

ELECTROCHEMICAL STUDIES
WITH THE QUARTZ CRYSTAL
MICROBALANCE

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



Anthony Harold Gafin

15 day of July 1994

TO MY GRANDMOTHER,
WHO TAUGHT ME TO KEEP ON ASKING.

ABSTRACT

A quartz microbalance electrode (QME) was constructed for the investigation of the electrochemistry of electroless plating baths. To this end, the electronic oscillator circuitry required for the microbalance was developed from literature examples, and the techniques of forming electrodes and mounting the crystal in an appropriate holder were established. The device thus developed was compact, allowing for *in situ* frequency and electrochemical measurements to be made in a commercially available 100 mL Metrohm cell. The precision and accuracy obtained with the home-built device were shown to be adequate for electrochemical research, and the sensitivity was found to be consistent with the value expected from the Sauerbrey equation.

Two similar electroless nickel baths, using hypophosphite and dimethylamine borane as respective reducing agents, were investigated with the QME. The potential dependence of the partial processes in the two baths are significantly different, and the nickel plating rates also differ from those observed when the electrode is held at the normal plating potential, but in the absence of any reducing agent. In both baths the presence of the anodic partial process leads to a substantial increase of the rate of nickel electrodeposition, indicating the existence of important interactions between the partial processes at the mixed potential.

Anodic stripping voltammograms of electroless nickel-phosphorus films showed two distinct peaks, which were attributed to the presence of two distinct solid phases. Partial anodic stripping, leaving the more noble material intact, yielded a phosphorus-rich surface. The QME was used to monitor the early stages of both open circuit and fixed potential plating in the hypophosphite-based electroless nickel plating bath on

this surface, as well as on normal electroless nickel-phosphorus and pure nickel films. The partially stripped film exhibited considerably higher plating rates, a phenomenon which is more readily explained in terms of enhanced catalytic activity rather than a simple surface area effect. The various nickel deposits were characterised by energy dispersive analysis by α -rays and x-ray photoelectron spectroscopy.

Electroless nickel-boron films exhibited only one stripping peak. The deposit formed in the electroless nickel-boron bath was found to have slightly higher activity towards autocatalytic deposition than did pure nickel. This was attributed to spill-over or synergistic effects, brought about by the presence of boron in the deposit.

Two electroless copper baths were studied. The rate of copper deposition was determined as a function of the concentration of triethanolamine (TEA). Here, TEA was present as a ligand for copper(II).

The nature of the ligand, i.e., TEA or EDTA, was found to affect the mechanism of copper deposition in electroless copper baths.

The effect of two additives on the plating rate and mechanism of copper deposition was investigated. The additives were 7-iodo-8-hydroxyquinoline-5-sulphonic acid, and 8-hydroxyquinoline-5-sulphonic acid. The former additive enhanced the plating rate at intermediate concentration, the most probable mode of influence via a bridging ligand effect, thereby facilitating electron transfer between the aqueous copper complex and the active surface. The latter additive did not enhance the electroless copper deposition rate.

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LIST OF SYMBOLS

A	area or anodic process
a	activity
aq	aqueous
C	cathodic process
c_i	concentration of species i
D_i	diffusion coefficient of species i
E	applied electric field, electrode potential
E_e	equilibrium electrode potential
E_e^0	standard electrode potential
E_{pl}	electrode potential during electroless plating
F	F distribution
F	Faraday constant, 96485 C mol^{-1}
f	frequency
f_0	fundamental frequency of a piezoelectric element
j	current density
J	flux
I	electrical current
i_l	limiting current
K	adsorption equilibrium constant
K	stability constant
k_x	rate constant of process x
M^{n+}	metal ion, $n+$ oxidation state
Δm	mass change determined with a QME
Δm_0	mass change calculated from the Faraday law
n	number of electrons transferred, number of moles of electrons transferred
n_i	number of moles of species i
$Ox,$	
O	oxidised species
Q	charge

R	gas constant
R_r	
Red	reduced species
R_d	electroless deposition rate
s	solid
s	drift speed
T	temperature
t, t	time
u	mobility
V_x	velocity of solution at distance x from electrode
.	rate of a process
X_{ads}	adsorbed X
X_{surf}	surface bound X
x	distance from an electrode
α	transfer coefficient
β	symmetry factor
δ	thickness of shear wave
ϕ	Galvani potential
η	overpotential
η_l	viscosity of liquid l
λ	partial charge transfer coefficient
μ_i	electrochemical potential of species i
μ_q	shear modulus of quartz
ν	kinematic viscosity, stoichiometric number
θ_e	fractional equilibrium surface coverage
ρ	density
ω	angular velocity, frequency of shear wave

LIST OF ABBREVIATIONS

a.c.	alternating current
AD	analog to digital
ASV	anodic stripping voltammetry
CE	counter electrode
CD	current density
DA	digital to analog
DME	dropping mercury electrode
d.c.	direct current
df	degrees of freedom
DMAB	dimethylamine borane
CV	cyclic voltammetry, cyclic voltammogram
EDTA	ethylenediaminetetraacetic acid
G.C.	glassy carbon
GH	guanidine hydrochloride
HEA	(2-hydroxyethyl)ethylenediamine
HIQSA	7-iodo-8-hydroxyquinoline-5-sulphonic acid
HQSA	8-hydroxyquinoline-5-sulphonic acid
HMDE	hanging drop mercury electrode
HPA	hydroxypropylethylenediamine
Hypo	H_2PO_4^- anion
LSV	Linear Sweep Voltammetry
MFE	mercury film electrode
MG	methylene glycol
MS	Mean square
NAND	not AND operator
NHE	normal hydrogen electrode
Ni-B	nickel-boron (alloy)
Ni-P	nickel-phosphorus (alloy)
NTA	nitrilotriacetic acid
p-level	probability level (tail area)
pzc	potential of zero charge
QCM	quartz crystal microbalance
QME	quartz microbalance electrode
R.A.	reducing agent

DE	rotating disc electrode
r.d.s.	rate determining step
RE	reference electrode
RLC	resistance-inductance-capacitance
RRDE	rotating ring disc electrode
SCE	saturated calomel electrode
SME	scanning microelectrode
STM	scanning tunnelling microscope/microscopy
TIPA	triisopropanolamine
TTL	transistor-transistor logic
VLSI	very large scale integration
WE	working electrode
XPS	x-ray photoelectron spectroscopy

PUBLICATIONS ARISING FROM THIS WORK

Publications and Conference Proceedings:

1. "Investigation into mechanisms of electroless plating using a quartz crystal microbalance electrode." Gafin, A.H. and Orchard, S.W. Proceedings of the Carman National Physical Chemistry Convention, Durban, Natal, 29-31 January 1992.
2. "Current-potential relationships for the half-reactions in two electroless nickel plating baths using the quartz crystal microbalance electrode." Gafin, A.H. and Orchard, S.W. *J. Appl. Electrochem.* 22 (1992) 830-834.
3. "Catalytic aspects of autocatalytic nickel deposition." Gafin, A.H. and Orchard, S.W., *J. Electrochem. Soc.* 139(8) (1992) 428C. (Paper presented at the Electrochemical Society 182nd. Meeting, Toronto, 11-16 October 1992. Abstract number 349.)
4. Catalytic effects in the initiation of autocatalytic nickel deposition on nickel containing substrates." Gafin, A.H. and Orchard, S.W., *J. Electrochem. Soc.* 140(12) (1993) 3458-3462.

Posters:

1. "Interactions between surface processes: a comparison between heterogeneous catalysis and electrode reactions." Gafin, A.H. and Orchard,

S.W., presented at Catalysis and Catalytic Processing Conference, Gordons Bay, 1990.

2. "Electroless nickel deposition studied using the quartz crystal microbalance." Gafin, A.H. and Orchard, S.W., presented at the South African Chemical Institute 31st. Convention, Grahamstown, 1991.

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 ELECTROCHEMICAL STUDIES WITH THE QUARTZ CRYSTAL MICROBALANCE

Electrochemical studies are most commonly carried out at solid electrode surfaces, or at mercury drop or film surfaces. Fundamentally, the experimenter can measure the electrode potential relative to some reference electrode, or the cell current corresponding to an electrochemical process occurring at the electrode.

The quartz (crystal) microbalance electrode is an electrode located on a quartz piezoid (piezoelectric transducer) which is set to act as a frequency controlling element of an electronic oscillator circuit. A change in mass of the piezoid influences the resonance frequency of the piezoid, which may easily be measured. Thus electrochemical processes which cause a mass change of the electrode may be monitored in the usual way (i.e., potential or current), with the third parameter of mass change also being measured *in situ*. Mass changes which may be detected with a quartz microbalance electrode are in the order of $18 \text{ ng cm}^{-2} \text{ s}^{-1}$, such that extremely small amounts of material deposited on or removed from the electrode may be monitored.

Electroless plating, also referred to as autocatalytic deposition, is a process which results in a mass increase of the substrate on which it occurs. The process, which is electrocatalytic in nature, has been found to take place via a multi-step mechanism. Some

degree of controversy surrounds the mechanism or mechanisms of autocatalytic deposition.

The focus of this work is the study of electroless plating systems using a quartz microbalance electrode. The designing and building of the quartz microbalance electrode device formed part of the project, since at the time of commencement none could be purchased. All studies using the device at that time were achieved using home-built circuits and electrode holders. The quartz microbalance electrode built and used for this project is, to date, the only one in South Africa (FRD Council Report 1992/93 p. 24).

The remainder of the chapter provides a general description of electroless plating and sets out the project objectives. Chapter 2 presents some aspects of electrochemical theory which are used in later arguments. Chapter 3 contains a detailed description of the technical aspects of the quartz microbalance electrode, and reviews some of the literature pertaining to studies using the device. A literature review of studies in the field of electroless plating is presented in Chapter 4 and the experimental procedures and methodology adopted in this work are given in Chapter 5. The remaining chapters deal with the results, discussion and conclusions of studies of autocatalytic nickel and copper deposition.

1.2 ELECTROLESS PLATING

1.2.1 Definition of the electroless process

Electroless plating is a surface-sensitive, heterogeneously catalysed, chemical reduction of metal ions from aqueous solution. The term "electroless" was coined by the inventors of the process (Brenner and Riddell 1946) in order to differentiate this plating technique from electrolytic metal plating, yet retain the information that film formation occurs via electron transfer. The latter point thus excludes, for example, metallisation by evaporation.

An electroless plating bath consists of the following essential components:

- metal salt(s) in aqueous solution
- complexing agents
- a reducing agent
- acid or base to adjust pH.

Other components may be present to enhance or modify bath characteristics. Examples of these are brighteners, stabilisers and accelerators (Feldstein and Lancsek 1971). A schematic representation of the surface catalysed reaction is given in Figure 1.1.

The overall reaction of electroless plating is



Aqueous metal ions are represented by M^{n+} and the reducing agent and oxidised product of the reducing agent (both aqueous) are represented by Red and Ox,

respectively. The solid metal deposit is represented by M. The metal ions are usually stabilised in complexes with one or more ligands.

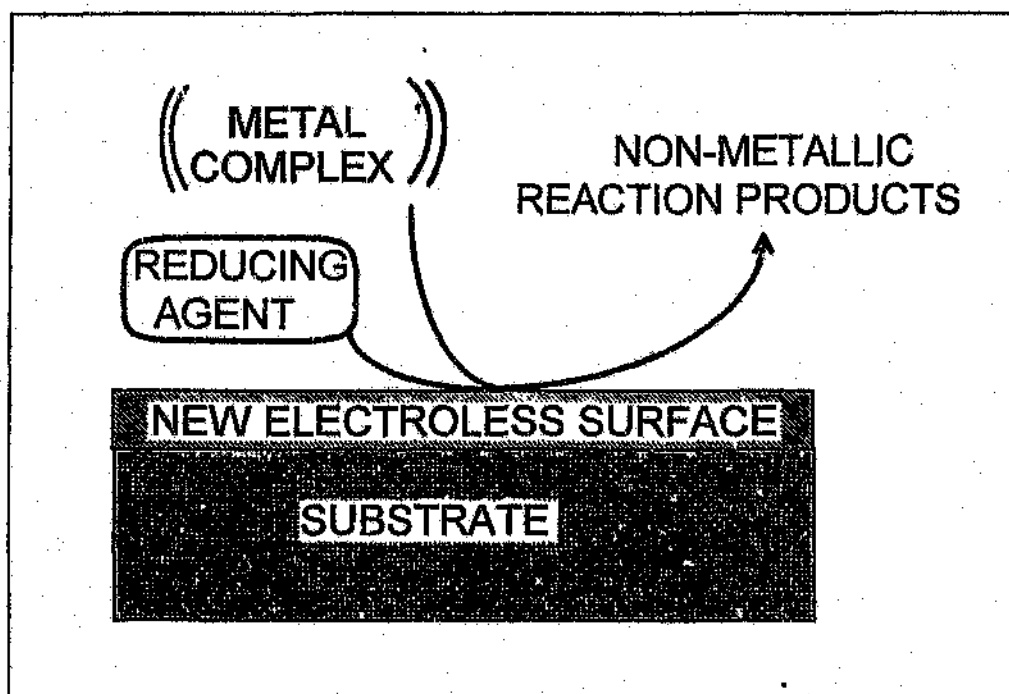
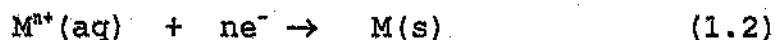


Figure 1.1 Schematic representation of electroless plating.

Electroless plating is a reduction-oxidation (redox) process, hence two partial processes may be identified. The generalised partial processes of the electroless system are given in reactions (1.2) and (1.3).



Reaction (1.2) represents the reduction of metal ions by electrons transferred at or via the substrate surface from reaction (1.3), the oxidation of the reducing agent. The number of electrons provided by the oxidation of one molecule of reducing agent need not

necessarily equal the number of electrons required for reduction of the metal ion.

Although the metal complex and reducing agent are both in solution, the homogeneous redox process does not take place. Heterogeneous catalysis is required in order for the reaction to proceed. Catalytic sites may be intrinsic to the surface of the substrate or they may be the result of a pre-treatment procedure.

The requirement of a catalyst to enable the redox process to proceed implies that kinetic stability of the bath exists. Thermodynamic instability, however, ensures that in the presence of the catalyst, the pertinent reduction and oxidation processes will proceed.

Experimentally it has been found that the electroless deposit is often not a film of pure metal, but an alloy of the metal M and at least one other element originating from the reducing agent. The minor component is a secondary reduction product. The existence of secondary products depends on the nature of the reducing agent.

1.2.2 Electroless plating - a materials processing technique

An adherent metal film covering some substrate is a materials processing phenomenon which has countless applications, ranging from decorative finishing of plastics to specialised-morphology thin metal films for electronic devices (Saubestre 1973, Arnyanov and Sotirova 1989).

Numerous methods have been developed for metal coating (or metallising) of diverse substrates. The manner in which the film is produced on the substrate differs according to the requirements and specifications of the resultant surface, end use, and the nature of the substrate. For example, an electrolytic plating method cannot be used to coat an electrically non-conducting object. Similar limitations exist for other techniques. Some of these techniques are summarised in Table 1.1.

Table 1.1 Comparison of metal coating techniques.

Plating Technique	Possible Substrate		Film Formation Process	Surface Selective
	Conductor	Insulator		
electrolytic	yes	no	aqueous ion reduction	cathode only
electroless	yes	yes	autocatalytic redox reduction	yes
homogeneous chemical reduction	yes	yes	redox in solution	no
evaporation	yes	yes	condensation	no
ion sputtering	yes	yes	atomic deposition	no

Areas of technology where electroless plating is used or has been investigated include

- very large scale integrated circuit (VLSI) manufacture (Ting 1988)
- printed circuit board manufacture (Henry 1987)
- optical fibre coating (Chatterjee 1984)
- automotive industry for metal-like "trims" (Henry 1987)
- metal matrix composites (Judd 1970)
- electromagnetic interference shielding (Hajdu and Krulik 1983)

- medical: ferromagnetic implants for the treatment of carcinomas (Graef and Chandler 1990)
- corrosion protection: electroless deposits have been shown to be better than electroplated coatings on equivalent specimens (de Minjer and Brenner 1957)
- preparation of supported metal catalysts (Coville et al. 1993).

Bayes and House (1991), and Smith (1991) describe applications of electroless plated articles in harsh environments (for example, a North Sea oil rig), and the production of composite films. These may be nickel films containing diamond, silicon carbide or Teflon powders.

1.2.3 Variety in formulations and conditions for electroless plating

The wealth of literature and the complex results therein, regarding the mechanism of electroless plating, suggest that the process is not a simple bimolecular redox reaction between metal ions and reducing agent. Some of the variations on the general electroless plating theme are set out below.

1.2.3.1 Metals and alloys

Metals which have been successfully deposited by the electroless technique include copper, gold, nickel, silver, cobalt and palladium (Pearlstein 1973, Okinaka 1974). These metals are usually about 90 - 97% pure.

Binary and ternary alloys can be produced, e.g., gold-copper (Molenaar 1982), nickel-cobalt-phosphorus (Armyanov and Sotirova 1989) and nickel-molybdenum-phosphorus alloys (Osaka, et al. 1988).

1.2.3.2 Reducing agents

A number of reducing agents have found application in electroless plating. For example, nickel may be reduced by the hypophosphite anion (H_2PO_2^-) or by dimethylamine borane (DMAB) (Feldstein 1970). Other compounds have also been used as reducing agents, e.g., sodium borohydride and hydrazine (Pearlstein 1973). Formaldehyde is used as a reducing agent in electroless copper baths (Chatterjee 1984). It is also possible to use a less noble metal ion as a reducing agent, as in the case of the autocatalytic deposition of bismuth using Ti(III) as reducing agent (Rutkevich et al. 1992, 1993).

1.2.3.3 Temperature

Depending on the bath formulation, electroless plating may proceed at temperatures ranging from about 20°C (Feldstein 1970) to about 90°C (Gruss and Pearlstein 1983).

1.2.3.4 pH ranges

Plating baths have been developed to operate in the acid and basic pH ranges (Pearlstein 1973).

Although the parameters mentioned above have been well investigated and documented, and applications for electroless films are numerous, a complete and universally accepted mechanism whereby the reaction occurs remains undiscovered or undisclosed. Clearly, if one mechanism exists for the electroless deposition of metals, it must be operative under a variety of conditions. If more than one mechanism is responsible for the process, it is of more than academic interest to know how these differ and how many there may be. This knowledge could possibly lead to further understanding of other heterogeneous catalytic processes. The industrial importance of electroless plating suggests that mechanistic understanding could be exploited in the development of tailor-made and efficient plating bath formulations.

1.3 PROJECT OBJECTIVES

In this project a quartz microbalance electrode (QME) was developed and applied to the study of electroless nickel and copper plating. The apparatus was designed and built in-house, where necessary, and assembled to give an instrument capable of performing electrochemical experiments (e.g., voltammetry, potentiometry, amperometry) and simultaneous *in situ* gravimetry. The latter analytical method was especially suitable for the reactions under study since the major product of interest was a solid.

It was hoped that the capability to measure two parameters simultaneously (e.g., electrode current and plating rate) would overcome many of the limitations of other, more classical techniques used in research in

electroless plating (the methods referred to here are described in Chapter 2).

Once the technique of using the QME was validated by comparison of initial results to existing data, a more detailed study of electroless plating systems could commence.

It has been stated that electroless nickel plating may be achieved under a variety of conditions. It is possible, for instance, to formulate a nickel plating bath which will operate at room temperature. The autocatalysis of nickel deposition may be based on a number of reducing agents including the hypophosphite anion and dimethylamine borane. These systems were the focus of study in this work. In addition, the behaviour of electroless copper baths of various formulations was investigated, with special attention given to the influence of additives (stabilisers and accelerators) and complexing agents, on the rates of the anodic and cathodic partial processes.

During the course of the research a property of the Ni-P alloy, viz., the existence of two phases, was observed. Although previously documented and indeed studied (Cargill 1979, Benje et al. 1988), this property has not been exploited in studies of autocatalytic deposition mechanisms. In this work, extensive investigation was carried out to determine the role of these phases in the electroless process.

CHAPTER 2

THEORETICAL CONSIDERATIONS

CHAPTER 2 THEORETICAL CONSIDERATIONS

2.1 ELECTRODE PROCESSES

2.1.1 Introduction

Electroless plating is a heterogeneous electron transfer reaction and, as such, may be studied as an electrochemical reaction with a variety of electroanalytical techniques. Chapter 2 introduces those important principles of electrochemistry which are of relevance to the work reported in this thesis. The factors which affect the course of an electrode process will also be described.

2.1.2 Mass transport

Electrochemistry is concerned with transformations of chemical species at the electrode-solution interface, by virtue of electron transfer. Solution species which may react at the interface are usually of particular interest. Thus it is important to understand by what means, and how quickly, these species get to and from the electrode.

Mass transport of species in solution may be by one or a combination of three different modes, namely diffusion, convection and migration.

2.1.2.1 Diffusion

Solution species are in constant random motion. A particular species may move predominantly in a given direction because a concentration gradient (or, more correctly, a chemical potential difference) exists in the solution. The chemical potential acts like a force. Atkins (1982, p. 903) describes this as a "phantom" force, because there is no actual force at all, only a tendency for the solution to achieve maximum entropy. At an electrode, the consumption or production of species produces a concentration gradient. The rate of diffusion of a species may be determined from Fick's laws (Atkins 1982, pp. 903-907).

For purposes of electrochemistry, Fick's first law can be expressed in terms of the rate of diffusion of particles through a plane parallel to the electrode (the electrode is assumed to be perfectly flat and of infinite dimensions). The rate of diffusion is the flux (J) which, in the S.I. system, has units $\text{mol m}^{-2} \text{s}^{-1}$ (Equation 2.1). The diffusing entities may be ions (species i), giving rise to a charge flux.

$$J = -D_i \frac{dc_i(x)}{dx} \quad (2.1)$$

In Equation 2.1, the concentration of i at a distance x from the electrode is $c_i(x)$, and $dc_i(x)/dx$ is the concentration gradient. The minus sign ensures that species are shown to move from an area of high concentration to one of low concentration (Pletcher 1991, pp. 18-20). D_i is the diffusion coefficient of species i and, typically, has a value of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C .

The rate of change in concentration of species i as a consequence of diffusion is described by Fick's second law (Equation 2.2). This law is derived by treating the rate of change of concentration of i at the centre of an element of solution bounded by two planes parallel to the electrode (Southampton Electrochemistry Group 1985 pp. 26-29).

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad (2.2)$$

Instrumental methods such as chronopotentiometry, chronoamperometry and cyclic voltammetry are based on the integrated form of Equation 2.2, with appropriate boundary conditions.

2.1.2.2 Convection

Mechanical agitation, or density or temperature variations give rise to bulk movement of solution. Natural convection is a non-quantifiable effect, where random vibrations and temperature effects cause solution movement. Forced convection may be used to overcome the problem of natural convection. The hydrodynamics of forced convection can be quantified under controlled conditions, such as in the case of the rotating disc electrode (*vide infra*), or the wall-jet electrode.

2.1.2.3 Migration

An electric field will cause charged species to move within the solution as a result of electrostatic forces (Pletcher 1991, pp. 17-18). Cations will migrate

towards the negatively charged electrode while anions migrate towards the positively charged electrode. The drift speed, $s_{\pm}$, of an ion is proportional to the strength of the applied field, E (Equation 2.3). The proportionality constant is the mobility, denoted by $u_{\pm}$. The subscript ($\pm$) indicates the sign of the charge on the ion.

$$s_{\pm} = u_{\pm} E \quad (2.3)$$

The mobility of an ion is related to ionic size, charge and the solution viscosity (Atkins 1982, pp. 896-905).

Many electrochemical techniques are based on well defined conditions of ion transfer to and from the electrode surface. In order to simplify the conditions, it is common to suppress the migration of electroactive species. This is achieved by the addition of a non-electroactive ionic compound (e.g., KCl) to the solution, such that the concentration of the supporting electrolyte is far greater than that of any electroactive species. Mass transport of the electroactive species is then almost exclusively brought about by diffusion and convection.

2.1.3 Electrode Reactions

2.1.3.1 Introduction

Electrode reactions involve electron transfer reactions occurring at a phase interface. The electrons are transferred between a species in the electrolyte and

the electrode. For purposes of this discussion, an electrode is considered to be a solid surface.

Electron transfer can only take place when the electroactive species is within molecular distance from the electrode. In addition, the area of contact between the electrode and electrolyte is finite. As a consequence of these two conditions, the rate at which electron transfer can take place may be limited by the rate of mass transfer of electroactive species to or from the electrode. The reaction is then said to be under mass transport control.

