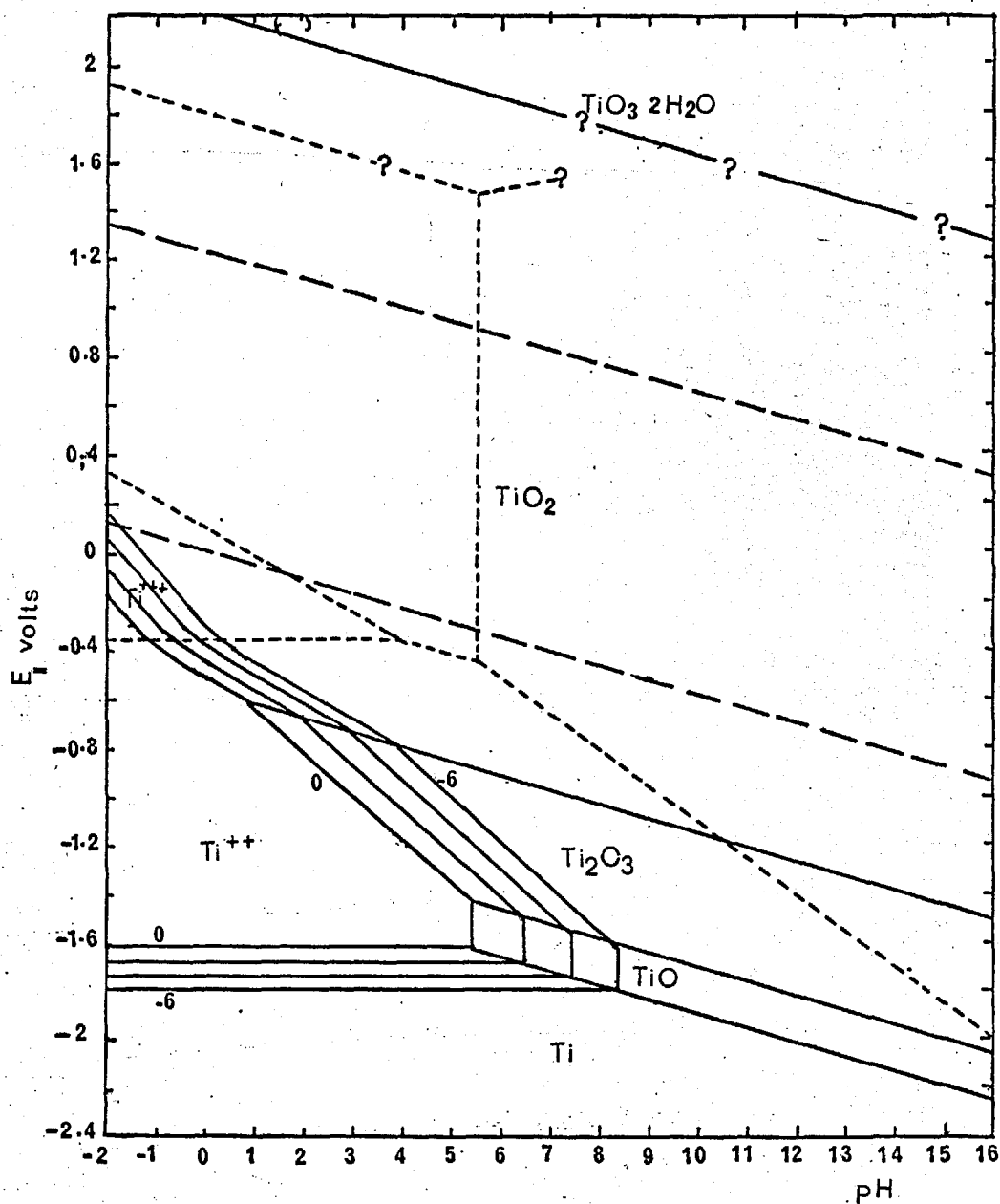


FIG. 4 pH-POTENTIAL DIAGRAM FOR THE
SYSTEM TITANIUM-WATER⁽¹³¹⁾

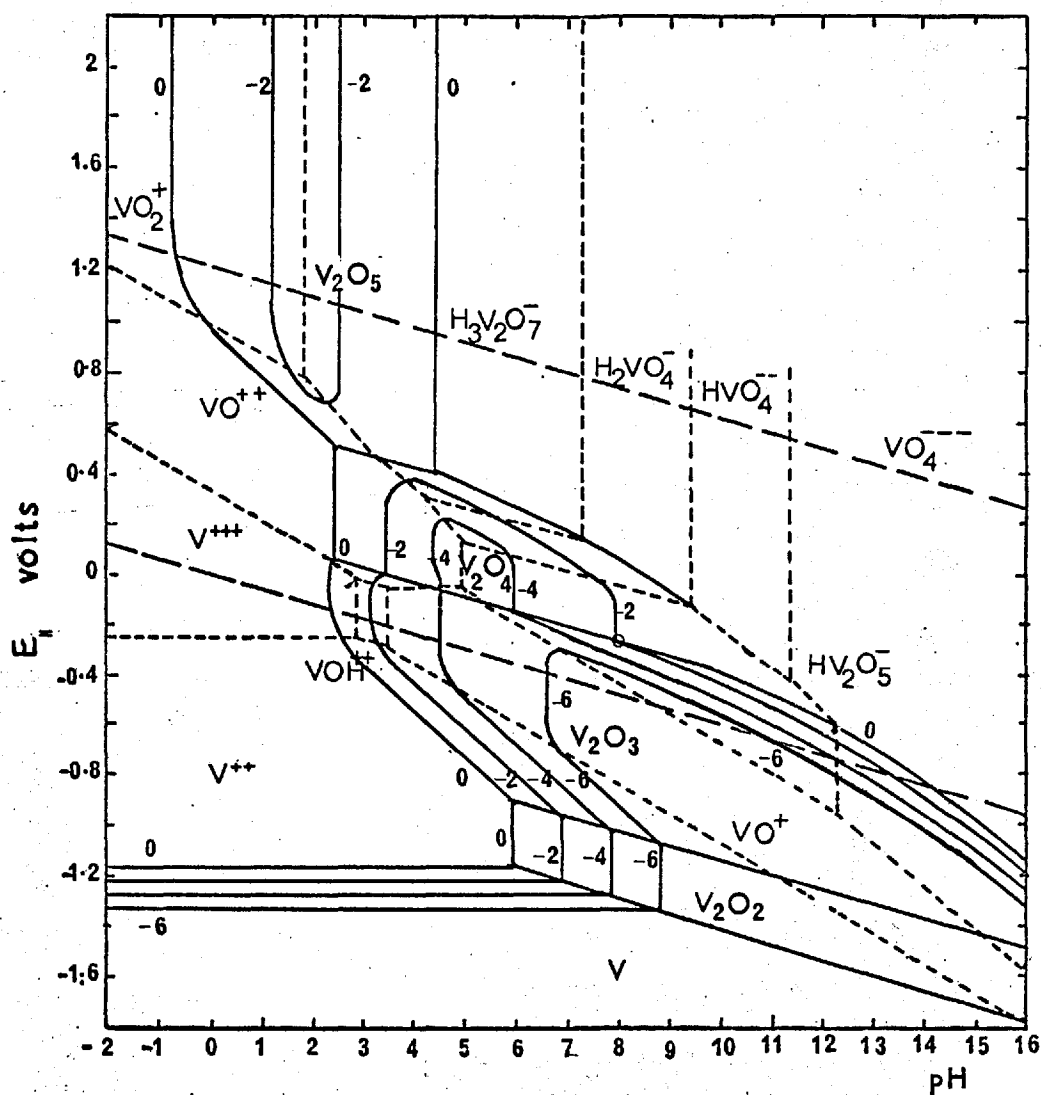


FIG. 5 POTENTIAL-pH DIAGRAM FOR THE SYSTEM VANADIUM-WATER⁽¹³³⁾

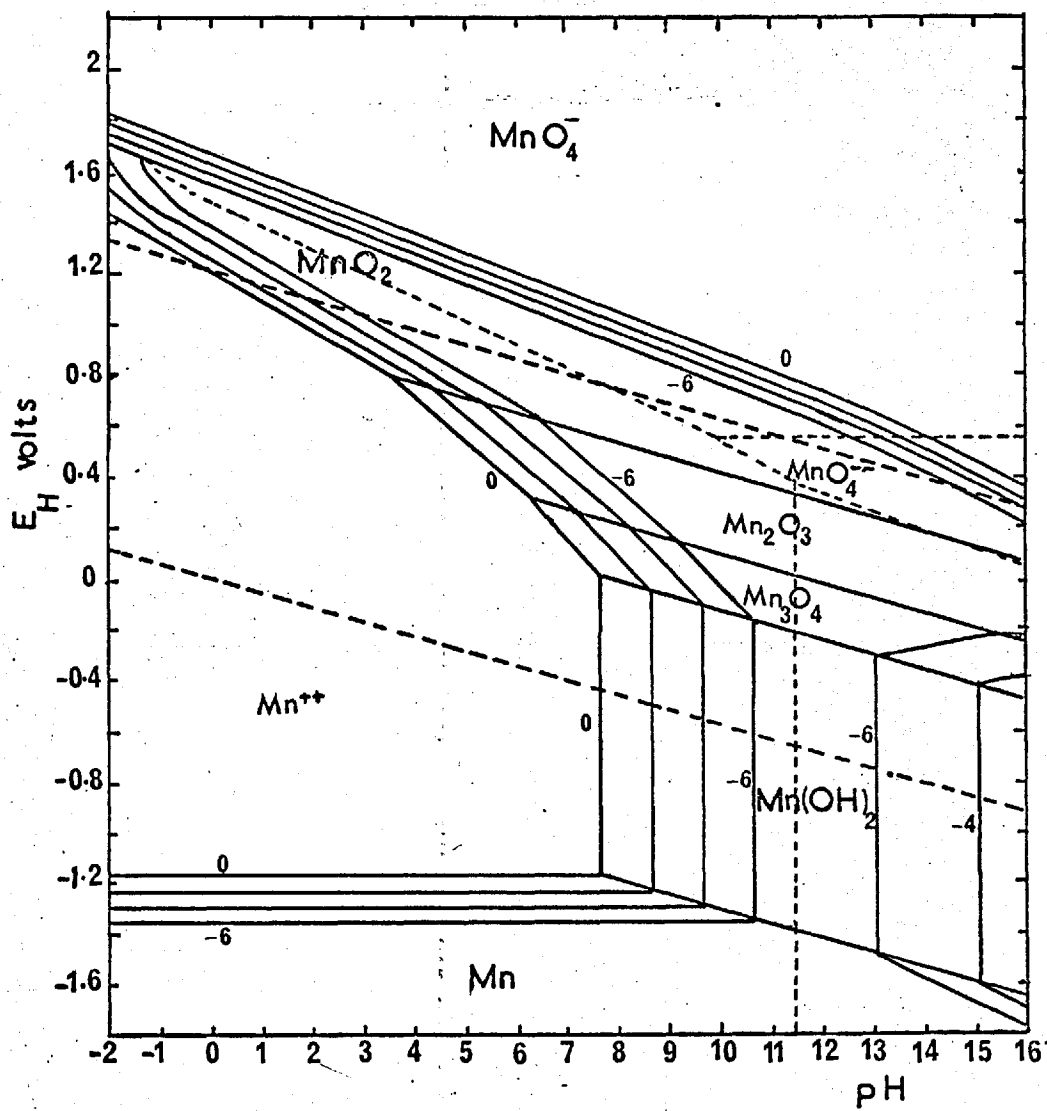


FIG. 6 pH POTENTIAL DIAGRAM FOR THE SYSTEM MANGANESE-WATER.⁽¹²⁰⁾

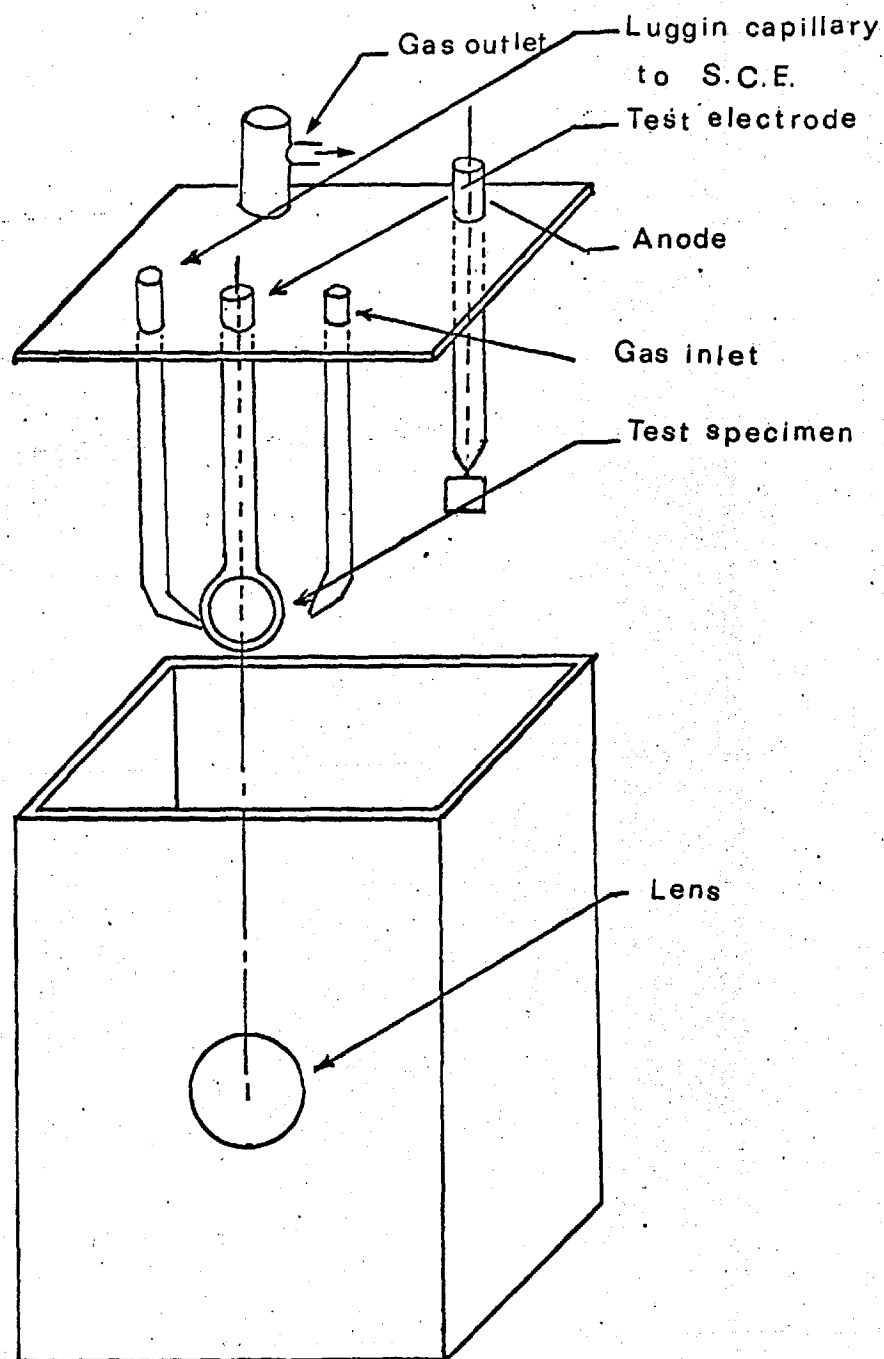


FIG.7 CELL USED IN CORROSION RATE MEASUREMENT

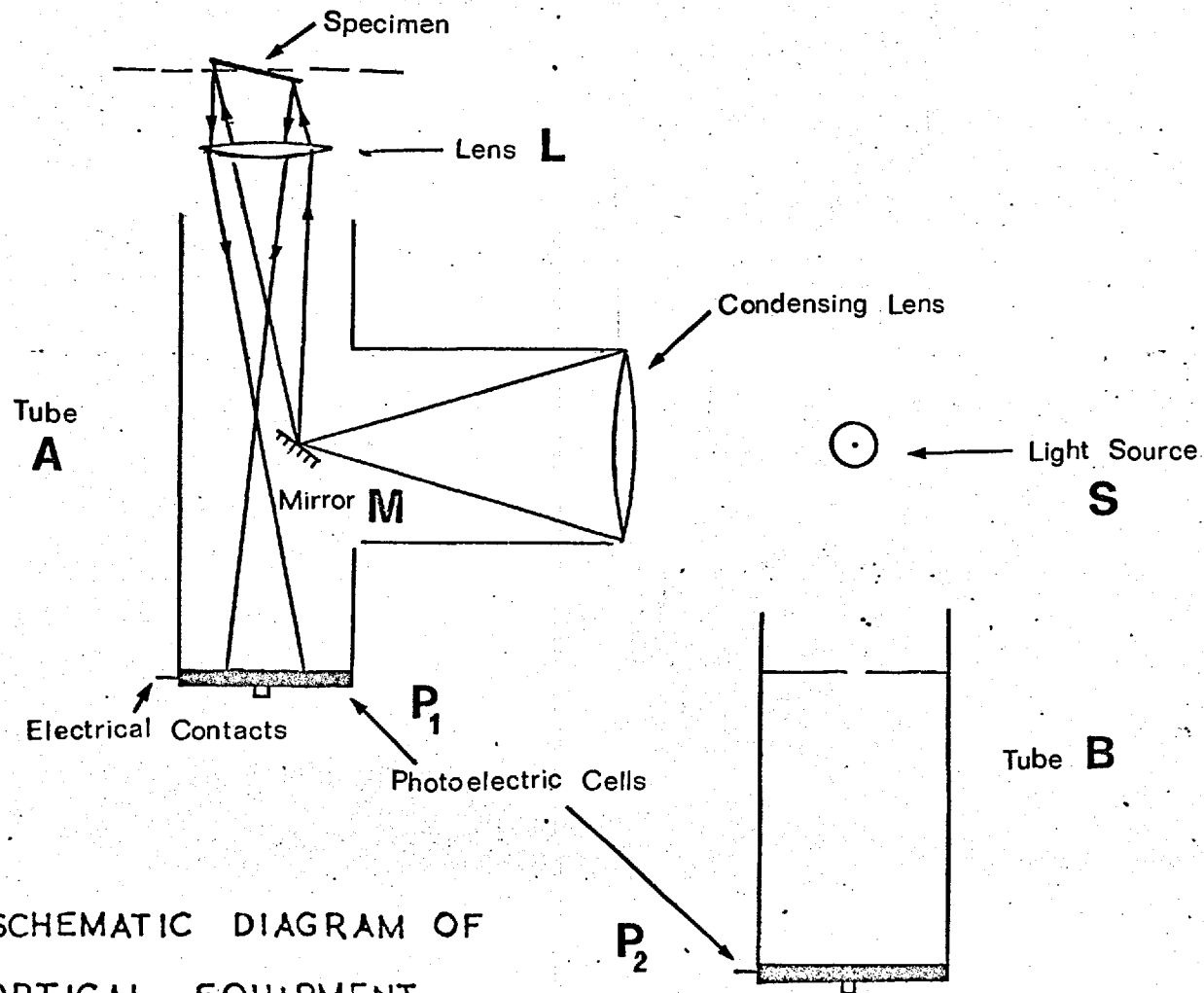


FIG.8 SCHEMATIC DIAGRAM OF
OPTICAL EQUIPMENT