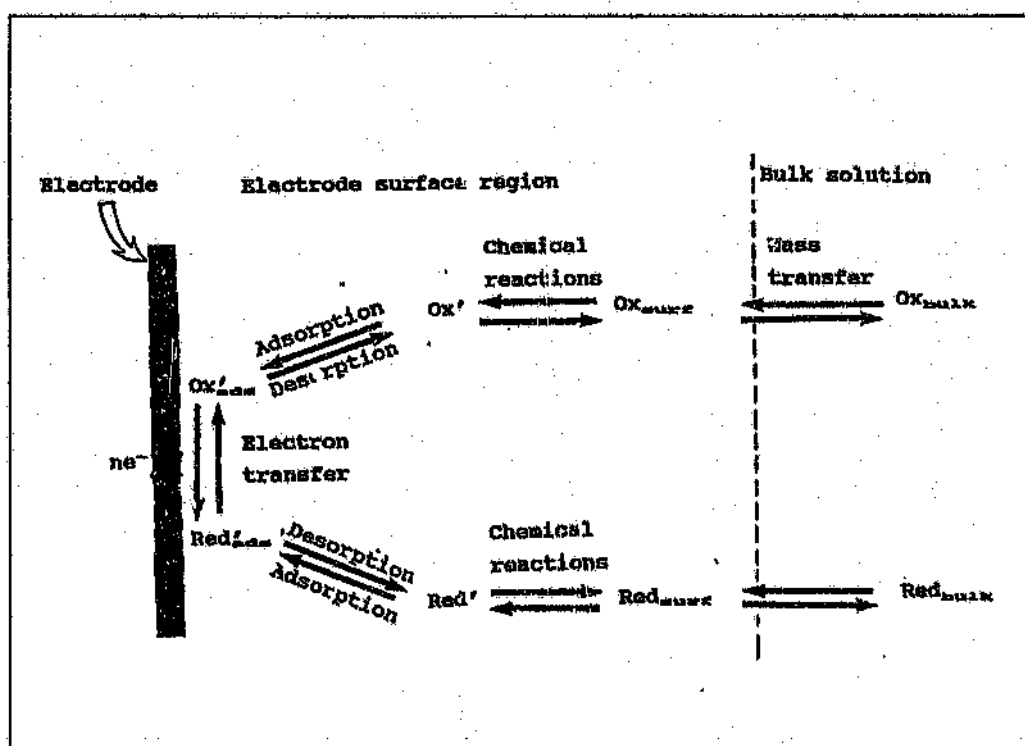


Figure 2.1 Schematic pathway of a general electrode reaction (redrawn from Bard and Faulkner 1980, p. 21).

An anodic reaction (e.g., Equation 2.4) is defined as an electrode reaction where electrons are passed from either surface atoms, surface bound molecules or a species in the solution phase (Red) to the electrode. The opposite is true for a cathodic reaction.



Electrode processes which occur when electrons are transferred across the electrode-solution interface are called faradaic processes. This term is used because the amount of chemical reaction occurring is proportional to the amount of electricity passed.

A non-faradaic process is one where there is no charge transfer across the interface but an external current does flow (even if only transiently). Non-faradaic processes include adsorption or desorption of species and structure change or charging of the electrical double layer (Bard and Faulkner 1980, pp. 6-8).

The explanations and discussion in this chapter relate to faradaic processes unless specified otherwise.

2.1.3.2 Faraday's laws

From the proportional relationship between amount of chemical reaction and amount of electricity flowing (Faraday's first law), it follows that the rate of chemical change is proportional to the current flowing. Electric current is the rate of flow of charge (Equation 2.5)

$$I = \frac{dQ}{dt} \quad (2.5)$$

In Equation 2.5, I is a current, Q the charge and t is time. For an oxidation process, e.g., (2.4), n_{ox} is the number of moles of Ox formed in the reaction, n is the

number of moles of electrons required per mole of Ox and F is the Faraday constant.

$$\frac{Q}{nF} = n_{ox} \quad (2.6)$$

Thus the rate of formation, ζ , in mol s^{-1} is given by

$$\zeta = \frac{dn_{ox}}{dt} = \frac{I}{nF} \quad (2.7)$$

Since an electrode process is a heterogeneous process, the rate, v , is usually expressed on a per unit area basis. This can be accomplished by using j , the current density (current per unit area) in place of I :

$$v = \frac{I}{nFA} = \frac{j}{nF} \quad (2.8)$$

A current density is a charge flux and thus the relationship between j and the flux of electroactive species J to or from the electrode surface can be seen.

2.1.3.3 The electrochemical interface

The electrified interface, referred to as the double layer, is a region adjacent to the electrode surface which adopts a structure as a consequence of charge build-up on the electrode, and the presence of charged solution species. As a consequence of charge build-up in the double layer, high electric fields may develop across the interfacial region (in the order of 10^7 V cm^{-1}). The presence of this electric field at the interface of electrolyte and electrode is the basis of electrochemistry (Bockris and Reddy 1970 p. 630).

The Helmholtz-Perrin model of the double layer treats the charged interface as a parallel plate capacitor. The net charge of the electrode surface is considered as one plate, and a layer of ions in the electrolyte, having aligned themselves at the interface, form the second plate. Counter-ions in solution are aligned at molecular distance from those ions attracted to the surface. This charge alignment forms the basis of the term "double layer". It has subsequently been shown that the Helmholtz-Perrin model is insufficient to completely describe the behaviour of the charged interface.

Gouy and Chapman, working independently, relaxed the constraints on the solution species, developing what is referred to as the Gouy-Chapman Diffuse-Charge model. The ions are no longer constrained to a flat plate adjacent to the electrode. A time-averaged distribution of charge accumulation near the electrode surface is brought about by the equilibrium attained between thermal forces in solution disrupting any structure of ion build-up, and the electrical force causing the build-up. The resulting picture is not of a fixed, charged layer as in the Helmholtz-Perrin model, but of a diffuse layer, with a net charge density falling off with distance from the interface. Notwithstanding the fact that experimental evidence of the behaviour of double layer capacitance cannot be reconciled with this model, it has served to facilitate further understanding of charged interfaces, leading to the development of the Stern model.

The Stern model of the charged interface allows for a combination of the effects described by the former two models. Ions are considered as finite-sized particles rather than point charges. Solvent molecules, e.g.,

water, adhere to the electrode by virtue of dipolar forces, and prevent the ions from reaching the electrode. Consequently, a layer of "fixed" ions is arranged at a certain distance from the electrode. This gives rise to a potential difference, which varies linearly with distance from the electrode. A diffuse layer of ions is found beyond the fixed layer. The charge density drops off with distance from the electrode as suggested by the Gouy-Chapman model. This drop-off constitutes a second potential variation, which is exponential (Figure 2.2).

A number of practical effects can be explained by the Stern model of the interface. These effects include the charging of the double layer and the energetics of adsorption of hydrated ions to the electrode surface. The presence of the water molecules adhering to the electrode (in an aqueous system), and the double layer, pose an energy barrier to adsorption of other species. (Bockris and Reddy 1970 pp. 718-737)

The locus of centres of closest approach of hydrated ions to a hydrated electrode is called the outer Helmholtz plane (OHP). When an ion loses its hydration sheath on the side closest to the electrode, and displaces water molecules from the electrode surface, the locus of centres of the ions adjacent to the electrode is what is called the inner Helmholtz plane (IHP). If the Gibbs function is negative, for the process of the ion divesting itself of part of its hydration sheath, and displacing water molecules, then contact adsorption occurs. In general, in aqueous systems, strongly hydrated ions do not contact adsorb. (Bockris and Reddy 1970 pp. 742-744)

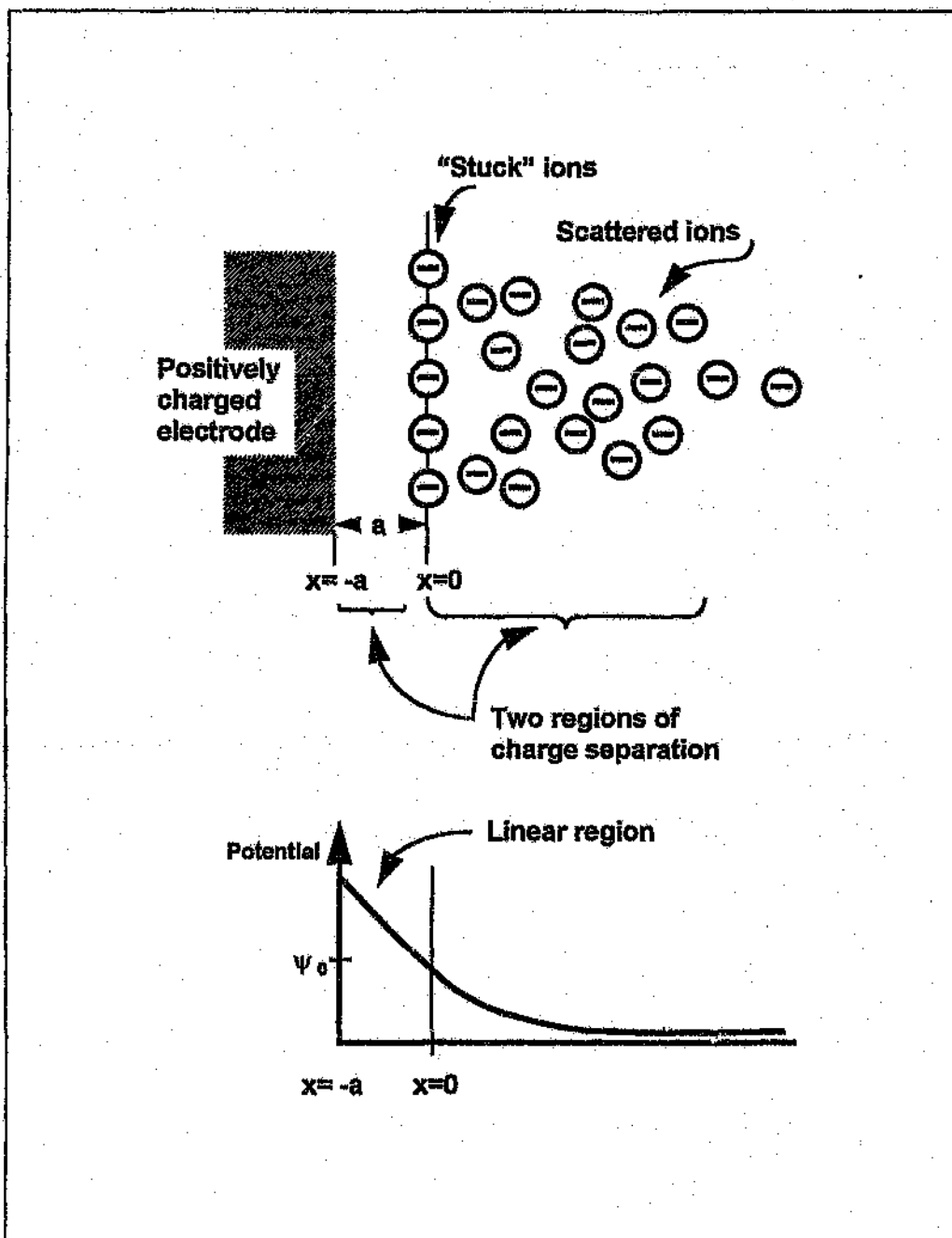


Figure 2.2 The electrode-solution interface according to the Stern model. A layer of (-) excess charge is stuck to the positively-charged electrode, with the remainder randomly distributed. The locus of centres of the stuck ions is at distance a from the electrode. Water molecules have been omitted, but these molecules prevent closer approach of the ions (Bockris and Reddy 1970 pp. 734-735).

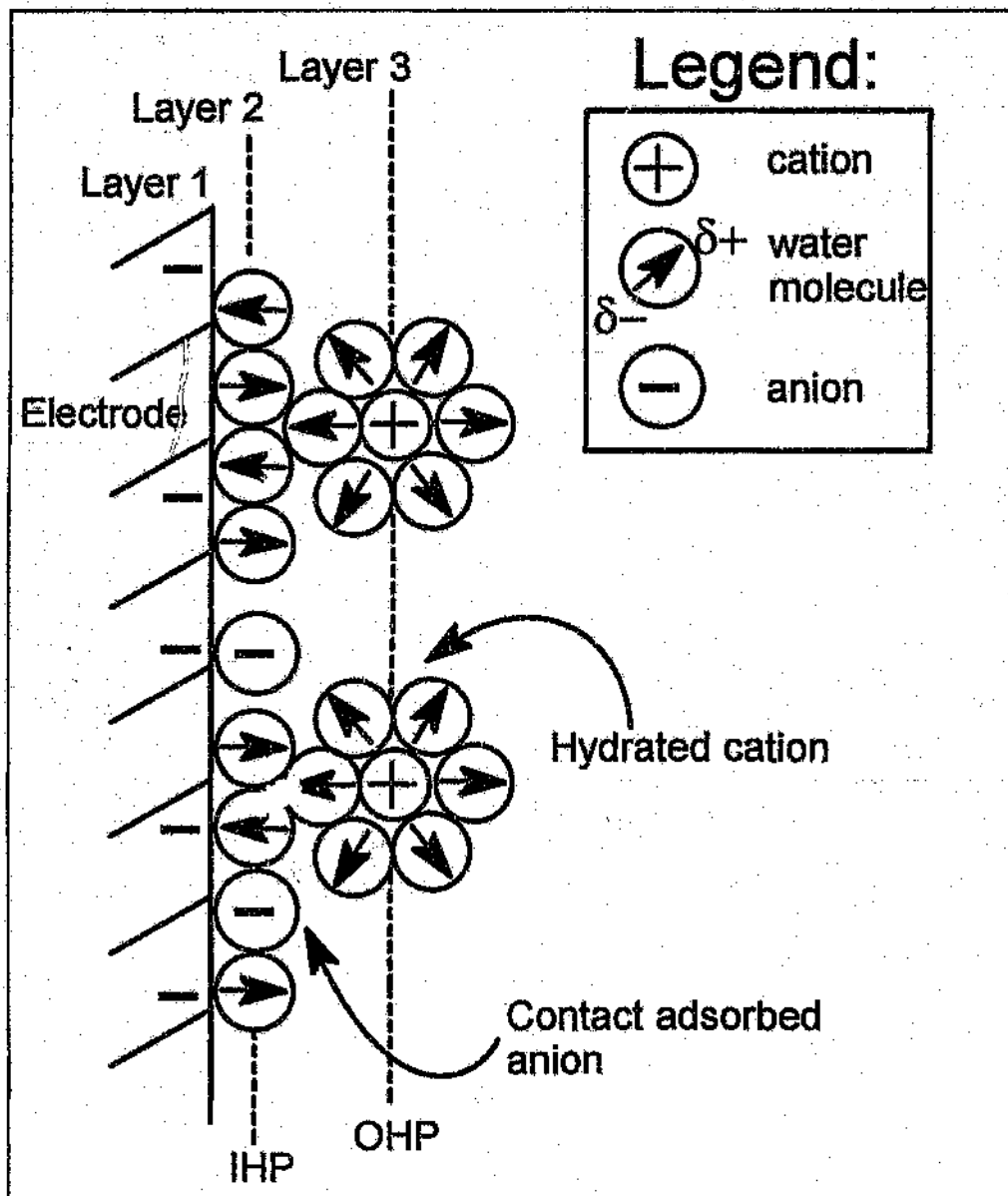


Figure 2.3 Arrangement of ions at an electrode, showing the Inner Helmholtz Plane (IHP) and Outer Helmholtz Plane (OHP). The existence of these planes gives rise to an electrical triple layer, the first being the layer of charge of the electrode surface. Counter-ions have been omitted (Bockris and Reddy 1970 p. 750).

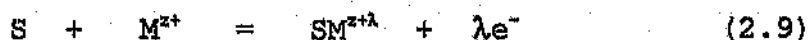
2.1.3.4 Adsorption at electrodes

Contact, or specific adsorption, is a term used to describe adsorption of a species to an electrode when coulombic as well as other attractive forces operate, e.g., weak electron orbital overlapping. This may be seen as one limiting case of adsorption at electrodes. Other limiting cases are pure electrostatic adsorption, adsorption of neutral molecules (including dipoles) and chemisorption. The latter type of adsorption involves the breakage of chemical bonds in the adsorbate and formation of chemical bonds between adsorbate and electrode. Charge transfer takes place across the interface during the chemisorption process. Adsorption of neutral molecules requires the displacement of water molecules from the surface. This process does not take place easily on a polarised electrode, where dipolar water is strongly attracted to the surface (Bard and Faulkner 1980 p. 515).

Adsorption on non-ideal surfaces is complicated by the exposure of the various crystallographic planes to the solution, as well as by the presence of surface defects.

The energetics of adsorption is described by various adsorption isotherms. These are described below, with reference to their limits of applicability.

Consider the adsorption of a charged species M^{z+} to a metal electrode surface S (Equation 2.9).



with λ (the partial charge transfer coefficient) = 1

The Langmuir isotherm (Equation 2.10) relates the degree of surface coverage to electrode potential, ignoring lateral interactions between adsorbate molecules. This isotherm is the simplest isotherm describing the adsorption of a charged species M^{z+} to surface S.

$$\frac{\theta_e}{1-\theta_e} = Ka \exp(-FE/RT) \quad (2.10)$$

where

- θ_e = fractional equilibrium surface coverage
- a = activity of adsorbate in solution
- E = electrode potential
- F = Faraday constant
- K = adsorption equilibrium constant
- R = gas constant
- T = temperature

The Frumkin and Temkin adsorption isotherms treat the Gibbs function of adsorption as an exponential function of coverage and lateral interaction parameters of adsorbed species, thus accounting for the non-ideality of interacting adsorbate (Calvo 1986 pp. 58-62).

2.1.3.5 Thermodynamics of electrode reactions

In this section, the relationship between the potential of an electrode and the current density is described. Only a single redox couple is considered:



O is the oxidised species and R is the reduced species. The rate constant of the forward process is k_c and the rate constant of the reverse process is k_a (the subscripts C and A stand for cathodic and anodic, respectively). The assumption is that mass transport is not limiting in the process. Then, only interfacial dynamics control the rate of the processes.

It has already been shown that current density, j , is a measure of the rate of an electrochemical process. The current density of the forward (cathodic) process is j_c and for the reverse (anodic) process is j_a . The convention adopted in this work is that current densities of anodic processes are positive and current densities for cathodic processes are negative. Thus, when the process (2.11) above is at equilibrium, the overall current density j is zero:

$$j = j_c + j_a = 0 \quad (2.12)$$

At equilibrium, the rate of the forward process is equal to the rate of the reverse process. The exchange current density is j_0 .

$$j_0 = -j_c = j_a \quad (2.13)$$

Since the reactants and products of a process such as (2.11) are generally charged species, the Gibbs function of the components can be changed at constant composition by altering the electrical potential of the phases (i.e., the potential difference across the electrode-solution interface at which the process takes place). The electrochemical potential of species i is $\bar{\mu}_i$, and is defined by Equation 2.14,

$$\bar{\mu}_i = \mu_i + z_i F \phi \quad (2.14)$$

where μ_i is the chemical potential of species i , $z_i F$ is the charge per mole of i , and ϕ is the potential of the phase in which the species is situated, referred to as the inner or Galvani potential. The second term thus accounts for the Gibbs function change brought about by altering ϕ . Furthermore, the chemical potential of species i is related to the activity:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (2.15)$$

where μ_i° is the standard chemical potential of species i and a_i is its activity. Since $\Delta\phi$ (the potential difference between the metal electrode and solution, or Galvani potential difference) cannot be measured directly, in practice, potentials are measured relative to a reference electrode. Equations 2.14 and 2.15 are fundamental in the derivation of the Nernst equation (2.16), which relates E_e , the equilibrium electrode potential to the ratio of activities of species O and R (a_o and a_r respectively) and E_e° , the standard electrode potential (i.e., when $a_o = a_r = 1$):

$$E_e = E_e^\circ + \frac{2.3RT}{nF} \log \frac{a_o}{a_r} \quad (2.16)$$

(Southampton Electrochemistry Group 1985 pp. 76-80)

In most cases of solution electrochemistry, the approximation is adopted that activity coefficients in dilute solutions are unity, so that the Nernst equation is written in terms of the concentrations of O and R (a_o is replaced by c_o , the concentration of O, and a_r is replaced by c_r , the concentration of R).

2.1.3.6 Kinetics of electrode processes

Equation 2.11 is used as the model reaction in this section.

An electrode immersed in a solution of electroactive species can be forced to adopt a potential E different to the equilibrium electrode potential E_e , for example, by application of a potential from an external source. The difference between E and E_e is the overpotential, η :

$$\eta = E - E_e \quad (2.17)$$

If an overpotential is positive, the system will tend towards a new equilibrium by altering the concentrations according to the Nernst equation (c_o increases and c_r decreases). The rate of the reverse process of (2.11) must increase, such that an anodic current flows, since the magnitude of j_a becomes larger than that of j_c . A negative overpotential has the opposite effect and a cathodic current flows, with a resultant increase in the concentration of R and a decrease in the concentration of O.

It is of interest to know the relationship between η and j . Early research suggested an exponential relationship between overpotential and current as illustrated by the Tafel equation (1905):

$$\eta = a + b \log |I| \quad (2.18)$$

In the Tafel equation, a and b are constants which may be determined experimentally. The accepted, practical relationship between overpotential and current density

(use of current density is preferable to the use of current) is somewhat more complex but retains the exponential form. This relationship (Equation 2.19) is known as the Butler-Volmer equation (Southampton Electrochemistry Group 1985 p. 81).

$$j = j_0 \left\{ \exp\left(\frac{\alpha_a n F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c n F \eta}{RT}\right) \right\} \quad (2.19)$$

In the Butler-Volmer equation, R is the gas constant, T the temperature and F the Faraday constant. The terms α_a and α_c are the transfer coefficients for the anodic and cathodic half-reactions respectively. Transfer coefficients are constants, defined, in the case of a multi-step process, such that $\alpha_a + \alpha_c = n/v$. Here n is the number of charges passing in one act of the overall reaction and v is the stoichiometric number. This is the number of times the rate determining step must occur per occurrence of the overall reaction. The transfer coefficient can be shown to include a term in β , the symmetry factor, which describes the Gibbs function for the electron transfer process. Stated briefly, a Gibbs function maximum exists for the process, related to the activation energy for the electron transfer. β describes the symmetry of the Gibbs function about the energy barrier. A detailed description of α and β is given in the text by Bockris and Kahn (1993 pp. 272-277). Values of α are usually between 0.3 and 0.7 and are frequently close to 0.5 (Pletcher 1991, pp. 7-12, Bard and Faulkner 1980, pp. 91-97).

The Butler-Volmer equation is only applicable when
(a) electron transfer is the rate determining step in the electrode reaction and

(b) when no resistive film forms on the electrode during the process.

In practical electrochemistry, approximations to the Butler-Volmer equation are often made (Southampton Electrochemistry Group 1985 p. 83). These are the high field and low field approximations. When η is large and positive (i.e. $\eta \gg RT/\alpha_a nF$) then the second exponential term in the Butler-Volmer equation becomes negligible. Equation (2.19) can then be reduced to the form

$$\ln j = \ln j_0 + \frac{\alpha_a n F \eta}{RT} \quad (2.20)$$

for positive overpotentials. This is the high-field approximation for anodic potentials, exhibiting an exponential relationship between j and η .

Similarly, for negative overpotentials i.e. when $\eta \ll -RT/\alpha_c nF$ the cathodic high-field approximation of the equation is

$$\ln(-j) = \ln j_0 - \frac{\alpha_c n F \eta}{RT} \quad (2.21)$$

The value of j is negative and a cathodic current is observed.

The two equations above take the form of the Tafel equation. Tafel plots are semi-logarithmic (i.e., $\ln(j)$ vs. η) graphic representations of the current-potential relationship. Values for the transfer coefficient can be calculated from the slope of a Tafel plot and a value for j_0 can be found by an extrapolation of the line to the point where $\eta = 0$ V.

The linear or low field approximation is made when the overpotential is small ($|\eta| < 10 \text{ mV}$ at 25°C). Then, using the approximation that $\exp(x) = 1 + x$ for small x , and $\alpha_a + \alpha_c = 1$, the Butler-Volmer equation reduces to

$$j = j_0 \frac{nF}{RT} \eta \quad (2.22)$$

Here the current density is proportional to overpotential (Pletcher 1991, pp. 13-15, Bard and Faulkner 1980, pp. 91-105). The linear and exponential forms of the Butler-Volmer equation are depicted in Figure 2.4.

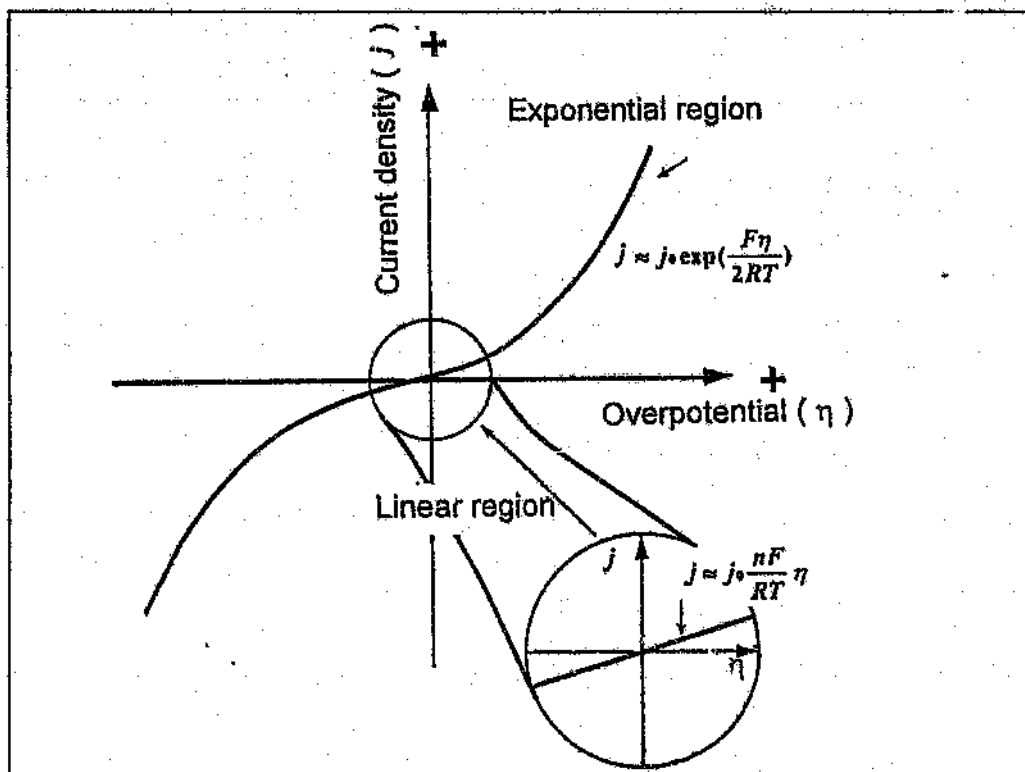


Figure 2.4 Graphical representation of the Butler-Volmer equation, showing the linear region and the exponential region, which are used in the low and high field approximations, respectively. The relationship shown here is symmetrical, which is true for the case $\alpha = 0.5$. Redrawn from Bockris and Reddy (1970 p. 886).

2.1.4 Mechanisms of Electrode Processes

For an electrode process occurring via more than one step, it is most likely that one will be inherently slower than the others. This is the rate determining step (r.d.s.). The individual steps are collectively called the mechanism of the process.

The symbol conventions of Bard and Faulkner (1980, pp. 429-430) are used in this work. Thus E represents an electron transfer step and C a homogeneous chemical reaction. Electrode processes which involve only one step, that is an electron transfer, have a mechanism known simply as electrochemical (E). A chemical-electrochemical (CE) mechanism is one where a chemical reaction occurs on or near the electrode before the electron transfer step. The steps may be in the reverse order, if the chemical step follows electron transfer. In this case, the mechanism is EC, following the pattern above. The sequence of steps can be built up further, as the complexity of the electrode process increases.

In most electrode reactions, a number of physical processes need to be considered regarding the overall rate of the reaction. These may be one or more of phase formation (e.g., gas bubbles or solid film), chemical reactions preceding or following the electron transfer, and adsorption or desorption of species at the electrode surface. When a particular electrode reaction involves the transfer of more than one electron, there are usually chemical reactions or rearrangements separating the individual electron transfer steps (Pletcher 1991, p. 3).

2.2 MIXED POTENTIAL SYSTEMS

2.2.1 Introduction

The thermodynamic equilibrium electrode potential has been defined as the potential observed when the net current density across the interface is zero (Section 2.1.3.5). This is true when there is only one electrode process taking place at the electrode, and the electronation and de-electronation reactions are taking place at the same rate. The net current density across an interface may also be zero under a different set of conditions, viz., when two separate electronation and de-electronation reactions are occurring at exactly the same rate.

The two (or more) reactions which are simultaneously occurring are known as partial processes. The potential observed at the electrode is not the equilibrium electrode potential, but a steady state, compromised potential, fixed by the kinetics of the two partial processes. Figure 2.5 represents this situation by showing the mixed potential as being the ordinate value of E corresponding to the point at which the anodic partial process current density is equal to that of the cathodic partial process.

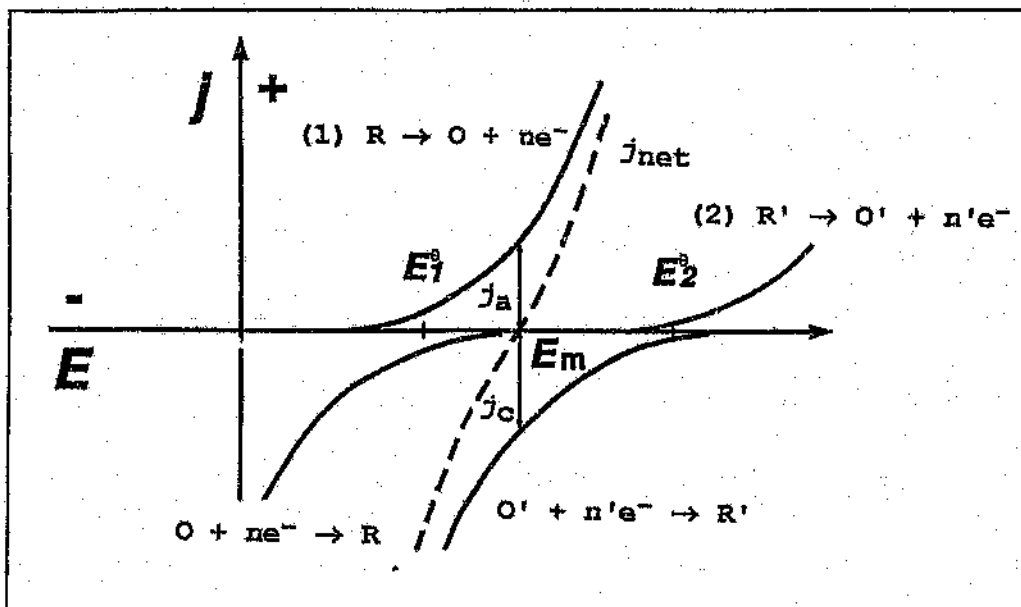


Figure 2.5 Schematic representation of the mixed potential system. Two redox processes (1) and (2), with formal equilibrium electrode potentials E_1^0 and E_2^0 , respectively, occur. The mixed potential is E_{mix} and the measured current density is shown by the broken line. Redrawn from Calvo (1986) p. 70.

The current density curves of the partial processes are affected by mass transport conditions and surface area. Consequently, the mixed potential may be susceptible to these kinetic factors, and the value of the mixed potential is governed by the kinetics of the fastest partial process (Calvo 1986 pp. 68-71, Bockris and Reddy 1970, p. 1104). This is in contrast to the equilibrium electrode potential of each partial reaction, which is governed only by thermodynamics.

Wagner and Traud (1938) studied corrosion of zinc amalgams and attributed the corrosion potential to a compromised, or mixed potential, of two separate processes: one reduction and one oxidation, both occurring at the same rate. By measuring the rates of the two processes, current density curves attributable to each of these processes were constructed and plotted on one graph. Wagner and Traud were instrumental in the

development of understanding of such so-called "mixed potential systems".

It is important to note that the Wagner and Traud mixed potential was defined for independent processes. The current density curves of Wagner and Traud were found to be identical when derived from a situation where the processes were taking place simultaneously and when they were made to occur in isolation. The term mixed potential has frequently been used in electroless plating. The validity of this terminology in the field of electroless plating will be debated in the results and discussion chapters of this work, since simultaneously occurring anodic and cathodic processes may interact. In this work, the term "mixed potential theory" refers to the classical theory of Wagner and Traud.

The mixed potential theory has been significantly developed by Spiro (Bockris and Kahn 1993 p. 754). In particular, Creeth and Spiro (1991) presented a reformulation of the Wagner and Traud additivity principle (the latter workers did not in fact suggest that the principle was valid for all mixed potential systems). Creeth and Spiro restated the additivity principle thus: "The current-potential curve of a mixture of couples can be obtained by adding, algebraically, at each potential, the currents given by each of the couples present, provided these have been determined in circumstances which correspond to those in the mixture."

In the field of corrosion study, Evans diagrams are frequently used for data presentation. These diagrams are semi-logarithmic plots of electrode potential vs. the logarithm of the absolute value of current density.

Two separate processes, one anodic and the other cathodic, can be represented on an Evans diagram. The point of intersection of the two lines then represents the corrosion, or mixed potential.

2.2.2 Coupled reactions

The mechanism of an electrode process has been described in Section 2.1.4 as consisting, in many cases, of a number of sequential steps. These steps are chemically coupled because the product of one step is the reactant of the next.

The partial processes in a mixed potential system are electrically coupled, i.e., the electrons liberated by the anodic partial process are consumed by the cathodic partial process and, as such, the processes must proceed at equivalent rates. It is also possible for the processes to be chemically coupled, e.g., as a consequence of pH effects. Although this is possible it is not ubiquitous in mixed potential systems (Smyrl 1981 pp. 104-105).

Another class of coupling may be identified: when the reaction product, an intermediate, or starting material of one partial process is a catalyst for another partial process. The rates of both partial processes may then be affected, along with the value of the mixed potential (Feldman and Melroy 1989, *op. cit.*).

2.3 ELECTROCATALYSIS

An electrocatalyst is an electrode material which enhances the rate of an electrode process at

overpotentials close to the equilibrium potential. Whereas many simple electron transfer reactions have large rate constants on a wide range of electrode materials, multi-step processes often require large overpotentials to achieve a practical current density (Pletcher 1991, p. 120). Electrocatalysts provide an alternative pathway from reactants to products, involving steps with lower activation energies than the uncatalysed route.

[The definition of catalysis as a physical chemistry phenomenon has long been debated because the nature of the interaction between the catalyst and reagents remains moot. Berzelius, who in 1835 coined the term catalysis, perceived these materials as causing a reaction between two compounds which would not take place in the absence of the catalyst. Later, W. Ostwald described the effect of the catalyst as releasing the reaction, since he appreciated that the reaction would occur but for an energy barrier retarding the process. Hence the philosophy of release-causality is more appropriate for the description of catalysis than causal-causality (Christoffel 1989). Christoffel suggests that the Chinese term "tsao mei", meaning marriage broker, may be better than the term "catalysis", originating from the Greek $\kappa\alpha\tau\alpha/\lambda\upsilon\sigma\epsilon\iota\nu$ (kata=down/lysein=split).]

The cathodic high field approximation of the Butler-Volmer equation (2.21) can be rewritten in a form which reveals that the rate of an electrode reaction (e.g., an electronation reaction) depends on both the Galvani potential difference across the interface ($\Delta\phi$) and on a term in the rate constant of the process - a purely chemical aspect (Bockris and Reddy 1970 p. 1142):

$$j = nFC_0k_c \exp\left(\frac{-\alpha_c F\Delta\phi_{pzc}}{RT}\right) \exp\left(\frac{-\alpha_c F(\Delta\phi - \Delta\phi_{pzc})}{RT}\right) \quad (2.23)$$

$\alpha_c =$ transfer coefficient for the cathodic process

$\Delta\phi =$	potential difference across the interface
$\Delta\phi_{pzc} =$	potential difference across the interface at potential of zero charge
$c_o =$	concentration of oxidised species
$k_c =$	rate constant of cathodic process
$F =$	Faraday constant
$j =$	current density
$n =$	number of electrons transferred
$R =$	gas constant
$T =$	temperature

Clearly, by altering the potential of an electrode which is acting as an electrocatalyst, the rate of the electrode process can be significantly affected. This is not the case with a purely chemically catalysed reaction.

The basis for comparison of different electrocatalysts for a given reaction lies in the comparison of the current density for the reaction at each surface. Consider two electrocatalysts 1 and 2, on which the current densities for a given electronation reaction are j_1 and j_2 respectively. The better electrocatalyst will allow the reaction to proceed with the higher current density. The overpotential is $\eta = \Delta\phi - \Delta\phi_e$, thus

$$j_1 = (j_0)_1 \exp [(-\alpha_c)_1 F(\Delta\phi - \Delta\phi_e) / RT] \quad (2.24)$$

and

$$j_2 = (j_0)_2 \exp [(-\alpha_c)_2 F(\Delta\phi - \Delta\phi_e) / RT] \quad (2.25)$$

If the electrocatalytic reaction has the same mechanism on both surfaces, it can reasonably be assumed that

$(\alpha_c)_1 = (\alpha_c)_2$ which renders the two exponential terms equal. Thus

$$\frac{j_1}{j_2} \approx \frac{(j_0)_1}{(j_0)_2} \quad (2.26)$$

Comparison of the current densities on two electrocatalysts at a given relative electrode potential is effectively a comparison of the exchange current densities on the two substrates.

It can be shown that the enthalpy of activation of an electrocatalysed electrode reaction is independent of the electronic properties of the substrate if the process involves only electron transfer between the substrate and ions in solution. This is not so, however, for an electrocatalysed reaction involving adsorbed species. In such cases, the nature of the substrate is an important factor determining the rate of the electrode process (Bockris and Reddy 1970 pp. 1143-1153).

Many electrode processes, such as the hydrogenation of unsaturated organic compounds, are thus affected by the choice of electrode. Because electrocatalysis often involves adsorption or complex formation of reactants or intermediates on the electrode, the material used must have a suitable electronic structure (viz., d-level vacancies, either in the pure metal, or induced as a result of alloying or cluster formation). It is for this reason that transition metals and oxides of transition metals function as electrocatalysts. Bockris and Kahn (1993 pp. 297-300) have cited examples of important electrocatalytic reactions which involve spill-over in alloy catalysts and catalysis by glassy metals (spill-over is the activation of a species at

one site, followed by migration and further reaction of the species at another site).

Geometric dilution, where active sites are spatially separated from one another, surface morphology and exposed crystal faces are all factors contributing to the characteristics of electrocatalytic reactions. In straightforward mass transport controlled electrode processes, the rate of the process is independent of the surface roughness, provided that the rugosity is small when compared to the diffusion layer thickness (Southampton Electrochemistry Group 1985 p. 251).

Impurities in the electrolyte, which can adsorb on the electrode, may force the reactants or intermediates to compete for catalytic sites, thereby reducing the efficiency of the electrocatalyst. Such compounds are aptly called poisons.

In electroless plating, only certain metals and alloys initiate the autocatalytic process. Trace amounts of non-electroactive species can change plating rates.

Thus electrocatalysis is an important concept in the study of electroless plating. Numerous electro-analytical techniques are used to study electrocatalysis. One of the recommended approaches is the measurement of steady state currents (or current densities) as a function of potential in a regime where mass transport is not limiting. Tafel slopes are then compared to those calculated for feasible mechanisms (Southampton Electrochemistry Group 1985 p. 232).

The simplest example of an electrocatalytic reaction is hydrogen evolution. In acid solution, the overall reaction is



Two mechanisms can be described for this process (Pletcher 1991, pp. 112-119), both involving adsorption of protons on an electrode surface. It has been found experimentally that exchange current densities for hydrogen evolution differ on different metals, with a range of ten orders of magnitude. Some representative values are shown in Table 2.1.

Table 2.1 Exchange current densities for H_2 evolution. Data obtained in 1 mol L^{-1} H_2SO_4 solution (Pletcher 1991, p. 119) (temperature not specified).

Metal	$\log(j_0/\text{A cm}^{-2})$
Pb	-8.6
Ag	-2.4
Pt	0.7

Clearly, the nature of the surface can be an important factor governing the rate of an electrode process.

Electrocatalysis is of prime importance in the area of fuel cell development. Conversion of chemicals to electrical energy, by means of "cold combustion" of CO and hydrogen, for example, can be achieved by electrocatalytic oxidation at one electrode of a cell, while reduction of oxygen takes place at the cathode (Bockris and Reddy 1970 p. 1394, Bockris and Kahn 1993 pp. 861-894).

Prevailing environmental regulations in most first world countries regarding emissions from automobile exhausts have created impetus for the development of cleaner power sources. Fuel cells require considerable development for widespread use, and a better understanding of electrocatalysis will assist in the maturation of the technology.

2.4 AUTOCATALYSIS

Autocatalysis is the catalysis of a reaction by one of the products of that reaction. This is to say that initially the reaction occurs either as a slow step after an induction period, or by being catalysed by some "third-party" material. In the latter case, the initial catalyst may become insignificant as the reaction products are formed. An example of autocatalysis in organic chemistry is the halogenation of aldehydes (Streitwieser and Heathcock 1981, p. 376).

Two situations may arise during the formation of an electroless film which illustrate that the redox process and metal deposition is autocatalytic. The first is when only isolated areas of the surface are catalytically active to electroless deposition, and the major part of the surface is inactive. This is typical of a treated surface where catalyst nuclei are formed. The catalytic "islands" may initiate the electroless reaction but in order for the localised islands of depositer material to grow together to form a coherent film, the edges of the initially-reduced metal must further catalyse the process (Feldstein et al. 1974).

The second situation illustrating the autocatalytic nature of electroless deposition resides in the fact

that films grow in thickness to significantly more than one monolayer. For this to happen, the first and subsequent monolayers need to be catalytically active.

2.5 ELECTROANALYTICAL TECHNIQUES

2.5.1 Voltammetry

2.5.1.1 Cyclic Voltammetry

Cyclic voltammetry (CV) was employed only qualitatively in this work. In cyclic voltammetry a cyclic, linear potential sweep is applied to an electrode in an unstirred solution. The current response is measured and current peaks are obtained as each electroactive species is oxidised or reduced as the case may be. In the qualitative application of cyclic voltammetry it is not possible to calculate the kinetic parameters of the electrode processes, but it is possible to obtain an "electrochemical spectrum" for the species present in the solution. A typical cyclic voltammogram for the reversible couple $O + e^- \rightleftharpoons R$ where O is the oxidised species and R the reduced species is given in figure 2.6.

CV can be used to study reversible, irreversible and quasi-reversible electrode processes. By altering the sweep rate of the potential it is possible to identify fast and slow electron transfer steps and to identify the formation of reaction intermediates. A properly designed experiment using the CV technique is

indispensable in the elucidation of electrode process mechanisms. The formal electrode potential of a reversible couple can be determined using CV, being centred between the peak cathodic potential and the peak anodic potential. (Southampton Electrochemistry Group 1985 pp. 178-185; Kissinger and Heineman 1984 pp. 86-94).

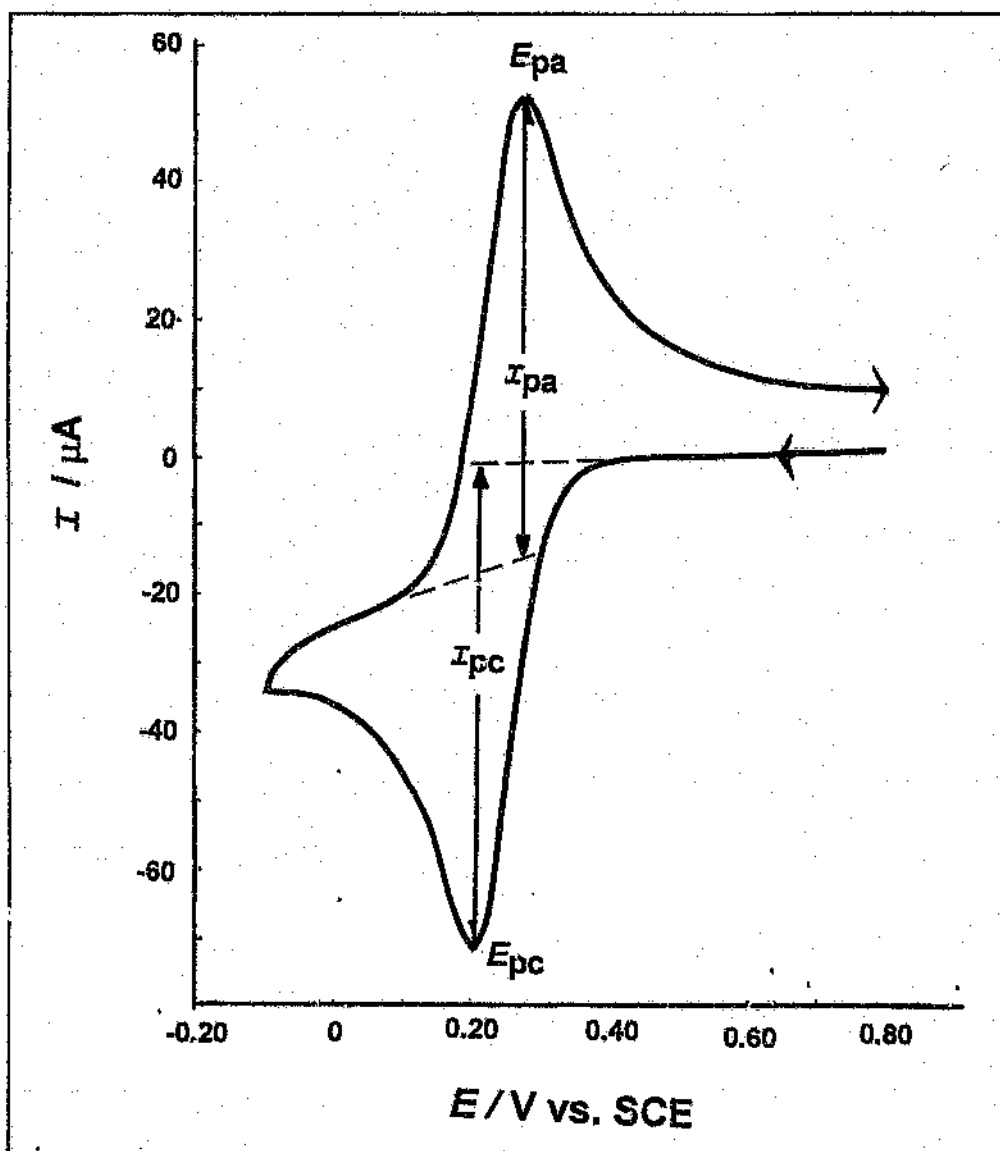


Figure 2.6 Cyclic voltammogram of 10.0 mmol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 mol L^{-1} KCl (25.2°C). Scan initiated at 0.80 V vs. SCE in a negative direction at 100 mV s^{-1} . Platinum electrode 0.0314 cm^2 . E_{pc} = peak cathodic potential, E_{pa} = peak anodic potential. I_{pc} = peak cathodic current, I_{pa} = peak anodic current.

2.5.1.2 Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) is the generic name for a range of techniques which have been developed for the determination of trace metals in solution. A description of the quantitative method follows.

An electroactive species in solution may be deposited on to an electrode surface by means of the application of a potential more cathodic than the reduction potential of that species. Electrodes commonly used for ASV are the mercury film electrode (MFE) on carbon paste or glassy carbon, the hanging drop mercury electrode (HMDE) and the dropping mercury electrode (DME). The deposition of the species on to the electrode is known as the preconcentration step, and is carried out in a reproducible manner (i.e., constant stirring rate, temperature and deposition time, as well as identical electrode surface, for each set of experiments). Following the preconcentration step, a rest period is allowed for the solution to become quiescent and for the preconcentrated species to diffuse uniformly within the mercury of the electrode. This step is performed in either the original solution or in an appropriate stripping solution. An anodic-going linear potential sweep applied to the electrode in the original solution or in a separate stripping solution will result in the oxidation of the deposited species. The current density of this oxidation process is measured, and the peak height related to the concentration of the electroactive species in the original solution. The potential at which the peak occurs is characteristic of the identity of the analyte.

A more sensitive variation of the ASV technique is when a periodic square wave pulse is applied to the anodic potential sweep. This serves to minimise the residual current effects arising from double layer charging. The pulse also increases the effect of sweep rate on the peak current. The detection limits are usually improved when square wave techniques are employed.

(Ellis 1973, Bard and Faulkner 1980 pp. 413-420)

2.5.2 Rotating Disc Electrode

The rotating disc electrode (RDE) is an important device in electroanalytical chemistry. A fast rotating disc electrode causes a well defined hydrodynamic condition near its surface. The rotation moves the solution near the electrode surface in an outward radial direction. The resulting fluid flow is shown in Figure 2.7. The velocity of the solution movement V_x perpendicular to and in the direction of the disc is a function of the rotation rate ω and the distance from the electrode.

$$V_x \propto \omega^{1/2} x^2 \quad (2.28)$$

The influence of forced convection on the mass transport is thus diminished at small distances from the electrode surface.