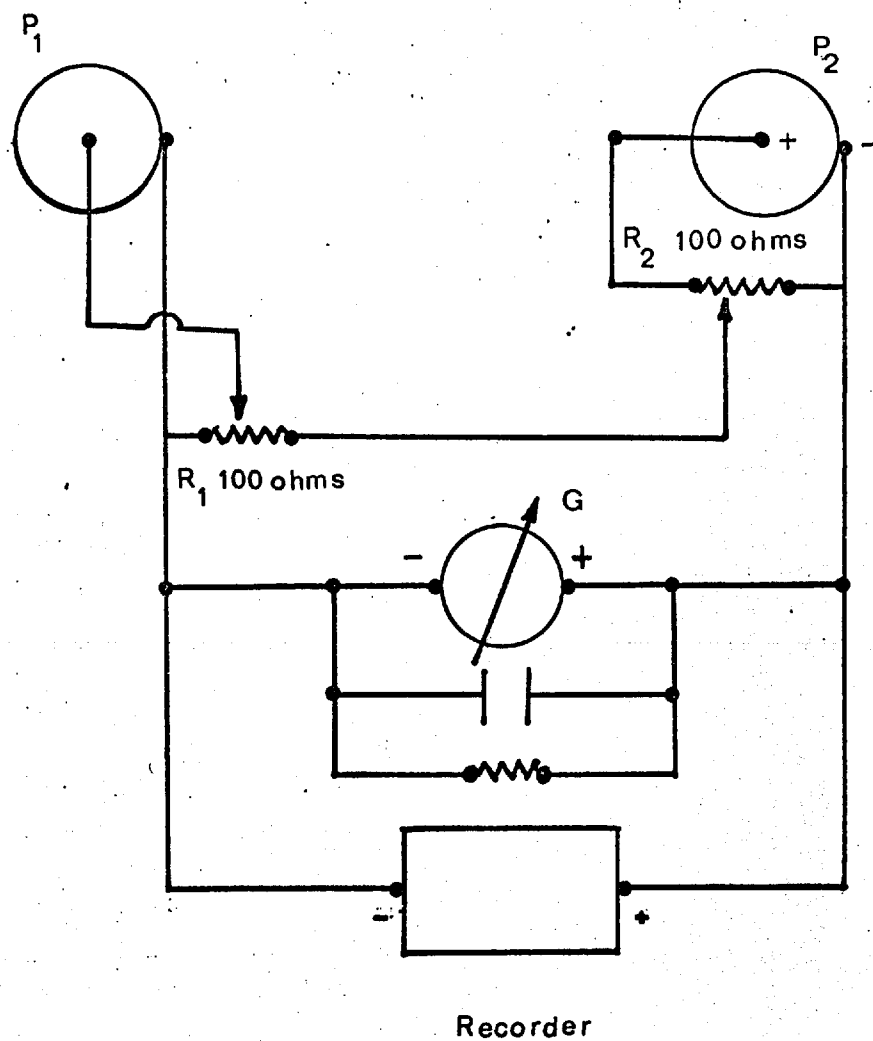
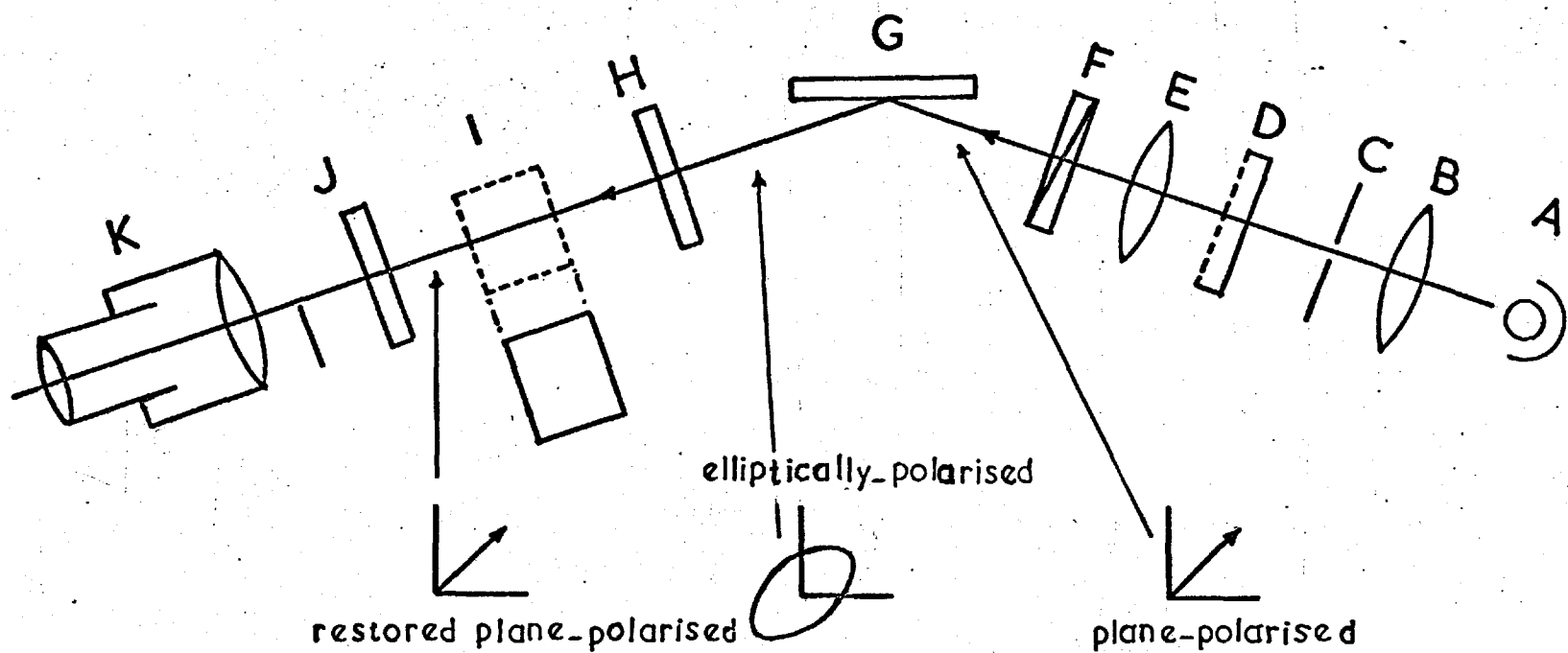


FIG.9 ELECTRICAL CIRCUITRY OF THE OPTICAL EQUIPMENT



- | | | | | | |
|---|----------------|---|--------------------|---|---------------------------------|
| A | light source | E | collimator lens | I | Tronstad ellipticity half shade |
| B | condenser lens | F | plane polariser | J | analyser & half shade |
| C | aperture | G | specimen | K | telescope |
| D | filter | H | quarter wave plate | | |