Rotating disc electrodes are used for the study of the kinetics of electrode processes. For example, the rate constant for the "C" step of an ECE mechanism can be determined by measuring the limiting current as a function of rotation rate. The limiting current of the electrode process is given by the Levich equation (Equation 2.29). A voltammogram for the reduction of

$K_3Fe(CN)_6$ at a rotating disc electrode is given in Figure 2.8.

$$i_l = 0.620 n F A c^\infty D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (2.29)$$

where

ω = angular velocity of the disc, i.e., $\omega = 2\pi N$, N is the rotation speed in revolutions per second

ν = kinematic viscosity of the fluid, $cm^2 s^{-1}$

i_l = limiting current, A

A = geometric surface area of disc, cm^2

c^∞ = solution concentration of the electroactive species, $mol cm^{-3}$

D = diffusion coefficient of the electroactive species, $cm^2 s^{-1}$

F = Faraday's constant

n = number of electrons transferred

It is clear that the current densities expected at a RDE for a mass transfer controlled process are higher than those measured in non-convective systems.

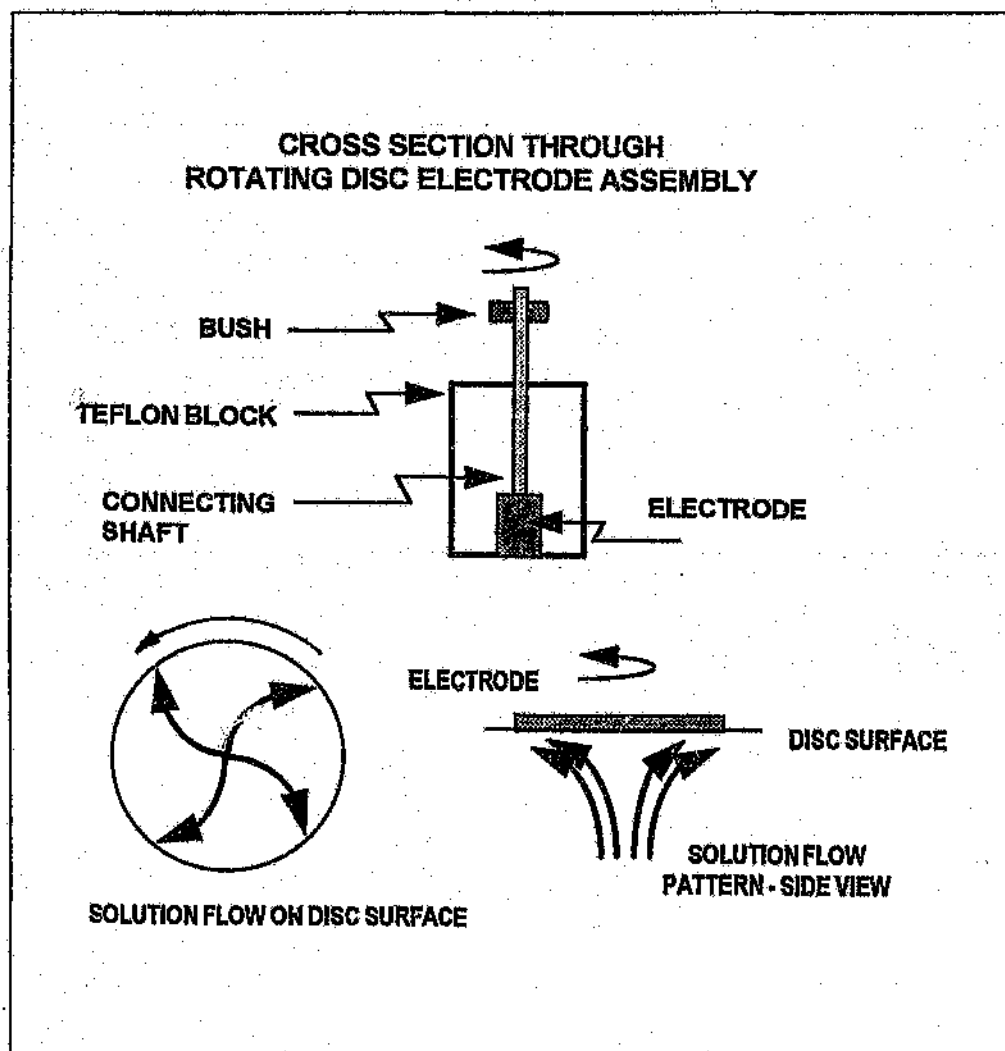


Figure 2.7 Hydrodynamics at a rotating disc electrode (redrawn from Southampton Electrochemistry Group 1985 p.116).

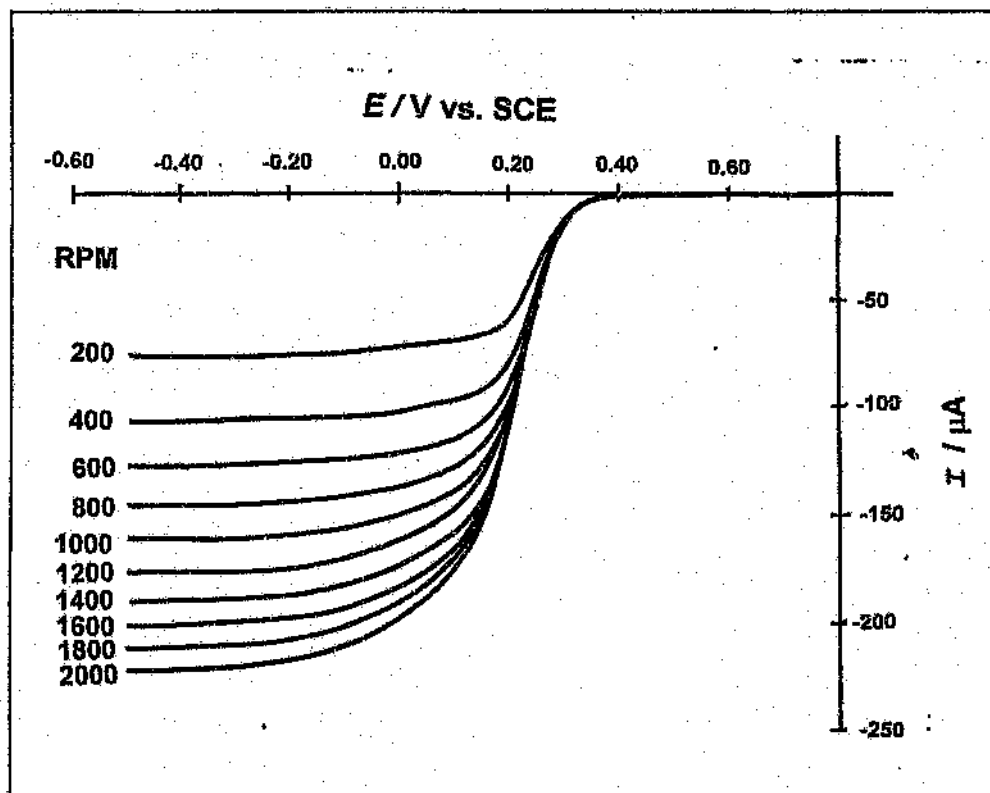


Figure 2.8 Voltammogram of $10.0 \text{ mmol L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$ in $1 \text{ mol L}^{-1} \text{ KCl}$ (25.2°C), at a platinum RDE. Scan initiated at 0.80 V vs. SCE in a negative direction at 50 mV s^{-1} . Platinum electrode area 0.0314 cm^2 .

2.6 TECHNIQUES FOR STUDYING ELECTROLESS PLATING

Studies of the electroless plating process have employed a variety of techniques and approaches (a detailed literature survey is presented in Chapter 4). Plating rates have usually been determined gravimetrically, by measuring the mass change of a sample substrate of known surface area. It is possible to determine the rate of the anodic process provided that the rate of formation of a non-solid product can be followed by an appropriate technique (e.g., spectroscopy).

Over the last two decades, electrochemical techniques have come to the fore in electroless plating research (e.g., voltammetry, potentiometry and amperometry). A metal surface plating in an electroless bath adopts a steady state potential with respect to the solution. This potential is a mixed potential, and the cathodic and anodic processes occur at the same rate. Observation of the mixed potential under suitably varied conditions has been a *modus operandi* adopted by researchers in the field (Feldstein and Lancsek 1971, Paunovic 1968).

When the potential of the plating surface departs from the steady state value, under the influence of an externally applied potential, plating is no longer truly electroless. However, the cathodic and anodic processes still occur, but at unequal rates (Feldman and Melroy 1989, Orchard 1988b, Paunovic 1968). Hydrogen evolution is usually a cathodic co-process. If this reaction occurs at a significant rate, it may affect the calculation of the anodic process current density described below.

The partial current densities of the two half-reactions can be derived from

(a) the net current density, j_{net} , as calculated from the current measured in the external circuit, and

(b) the plating rate converted to a current density using Equation 2.8. These give the anodic and cathodic partial current densities, j_a and j_c , respectively. The relationship is

$$j_{\text{net}} = j_a + j_c \quad (2.30)$$

(Note that lower case subscripts are used here to differentiate these current densities from those in Equations 2.12 and 2.13. Equation 2.30 represents current densities of two different partial processes.) Tafel-type plots can be made using this data and the relevant electrochemical parameters may be extracted.

Another technique used in the study of electroless plating has involved the use of an electrochemical cell design which keeps solutions of the metal ion and reducing agent separate by means of a membrane or frit. While mixing of the solution species is avoided, ionic transport by a supporting electrolyte is allowed (El-Raghy and Abo-Salama 1979). This type of experiment is performed to determine the dependence of one half-reaction on the other. Wiese and Weil (1987) used an elaborate arrangement of electrical separation of the partial processes. The results and conclusions of the various works cited here will be discussed in more detail in Chapter 4.

The rotating disc electrode has been used (Orchard 1988a and 1988b) to measure plating rates under controlled hydrodynamic conditions.

Mechanistic information was obtained by electrochemical mass spectrometry (Jusys and Vaškelis 1992, *op. cit.*). In this series of studies, gaseous products from isotopically labelled electroless baths were analysed by mass spectrometry. To accomplish this, a thin Teflon membrane was used to support the electrode. Gases were sucked through the membrane, into the mass spectrometer.

Most classical techniques, however, have the limitation that they interfere with the very process which they

are investigating. The long plating times required to obtain a measurable mass change may lead to significantly altered reagent concentrations. This is exacerbated when the bath being studied operates at a temperature where a volatile component evaporates. Thus the development of an experimental strategy which examines the process rapidly, and with less of a disturbing effect, could yield useful and as yet undiscovered information.

A relatively new device, the electrochemical quartz crystal microbalance, or quartz microbalance electrode, has attributes which are of great use in the mechanistic studies of electroless plating. A description of the quartz microbalance electrode follows in Chapter 3.

CHAPTER 3

THE QUARTZ MICROBALANCE -

TECHNICAL DESCRIPTION

CHAPTER 3 THE QUARTZ MICROBALANCE - TECHNICAL DESCRIPTION

3.1 QUARTZ CRYSTALS*

Alpha-quartz is the crystalline form of silica (SiO_2) which is stable at temperatures below 573°C . The non-centrosymmetric crystal structure of alpha-quartz gives rise to a number of physical properties, one of which, the piezoelectric effect, is discussed in the following section.

Crystalline quartz, specifically alpha-quartz, occurs naturally as a geochemical phenomenon. An industrial process also exists whereby scarcely-flawed crystals may be grown on to seed crystals from an alkaline, aqueous solution. This is the hydrothermal route of quartz crystal production. Crystals obtained from the latter process were exclusively used for the purposes of this project.

* Bibliographic note : Technical information and descriptions in this section were obtained by consulting pertinent texts (Bottom 1982, Frerking 1978). Other sources are acknowledged as they are cited.

3.2 THE PIEZOELECTRIC EFFECT

3.2.1 Explanation of the piezoelectric effect

The term "piezoelectricity" is derived from the Greek word, *piezo*, meaning "press", hence "pressure electricity". Because of the polar anisotropy in the unit cell of the crystal, a pressure on a section of crystal (or piezoid) results in a shift in charge distribution. This can be detected as a change in the electric field between the faces of the crystal section and is referred to as the *direct piezoelectric effect* (Figure 3.1).

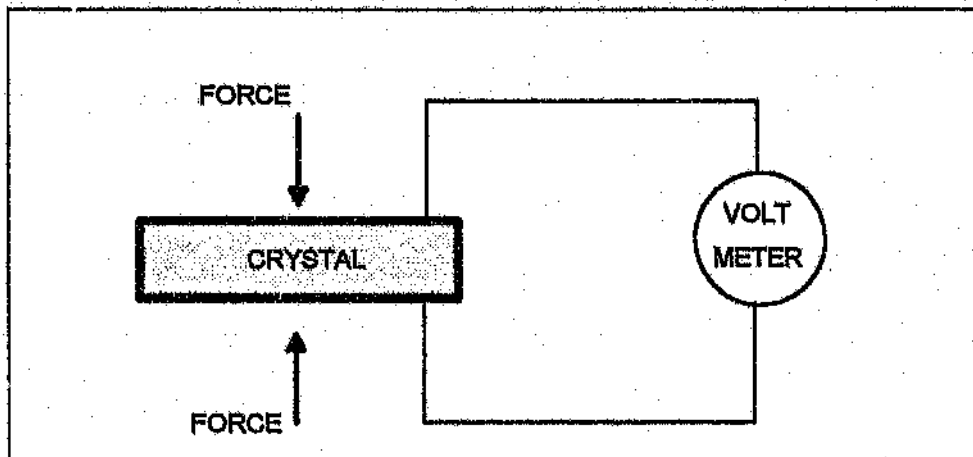


Figure 3.1 The direct piezoelectric effect.

The *converse piezoelectric effect* is the phenomenon whereby a physical displacement of atoms in the piezoid occurs as a result of an imposed electric field (Figure 3.2).

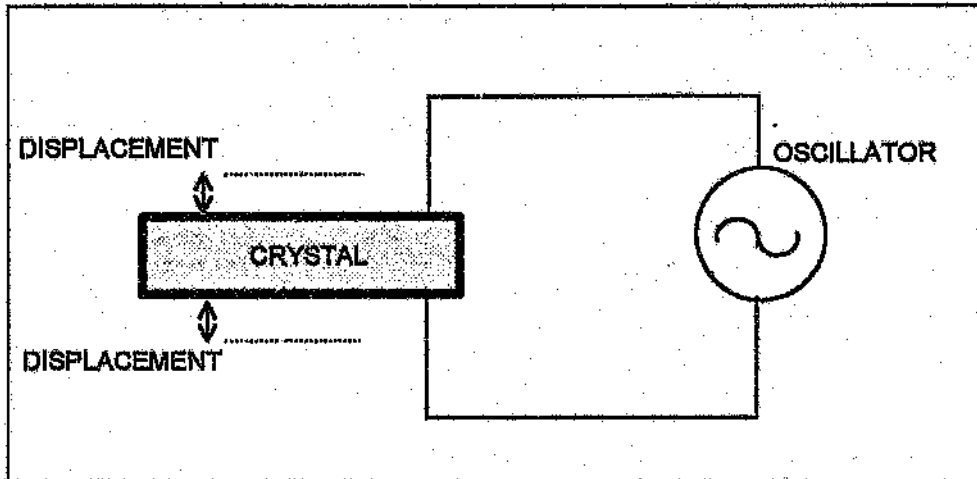


Figure 3.2 The converse piezoelectric effect.

It is this phenomenon which is utilised in frequency control applications and the quartz crystal microbalance (QCM).

The fabrication process produces piezoids which are wafers of crystal usually less than one millimetre thick. These are cut at specific orientations to the z , or optical, axis of symmetry of the single crystal (Figure 3.3).

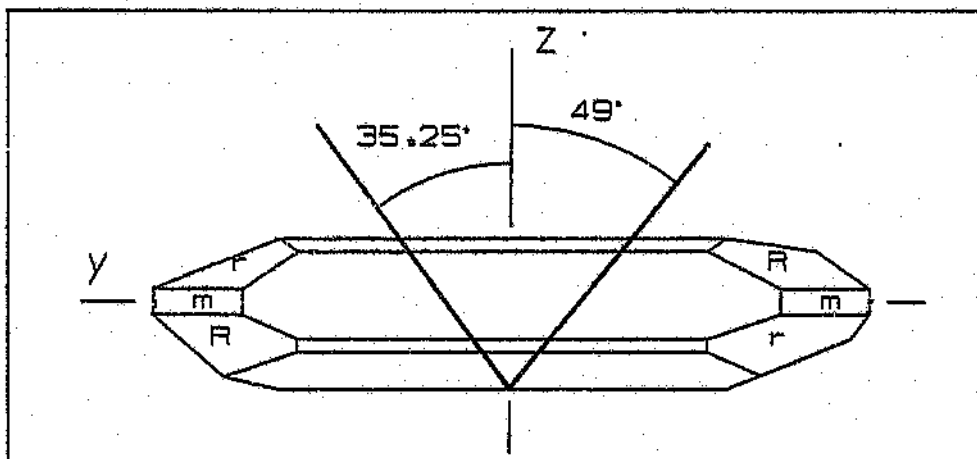


Figure 3.3 The orientation of AT and BT cut crystal wafers. R, m and r represent the specific faces of the crystal.

The two possible cuts shown in Figure 3.3 are referred to as AT (35.25° to z axis) and BT (-49.00° to z axis) cuts. Both cuts form plates which are parallel to the x axis. Since piezoid is a solid body, the vibrations which are caused by an oscillating electric field can occur in identifiable directions and at resonance frequencies dependent on the mass, thickness and shape of the piezoid and the orientation of the field relative to the optical axis, i.e. the cut. These vibration directions, called modes, include bend, torsion and shear displacements.

Piezoids used in frequency control and quartz microbalances are usually disc shaped. In order to apply the required electric field to the crystal, it is necessary to apply conductive layers to opposite faces of the disc whereby leads to a suitable field generator (oscillator) can be attached. This is commonly done by evaporating metals such as silver or gold on to the faces to form electrodes. Most of the vibration occurs where the electrodes overlap - this is the piezoelectrically active area (Figure 3.4). As mentioned above, the resonance frequencies (or harmonics thereof) are governed by physical characteristics, including mass. Thus an increase in mass will change the resonance frequency only if this mass change occurs within the piezoelectrically active area.

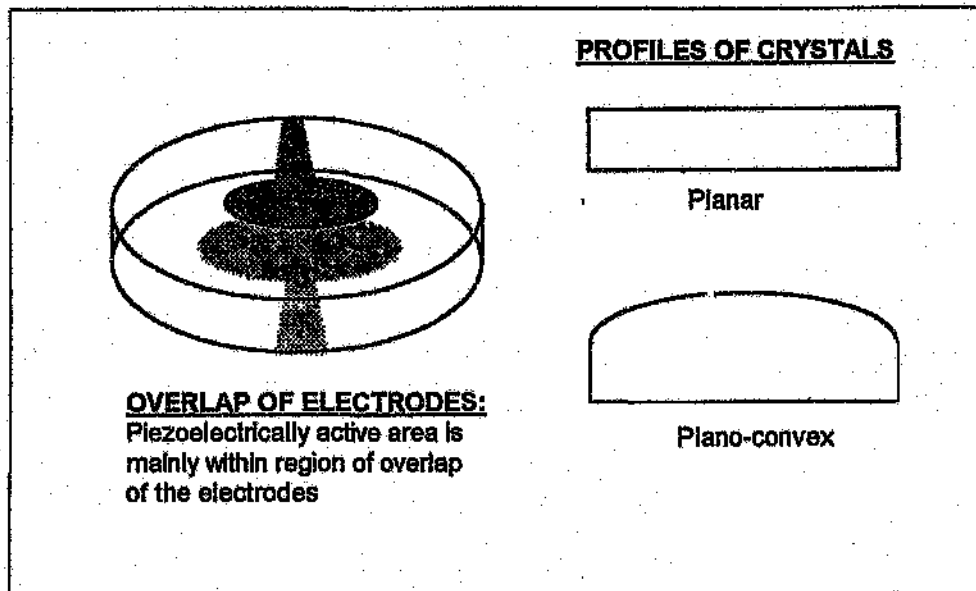


Figure 3.4 Perspective view of a quartz crystal piezoid, showing overlapping region of electrodes with unequal radius, and profiles of planar and plano-convex crystal wafers.

3.2.2 Shapes of crystals

Planar, disc shaped crystals exhibit greatest piezoelectric activity of electrode overlap. The vibrations are not, however, wholly limited to the overlapping region but do extend radially outwards. This effect is often deleterious to the operation in a quartz microbalance, and can be minimised in two ways (Ward and Delawski 1991). The first is by judicious choice of the relative electrode sizes and their size relative to the dimensions of the crystal. An optimum ratio of the diameters of electrode area and crystal exists. This reduces the effect of shear waves extending radially and being reflected back by the edge of the crystal.

The second method of minimisation involves the use of a contoured, plano-convex piezoid. As a result of the central region being thickest, so-called energy trapping occurs, maximising the amplitude of the vibration in the centre and minimising it outside the electrode overlap area. These contoured discs exhibit better frequency stability than planar crystals, are better suited for use in the QCM.

Bácskai, Láng and Inzelt (1991) performed a similar mapping of the radial sensitivity of the quartz microbalance to that undertaken by Ward and Delawski. Bácskai and co-workers addressed the problem of uneven thickness of polymer films on the QME, and concluded that for uneven films, the differential sensitivity function of the resonator must be known for meaningful results.

3.3 THE QUARTZ CRYSTAL AS AN OSCILLATOR ELEMENT

3.3.1 Quartz crystals as resonators

When a xylophone bar is struck by a hammer, the bar will vibrate at a frequency determined by the dimensions of the bar and the points of support. A quartz piezoid is excited into vibration, not by being struck, but by an externally applied, oscillating electric field. By virtue of its solid characteristics, resonance may be attained.

In order to sustain this vibration, the applied field must change in a periodic manner. When conditions have been carefully designed to meet the numerous electrical parameters of importance, a resonance frequency can be established where the crystal controls the rate of voltage change in the external, driving circuit; this circuit is an oscillator. It is this principle which is exploited in telecommunications, radio, microprocessor clock circuits and in fact, any context where isochronous electronic timing is desired. Well-built crystal units incorporated into carefully designed oscillators may give frequency stability of a few parts in 10^{13} (Frerking 1978, p. v).

3.3.2 Oscillators

In the present context, oscillators are electronic circuits which convert a direct current (d.c.) voltage into an alternating current (a.c.) voltage. Basically, an oscillator consists of a supply voltage, an amplifier and a feedback loop (Figure 3.5).

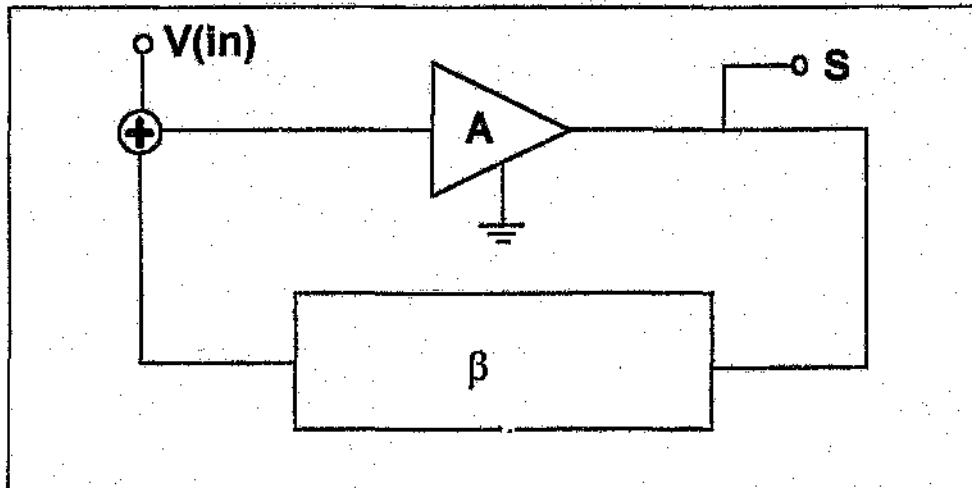


Figure 3.5 The elements of an oscillator. A = amplifier, β = feedback network, $V(in)$ = supply voltage, + = mixer and S = signal.