FIG.10 SCHEMATIC DIAGRAM OF THE ELLIPSOMETER

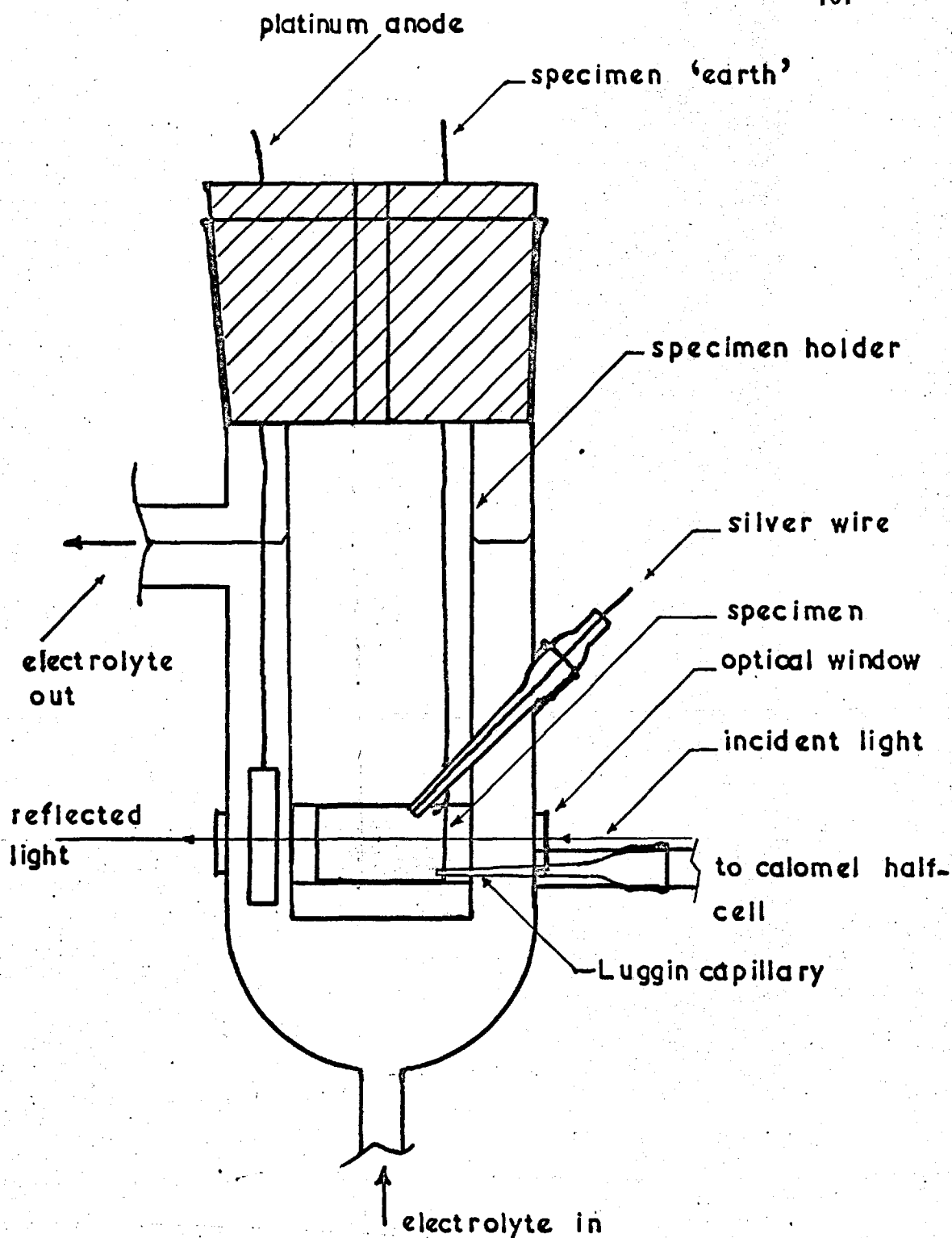


FIG.11 CORROSION CELL USED IN ELLIPSOMETRIC MEASUREMENTS

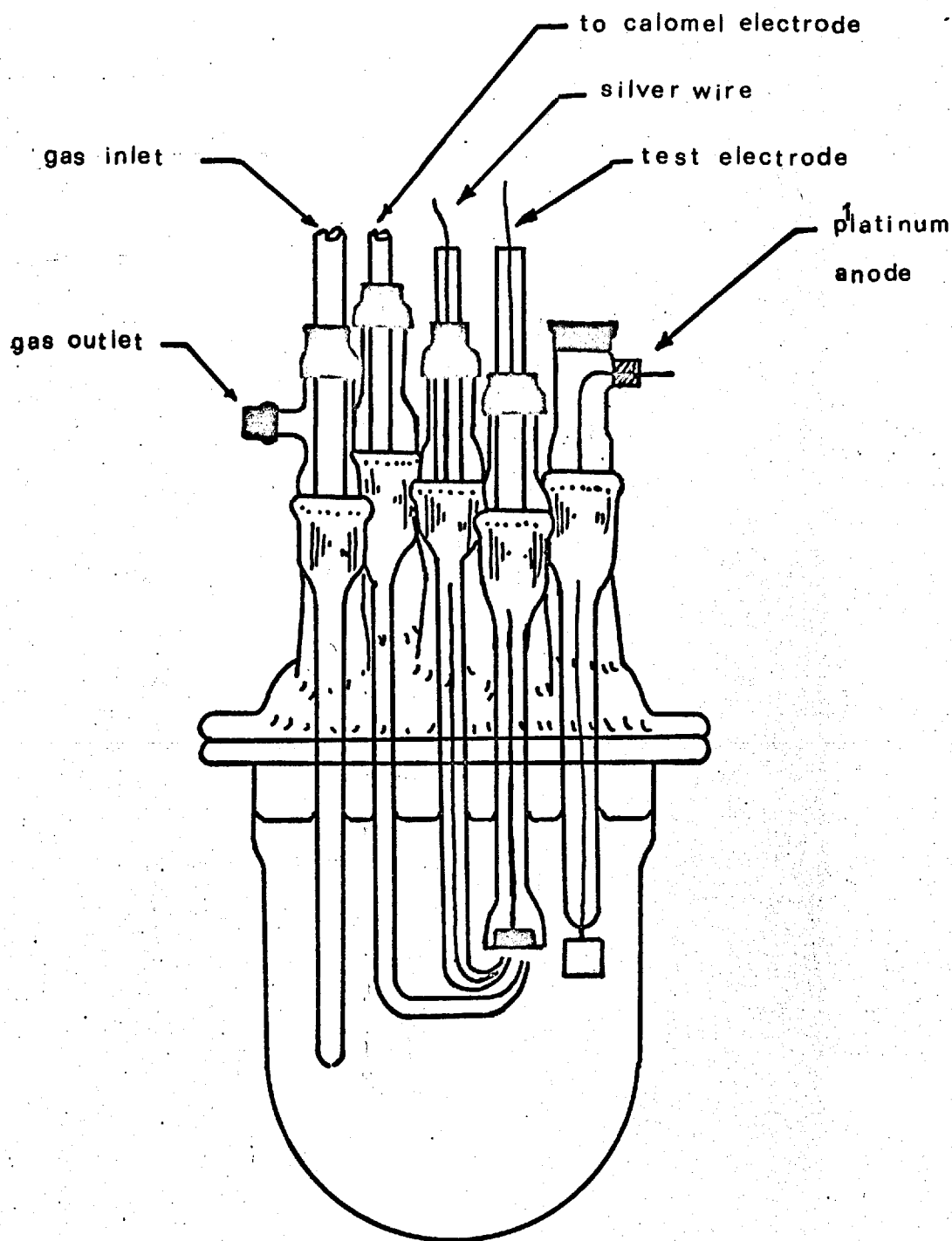


FIG. 12

CELL USED IN IMPEDANCE MEASUREMENTS

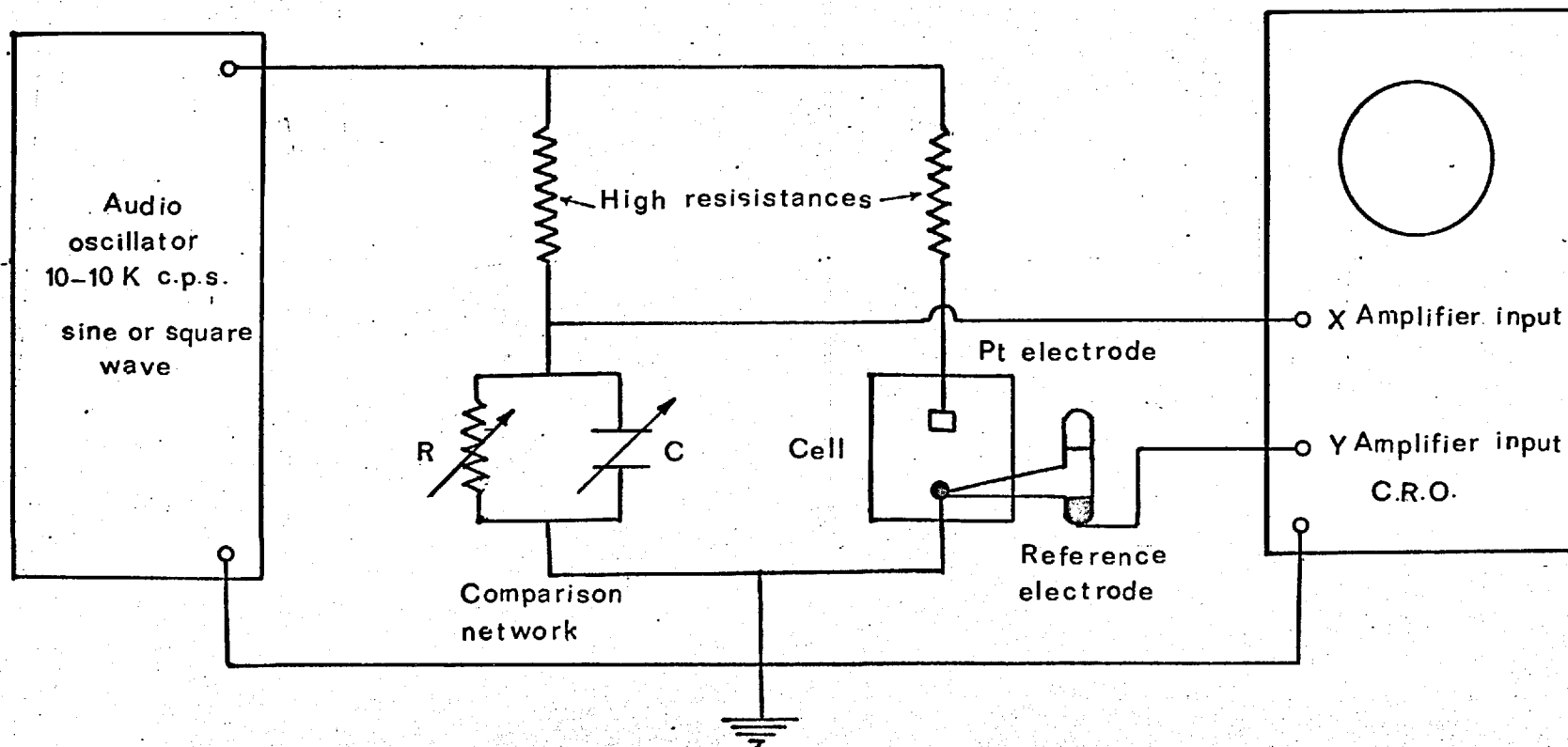
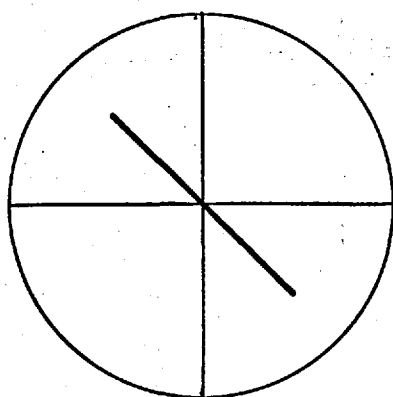
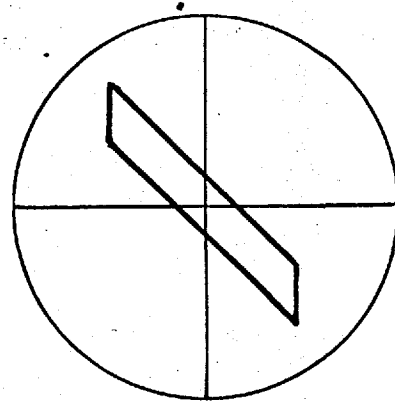
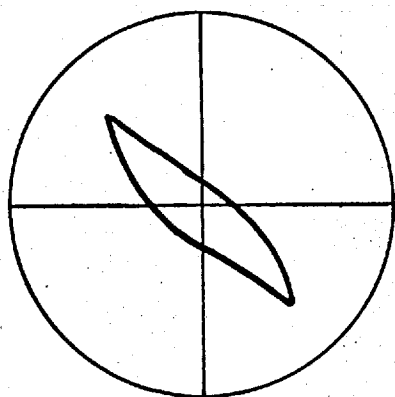
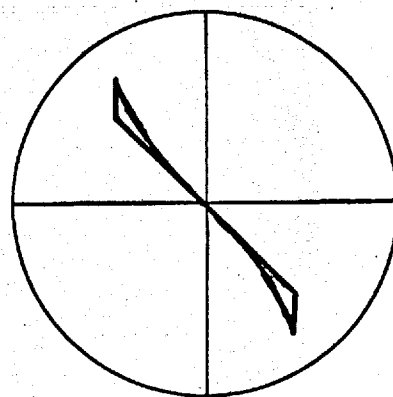


FIG.13 SCHEMATIC DIAGRAM OF IMPEDANCE-MEASURING
EQUIPMENT

**a****an ideal balance****b****an ideal balance with
uncompensated series
resistance****c****balance with distortion
caused by a smaller
time constant****d****compensation for apparent
series resistance****FIG.14 SHAPE OF TRACE ON OSCILLOSCOPE**

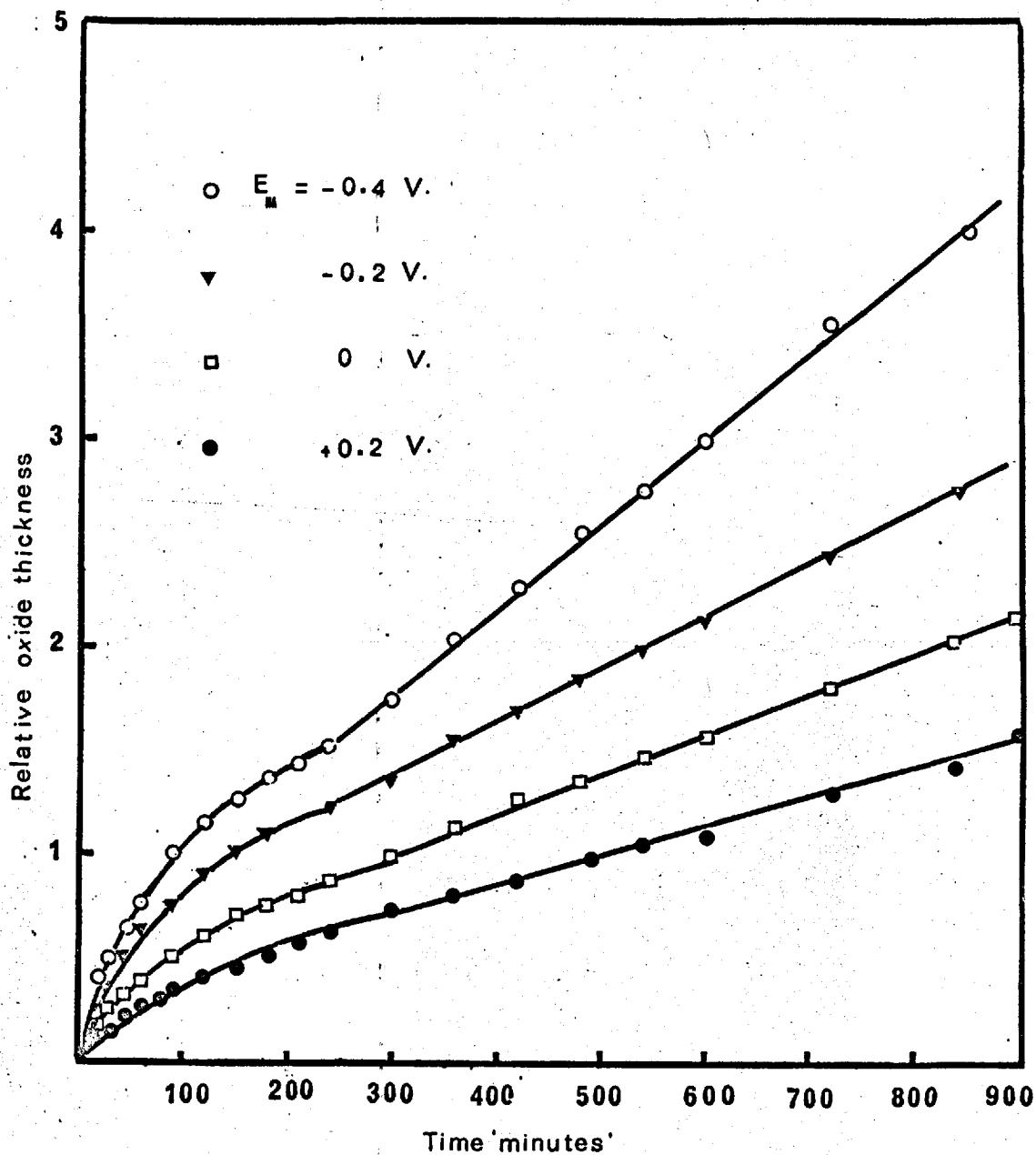


FIG. 15 EFFECT OF CATHODIC POLARISATION
ON U-12wt.% Mo, pH 5.4 $T = 40$ °C

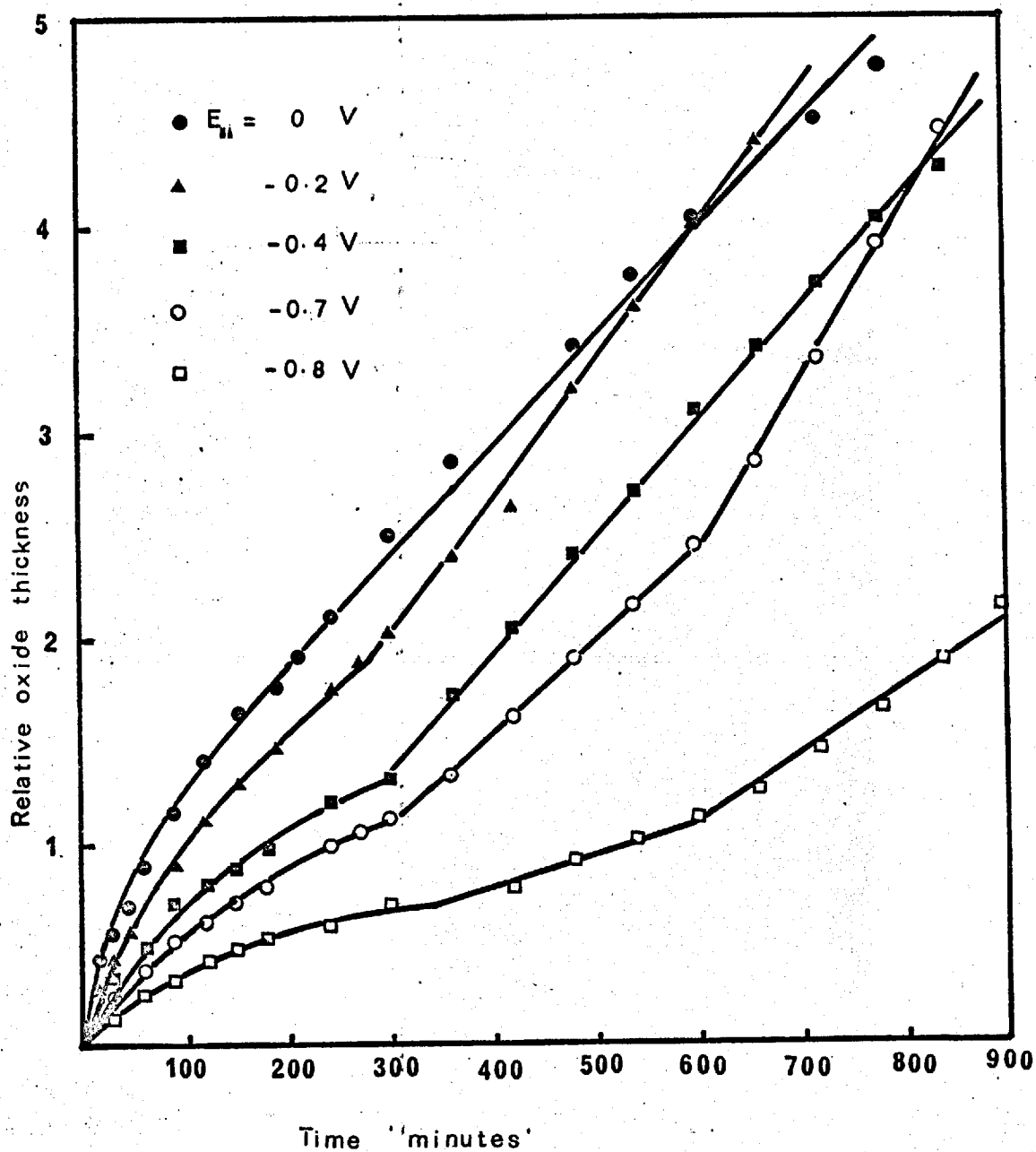


FIG. 16 EFFECT OF CATHODIC POLARISATION
ON CORROSION RATE. U-5wt.%Zr pH 9.7
ROOM TEMP.

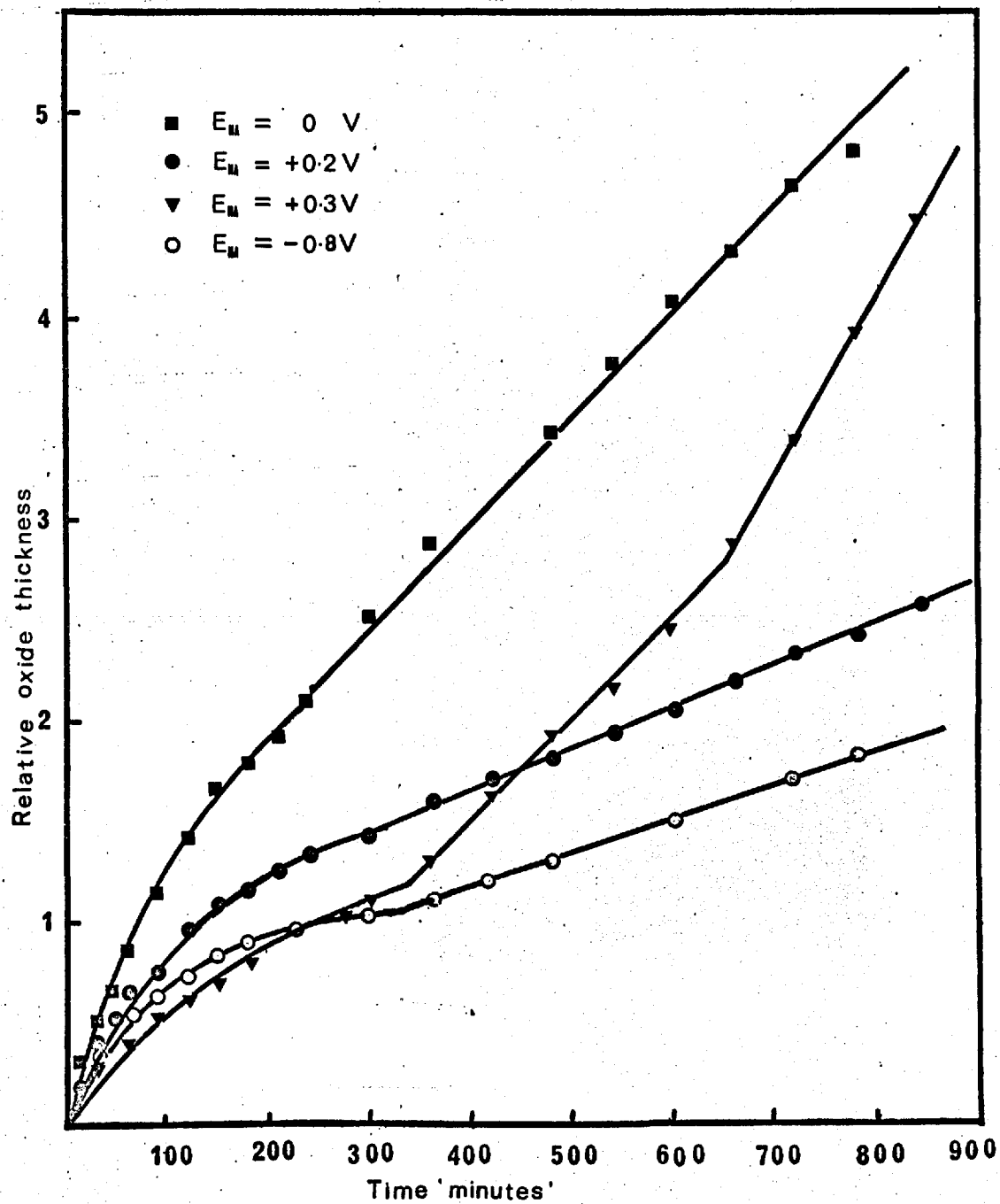


FIG.17 EFFECT OF ELECTRODE POTENTIAL

U-5wt.%Zr pH 9.7 ROOM TEMP.

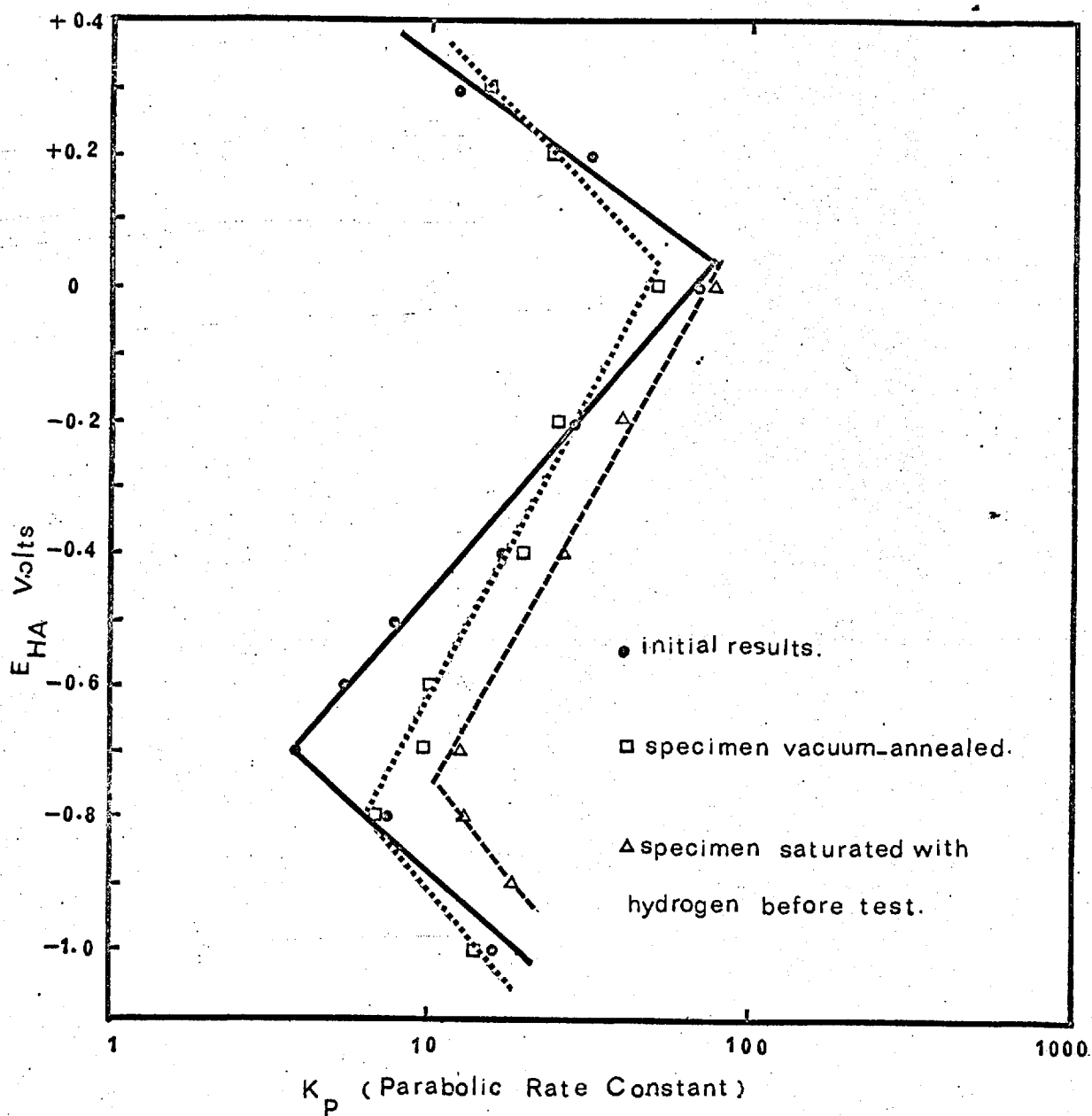


FIG.18 EFFECT OF POTENTIAL ON CORROSION
RATE U-5wt.% Zr. pH 9.7

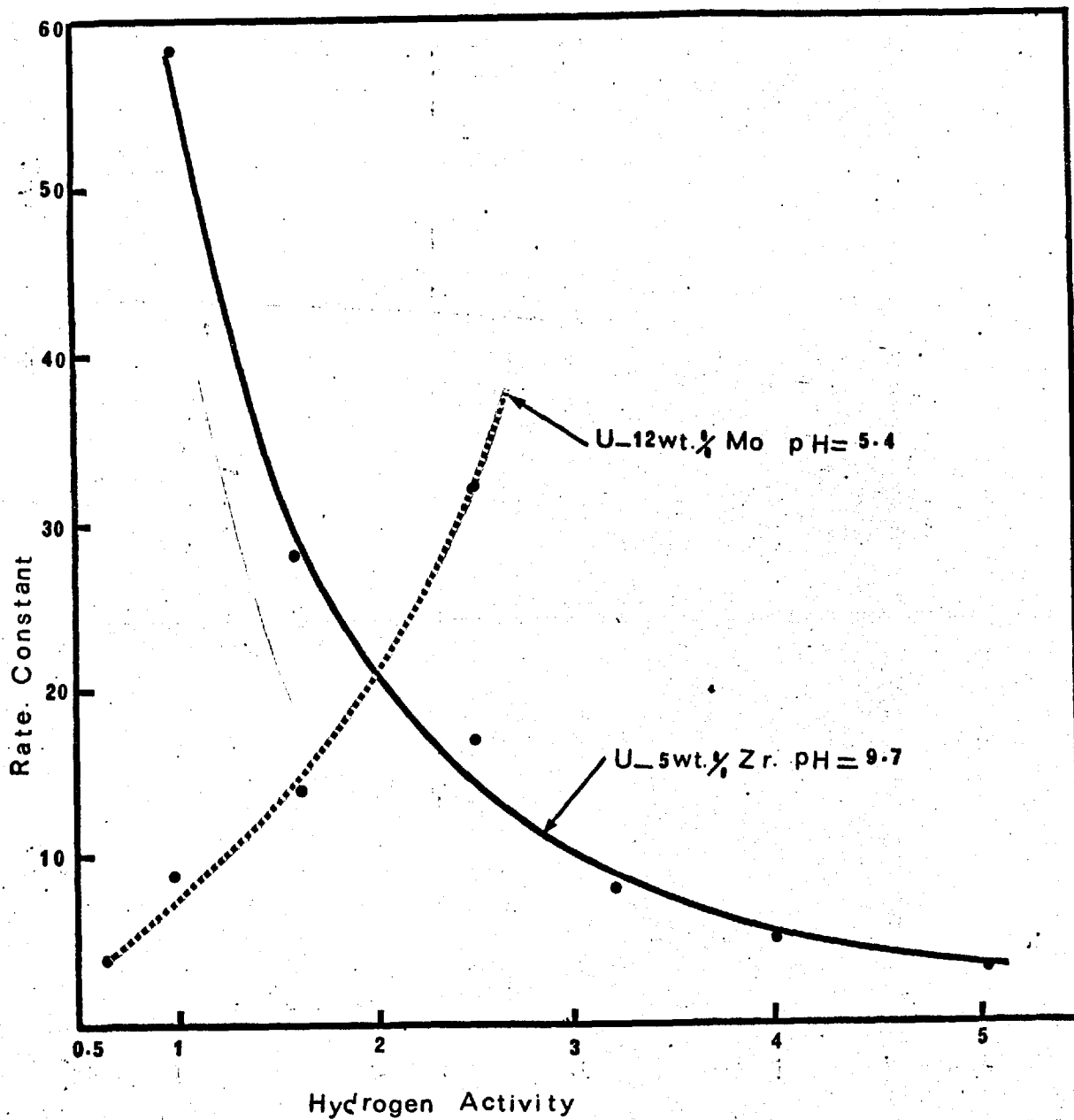


FIG.19 CORROSION RATE AS A FUNCTION
OF HYDROGEN ACTIVITY

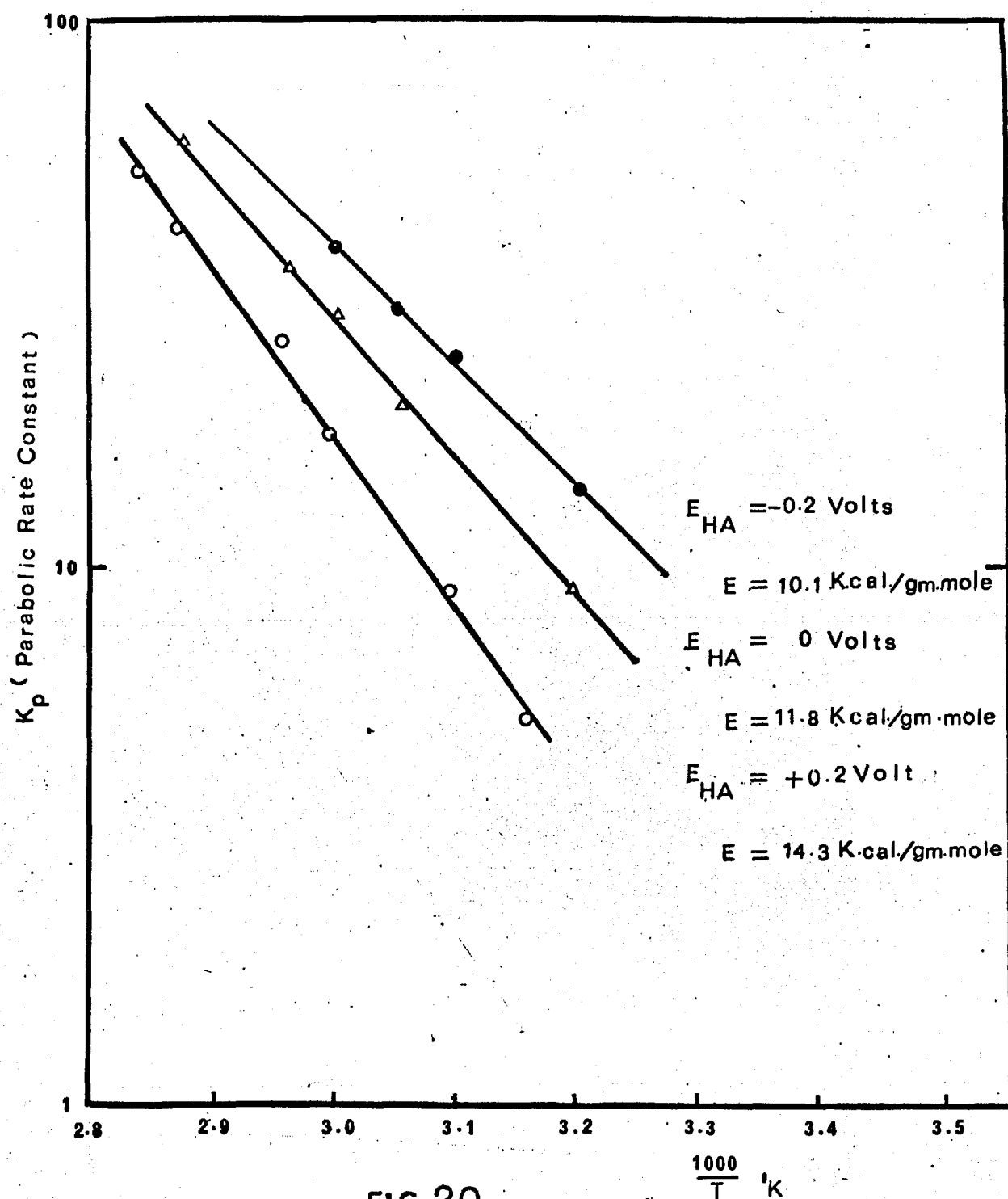
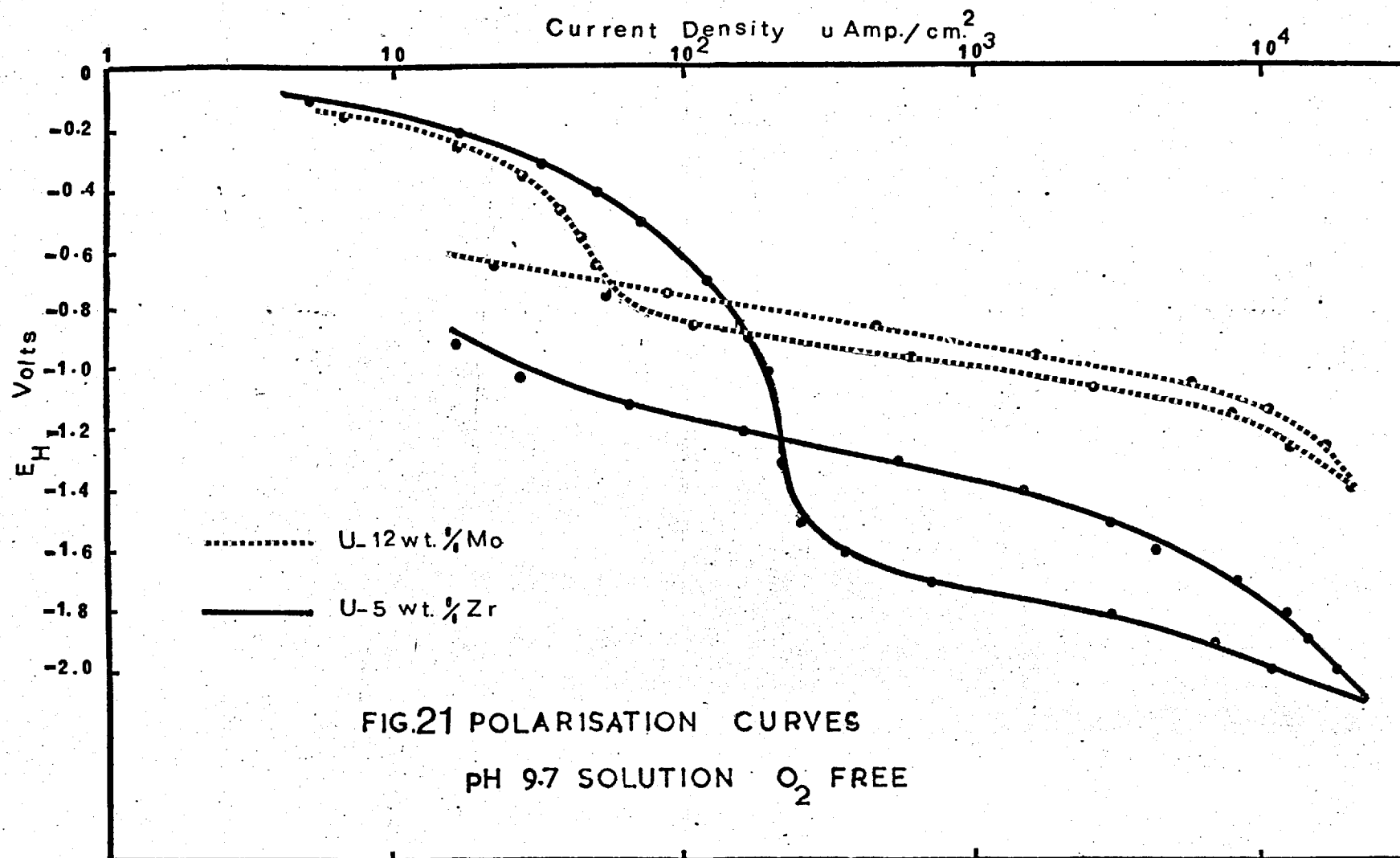