When Barkhausen's criterion (Boylestad and Nashelsky 1987, p. 758) is satisfied, the amplifier/feedback combination acts as an oscillator. The criterion requires that the overall gain of the system must be infinitely large, and that the feedback signal is in phase with, and adds to, incoming signals (Glasspoole 1987). The crystal represents, to the circuit, a resistance-inductance-capacitance (RLC) network (Figure 3.6):

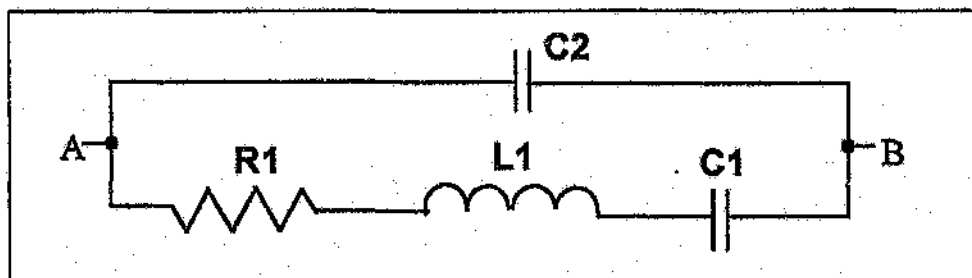


Figure 3.6 The equivalent circuit of a quartz crystal resonator. $R1$, $L1$ and $C1$ comprise the reactance of the crystal and $C2$ is the mounting capacitance.

On the basis of oscillator theory, and taking into account the behaviour of crystals as RLC components, numerous oscillator circuits have been developed. Some of these are given in Figures 3.7 to 3.11. (These diagrams are for illustration and do not contain sufficient information for construction.)

The oscillator circuits illustrated have certain fundamental differences, depending on where in the circuit the crystal resonator (Y1) is situated and what relationship exists between the values of crystal reactance, mounting capacitance and circuit components. These considerations will not be discussed further.

Circumstances dictate the choice of oscillator for a particular application. Most communication and microprocessor devices require high stability. The amplitude of actual physical vibration is not generally a consideration, but circuitry must provide constant frequencies over long periods of time. In the case of the QCM, however, a more "pullable" oscillator is necessary. This means that the circuit will be capable of attaining resonance with the crystal at excursions from the original frequency to which the circuit was tuned. These excursions may be in the order of 0.5%. The quartz microbalance electrode also requires that the a.c. signal be decoupled from that side of the device which acts as the electrode in the electrochemical cell, so that this signal does not influence the electrode potential.

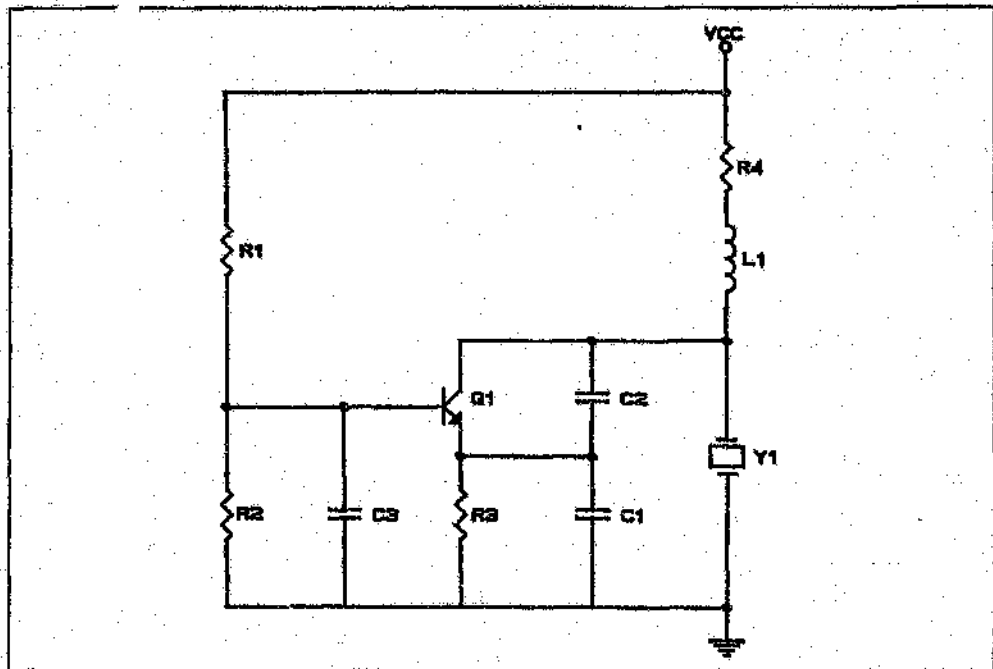


Figure 3.7 Clapp crystal oscillator (Frerking 1978 p. 85).

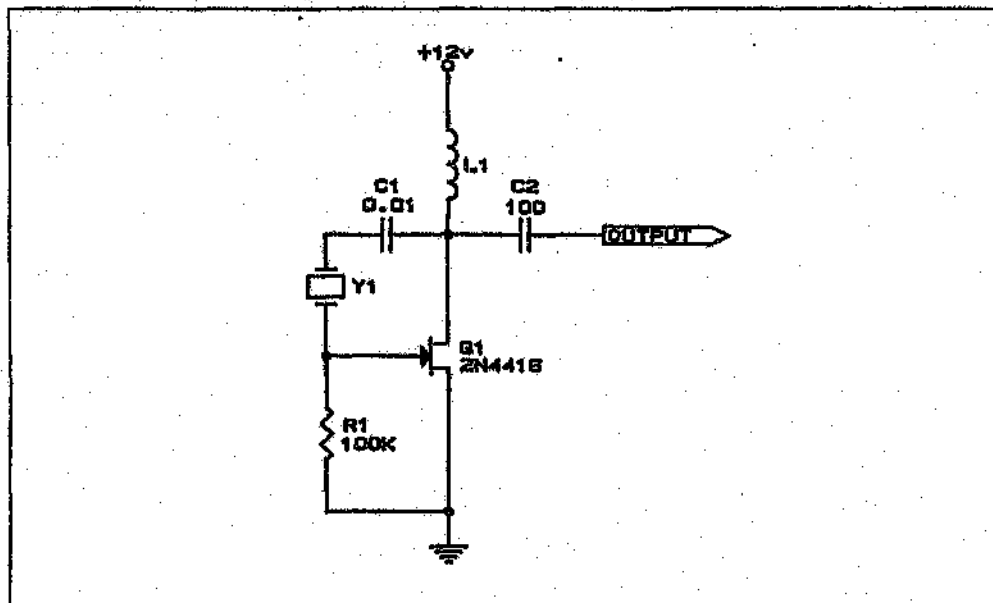


Figure 3.8 Pierce crystal oscillator (Wolfgang and Hutchinson, 1991, p. 10-1).

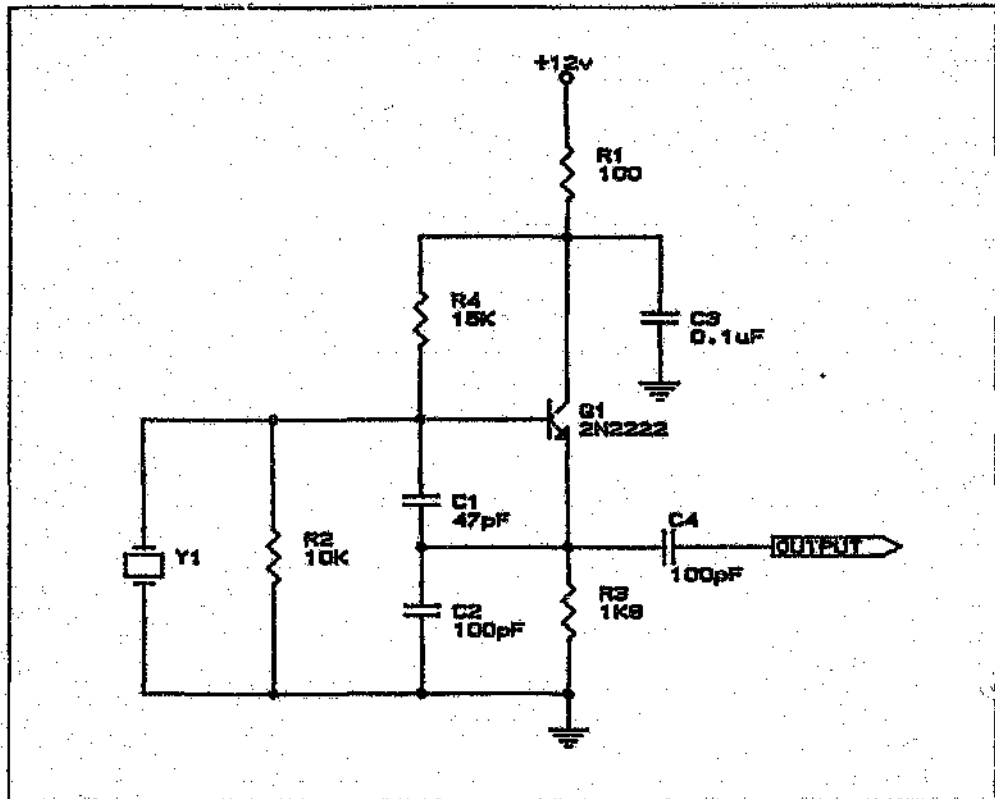


Figure 3.9 Colpitts crystal oscillator (Wolfgang and Hutchinson 1991 p. 10-1).

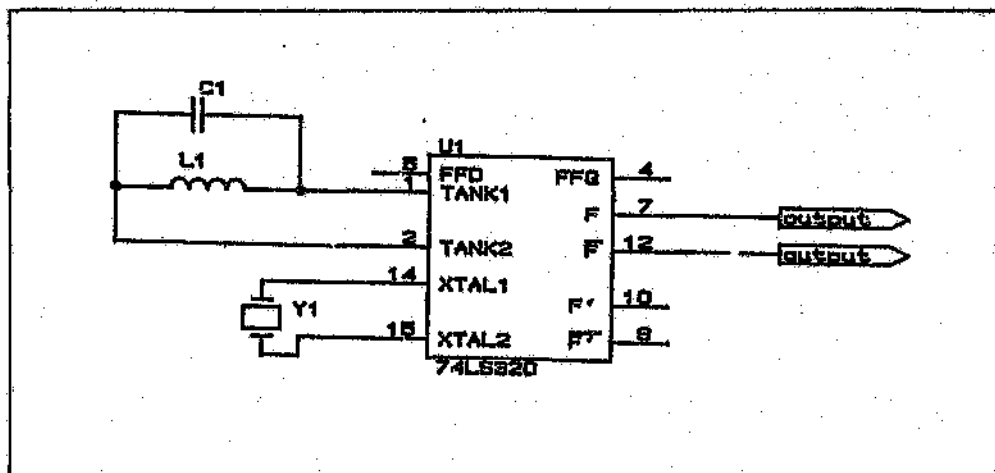


Figure 3.10 74LS320 integrated circuit crystal controlled oscillator (Hardy 1983 p. 7-466).

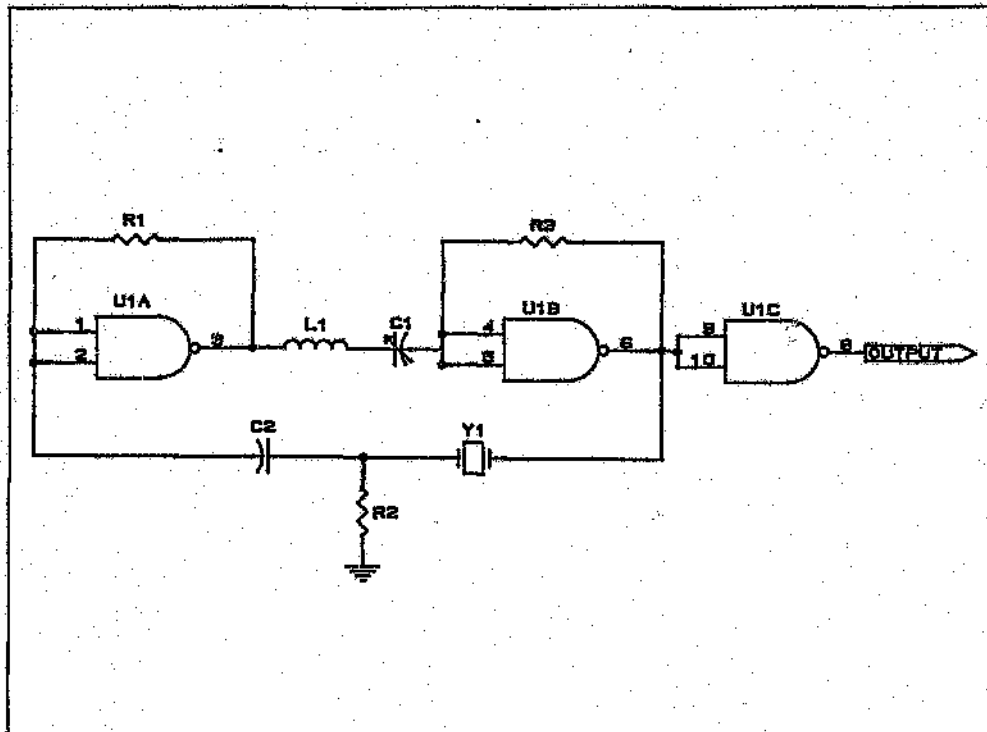


Figure 3.11 Dual-input NAND-gate oscillator
(Frerking 1978, p. 107).

3.4 MASS CHANGES AND RESONANCE FREQUENCIES

3.4.1 Mass change - resonance frequency relationship

3.4.1.1 The Sauerbrey equation

It was stated in Section 3.2.1 that the resonance frequency of a quartz piezoid depended, in part, on the mass of the piezoelectrically active area of the crystal. This phenomenon will be described in this section. AT-cut quartz disc piezoids oscillate at the fundamental frequency or odd harmonics of this frequency. The proof of this is lengthy and may be found in the text by Bottom (1982, pp. 134-136).

Factors which affect the resonance frequency and deviations from this frequency include:

- physical properties of the quartz disc (thickness, density and shear modulus)
- density and viscosity of the phases adjacent to the piezoid
- ambient temperature and pressure difference across the disc
- mass of attached electrode or of adsorbate on attached electrode.

(Deakin and Buttry 1989, Deakin and Melroy 1989)

Other factors may also contribute to frequency change. These will be discussed in Section 3.4.2. The

general relationship, taking only attached electrode mass into account and maintaining all other parameters constant, is given by Equation 3.1 (Sauerbrey 1959):

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\rho_q \mu_q}} \quad (3.1)$$

Here, f_0 is the fundamental frequency of the crystal and Δf is the frequency shift from the resonance value. Δm is the mass change causing the frequency shift. The surface area which is piezoelectrically active is represented by A , while ρ_q and μ_q are the density and shear modulus of quartz respectively.

Equation 3.1 shows that the change in frequency is linearly related to mass change. A rearrangement (Equation 3.2) of the Sauerbrey equation is used to determine the sensitivity and linearity of response of the QCM. This rearrangement expresses the ratio $\Delta f/\Delta m$ in terms of f_0 and the physical parameters. Equation 3.2 shows that for a crystal of a given fundamental resonance frequency, the ratio on the left-hand side should be constant. By depositing a known mass on the face of a crystal, and observing the frequency change, an experimental ratio can be obtained and compared to the theoretical value (Stöckel and Schumacher 1987).

$$\frac{\Delta f}{\Delta m} = -\frac{2}{A\sqrt{\rho_q \mu_q}} f_0^2 \quad (3.2)$$

Clearly, the higher the fundamental resonance frequency of the crystal, the better the mass

sensitivity. A problem arises with high frequency crystals, however, because these are very thin discs and are consequently difficult to mount, coat etc. This limitation can be circumvented by operating a thicker piezoid at higher harmonics to achieve better sensitivities. In such cases, odd harmonics of the resonance frequencies are used, as has been done in the study of underpotential deposition of lead on gold (Melroy, et al. 1986), for measurement of sub-monolayer depositions. In order to force a thicker crystal wafer to have a harmonic resonance frequency, the wafers are overtone polished. This process leaves the wafer with a much smoother surface. Overtone polished crystals have found favour where measurements are made at the theoretical limits of the detection of the fundamental mode (e.g., $18 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ for a 5 MHz crystal).

3.4.1.2 Limitations of the Sauerbrey equation

Benes (1984) examined the theoretical and practical aspects of mass sensing using a quartz microbalance. The limiting conditions were discussed, and the z-match technique was suggested as being a more accurate model for the conversion of frequency changes to areal mass changes. The z-match technique considers the importance of the acoustic impedance of the depositing material as being significant in the calculation. Use of the z-match technique was recommended particularly when extremely high loading of the crystal was anticipated.

A detailed study of the radial mass sensitivity of the QME was undertaken by Hillier and Ward (1992), using a scanning microelectrode (SME) in close proximity to a QME. This study expanded and improved on earlier work (Ward and Delawski 1991). Here, it was pointed out that the use of the Sauerbrey equation must be accompanied by certain assumptions. It is assumed that the added mass is uniformly distributed, that a rigidly elastic thin film is deposited and that any local deposit is treated as a thin film over the entire electrode area. Clearly these assumptions represent the ideal case. By scanning the microelectrode outward from the centre of the crystal in a spiral pattern, they were able to deposit controlled amounts of copper or to insert controlled amounts of ions into polymer films on the QME while measuring the frequency change. The position of the points of deposition was known with a precision of 4 nm. In this way, mapping the crystal surface with the SME was achieved.

Hillier and Ward thus investigated energy trapping, as a function of crystal shape, electrode orientation and relative size. In addition the sensitivity as a function of mass loading, solution viscosity and electrode orientation was quantified. They acknowledged that their results with ion insertion were not as reliable as those for copper deposition, as a result of the viscoelastic properties of the substrate. They concluded that depending on the experimental arrangement and type of deposit, the Sauerbrey equation could be in error by as much as 25%. This is particularly so for plano-plano crystals with high mass loading of viscoelastic films. It was

recommended that calibration be done in all cases, with a film with properties as close as possible to the experimental film.

3.4.2 Factors contributing to apparent mass change

3.4.2.1 Coupling of the solvent with the oscillating crystal

Two aspects may be of consideration in terms of liquid media coupling with the crystal. The first type of coupling is electrical coupling. It has been suggested (Kurosawa, et al. 1990) that electrolyte solutions may modulate the inductance of the piezoid. This has not been fully investigated and the results to date are ambiguous and inconclusive.

The second, more important type of coupling is the damping effect the liquid has on the shear motion.

Kanazawa and Gordon (1985a and 1985b) quantified the effect of a thin layer of solution closest to the crystal surface on the fundamental frequency of the crystal. They proposed that this thin layer of solution was translated in a shear motion with the crystal surface. The magnitude of the shear wave in the bulk solution (i.e., beyond the thin layer) is damped as a result of energy losses due to viscous drag. Kanazawa and Gordon were able to predict the

thickness of the shear wave as a function of the frequency of oscillation and the properties of the liquid (Equation 3.3). In addition, an expression for the frequency change expected when an oscillating crystal is immersed in a liquid was derived (Equation 3.4).

$$\delta = \sqrt{\frac{2\eta_l}{\omega\rho_l}} \quad (3.3)$$

- δ = thickness of shear wave in liquid
- η_l = viscosity of the liquid
- ρ_l = density of the liquid
- ω = frequency of the shear wave

$$\Delta f_M = -f_0^{3/2} \sqrt{\frac{\rho_l \eta_l}{\pi \rho_q \mu_q}} \quad (3.4)$$

- Δf_M = change in mechanical frequency of oscillation
- f_0 = fundamental resonance frequency of crystal
- η_l = viscosity of the liquid
- ρ_l = density of the liquid
- ρ_q = density of quartz
- μ_q = shear modulus of quartz

A relationship exists between the density and viscosity of the liquid, and the frequency of resonance relative to that in water (Equation 3.5) (Kurosawa, et al. 1990).

$$\Delta f_w \propto \sqrt{\rho_l \eta_l} - \sqrt{\rho_w \eta_w} \quad (3.5)$$

Δf_r is the resonance frequency change from water to a different liquid. ρ_l and η_l are the density and viscosity of the liquid respectively and ρ_w and η_w are the density and viscosity of water respectively.

Hager (1986) has used the influence of fluid characteristics on resonance frequency for fluid property evaluation. Other research efforts have also utilised this aspect of the microbalance, for example, the work by Murumatsu and co-workers (1988).

Kanazawa and Melroy (1993) give a complete summary of the mathematical treatment of the various effects governing frequency change brought about by liquid in contact with the resonator. The thickness of the shear wave which propagates into solution is approximately 2400 Å for water. This thickness is of sufficient magnitude to be of importance in electrochemistry, where the thickness of the double layer is in the order of 10 - 100 Å.

3.4.2.2 Surface roughness

A film of material being deposited on a QCM contributes directly to mass change of the piezoid. When the growing film is not smooth, as depicted in Figure 3.12, the liquid trapped within the depressions contributes to the inertia of the surface in shear movement and contributes to the apparent mass change. If a surface is considered to be uniformly rough, and the average depth, δ , of surface

depression is known, then the frequency shift due to entrapped liquid, $(\delta f)_{\text{rough}}$, can be calculated (3.6).

$$(\delta f)_{\text{rough}} = -\frac{2f_0^2}{\sqrt{\rho_q \mu_q}} \rho_l \delta \quad (3.6)$$

δ = average depth of surface depression

$(\delta f)_{\text{rough}}$ = frequency shift due to entrapped liquid.

Other parameters are as defined for Equation 3.4.

(Kanazawa and Melroy 1993)

The sensitivity of the QCM to surface roughness may also be used as an analytical tool. Schumacher, Borges and Kanazawa (1985) used the QME to probe surface reconstructions on gold electrodes in liquid. Copper and silver quartz microbalance electrodes which had been roughened electrochemically, were shown to undergo morphological reconstruction within a few hours (Schumacher, Gordon and Melroy 1987). Bittner, Wanner and Weil (1992) studied the role of surface microstructure of copper deposits during electroless plating in formaldehyde containing copper baths. This was achieved using a quartz microbalance in conjunction with Fourier transform infra-red spectroscopy and surface enhanced Raman spectroscopy.

Beck, Pittermann and Weil (1992) investigated the effect of surface roughness on the theoretical sensitivity of the QME by using the QME in conjunction with a.c. impedance spectroscopy. A silver plating and dissolution process with current efficiency known to be 100% was used as a means of creating a controlled surface morphology. These

workers found that they were able to differentiate between viscously coupled liquid (i.e. liquid which moves with the shear motion of the crystal irrespective of surface roughness) and rigidly coupled liquid (i.e. liquid entrapped in deep fissures in the surface (Figure 3.13)).

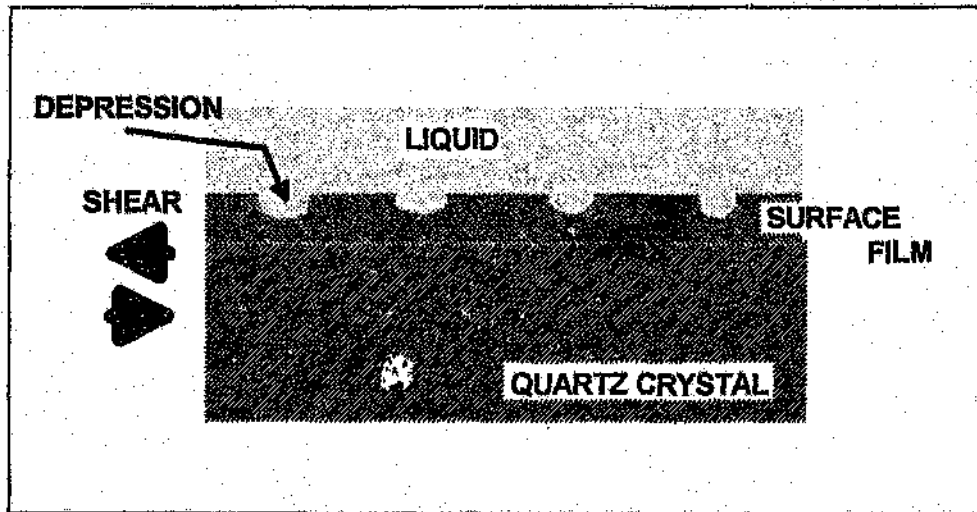


Figure 3.12 Surface depressions entrap liquid, which contributes to film mass during shear mode oscillation.