FIG. 20
TEMPERATURE DEPENDANCE OF CORROSION RATE
U 12wt.% Mo pH 5.4 OXYGEN FREE



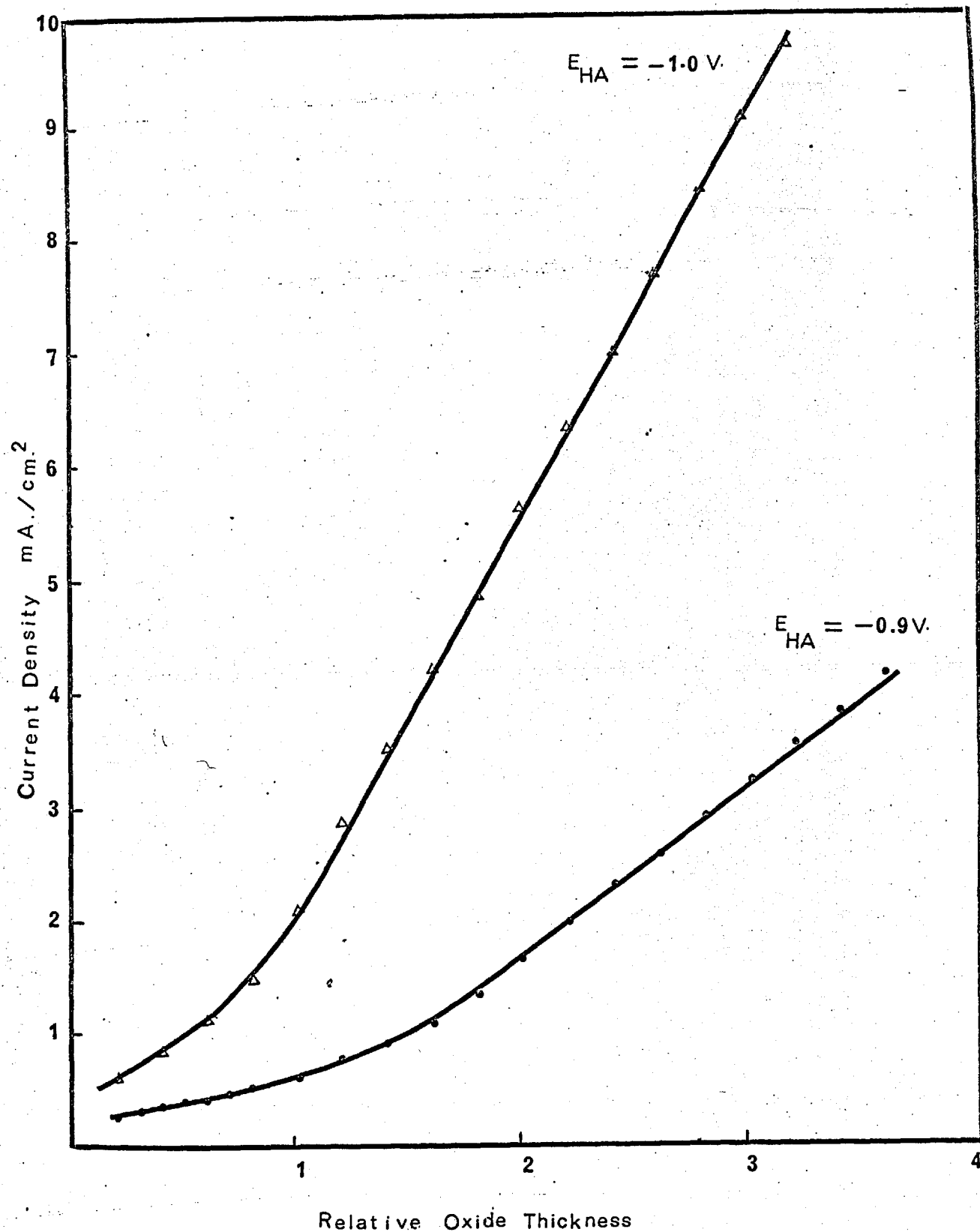


FIG. 22 CURRENT DENSITY AS A FUNCTION OF OXIDE THICKNESS U-5wt.%Zr pH 9.7

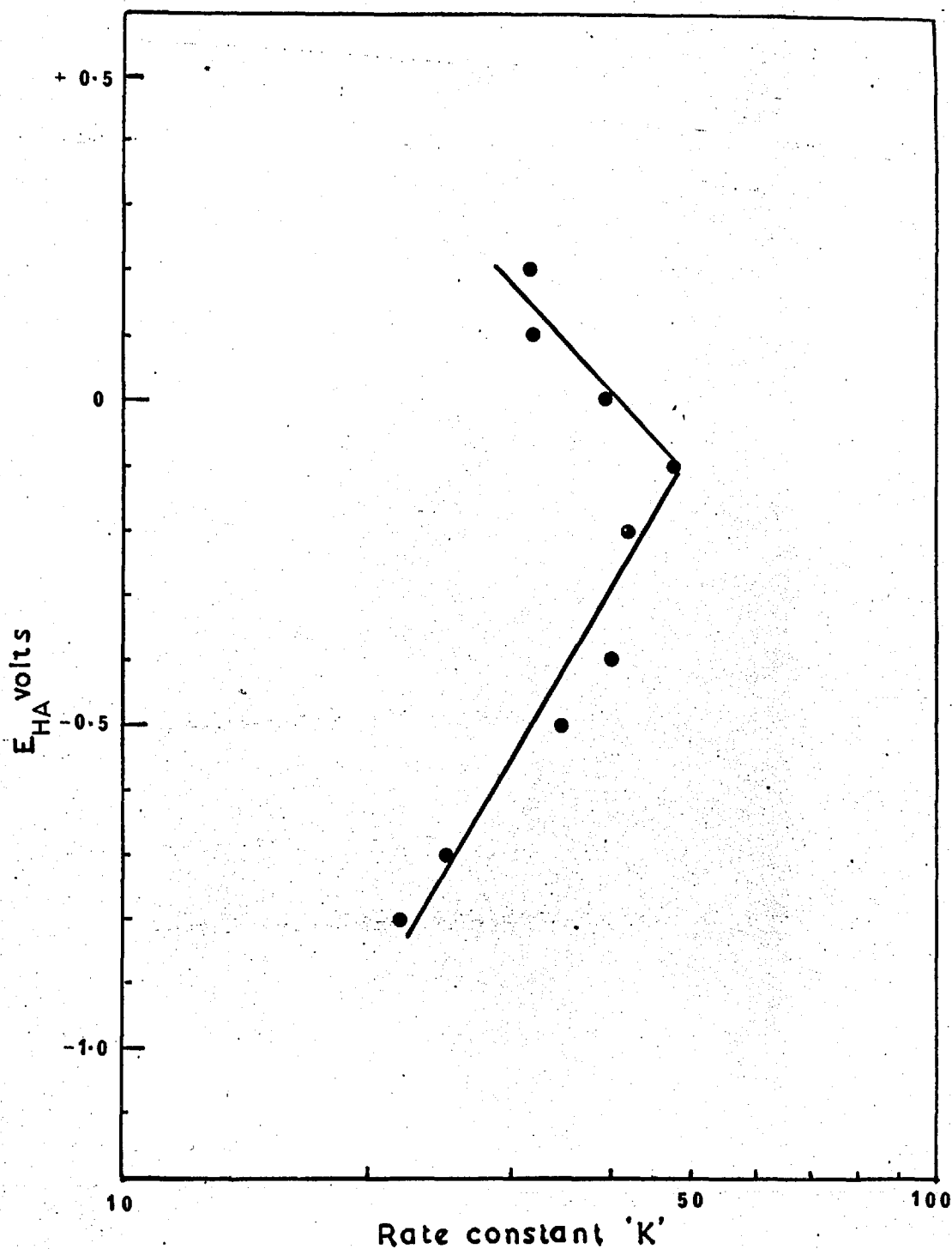


FIG.23 CORROSION RATE CHANGE
WITH POTENTIAL U-5wt.% Zr. pH 8.4

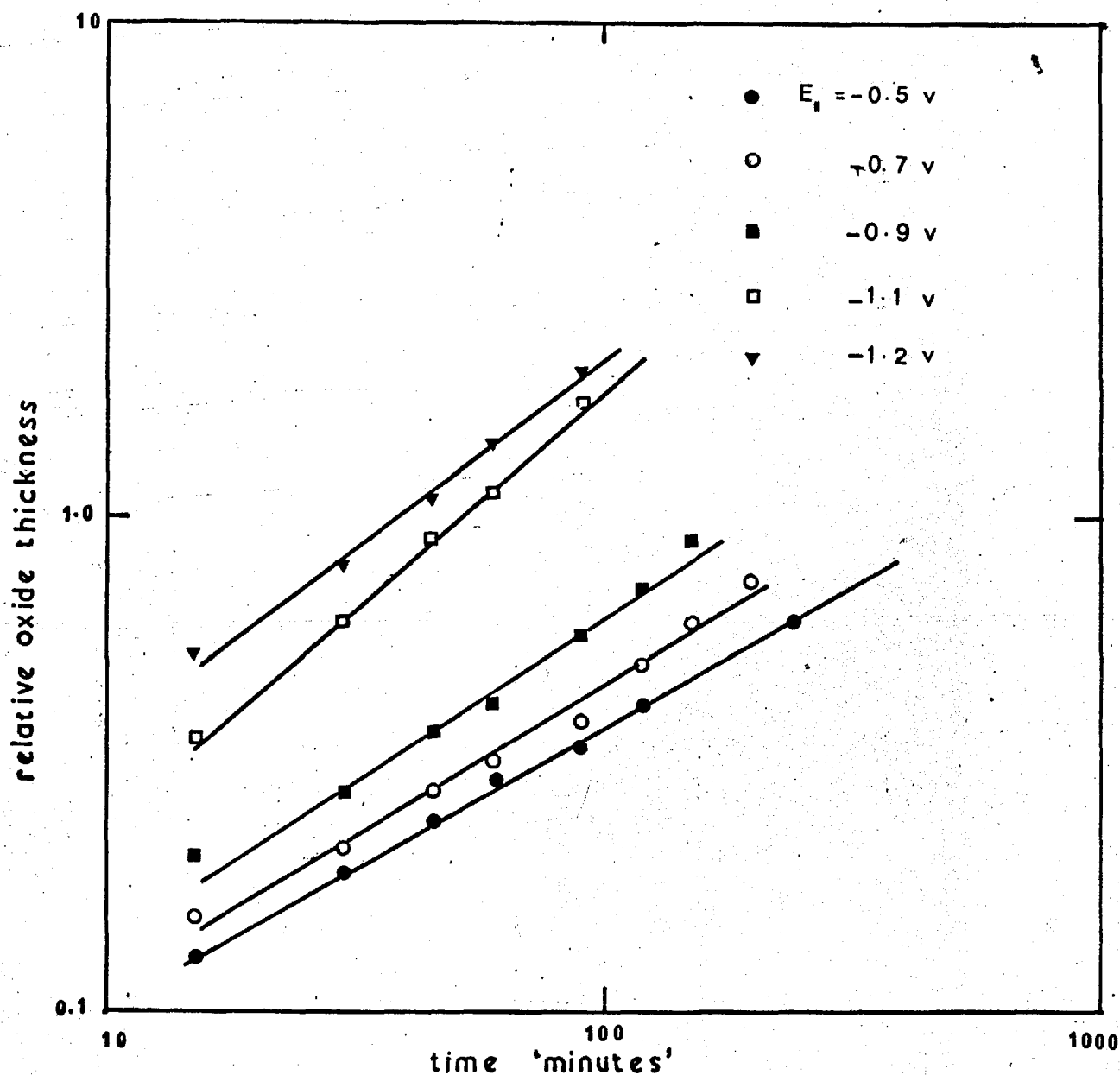


FIG.24 EFFECT OF CATHODIC POTENTIAL ON
CORROSION RATE - Ti - pH 9.7 - 70 °C
'OPTICAL ABSORPTION TECHNIQUE'

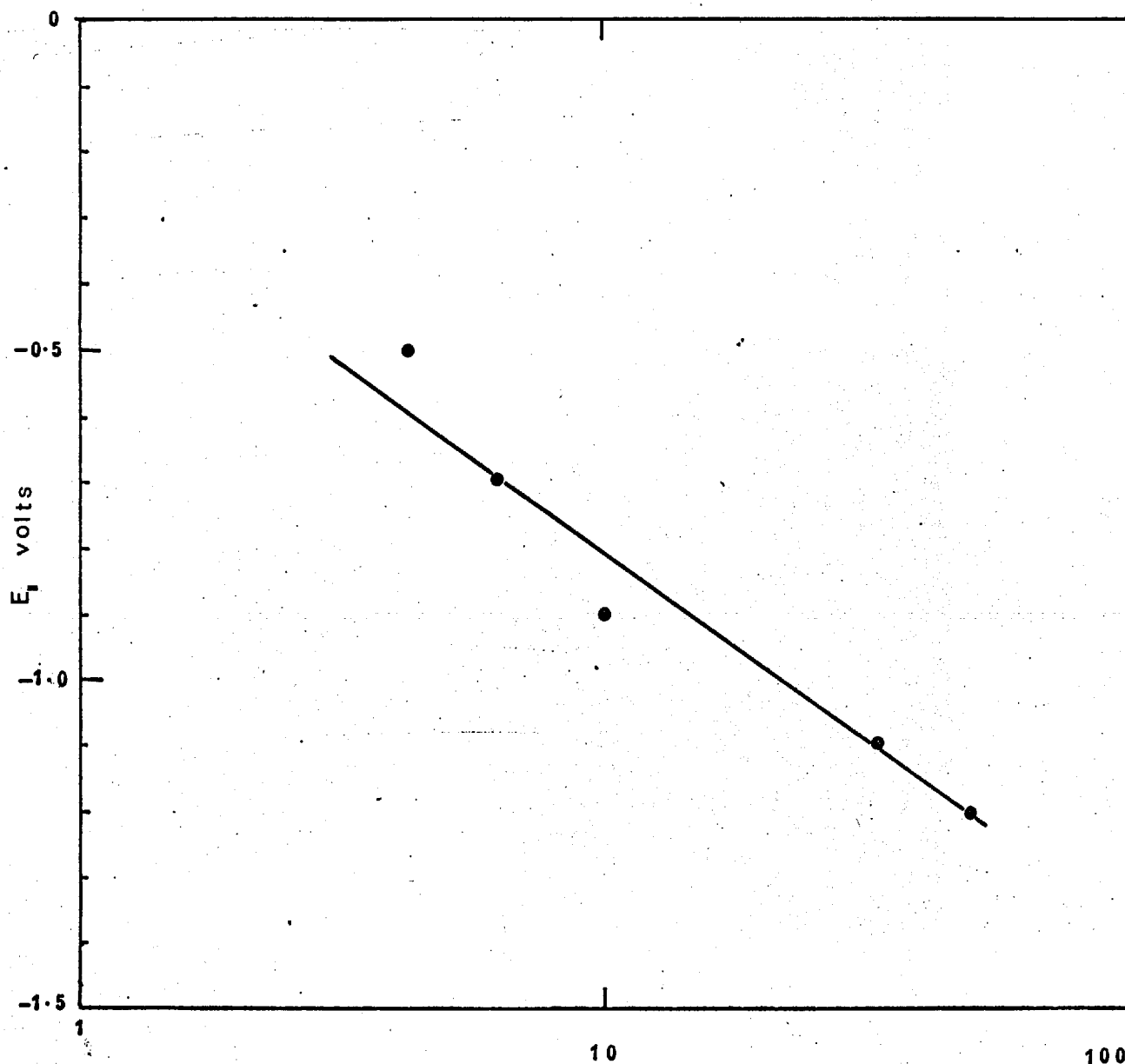


FIG. 25 POTENTIAL DEPENDENCE OF CORROSION
RATE OF TITANIUM — pH 9.7 — 70 °C
'ABSORPTION TECHNIQUE'

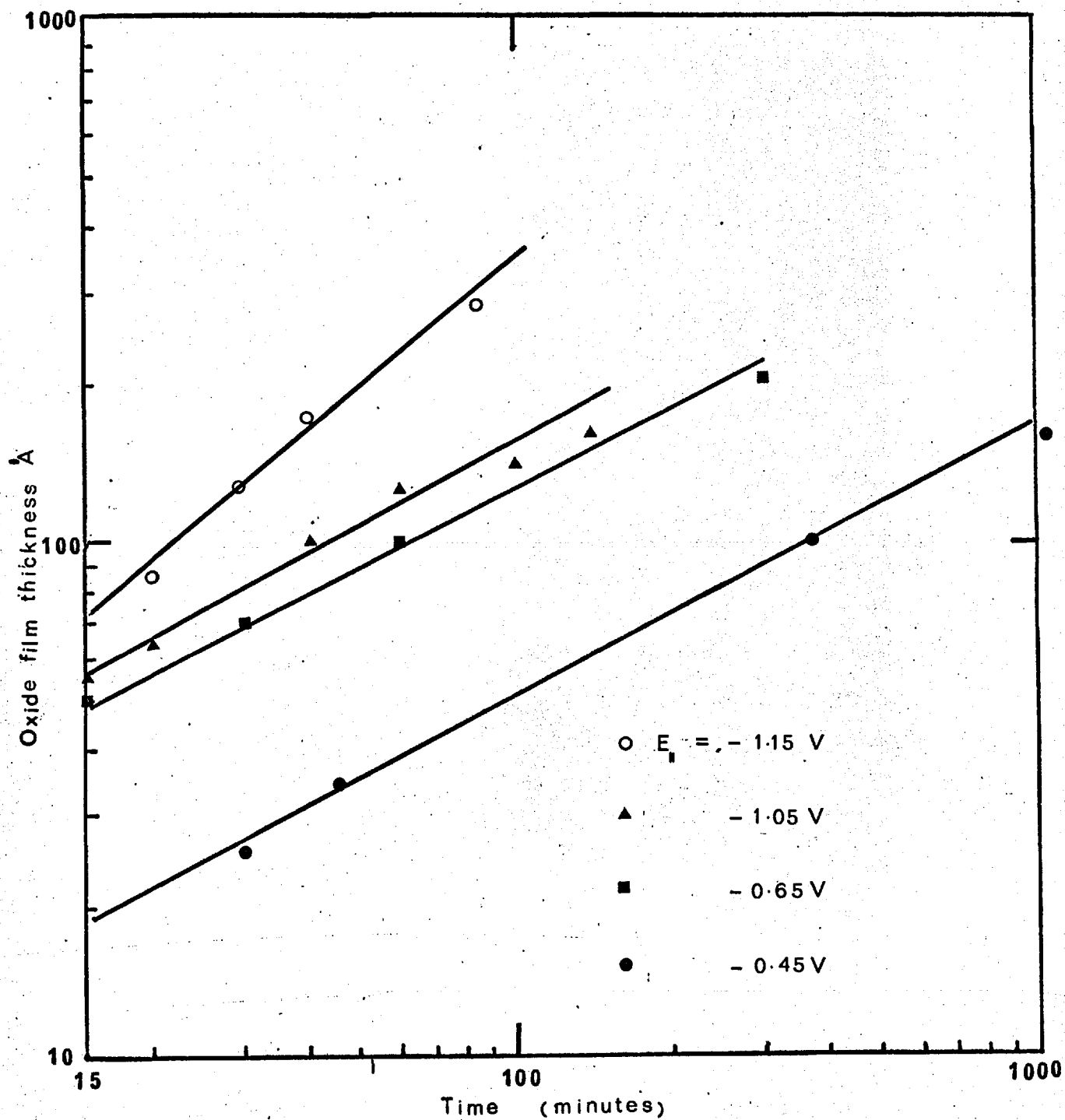


FIG.26 EFFECT OF CATHODIC POLARISATION ON Ti

pH 9.7 T = 70 °C

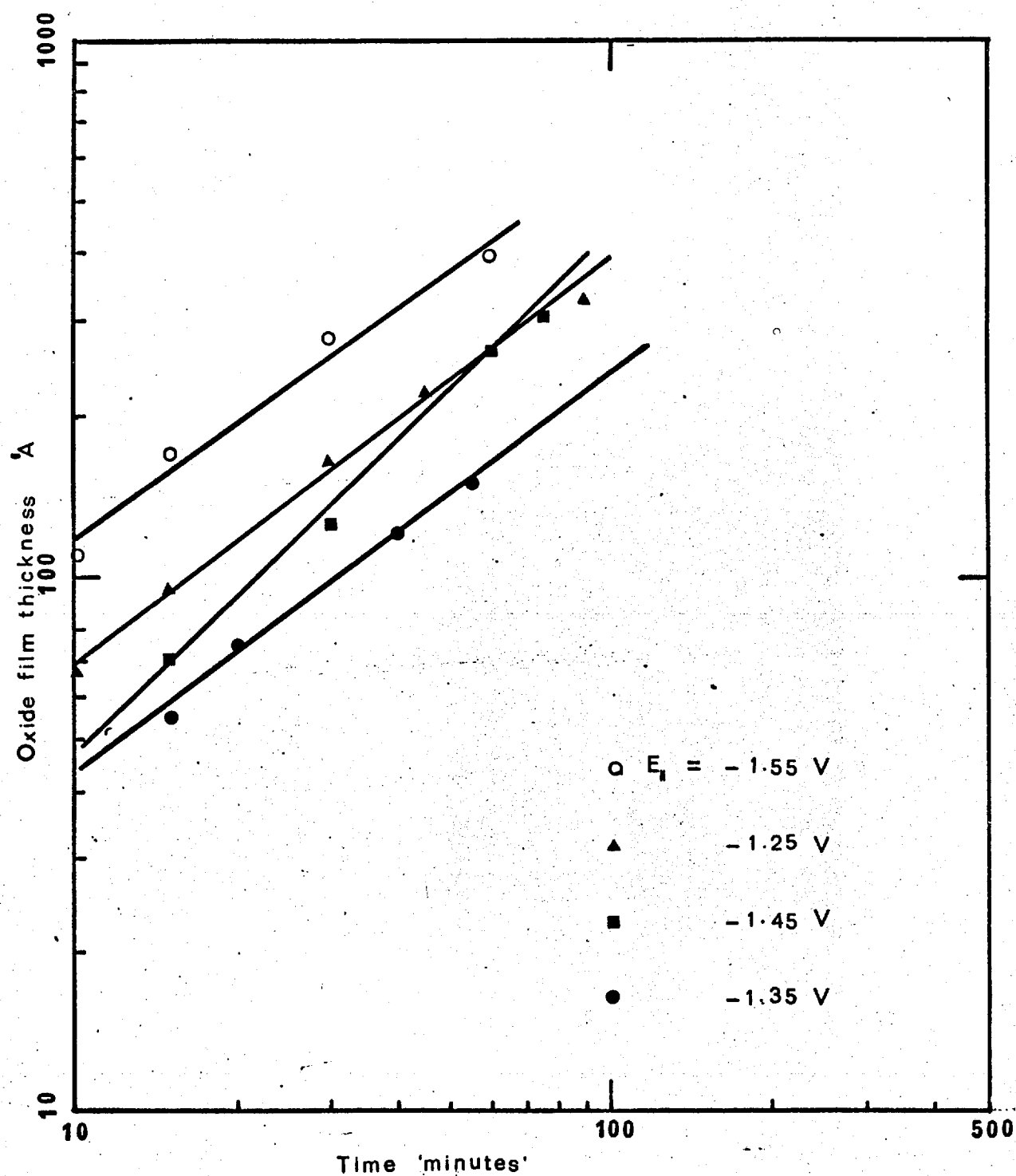
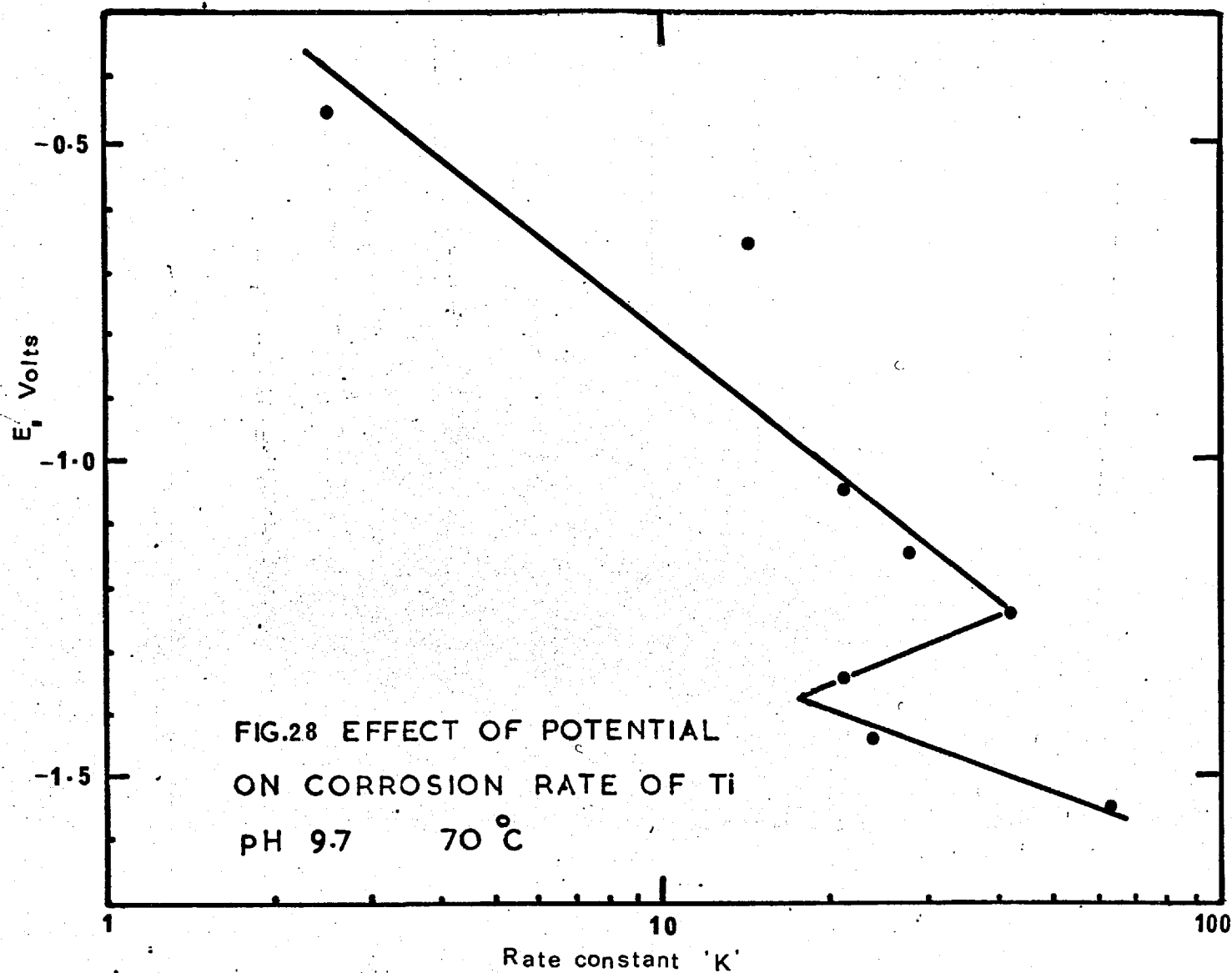


FIG. 27 EFFECT OF CATHODIC POLARISATION ON Ti

pH 9.7 $T = 70$ °C



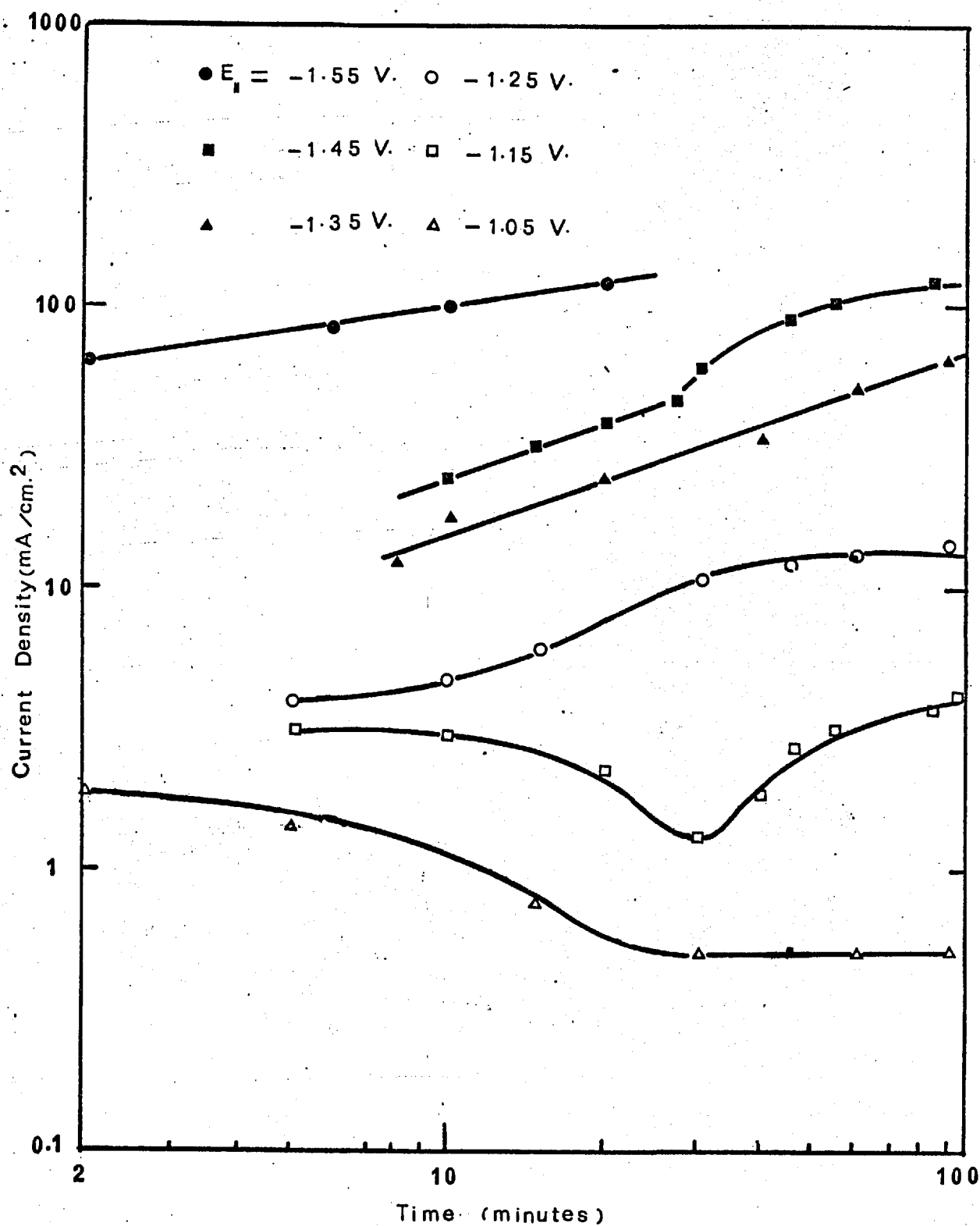


FIG.29 POTENTIOSTATIC CURRENT AS A FUNCTION OF TIME - Ti - pH 9.7 - 70°C

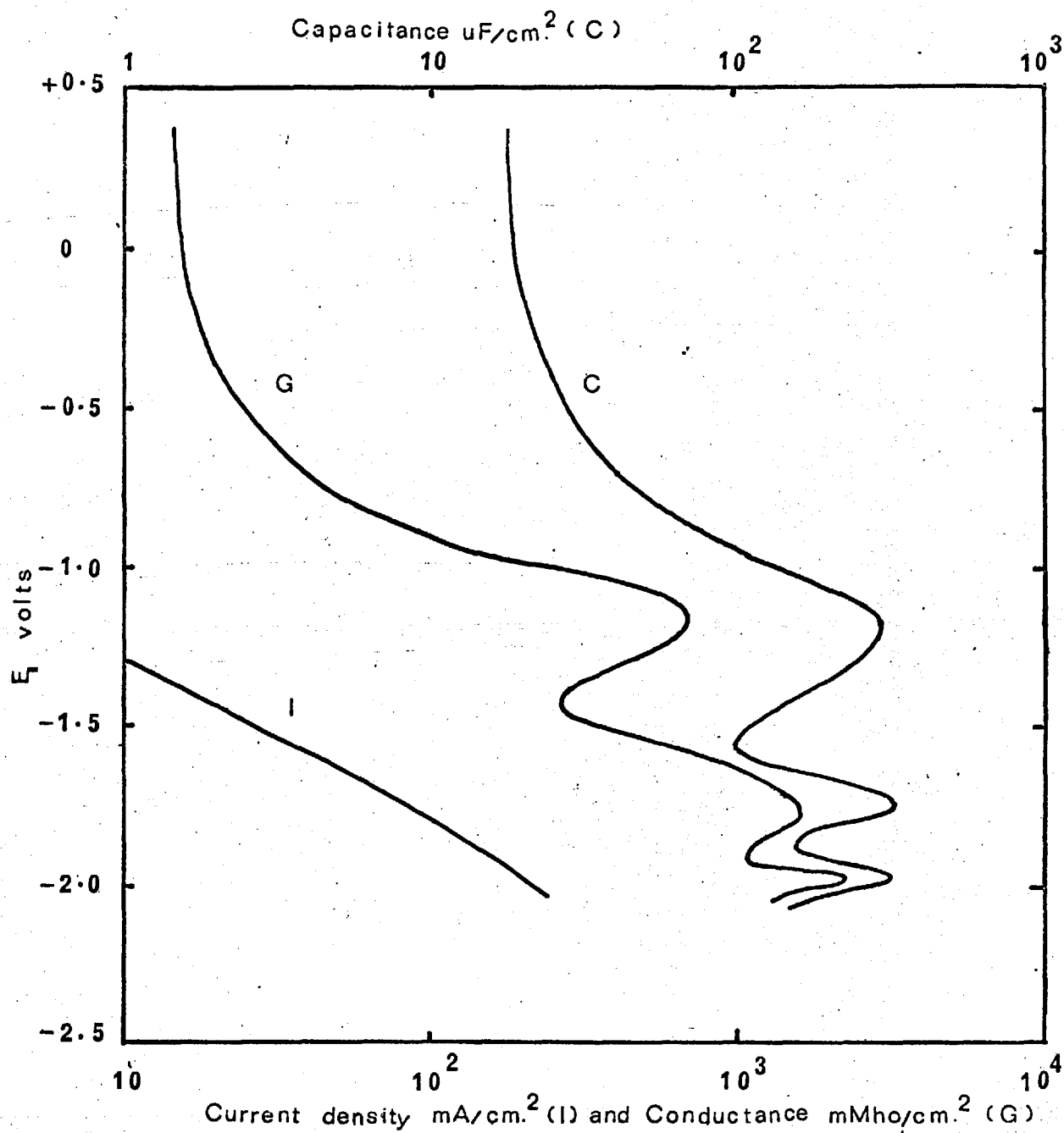


FIG. 30 IMPEDANCE CHANGE WITH ELECTRODE
 POTENTIAL - Ti - pH 9.7 - FREQUENCY = 1000 C.R.S.
 (after Leach⁽¹²¹⁾)