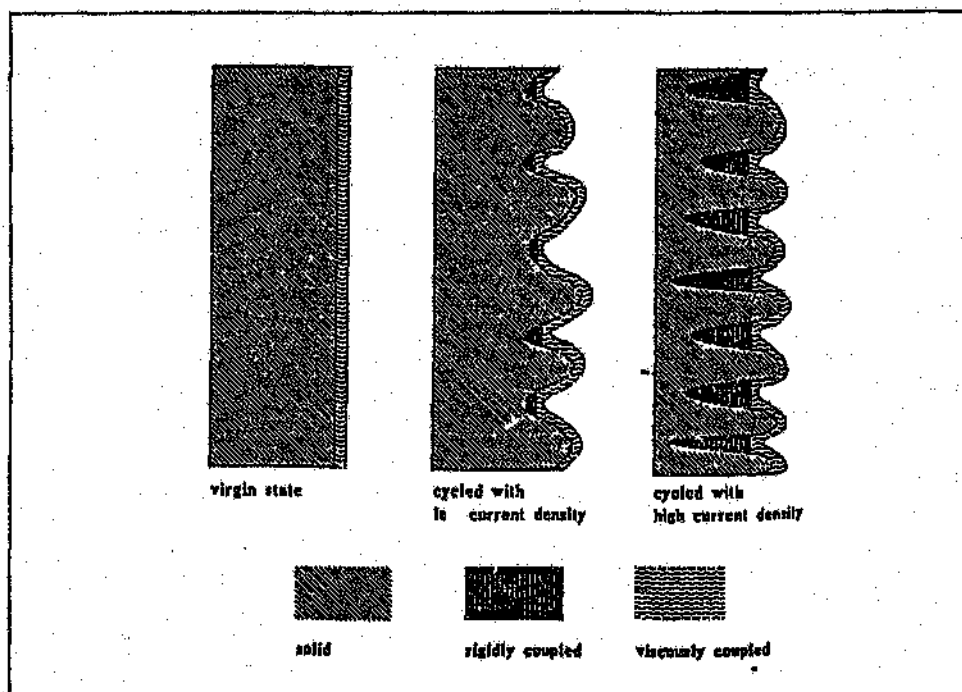


Figure 3.13 Schematic representation of rigidly and viscously coupled water (Beck, Pittermann and Weil 1992).

Beck and co-workers (1992) suggested that the QME should be used in conjunction with a.c. impedance spectroscopy whenever the current efficiency of the electrode process was unknown, or when details of the surface microstructure are of interest.

3.4.2.3 Adsorbed species

Solution species which adsorb to the surface may be of sufficient mass and concentration to contribute significantly to the frequency shift. Again, this behaviour is not always deleterious because it has found application in specialised analysis. Okahata and Ariga (1987) have performed *in situ* investigations on the deposition of Langmuir-Blodgett (LB) films, Okahata, Ebato and Taguchi (1987)

detected the adsorption of bitter substances on a lipid bilayer-coated quartz microbalance. Okahata and Ebato (1989) used a quartz microbalance to determine the smectic/nematic phase transition in liquid crystal and lipid multibilayers (these detections were performed with the crystal in air). Figure 3.14 illustrates the phenomenon of adsorption on a crystal in a liquid medium.

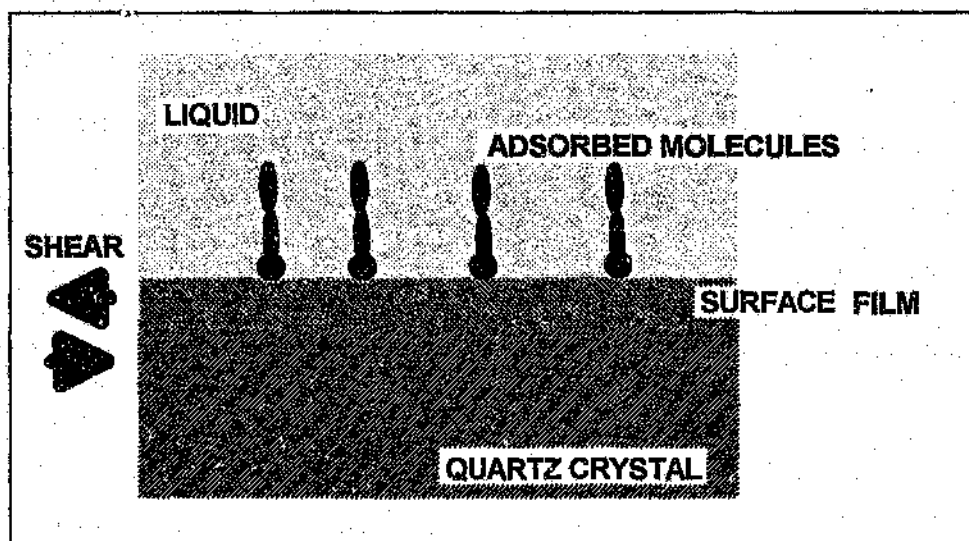


Figure 3.14 Adsorbed species contribute to mass of a crystal resonator in shear mode oscillation.

Absorption of ions into a surface film will affect the resonance frequency of a quartz microbalance. For example, poly(tetracyanoquinodimethane) electrodes were found to incorporate solvent molecules and ions upon electrochemical cycling (Inzelt 1990). Quartz microbalance studies of processes on polymer electrodes (operated in the shear mode) are subject to spurious results unless account is taken of changes in the viscoelastic properties of the

material, which may occur (Ward, Wang and Frostman 1992).

3.4.2.4 Effect of surface stress on frequency change

Newly-formed films may be stressed for a period of time, and absorption of atoms into a film may bring about surface stresses. Frequency change is effected by the surface stresses of the electrodes. These effects may be used as analytical probes. Heusler, et al. (1988) measured mass and surface stress on a QME. Gräsjo and Seo (1990) measured the absorption of hydrogen and deuterium into palladium during electrolysis, by observing the deviation from the Sauerbrey equation. Heusler and Pietrucha (1992) also investigated the surface stress of the Pd and H₂ or D₂ system, using a QME.

3.5 ELECTROCHEMICAL APPLICATION OF THE QUARTZ CRYSTAL MICROBALANCE

3.5.1 Introduction

Early use of oscillating quartz piezoids were made to determine mass changes on the crystal by virtue of molecules condensing from the gas phase. Examples of this include monitoring of the coating thickness in metal evaporation coating units. The initial

applications of the quartz microbalance to condensed phase analysis were achieved by making an initial frequency measurement in air, or a controlled environment, deposition of the material of interest in liquid and finally drying and re-measuring of the resonance frequency (Nomura and Hattori 1980). Later experiments were performed with piezoids immersed in organic liquids (Nomura and Okuhara 1982). Electrolytes were avoided because these would cause a closed circuit between the two poles of the crystal (i.e. shunting). The work by Bruckenstein and Shay (1985) paved the way for a two-pronged electrochemical technique when the QCM was first used in aqueous solution. By isolating one of the crystal faces from contact with solution, electrical shunting was avoided. In this manner, the standard electrochemical methods (voltammetry, potentiometry, amperometry) could be exploited, while performing simultaneous *in situ* gravimetry.

3.5.2 The quartz microbalance electrode

One of the faces of the quartz crystal serves a dual purpose in the QME. Whereas the electrode of one face of the crystal is isolated from solution, the other is immersed and connected to an electrochemical instrument such as a potentiostat, as well as to the oscillator and frequency counting instrumentation. This electrode can thus serve as a working electrode (WE) in an electrochemical cell. The counter and reference electrodes (CE and RE, respectively) are connected to the potentiostat in the usual manner. It

is thus possible to perform controlled potential, controlled current or open circuit experiments on a crystal electrode while it is operating as a piezoid. Judicious choice of circuitry and filtering allows the two sections of the QME instrument to operate independently.

3.5.3 Electronic circuit considerations for the quartz microbalance electrode

Standard voltammetric or amperometric electrochemical techniques rely on the application or measurement of a direct current. If an a.c. component is present at the WE, it is necessary to decouple (separate) it from the required d.c. signal. Two methods exist whereby this can be achieved.

3.5.3.1 Use of a common ground potential

For the purposes of this discussion, oscillators will be divided into two categories - one where one face of the crystal is at ground potential and the other where neither crystal face is held at ground potential. Two examples of circuits which include a ground-potential electrode are the Clapp oscillator and Pierce oscillator (Figure 3.7 and Figure 3.8, respectively).

A potentiostat which employs a grounded WE, such as the Wenking or Mintek design, may be successfully connected to the crystal (as a component of the QME)

without the risk of interfering with the oscillator circuitry or the oscillator interfering with the electrode potential. Weil and co-workers (Benje, et al. 1986) used this type of QME for studies of dissolution of nickel films.

3.5.3.2 Inductor filtering for non-grounded crystals

Circuits employing transistor-transistor logic (TTL) gates are designed such that neither crystal face is at ground potential. Figure 3.9, Figure 3.10 and Figure 3.11 are circuits for oscillators which have neither crystal face grounded. These are the Colpitts, Integrated and Dual-input NAND-gate oscillators respectively.

Bruckenstein and Shay (1985) used a parallel-resonance crystal oscillator. It was necessary to insert an inductor between the potentiostat and crystal (WE) electrode to remove the a.c. component of the current from the electrochemical signal. The principle of operation is that inductors are open-circuit elements to alternating current but closed-circuit to direct current.

3.5.4 Control and design of Quartz Microbalance experiments

3.5.4.1 Frequency measurement

The most convenient way to determine the resonance frequency of a crystal oscillator circuit is by means of a frequency counter. These instruments preferably have the following attributes:

- measurement of frequency changes to 0.01 Hz depending on instrument specifications
- sensitivity to signal in the order of 20-30 mV RMS depending on frequency and instrument specifications
- transfer of readings to an automated data logging device (e.g. computer) via either a digital or analogue interface
- multi-channel input allowing for use of reference signal if circuitry requires this feature.

3.5.4.2 Current and potential control and measurement

It has been stated that the QME is a two-pronged analytical tool. Measurement of frequency (mass) change is the one prong and an electrochemical technique, e.g., voltammetry, is the second. Thus electrode current and potential must be known simultaneously with resonance frequency. If a computer is used as the data logging device, it can

be set up to monitor and control electrochemical parameters as well as to read frequency. Many potentiostat/galvanostat instruments are equipped with output poles for external monitoring or control of the electrode potential or current. A computer equipped with digital/analogue interface circuitry (DA/AD) can perform this function. Voltage resolution depends on the DA/AD card in use and may vary from 0.61 mV for a 14-bit device to 2.4 mV for a 12-bit device if the measurable range is ± 5 V. Reading of frequency and current, for example, can be done in a fraction of a second and the rate of measurements is usually limited by the frequency counter gate time.

3.5.4.3 Data logging and manipulation

The data obtained by the techniques described above can be processed on line if time overheads are not a consideration. It is also possible to store the data by the usual magnetic means for processing after completion of the experiment.

3.5.5 Examples of the electrochemical applications of the quartz microbalance electrode

Apart from the applications cited in the sections above, the QME has been used in corrosion study (Hager, Reudisueli and Beuhler 1986, Chandler et al. 1991), as well as for the study of anodic deposition of FePO_4 from ferrous ions on gold (Seo et al. 1992).

The formation and disappearance of oxide or hydroxide films on metal surfaces has been monitored with the QME (Müller et al. 1988, Deakin and Melroy 1989, Bernard et al. 1991). Hessami, Armstrong and Kanazawa (1992) have achieved controlled hydrodynamic conditions at the QME by directing a jet of electrolyte at the electrode. In this manner they were able to measure the rates of electrodeposition and dissolution of copper and nickel thin films as a function of electrolyte velocity. Schmidt et al. (1993) investigated the deposition of metals from dilute solutions, in particular, for the determination of trace amounts of copper and lead in solution. Here, the QME was used in conjunction with anodic stripping voltammetry. Electrochromic materials are currently of great interest to electrochemists, and the research in this field has not ignored the QME. Ostrom and Buttry (1988) have used cyclic voltammetry and potential step techniques with the QME to investigate the properties of thin films of electrochromic diheptylviologen bromide. Bourkane, Gabrielli and Keddam (1988) were amongst the first to incorporate a.c. impedance techniques with the QME.

A growing number of research groups are using the QME to study diverse electrochemical and solid/solution interface processes. The citations given above are by no means exhaustive.

The description of the quartz microbalance theory has also been limited in scope. Two of the most recent reviews on the subject are the comprehensive article

by Buttry (1991) and that by Buttry and Ward (1992) in which attention is given to applications, techniques and theory. In the latter review, 133 references are cited covering the twelve years of *in situ* electro-gravimetric measurements using the quartz crystal microbalance (8 years in aqueous solution).

CHAPTER 4

LITERATURE SURVEY -

ELECTROLESS PLATING

CHAPTER 4 LITERATURE SURVEY - ELECTROLESS PLATING

4.1 GENERAL STUDIES IN ELECTROLESS PLATING

In common with many great scientific discoveries, electroless plating was invented by accident. The serendipitous event occurred while research was being conducted on improving electrolytic nickel plating bath properties. The discoverers (Brenner and Riddell 1946) explained their observation simply by reporting the phenomenon as a surface catalysed reduction of nickel by hypophosphite, producing an increasingly acidic solution.

Within one year of the initial publication a minimum of two patents had been filed, relating to the topic. To date, citation index and abstract searches reveal that hundreds of publications relating to electroless plating exist. One of the reasons contributing to this wealth of literature is the usefulness of electroless plating in the electronics industry. This industry has grown at a tremendous rate over the last forty years, with the demand for ever smaller, higher density circuitry requiring further research into fabrication techniques, including electroless plating. In the Proceedings of the Symposium on Electroless Deposition of Metals and Alloys, edited by Paunovic and Oh (1988), a number of papers dealing with the use of electroless plating and electronic circuitry are presented. The requirement for reliable, high density magnetic recording media in the computer industry has increased. The properties of certain electroless alloys

are suitable for this application. In his Ph.D. thesis, Homma (1992) gives an in depth review of the developments in this field. Many recent publications address the tailoring of electroless deposits, for example, bevel plating by anisotropic electroless nickel deposition (van der Putten and de Bakker 1993a and 1993b), and the prevention of recrystallization by annealing of fine-grained copper deposits (Mak et al. 1993). Sricharoenchaitkit (1993) used an electroless nickel film to act as a plasma barrier in an oxygen magnetron-enhanced reactive ion etching procedure.

Early mechanistic studies, published a few years after the discovery of electroless plating, investigated the effect of some fundamental parameters on electroless nickel plating rate (de Minjer and Brenner 1957). These included pH and component concentrations. The effect of inhibitors was also studied, as well as the composition of precipitates arising from bath decomposition. Various organic acids were investigated as accelerators. The addition of certain inhibitors (thiourea, selenic acid, potassium thiocyanate) resulted in a change in the overpotential of hydrogen evolution on the substrate. Plating rates were determined gravimetrically.

The possibility that the mechanism included the activation of nickel by the discharge of hydrogen was considered. These authors felt that the rate of hydrogen evolution could influence the rate of nickel deposition.

Levy (1963) proposed that most electroless plating reactions take place by a single mechanism. This hypothesis was based, in part, on the observation that all reducing agents used in electroless plating, up to

that time, contained hydrogen atoms, and gaseous hydrogen was always one by-product of electroless plating. Levy noted that a common factor amongst metals which were capable of being electrolessly plated was the presence of, or the ability to form inner orbital electron vacancies. Levy also critically assessed mechanistic work previously published. Reference was made to work by Cahill (1957) which showed that copper could be plated from solutions of Cu^{2+} and formaldehyde as a reductant, even when the reductant and metal ion solutions were separated by a porous frit, ruling out a direct chemical step between the metal ions and reducing agent. That is to say, a purely electrochemical mechanism was suggested. With this type of mechanism, interaction between the metal ions and any reducing agent species or intermediate is not required.

The influence of solution agitation on electroless plating rates was investigated in detail (Feldstein and Amodio 1969). Both electroless copper and nickel baths were investigated, with acidic and alkaline formulations. Trends observed in acidic and alkaline nickel baths led these authors to conclude that a similar mechanism existed for the two pH regimes. It was found that agitation has the greatest effect when the activation energy is high, bath temperature is low and agitation is achieved by mechanical stirring. For example, a low temperature alkaline nickel hypophosphite bath, with plating rate independent of Ni^{2+} concentration, was shown to have a plating rate independent of agitation at 35°C but to exhibit lower plating rate with increased agitation at 20°C . A low temperature nickel boron bath exhibited plating rate independent of agitation at 25°C but dependent on agitation at 35.5°C .

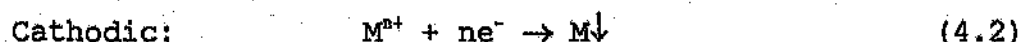
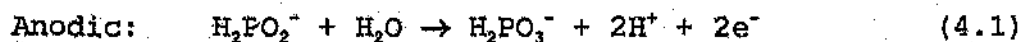
Potentiometric determination of the hypophosphite species in electroless nickel baths was investigated as an analytical technique for monitoring an industrial electroless process (Feldstein, Lancsek and Amick 1970). This was performed as a necessary maintenance of industrial electroless baths require the concentration of the reducing agent to be within certain limits. It was shown that chemical species known to be inhibitors of the hypophosphite-reduced nickel system could be used as titrants for the hypophosphite anion. Thiourea was one such titrant investigated. Paunovic (1980) described an electrochemical control system for electroless copper baths, using chronopotentiometry and voltammetry. It was suggested that the computerised monitoring and control of more than one bath component would be possible once a data base of ideal responses was collected.

The extensive research in the field of electroless plating has led to the proposal of many different mechanisms. These mechanisms have been supported by numerous painstaking and ingenious experiments.

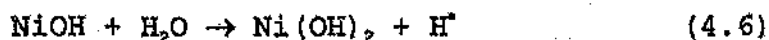
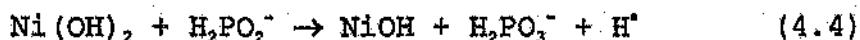
In a comprehensive paper on electroless plating mechanisms, observations of previous workers were brought together in an attempt to identify plausible and implausible mechanisms (Salvago and Cavallotti 1972). These authors presented a review of the first twenty-seven years of study in the field. A second comprehensive discussion on general electroless plating mechanisms was made by van den Meerakker (1981b). Both of these reviews scrutinised mechanisms in terms of available experimental results and postulated new reaction sequences which appeared to better fit the data, including those from their own research.

Van den Meerakker (1981b) proposed a uniform, general mechanism for different bath combinations and substrates. Listed below are the various pre-existing mechanisms on which his discussion was based. Proponents are as cited by van den Meerakker.

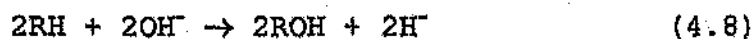
(i) The Pure Electrochemical Mechanism



(ii) The Metal Hydroxide Mechanism



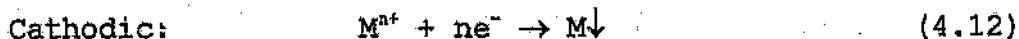
(iii) The Hydride Ion Mechanism



(RH is formaldehyde or hypophosphite)

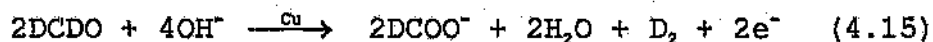
(iv) The Atomic Hydrogen Mechanism





(RH is formaldehyde, hypophosphite or borohydride)

Mechanism (i) has been suggested to be inadequate mainly because it is inconsistent with experimental results identifying the origin of the evolved hydrogen. Studies by Ogura, et al. (1990), where deuterated formaldehyde was used, support results cited by van den Meerakker to this effect. That is, the evolved hydrogen was found to originate from both the reducing agent (HCHO) and the solvent (H_2O). However, ECMS experiments performed by Jusys and Vaškelis (1992a) rejected outright the conclusion drawn by Ogura et al. By showing that the evolved hydrogen originates from the formaldehyde alone (4.15 and 4.16), Jusys and Vaškelis were able to give evidence in support of an electrochemical mechanism. The result of the work by Jusys and Vaškelis (1992a), for oxidation of heavy formaldehyde in water, was

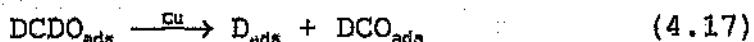


and for oxidation of formaldehyde in heavy water

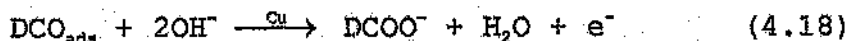


Jusys and Vaškelis suggested that the methodology adopted by Ogura et al. led to spurious results. They also pointed out that the oxidation of formaldehyde was not likely to be an elementary process. The catalytic mechanism of oxidation and dehydrogenation of formaldehyde (reactions 4.19 and 4.20, van den Meerakker 1981b) was cited in this regard. The

mechanism of the copper catalysed process, using DCDO, was given by these workers as



(dissociative adsorption on Cu, production of labile formyl)



(oxidation of the formyl moiety)

Recombination of the adsorbed D (or H in the case of HCHO) results in D₂ or H₂ respectively.

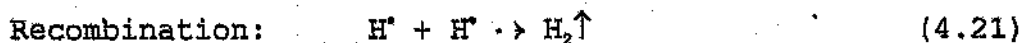
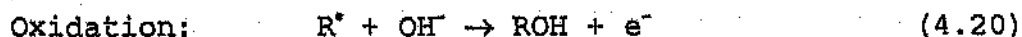
Experiments carried out in two-compartment cells, such as in the frequently cited work by El-Raghy and Abo-Salama (1979), using a copper(II)-tartrate/formaldehyde bath, exposed a weakness in mechanism (ii) since they proved that the chemical interaction described by this mechanism was not a requirement for electroless plating. (Donahue (1979) discussed the paper by El-Raghy and Abo-Salama, pointing out that experiments in separated compartment cells did not reveal certain interactions which might be expected in electroless plating reactions). The result presented by El-Raghy and Abo-Salama (and other works cited by Donahue) may thus represent a special case where independent anodic and cathodic processes could result in autocatalytic deposition.

Mechanisms (iii) and (iv) imply that hydrogen evolution should be at least equivalent to metal deposition. This is not what is observed in practice, as noted by van den Meerakker. Since there were flaws in all four mechanisms, van den Meerakker formulated a new mechanism consistent with experimental data.

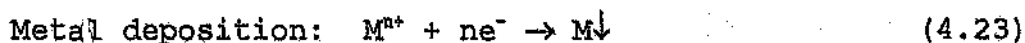
His mechanism is composed of the following steps:

Anodic:

Dehydrogenation:



Cathodic:



Hydrogen evolution:



Reactions 4.23 and 4.24 reflect behaviour in basic solution. The corresponding processes in acidic solution are thus



and



respectively. The co-deposition of phosphorus and boron with nickel in baths reduced by $H_2PO_2^{-}$ and boron compounds respectively was attributed to a third cathodic process.

The mechanism described above was claimed to apply to the following reducing agents: borohydride, dialkylamine borane (generic), hydrazine, formaldehyde

and hypophosphite. Detailed hypothetical reaction sequences were given.

Both the catalytic nature of electroless plating and some aspects of the mixed potential theory can be reconciled with this mechanism. However, the interdependence of the two half-reactions, which had previously been proposed by Donahue (1972), was not addressed.

Donahue's (1972) treatment of mixed potential systems emphasised the possibility of interdependence of the half-reactions but was subject to the assumption that Tafel slopes for the respective half-reactions in the complete bath are not different from those observed in electrode kinetic studies of the individual processes.

Bindra and Roldan (nee Tweedie) (1983) investigated the controversial issue of the applicability of the mixed potential theory to the mechanism of electroless plating. In their first (Bindra and Tweedie, 1983) of a series of publications, the effect of mass transport and concentration of reductant or oxidant on the mixed (plating) potential in a copper bath was examined. In this case, formaldehyde was used as the reducing agent. Evidence of the interaction of formaldehyde oxidation and copper reduction partial processes was noted, on the basis of comparison of the Tafel slopes obtained for formaldehyde oxidation in the plating solution and in the anolyte alone. Small differences between the two slopes were attributed to coupling of the anodic and cathodic partial processes, and to catalytic effects of the surface. A transfer coefficient of 0.41 for the anodic process was suggested to indicate specific adsorption of the reacting species. These conclusions may be contrasted to those of Paunovic (1968), who

attributed small differences in Tafel slopes to poor reproducibility on the solid electrode. The second paper (Bindra and Roldan 1985) reported on the catalytic activity of various metals for the oxidation of formaldehyde as determined with the aid of cyclic voltammetry. Comparison between formaldehyde oxidation in acidic and alkaline media were made. Decomposition of formaldehyde on metals takes place with hydrogen evolution if the free energy for hydrogen adsorption is positive (e.g. copper). On metals for which the free energy for hydrogen adsorption is negative, e.g. palladium, low catalytic activity towards formaldehyde oxidation was noted, and it was pointed out that autocatalytic deposition of these metals using formaldehyde as the reducing agent was not possible. Part three of the series (Bindra and Roldan 1987) examined the interaction (or interdependence) of the partial processes in electroless plating. The various possibilities of kinetic control of the overall process were considered and a mechanism was proposed. These workers suggested further that the overall mechanism of electroless plating could be determined by observing the mixed potential behaviour while varying the concentrations of the reacting species under controlled hydrodynamic conditions. This was limited to the cases of diffusion or electrochemical control. Under mixed control, more complicated theoretical treatment than that presented would be required.