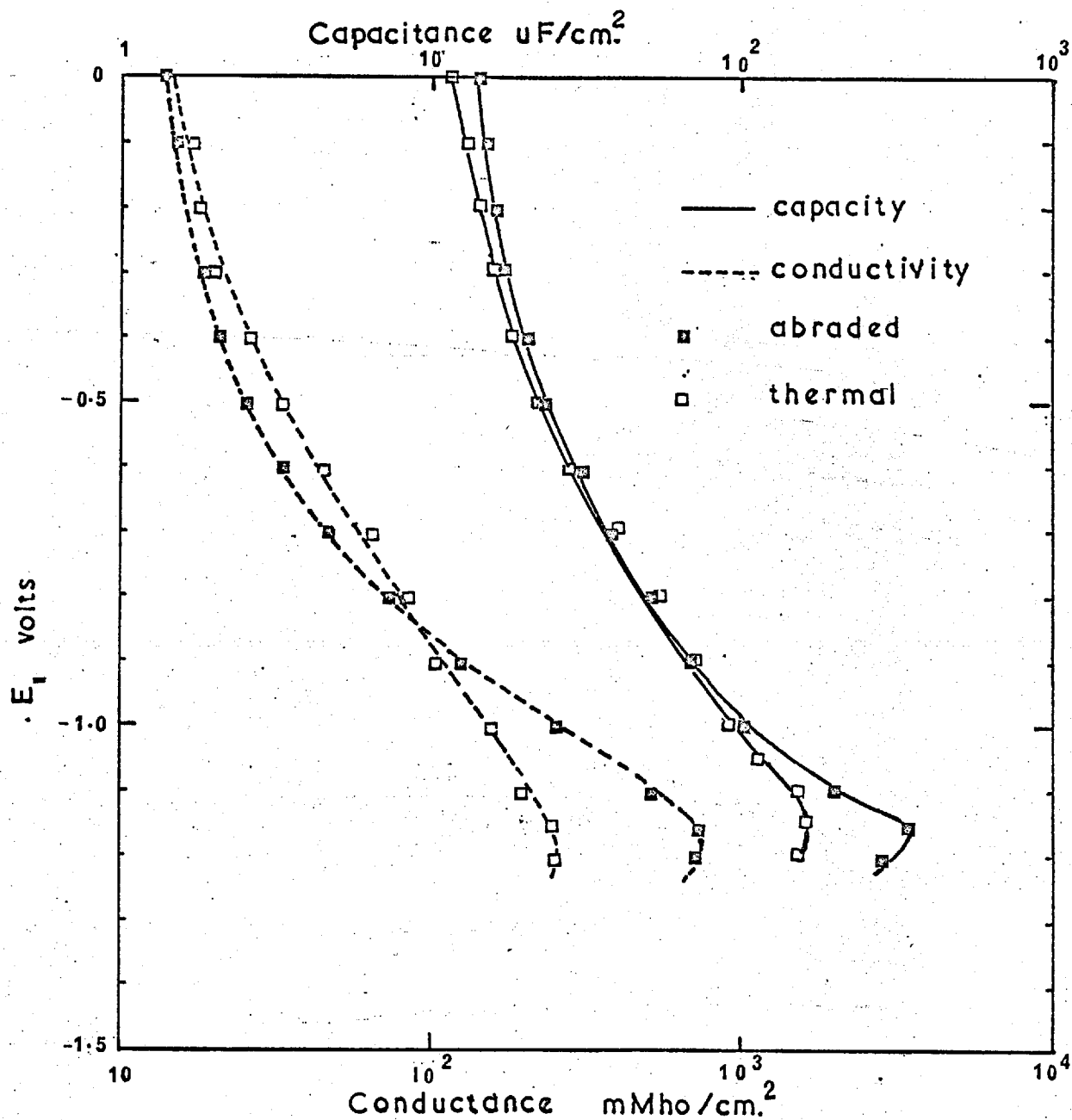
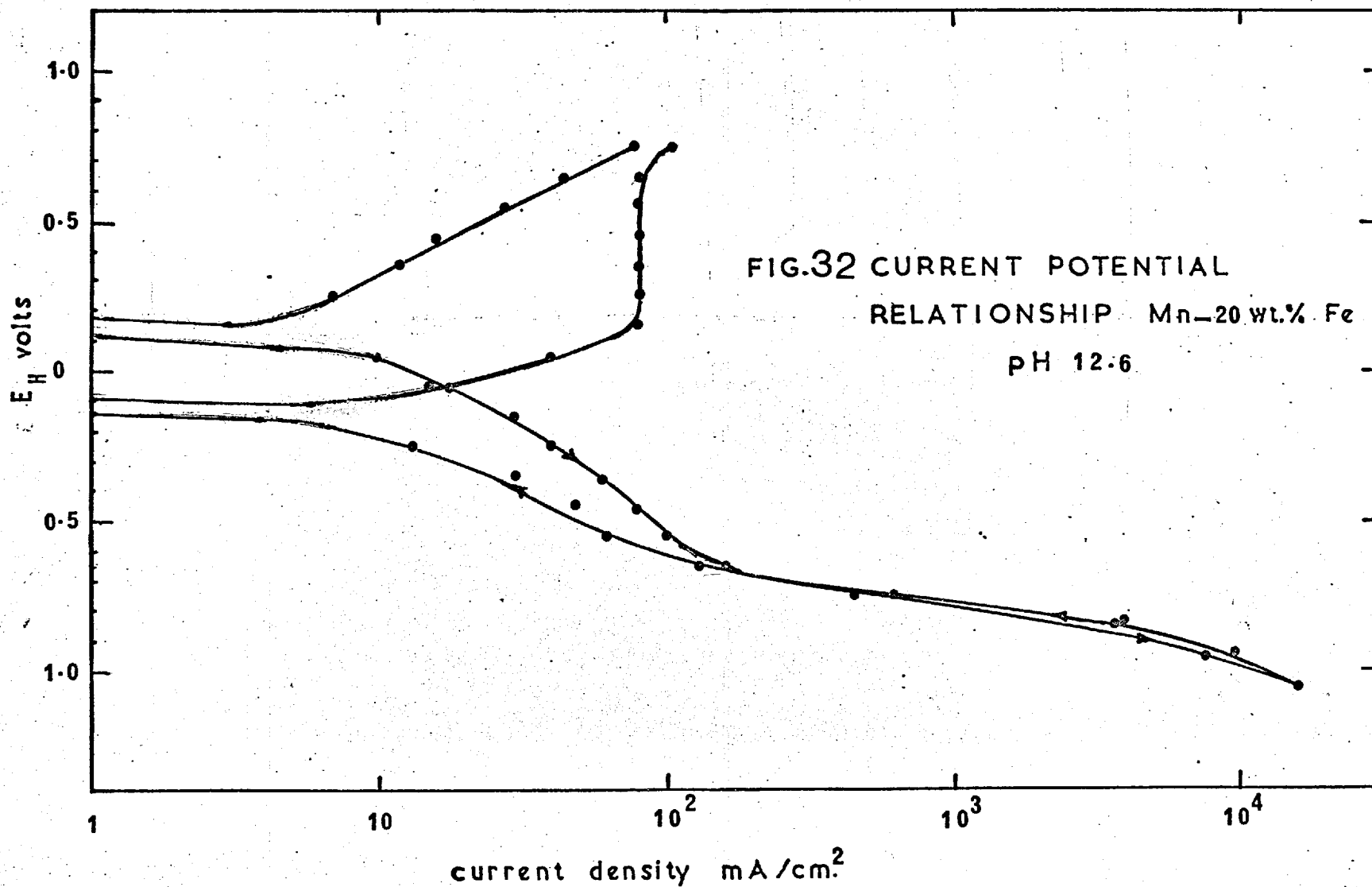


FIG.31 EFFECT OF ELECTRODE POTENTIAL
ON IMPEDANCE — Ti — pH 9.7



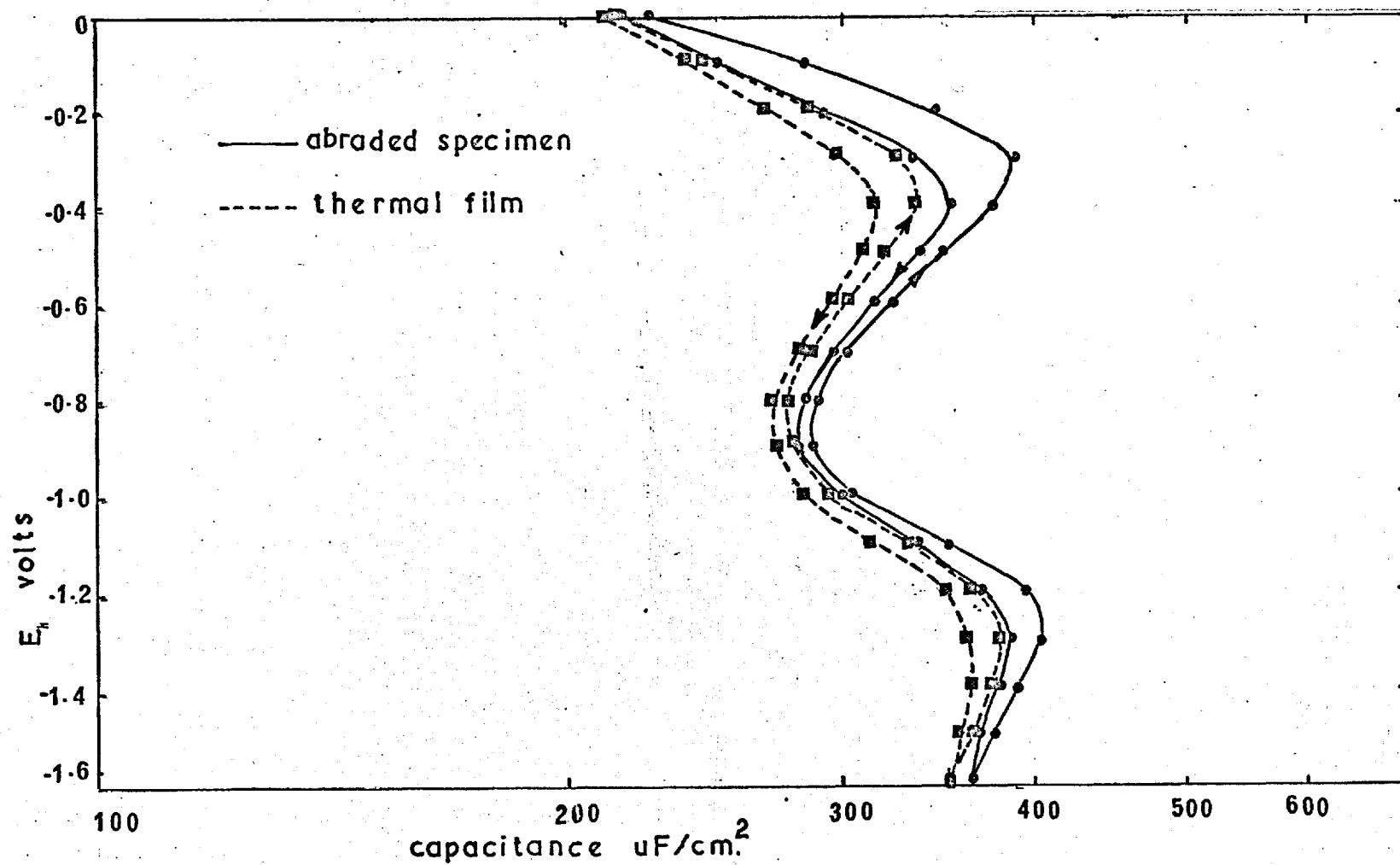


FIG.33 CAPACITANCE DEPENDENCE ON POTENTIAL -
VANADIUM — pH 9.7

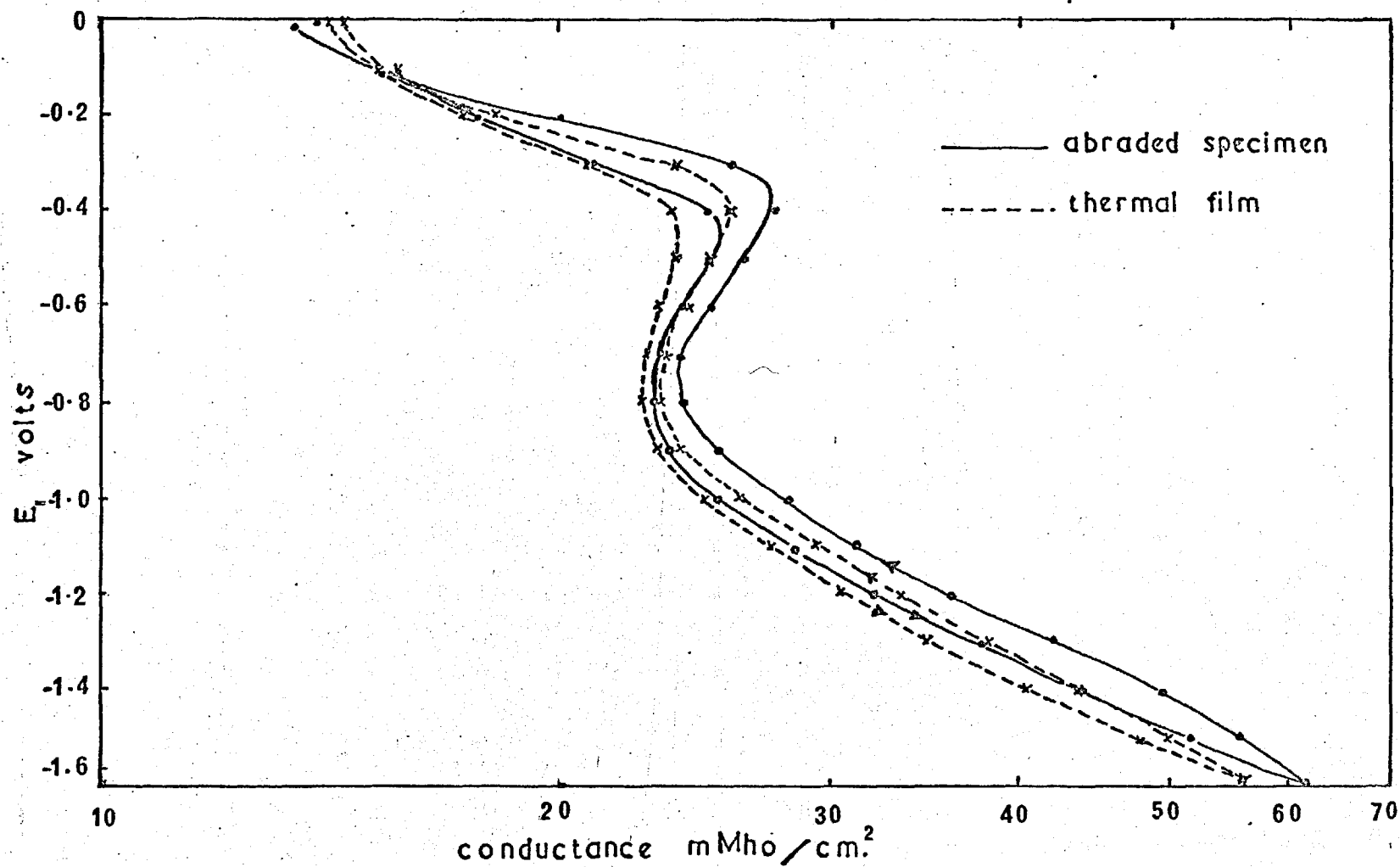


FIG.34 EFFECT OF CATHODIC POTENTIAL ON
CONDUCTANCE OF VANADIUM - pH 9.7

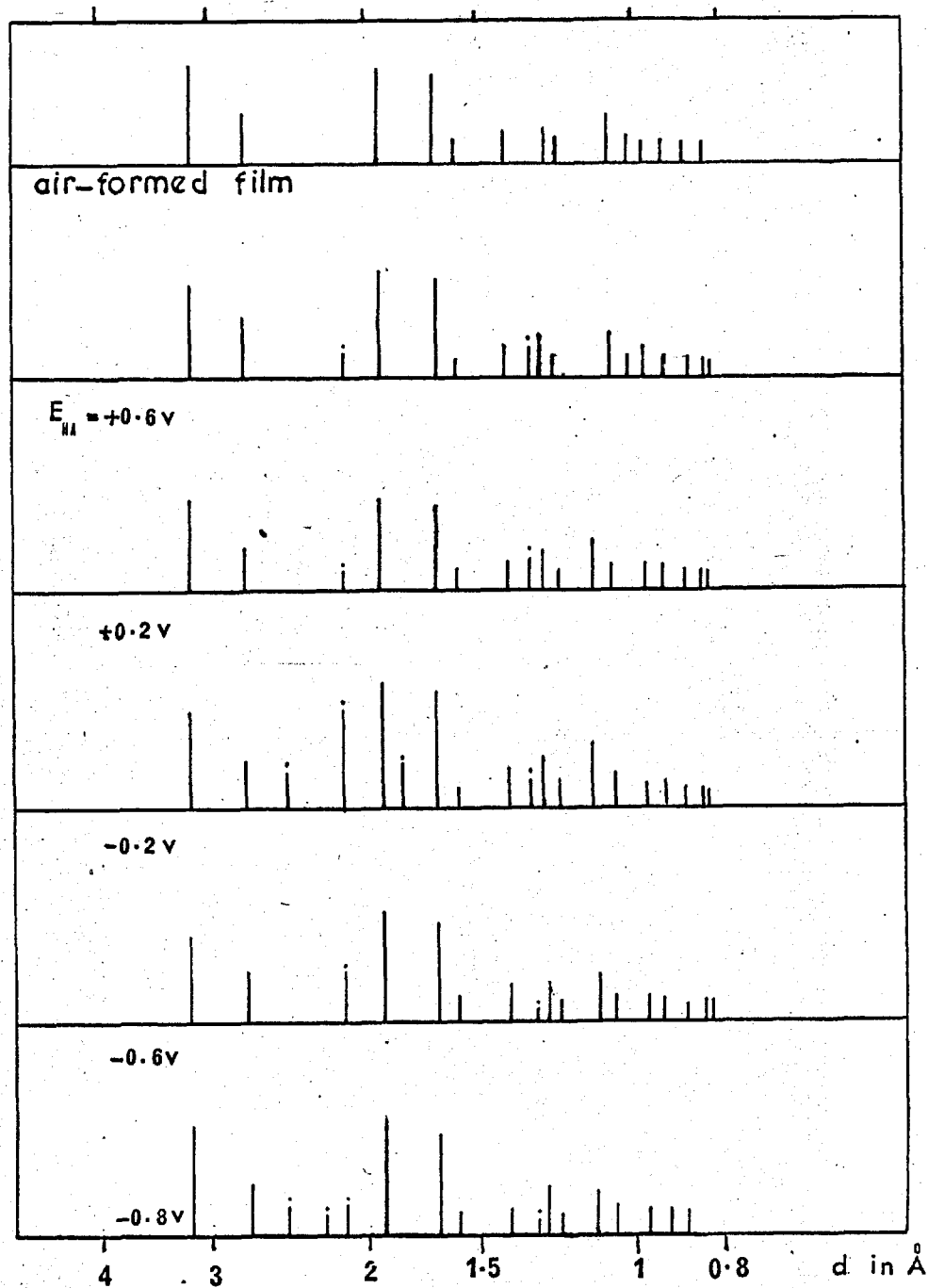
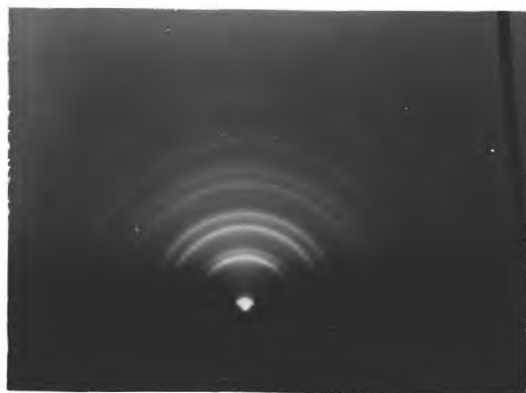
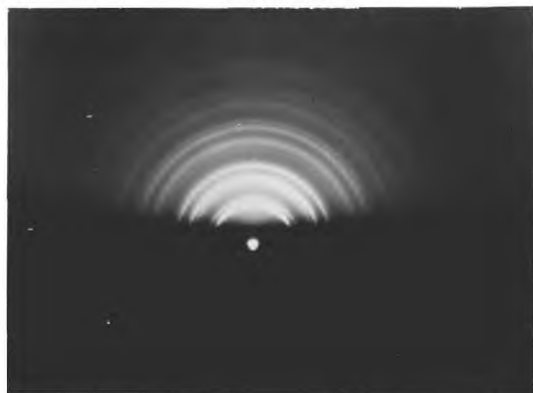