In a three part series, Flis and Duquette (1984a, b, c) investigated the role of the catalytic substrate on the nucleation and growth of electroless nickel deposits. Iron, nickel, nickel-phosphorus, molybdenum activated with palladium, copper, activated copper, gold and platinum were the substrates investigated by these workers. Techniques used in this work included linear

sweep voltammetry and scanning- and transmission electron microscopy (SEM and TEM, respectively). Nickel phosphorus alloys exhibited higher catalytic activity than pure nickel for the oxidation of hypophosphite and the electroless deposition of nickel. This phenomenon was attributed to low stability of surface oxides on the alloy as opposed to the pure nickel. Potential arrests during the incubation period of electroless nickel plating were noted on various substrates. These arrests were associated with oxide dissolution. The intrinsic catalytic activity of nickel and Ni-P was considered to be almost identical. Small amounts of electrolytically deposited nickel on copper, gold and palladium was found to enhance the electrocatalytic activity of these metals towards H_2PO_2^- oxidation, a phenomenon attributed to synergistic effects.

Vaškelis, Jagminiene and Prokoptchick (1986) and Vaškelis and Jagminiene (1987) used a glass electrode, covered in Pd-activated nylon netting, to measure the pH of the solution as close as possible to the solid / solution interface. In the former work, the surface layer pH in an electroless nickel bath with various additives was measured, while in the latter, an electroless copper bath was studied. These workers cautioned against the use of pH measurements in the bulk solution region of an electroless bath in kinetic studies, because a significant difference was noted between the interfacial and bulk pH.

Paunovic (1985) introduced the potentiostatic high overpotential technique in studies of electroless copper deposition in order to provide correlation between electrochemical and structural kinetic parameters. Nucleation parameters (number of nuclei, the nucleation rate constant, and the geometry of

nuclei) were thus determined by an electrochemical method.

Homma and co-workers (1991) employed TEM to define and compare the growth patterns of electroless copper and nickel deposits. The differing ability of these metals to adhere to ceramic substrates was attributed to the observation that in Ni-P deposition, finite nucleation occurs, allowing the deposit to grow into clefts in the substrate. In the case of copper, however, growth takes place along specific crystallographic axes, and large, orientated particles form which do not mechanically key in to the substrate. By observing the initial growth stages in electroless Ni-P using *in situ* scanning tunnelling microscopy (STM), Homma, Yamazaki and Osaka (1992) were able to confirm that the deposit grows by means of continuous nucleation of grains. The grains grow to a critical size, at which point new grains are nucleated on the surface. This is in contrast to the situation in electrolytic deposition, where grains grow to much larger dimensions. Gómez and co-workers (1992), studying electroless nickel, noted that under controlled potential and in the presence of certain sulphonated additives, progressive nucleation (similar to that observed by the previous workers) was found in the formation of electrodeposited films.

A detailed review on the electrochemical, catalytic and mechanistic aspects of electroless plating, as well as methods of determining deposition rates, was published by Ohno (1991). The electrochemical behaviour of electroless baths was discussed in terms of the mixed potential theory and the polarisation behaviour of the bath in the absence of one of the active components. It was shown that the sum of the net current density at a given potential, obtained from polarisation curves

(presented as logarithm (current density) vs. potential) for each of the reducing agent and metal ion in isolation, did not equal that measured in the full bath, thus proving interaction of the partial processes. The following observations point directly to the importance of the catalytic activity of the depositing metal:

- electroless deposition occurs exclusively on an active surface;
- if the surface is not inherently active then some form of activation procedure is required (e.g., immersion in a tin/palladium solution);
- an induction period is frequently observed prior to the onset of steady state plating;
- the selection of reducing agents for use in electroless baths is limited;
- the combinations of metal ion and reducing agent which function as electroless baths are specific;
- in many cases, hydrogen evolution accompanies electroless plating, and the hydrogen originates from the reducing agent;
- compounds known to be poisons for catalysts, e.g., thiourea and mercaptobenzothiazole, act as stabilizers in electroless baths.

A diagrammatic representation of the activity of certain metals for the oxidation of reducing agents at a reference current density was given, and is reproduced in Figure 4.1. It was noted that no correlation exists between the catalytic activity of a metal for H_2 evolution, and its catalytic activity for the oxidation of the reducing agents.

The experimental results given by Ohno revealed three types of polarisation curves for the anodic oxidation of the reducing agent. These are illustrated in Figure

4.2. The shapes of these curves were reconciled by Ohno with a mechanism of the oxidation process. The kinetic equations of this mechanism were used to develop a computational model for predicting the shape of the polarisation curve under a given set of conditions. Results obtained from the model were presented, and were shown to compare well to experimental observations.

Ohno also presented a discussion of the use of the polarisation resistance technique and a.c. impedance methods for prediction of the electroless plating rate.

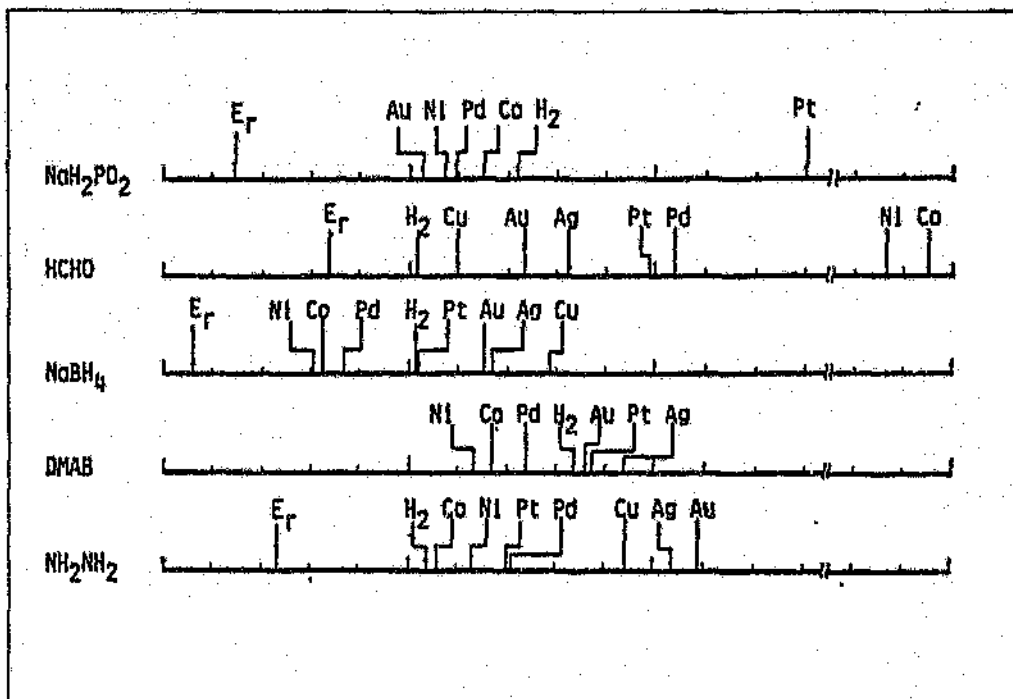


Figure 4.1 Catalytic activities of metals for the anodic oxidation of five reducing agents. E_r = standard reduction potential of the reducing agent, H₂ = reversible hydrogen potential (potentials at 10⁻⁴ A cm⁻²) (Ohno 1991). The bath compositions were specified by Ohno, respectively.

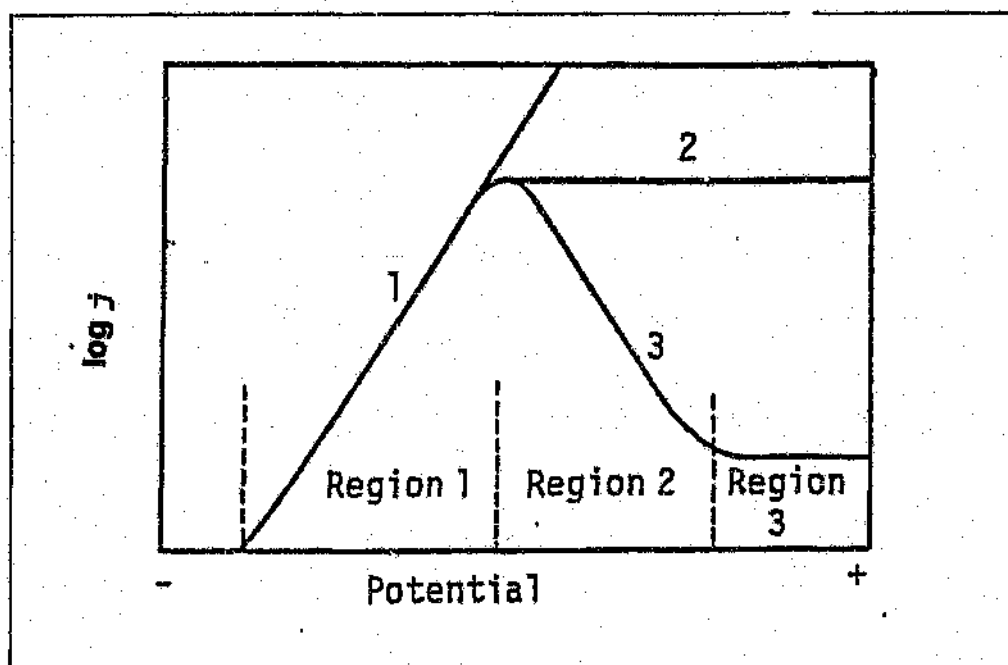


Figure 4.2 Schematic representation of the three types of $\log(\text{current density})$ vs. potential curve observed experimentally (Ohno 1991). 1 = Tafel behaviour, 2 = limiting current, 3 = volcano shape

The following investigations of deposition rates and rates of reductant oxidation in complete and modified baths corroborated Donahue's finding (1972) that the two partial reactions in some electroless plating baths are interdependent: Bindra and Roldan (1987) using a rotating disc electrode for electroless copper with HCHO reductant; simultaneous *in situ* gravimetric / net electrode current measurements: Wiese and Weil (1987a) (electroless copper) and (1987b) (separation of partial processes using an electronic circuit), Orchard (1988b) rotating disc, electroless nickel reduced by H_2PO_2^- , Feldman and Melroy (1989) - QME studies of electroless copper with HCHO reducing agent, Gafin and Orchard (1992) - QME studies of electroless nickel with H_2PO_2^- reducing agent. The discovery of interdependence opened many more possible avenues of research and interpretation, since independence of the anodic and

cathodic reactions is fundamental to the classical mixed potential theory of Wagner and Traud.

Thus, a chemical interaction of bath components (including reaction products) combined with purely electrochemical steps has become a more likely genre of mechanism for electroless plating.

4.2 ELECTROLESS NICKEL

Autocatalytic or electroless deposition was first observed with nickel (Brenner and Riddell 1946). The electroless nickel deposition process has received considerable attention for historic reasons. However, this attention could only be sustained if some commercial value could be attached to electroless nickel. The magnetic, wear and corrosion-resistant properties of electroless nickel alloys have ensured continued attention (Bayes and House 1991).

Feldstein (1970) published detailed information regarding two room temperature electroless nickel baths, both of which operate at alkaline pH. Studies of deposit composition, activation energy, solution complexes and plating rates were made. These baths have proven to be useful for mechanistic studies because loss of the most volatile component (ammonia) is much lower than for baths operating at elevated temperatures (Orchard 1988b).

Studies by Feldstein and Lancsek (1971) of the mixed potentials of nickel plating baths yielded mechanistic postulates accounting for the phosphorus content of the electroless deposit and the hydrogen evolution during plating. In this work, it was proposed that the

reduction of hypophosphite was not directly involved in the formation of elemental P. The phosphorus was thought to be a product of reaction of a short-lived intermediate, namely, metaphosphorous acid (HPO_2). Jusys, Liaukonis and Vaškelis (1992) utilised electrochemical mass spectrometry (ECMS) to investigate the mechanism of electroless Ni-P deposition. Experiments were performed with deuterated and ordinary hypophosphite, and H_2O and D_2O . In addition, experiments were performed at open circuit and controlled potential in the absence of one of the electroactive species. These workers suggested possible mechanisms of hydrogen evolution and P incorporation. Metaphosphorous acid did not, however, appear in their mechanism. (ECMS allows the monitoring of gaseous products of electrode processes. For example, a porous Teflon membrane is coated with nickel, which serves as the working electrode. Gaseous products are sucked through the membrane during the electrode reaction and are analysed by mass spectrometry. Judicious choice of deuterated or other isotopically labelled reagents expedites mechanistic studies.)

Zeller and Landau (1992), and Harris and Dang (1993) investigated phosphorus incorporation into Ni-P alloys formed by electrodeposition. Both groups favoured an indirect mechanism of P incorporation, with a PH_3 intermediate from a phosphorous acid starting material.

Gorbunova, Ivanov and Moiseev (1973) used sodium borohydride as a reducing agent for the electroless deposition of Ni-B alloys. A mechanism was proposed for this process and physical properties of the deposit were described. These workers found that Ni-B alloys containing 4.3% B consisted of two phases: a solid solution of B and H in fcc β -nickel, and an amorphous

phase. Alloys with higher fractions of boron were found to be amorphous. Lelental (1974) discussed the effect of substituents on amine boranes (viz., ammonia-borane, mono-methylamine borane, and di- and tri-methylamine borane) on the activity of autocatalytic deposition. A mechanism for the electroless reaction was proposed. Molecular orbital theory was used to explain aspects of the reactivity of the various amine boranes, in terms of the strength of the N-B bond. The critical coverage of Pd for electroless nickel plating with various amine boranes are given in Table 4.1.

Table 4.1 Critical coverage of Pd for catalysis of electroless nickel plating with various reducing agents, and relative N-B bond strengths (Lelental 1974).

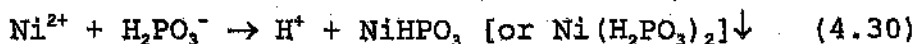
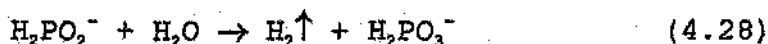
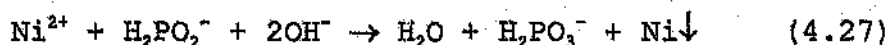
Reducing agent (0.17 mol L ⁻¹)	Critical coverage of Pd /atoms cm ⁻²	Relative N-B bond strength*
H ₃ NBH ₃	3.7 x 10 ¹³	0.4728
CH ₃ H ₂ NBH ₃	1.5 x 10 ¹⁴	0.4798
(CH ₃) ₂ HNBH ₃	5.8 x 10 ¹⁴	0.4892
(CH ₃) ₃ NBH ₃	>1.7 x 10 ¹⁶	0.5049

* Measure of N-B overlap

It was subsequently shown (Lelental 1975) that a copper dopant in an electroless Ni bath significantly improved the autocatalytic activity of the deposit when compared to pure nickel. It was proposed that this improvement was a consequence of the promotion of weak chemisorption of hydrogen on the surface. Lelental cited a number of works dealing with the enhanced catalytic activity of the Ni-Cu alloy over pure Ni, and the hypothesis was that the effect was due to d-band holes in the alloy. Molecular orbital theory arguments were used to describe the formation of weak, as opposed

to strong chemisorption of H_2 as a factor which improved electrocatalytic activity. Van den Meerakker and de Bakker (1990) also demonstrated that alloying influenced the electrocatalytic activity under potentiostatic conditions.

The substrate composition is an important factor in mechanistic considerations (van den Meerakker 1981a). Marshall (1983) reported low rates of $H_2PO_2^-$ oxidation at non-catalytic surfaces, as compared with nickel or palladium which were catalysts. The catalytic oxidation of $H_2PO_2^-$ on Ni was investigated in some detail by Jusys, Liaukonis and Vaškelis (1991), using ECMS. Anodic dissolution of nickel was suggested to influence the catalytic nature of the surface. Dissolution of nickel oxide, resulting in an "incubation period" has been proposed to be necessary prior to electroless plating (Flis and Duquette 1984a). It is important, however, to mention the difference in catalytic activity of pure nickel and Ni-P alloys. Whereas pure Ni has activity for the catalytic decomposition of $H_2PO_2^-$ (Marshall 1983), it shows reduced activity to electroless plating (Flis and Duquette 1984a, Hung and Ohno 1990). The Ni-P alloy, however, readily catalyses the electroless process. Sugita and Ueno (1984) proposed the following mechanism for the incorporation of phosphorus in the electroless deposit:



With regards the formation of an oxide film during anodic dissolution, Diegle et al. (1988) performed

detailed XPS studies on an alloy of Ni and P. These workers used XPS to assess the effect of anodic polarisation of an Ni-P alloy in sulphuric acid. A model for the passivation of a Ni-P alloy was proposed (Figure 4.3). The model illustrates the formation of a P-enriched layer close to the surface during anodic polarisation, in sulphuric acid medium, followed by oxidation of P to form a barrier layer of adsorbed H_2PO_2^- . This constitutes the passive state of the alloy. In the transpassive state, H_2PO_2^- is oxidised to H_3PO_3 , and stoichiometric alloy dissolution takes place through the P-enriched layer.

The technique of XPS is useful in the characterisation of a catalytic surface, and is thus often applied to catalytic materials at various stages in the history of the material, with respect to its active lifetime.

Hofmann and Weil (1993) expanded on the work of Diegle and co-workers by using a rotating ring-disc electrode to characterise oxidation products of electroless Ni-P deposits. In addition, a QME was used for further characterisation of the oxidation state of phosphorus species. In this publication, it was proposed that the peak separation of the two phases in the Ni-P alloy (Benje et al., 1988) was due to passivation, and not due to differing thermodynamic stability of the phases. It was found that the oxidation of phosphinate (P^{1+}) ions is less hindered on the crystalline phase than on the glassy phase. During anodic oxidation of the Ni-P alloy, the major product (in respect of oxidation of P) is phosphate, with a minor product being phosphinate. Two possible mechanisms were given in which the possibility of both phosphinate and phosphonate intermediates was described. The phosphinate, which is readily oxidized on the crystalline Ni-P, forms a

stable adsorbate on the glassy phase, as described by Diegle et al. (1988). Passivation of the glassy phase is the consequence of this reaction sequence. Hofmann and Weil attributed the ready dissolution of the Ni-P crystalline phase to the strong electrocatalytic activity of this material to oxidation of the P^{1+} species, and presented a diagrammatic model of the oxidation mechanism of the Ni-P alloy (Figure 4.4).

Schematic cross section of passivity model.

Short term situation (1-~10 s of polarisation) shows transition between air-formed film and final barrier layer.

Long term situation ($\geq 10^3$ s of polarisation) shows near steady-state barrier of hypophosphite anion.

Schematic cross section of transpassive dissolution: High overpotential induces oxidation of adsorbed hypophosphite anion to H_3PO_3 , accompanied by stoichiometric alloy dissolution through an enriched P layer.

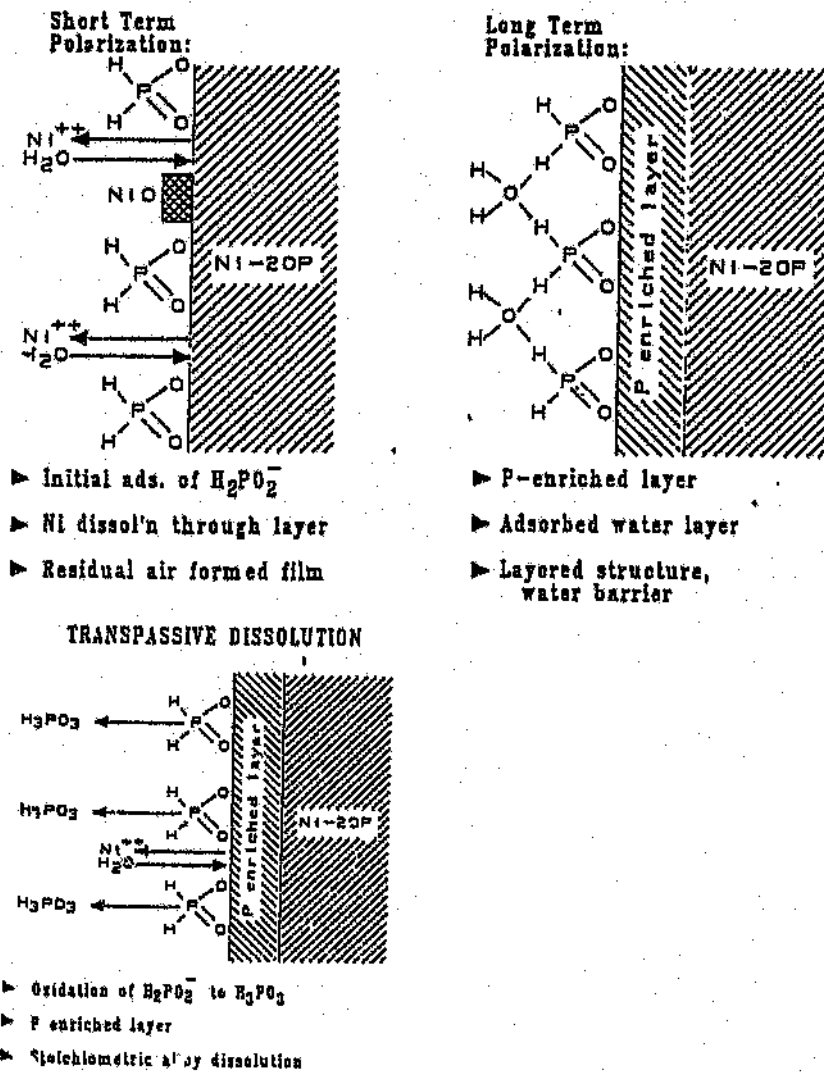


Figure 4.3 Passivation model of Ni-P alloy, resulting in the formation of a barrier layer of H_2PO_2^- (Diegle et al. 1988).

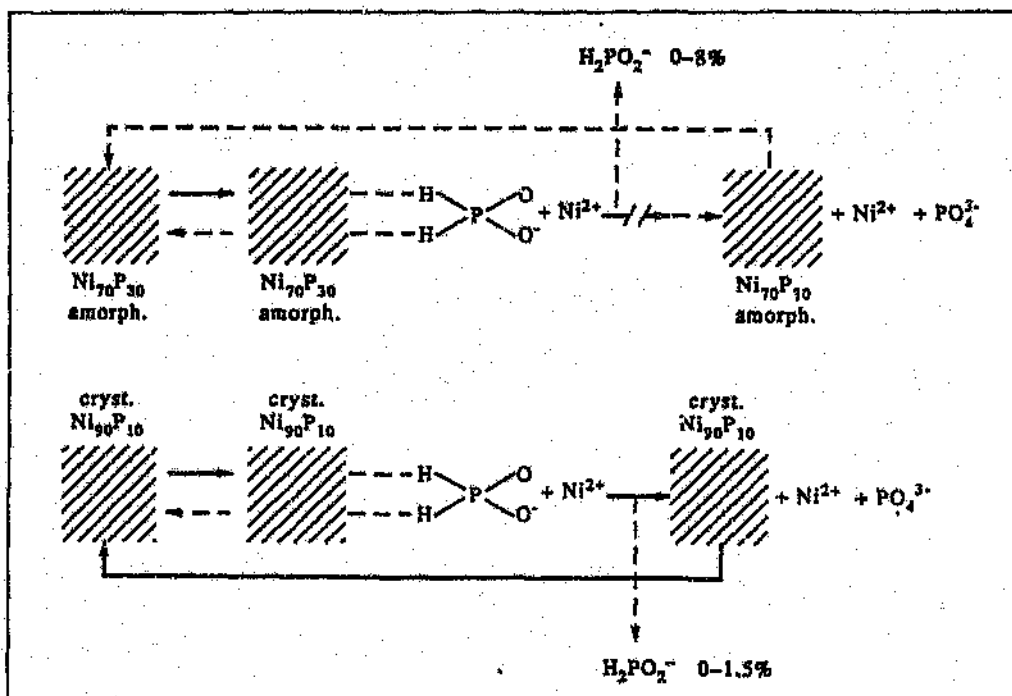
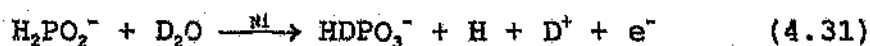


Figure 4.4 Schematic model of oxidation mechanism of Ni-P alloy, illustrating the formation of H_2PO_2^- (adsorbed) as an intermediate product (Hofmann and Weil 1993).