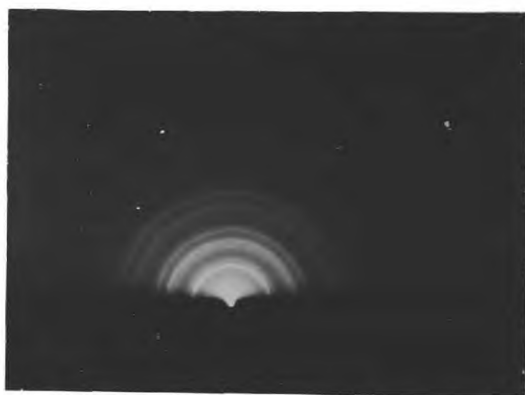
FIG. 35a EFFECT OF POTENTIAL ON OXIDE
FILM STRUCTURE U-5wt.% Zr pH 9.7



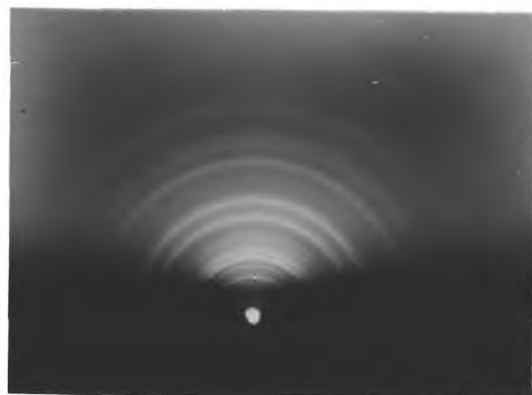
(a) air-formed film



(b) EHA = +0.6 V



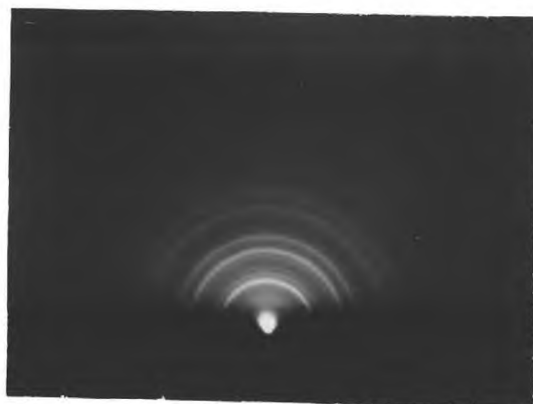
(c) EHA = +0.2 V



(d) EHA = -0.2 V



(e) EHA = -0.6 V



(f) EHA = -0.8 V

Fig. 35 b. Diffraction patterns of oxides formed on
U-5wt% Zr-pH 9.7-Oxygen-Free

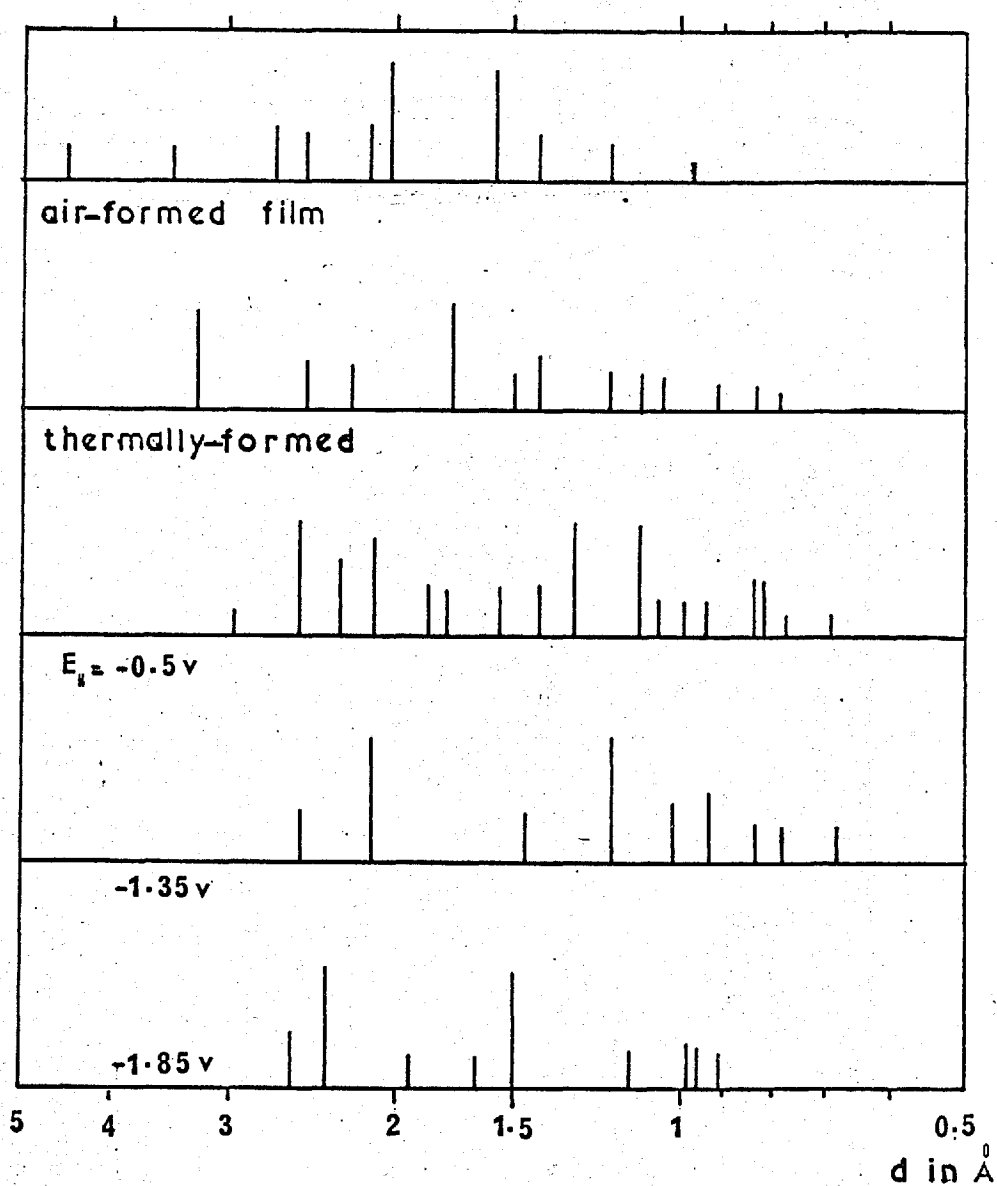
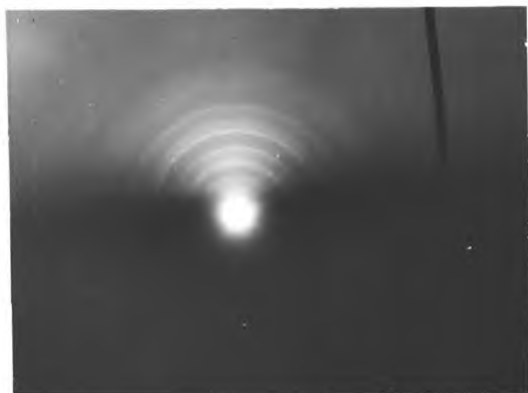
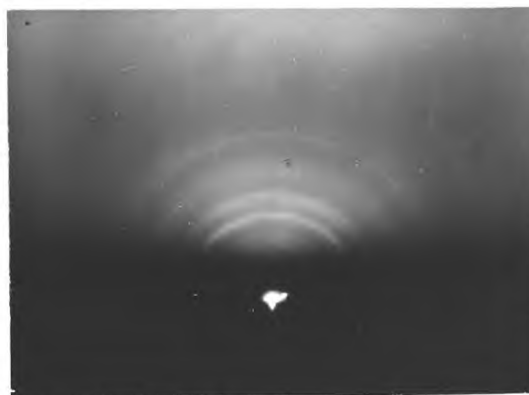


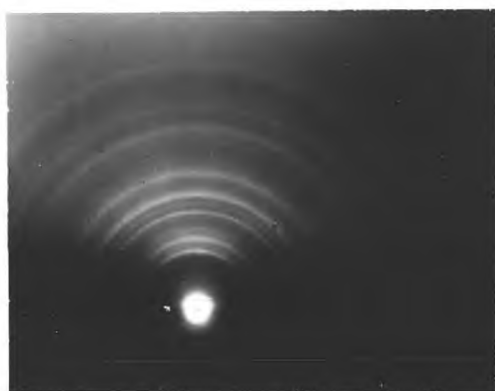
FIG.36a OXIDE FILM STRUCTURE CHANGE
WITH POTENTIAL - Ti - pH 9.7



(a) air-formed film



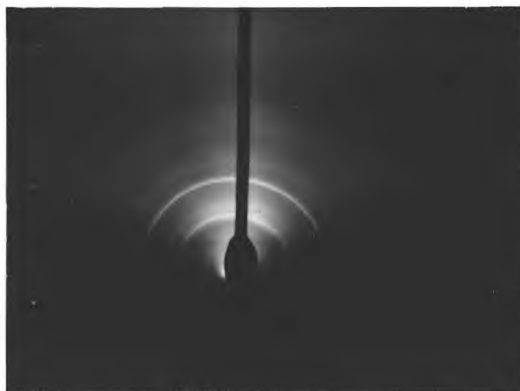
(b) Thermally formed film



(c) EH = -0.5 V



(d) EH = -1.35 V



(e) EH = -1.85 V

Fig. 36 b. Diffraction patterns of oxides formed on titanium -pH 9.7 Oxygen-Free

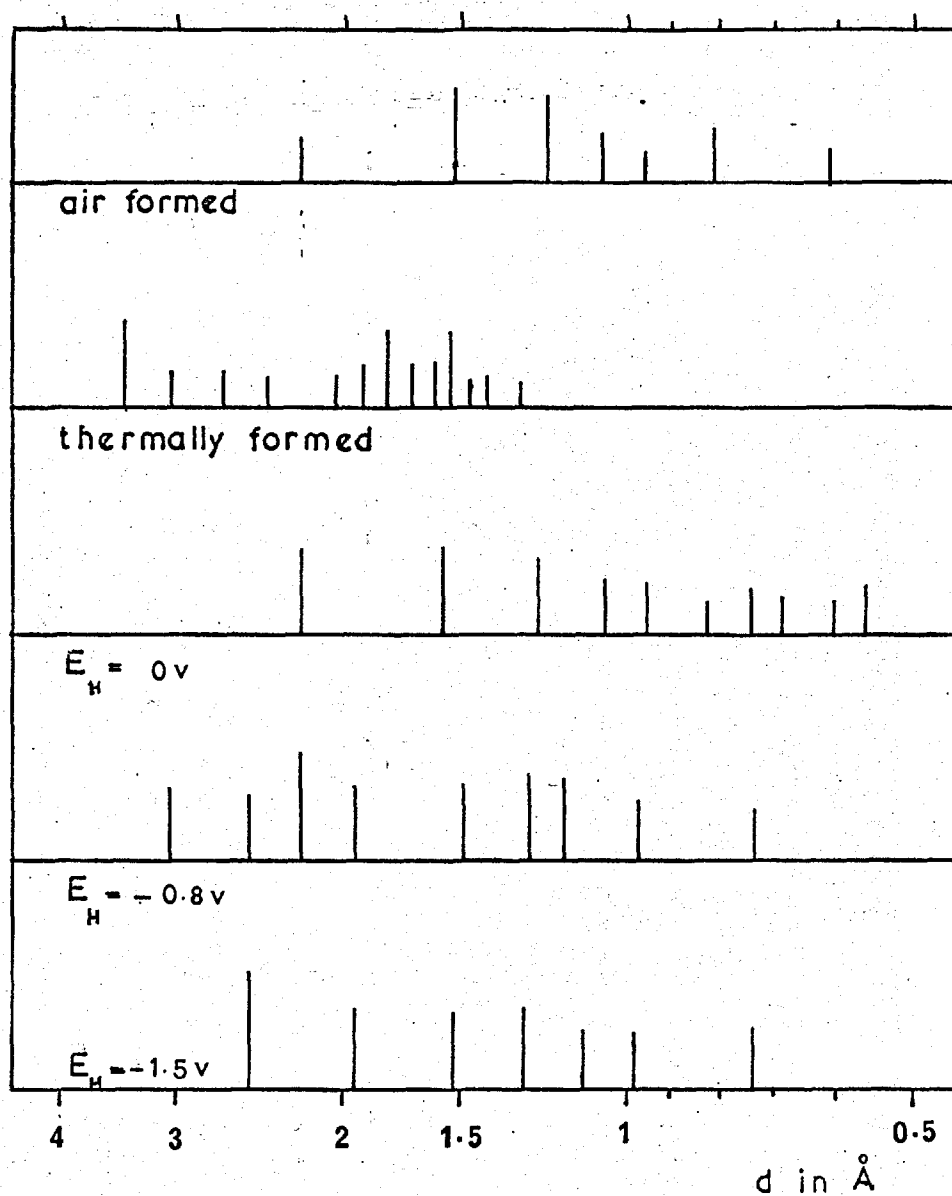
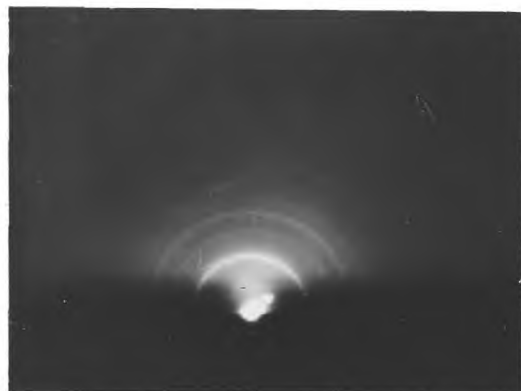
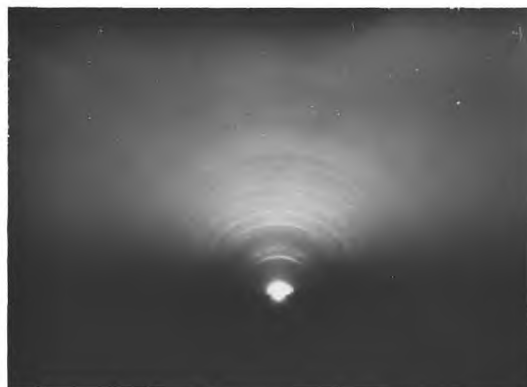


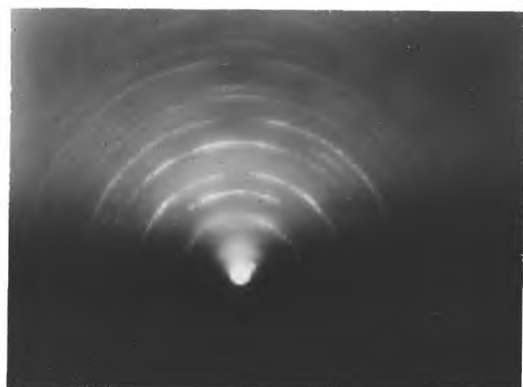
FIG. 37a OXIDE FILM STRUCTURE CHANGE WITH
POTENTIAL - VANADIUM - pH 9.7



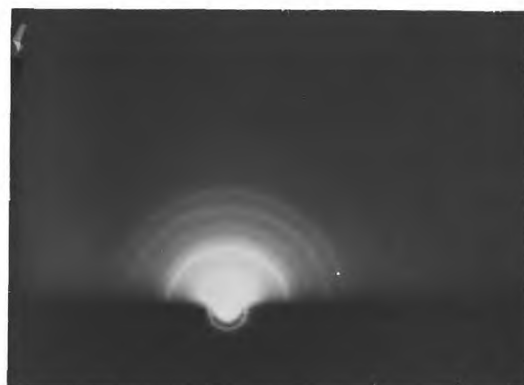
(a) air-formed film



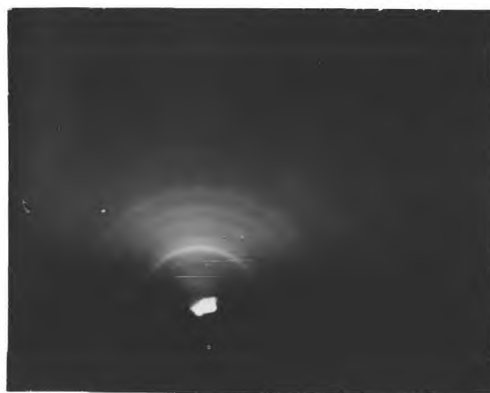
(b) Thermally formed film



(c) $E_H = 0 \text{ V}$



(d) $E_H = 0.8 \text{ V}$



(e) $E_H = -1.5 \text{ V}$

Fig. 37 b. Electron Diffraction Patterns of oxides formed on vanadium -pH 9.7- Oxygen-Free