Jusys, Liaukonis and Vaškelis (1992) alluded to the influence of surface composition in their study of the mechanism of electroless Ni-P deposition. Using a pure Ni electrode at the start of each experiment, these workers observed the behaviour of an electroless Ni bath employing H_2PO_2^- as reducing agent. An incubation period was noted for a steady state to be established at open circuit. The mechanisms of the various cathodic and anodic processes occurring during electroless plating suggested by these workers follows, and falls into the "electrochemical" mechanism category. The use of D_2O clearly illustrates the mechanism.



The last three reactions are cathodic, the first being the anodic oxidation of H_2PO_2^- in D_2O . An enhancement of the rate of oxidation of H_2PO_2^- was observed when Ni^{2+} was present in solution, over the rate observed in the absence of this cation. This was attributed to enhanced catalytic activity of the constantly renewing surface.

The rate of reaction 4.31 was found to be about ten times greater than that of reaction 4.34, thus the influence of the latter on the gas composition could be neglected. The rate of reaction 4.31 showed dependence on the Ni^{2+} concentration only at low values, i.e., up to about 0.02 mol L^{-1} . This reaction was found to follow the kinetic equation:

$$\frac{d[\text{H}_2\text{PO}_2^-]}{dt} = k[\text{H}_2\text{PO}_2^-]^n [\text{Ni}^{2+}]^0 = [\text{H}_2\text{PO}_2^-]^n$$

(4.35)

where $n = 1$ at $0 < [\text{H}_2\text{PO}_2^-] \leq 0.02 \text{ mol L}^{-1}$

or $n = 0$ at $[\text{H}_2\text{PO}_2^-] > 0.1 \text{ mol L}^{-1}$ and k is the rate constant.

At controlled potential, the rate of reaction 4.33 was found to be related to the presence, or contemporaneous reduction of Ni^{2+} (reaction 4.32). No direct evidence was found which suggested that the phosphorus content of the Ni-P alloy was responsible for its enhanced electrocatalytic activity when compared to pure Ni. The enhanced electrocatalytic activity was related to a favourable structure of the surface formed during the deposition of the alloy.

Los and Lasia (1992), extending the work of Lian, Kirke and Thorpe (1991), have shown that amorphous Ni-B can

have higher electrocatalytic activity than similar crystalline materials. (This effect is complicated by surface area effects, and in the study by Los and Lasia, the method of preparation of the Ni-B alloys and Ni-B/Ni alloys was by powder pressing. Chemical treatment of these materials was found to increase the surface area exposed to solution as a result of selective dissolution, as well as to expose active sites or modify the surface to render it more active.)

Heat treatment of electroless Ni-P alloys has been employed in order to modify the hardness of the deposit. High temperature was shown to affect the stoichiometry and crystallinity of electroless Ni-P deposits containing 3.2 - 12.5 w/o P (Randin et al. 1967, Randin and Hintermann 1968, Lin and Lai 1989). It was confirmed that heating the deposit to temperatures greater than 300°C resulted in the formation of continuous Ni, and Ni₃P. Randin and Hintermann suggested that the as-produced deposit contained Ni₂P and Ni, the former phase accounting for almost all of the P in the deposit. It was noted that the detection limits of the analytical techniques were not low enough to identify the presence of a small concentration of elemental phosphorus in the Ni matrix. Lin and Lai showed that the as-deposited alloy was amorphous.

4.3 ELECTROLESS COPPER

Electroless copper plating has found considerable application in the electronics industry, primarily in the production of printed circuit boards. The technique of "through-the-hole" plating allowed engineers to manufacture circuit boards with tracks and components on both sides, thus contributing to the diminishing

size of electronic devices (McDonald 1984 p. 440). Early attempts at producing electrically conducting plastics involved the coating of polymer powders with electroless copper (Shorokhova and Kuz'min 1964) and the use of electroless deposits as base layers for electrodeposition of decorative metals (Krulik 1978). Plating of plastics by electroless techniques has become a popular method of producing relatively cheap decorative plumbing and automotive parts (Marcott and Spatola 1990).

Whilst research regarding the mechanism of autocatalytic deposition of copper has progressed considerably, a significant segment of the literature on electroless copper plating deals with bath stabilization, acceleration of plating rates and fine tuning of the morphology of the deposit. To achieve the desired effects, compounds not ordinarily required in the autocatalytic recipe have been added to the baths. These compounds have thus become known as additives. The effects of additives, and their modes of interaction with the fundamental bath components and plating surfaces has been well documented.

4.3.1 General and mechanistic studies

Donahue (1980) attempted to quantify the kinetics of electroless copper deposition by investigating the mass transport effects on the plating rate. In the absence of forced convection, microconvection as a result of H_2 bubble formation was found to be the mode of mass transport of greatest importance. Inhibition of the electroless process by the addition of ligands was reported as a subsequent part in a series on the kinetics of the electroless copper plating (Donahue et

al. 1982). Further work on the transport properties of some electroless copper plating baths was published by Donahue and co-workers (Ying et al. 1988). In this technical note the kinematic viscosity and densities of selected copper baths, as well as the diffusion coefficients of a number of cupric ion complexes, were determined.

Bindra and Tweedie (1983) described the copper(II)-EDTA electroless system, employing formaldehyde as the reducing agent, as being a mixed potential catalytic process with interdependent half-reactions. Experiments were performed using an RDE and varying copper ion concentrations. The mixed (plating) potential was found to increase with both rotation rate and copper ion concentration, and to decrease with a higher concentration of reducing agent. These results suggested a diffusion controlled cathodic half-reaction coupled with an activation controlled anodic half-reaction. Subsequently, Bindra and Roldan (1987) expanded on this work, both experimentally and by theoretical assessment of the relationship between the mixed potential and rotation rate of the RDE. The new results showed that Tafel slopes of the half-reactions in the complete bath and in catholyte or anolyte only, were significantly different. The inference is that independence of the half-reactions, as suggested by the original precepts of the mixed potential theory, was not exhibited in the copper(II)/formaldehyde system.

Kinetic investigations of the copper(II)/formaldehyde system were performed by Schumacher, Pesek and Melroy (1985). These workers employed a closed loop control system which automatically monitored and adjusted the concentrations of hydroxide ions, cupric ions and formaldehyde in order to maintain them within specified

limits. Deposition rates were measured using a quartz microbalance electrode (QME). Under conditions where the electroless deposition of copper was controlled by the rate of electron transfer (i.e. where mass transport of copper is not limiting), it was found that the reaction is first order in respect of the methylene glycolate anion and zero order in respect of the cupric ion. (Methylene glycol (MG) is the dominant form of formaldehyde in a basic solution. Dissociation of MG to the methylene glycolate anion then occurs.) Tam (1985) tentatively identified the major peak on a cyclic voltammogram of a copper bath (during the cathodic scan) to MG and its Cu^{2+} adduct. The precise electron transfer process giving rise to this peak was not given. Gottesfeld et al. (1986) speculated on the mode of electro-dehydrogenation of an adsorbed methylene glycolate anion (Figure 4.5). These workers levelled some criticism against van den Meerakker's (1981a) treatment of HCHO oxidation on copper, claiming that an incorrect expression for electrochemical H atom ionisation had been used in this work.

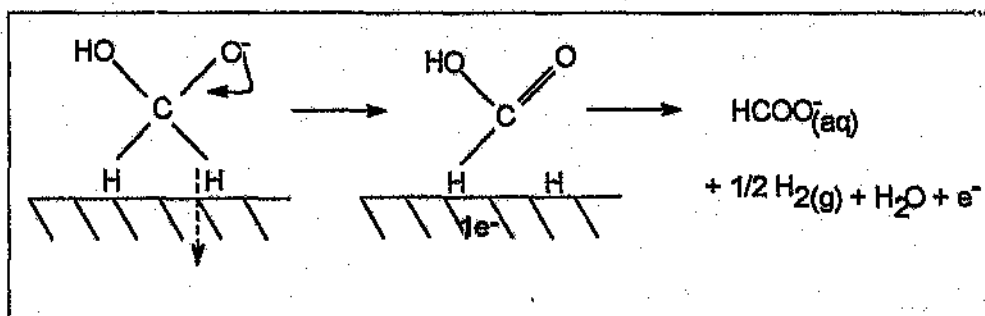


Figure 4.5 Schematic representation of the electro-dehydrogenation of an adsorbed methylene glycolate anion on a copper surface during electroless copper plating (Gottesfeld et al. 1986).

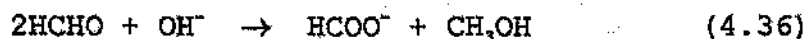
Wiese and Weil (1987a) employed a QME and an electrochemical cell capable of fast solution transfers in studies on autocatalytic copper deposition. No

evidence of direct electron transfer between reducing agent (HCHO) and metal ion (Cu^{2+}) was noted but the half-reactions were found to be interdependent. A parallel channel for the overall reaction including a direct electron transfer was mentioned as being possible, but most unlikely. Formaldehyde oxidation on copper surfaces was found to be enhanced when simultaneous copper ion reduction was taking place (and not simply when cupric ions were present in the solution). Formaldehyde was seen to generate a catalyst to enhance copper ion reduction. Electron transfer from the surface to the metal ions was suggested to take place via catalysts chemisorbed on the copper surface, e.g., the methylene glycolate anion. No evidence for direct adsorption of the copper(II)-EDTA complex to the electrode was found. When other ligands are present in solution, the possibility of formation of mixed complexes exists. These authors, however, showed that reduction of copper(II) could take place in a solution where no mixed complexes existed. It was also observed that the active, adsorbed species was capable of reducing more than one copper ion prior to desorption.

Similar results to those described above were reported by Feldman and Melroy (1989). *In situ* gravimetric measurements of copper deposition rates from copper(II)-EDTA complex, with formaldehyde as reductant, were made using a QME. The shapes of the current-potential curves for both half-reactions were shown to depend on the concentration of formaldehyde. In particular, the rate of copper deposition was found to be significantly enhanced even at low concentrations of HCHO (15 mmol L^{-1}). Catalysis of copper reduction in the complete bath was evidenced by the significant rate of copper deposition at potentials as positive as -0.6 V vs. Ag/AgCl, an important point, because in an

electroless plating bath, Cu^{2+} ions are stabilized by the complexing agents. The standard reduction potential of the $\text{Cu}(\text{EDTA})^{2-}$ complex is approximately -1.05 V vs. Ag/AgCl , and Feldman and Melroy noted that the foot of the voltammetric wave of reduction of this complex began only at about -0.9 V vs. Ag/AgCl (in the absence of formaldehyde). Catalysis of the reduction was clearly taking place in the complete bath. The formation of a complex of copper, EDTA and formaldehyde was suggested, but it was not certain whether this was a surface or solution species. Feldman and Melroy tentatively suggested a mechanism involving the adsorption, or formation, of the above-mentioned complex on the surface, followed by a concerted reaction in which copper was reduced and formaldehyde oxidised. The result of El-Raghy and Abo-Salama (1979) was acknowledged by these authors as contradictory to their observation, and the apparent mechanistic difference was attributed to the relative ease of reduction of the copper(II)-tartrate complex used by the earlier researchers.

Van den Meerakker and Scholtens (1989) followed the decomposition of formaldehyde in aqueous solution under conditions expected in an electroless copper bath. The kinetics of two modes of HCHO decomposition, namely the Cannizzaro reaction (4.36) and aldol condensation (4.37), were investigated. The former reaction was found, experimentally, to be the decomposition pathway below 70°C , while both reactions occurred above this temperature.



Expanding on earlier work (viz. Jusys and Vaškelis 1992a), Jusys and Vaškelis (1992b) used cyclic voltammetry in conjunction with ECMS for further studies of the copper - formaldehyde system. The electrochemical window between formaldehyde decomposition to methanol (cathodic) and CO_2 (anodic) was determined. Hydrogen evolution from HCHO and H_2O was determined as a function of pH, formaldehyde concentration, temperature and electrode potential. Catalytic dehydrogenation of formaldehyde was observed at open circuit conditions, and the deuterium tracer results were interpreted in terms of a two-stage catalytic dehydrogenation reaction starting with the methylene glycolate anion (this is formed as a result of hydration of formaldehyde in alkaline medium).

Hung, Hung and Ohno (1989) described a formulation for producing autocatalytic copper-nickel alloys. By including Ni^{2+} in the electroless bath, hypophosphite could be used to reduce both the Cu^{2+} and Ni^{2+} . The Ni in the deposit allowed the process to continue, whereas on pure copper the oxidation of H_2PO_2^- would not be catalysed. Hung and Chen (1989) found that addition of boric acid to a copper(II)/ H_2PO_2^- bath (which contained Ni^{2+}) assisted in the reduction of nickel(II), which in turn catalysed the oxidation of hypophosphite. It was found that only copper(II) complexes capable of forming dimeric structures showed significant plating rate.

Hung and Ohno (1990) presented polarisation curves for a copper(II)/hypophosphite bath and concluded that the process followed the classical mixed potential theory. These workers considered the possibility of side reactions or the interdependence of partial processes as reasons for discrepancies between polarisation curves obtained in complete baths and baths lacking in

metal ions or reducing agent. It was shown that the bath composition required nickel or cobalt ions and boric acid, in order to achieve autocatalytic copper deposition using H_2PO_2^- as reductant. This effect may be compared to the requirement of copper in electroless gold baths which use formaldehyde as reducing agent (Molenaar and Meenderink 1985). A pH effect was noted by Hung and Ohno, consistent with their proposed mechanism which included, as a first step, attack of OH^- on surface-bound H_2PO_2^- (Figure 4.6).

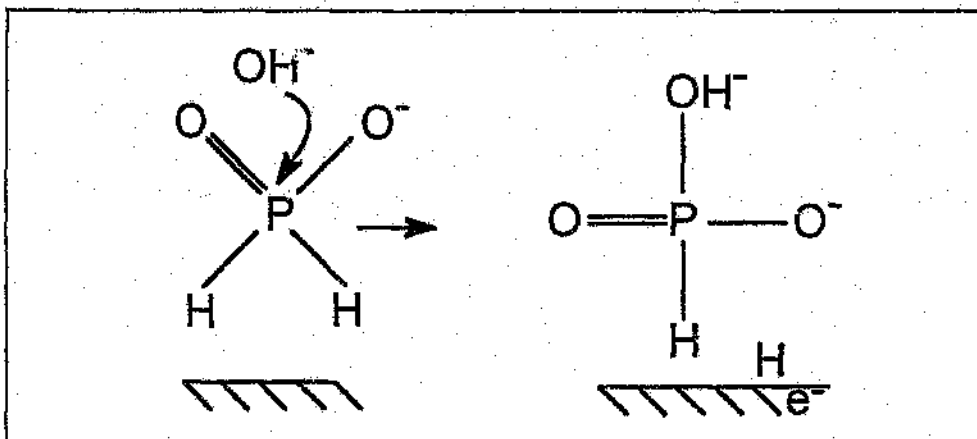


Figure 4.6 The OH^- attack on surface bound H_2PO_2^- (Hung and Ohno 1990).

Kondo et al. (1990, 1991) investigated the possibility of using novel ligands to enhance the efficiency of electroless copper baths. Triethanolamine (TEA, Figure 4.7) was the ligand suggested as being most promising, and adsorption kinetics of this ligand on the plating surface were presented.

An acceleration of plating rate at low concentrations of TEA was noted (Figure 4.8). This phenomenon was attributed to the adsorption of a monolayer of TEA (TEA_{ads}), followed by a monolayer of copper(II)-TEA on the active surface. With excess TEA, the copper(II)-TEA

layer was covered by the ligand, sterically hindering the oxidation of formaldehyde at the surface (Figure 4.9).

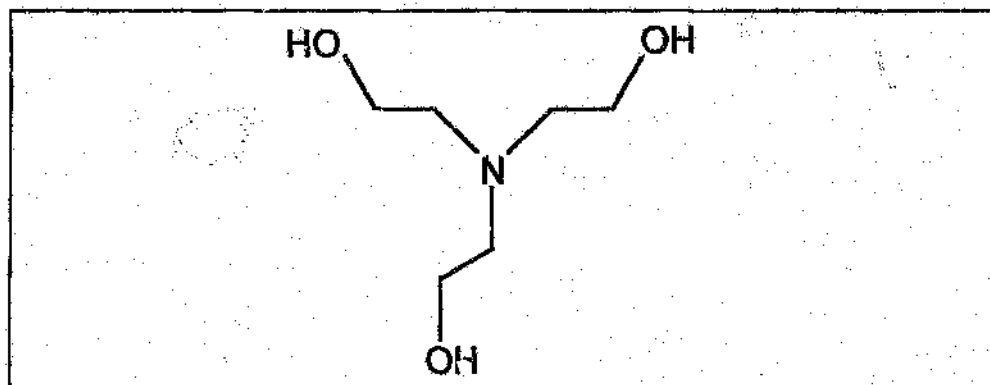


Figure 4.7 Projection formula for triethanolamine.

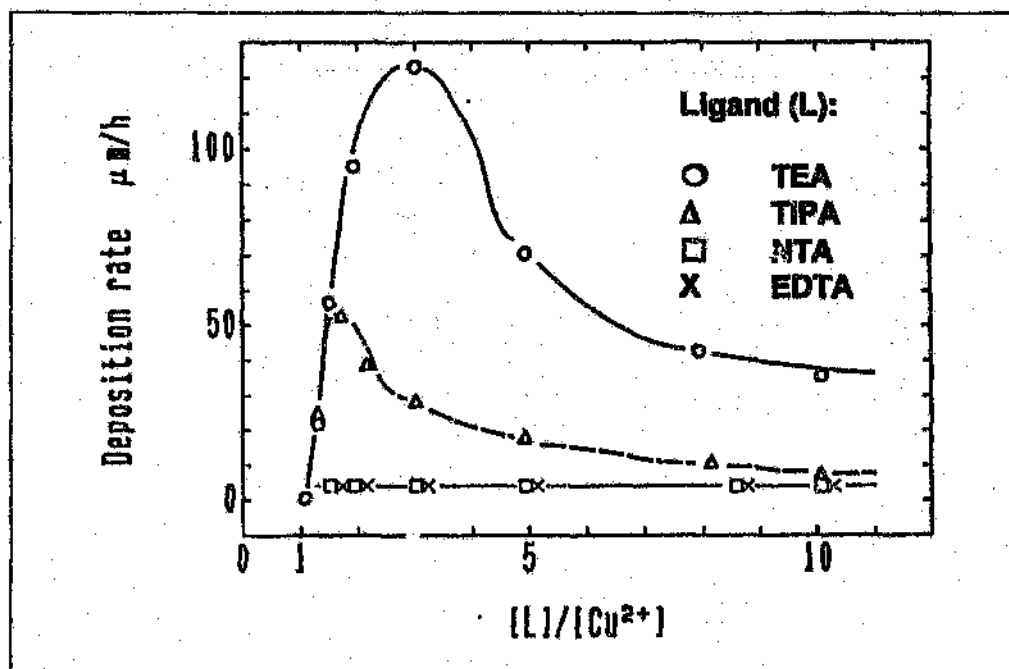


Figure 4.8 Dependence of copper deposition rate on the concentration of triethanolamine and other ligands, at 60°C. Kondo et al. (1990). Bath composition: [Cu²⁺] 0.060 mol L⁻¹, [HCHO] 0.22 mol L⁻¹, [K₄Fe(CN)₆] 20 ppm, [2,2'-dipyridyl] 10 ppm, [Ligand] variable, pH at 25°C = 12.8.

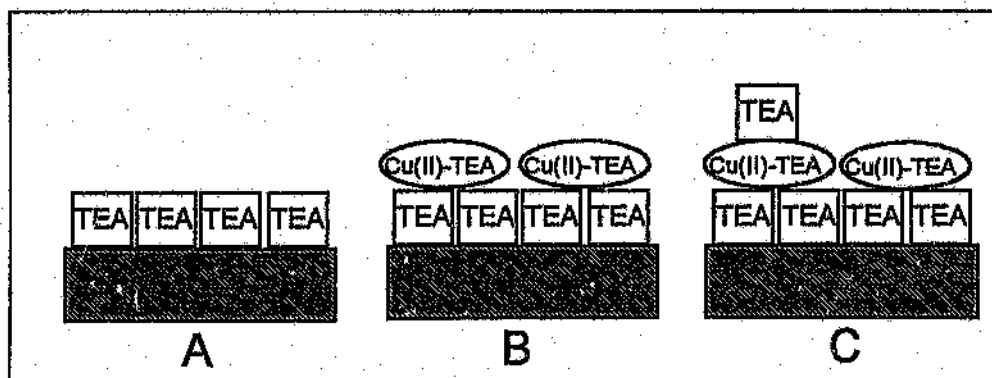


Figure 4.9 Schematic adsorption of triethanolamine (TEA) on a copper surface in an electroless plating bath (A). Adsorption of a Cu^{2+} -TEA monolayer (B), followed by adsorption of TEA (C) when there is excess ligand. This causes deactivation of the surface (Kondo et al. 1991).

The model for ultimate suppression of the deposition rate in excess ligand proposed by Kondo et al. (1991) involves three layers of adsorbate. According to these workers, the copper(II)-TEA complex is 1:1 in copper(II):TEA. The stability constant for the 1:1 complex - $(\text{CuL}(\text{OH})_2)$ - is $10^{18.4}$ (Sillén and Martell 1971). Thus, excess TEA is either in the solution bulk or it is adsorbed to the surface. Kondo and co-workers assumed that the free TEA adsorbed to the copper surface in preference to the complex. It was favourable, however, for the complex to adsorb over the adsorbed TEA. This effectively immobilised the complex near the interface. A further assumption made by Kondo and co-workers was that the catalytic oxidation of formaldehyde could only progress when this species was able to react at naked copper. Therefore, in vast excess of TEA, where surface coverage is complete, or at best very high, formaldehyde can not act as a reducing agent. Furthermore, coverage of the copper(II)-TEA complex by excess TEA is also conceivable. This surface condition, together with the

dramatic surface coverage by TEA, inactivated the copper metal as a catalyst for deposition. Kondo and co-workers investigated a number of other ligands, namely

triisopropanolamine (TIPA), nitrilotriacetic acid (NTA),

N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (HEA),

N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (HPA), and ethylenediaminetetraacetic acid (EDTA). EDTA and NTA are more hydrophilic than the other ligands, and as such they do not adsorb to the metal surface as strongly as the other ligands. It was for this reason that the acceleration effect noted with the other ligands (to a greater or lesser degree) was not observed with NTA and EDTA. In a subsequent publication (Kondo et al. 1992), the kinetics of adsorption of various ligands to a copper surface was described in detail. It was shown that the geometric structure of the complex, i.e. tetrahedral in the case of copper(II)-TEA and octahedral in the case of copper(II)-HEA, has a large influence on the likelihood of adsorption of the complex to already adsorbed free ligand.

Kondo and co-workers (1993a, 1993b) investigated the effects of potassium hexacyanoferrate(II) and 2,2'-dipyridyl on a copper(II)-TEA bath. The former compound was found to improve the surface morphology of the deposit, while preventing decomposition of the bath. 2,2'-dipyridyl, too, was found to contribute to a smoother deposit, and it was proposed that this compound adsorbs over adsorbed copper(II)-TEA, while in an EDTA bath the 2,2'-dipyridyl adsorbs on the naked copper surface. These workers also identified synergistic effects of these additives on the plating

rate and deposit quality (Kondo et al. 1993c) by virtue of different adsorption characteristics.

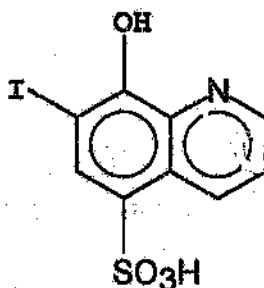
Bittner, Wanner and Weil (1992) used FTIR, SERS and a QME as analytical tools in a study of the role of the microstructure of copper deposits during electroless plating in formaldehyde baths. Innovative design of electrochemical cells allowed the QME to be used simultaneously with one or other of the spectroscopic techniques. A correlation was noted between surface roughness and catalytic activity. A synergistic feedback process was suggested whereby the copper deposition brought about by formaldehyde oxidation occurred in such a way as to produce a surface suitable for formaldehyde oxidation. Further evidence of interdependence was thus found, emphasising the importance of *in situ* studies of autocatalytic deposition processes. The influence of additives on the microstructure was investigated.

Mechanical properties (tensile strength, crystallite size) of electroless copper deposits were determined in conjunction with kinetic investigations of the autocatalytic process (Matsuoka, Murai and Iwakura 1992). A QME, as well as a.c. impedance techniques were used in this study, and a number of observations were made regarding the choice of base (of KOH, NaOH and LiOH, the latter was found to give the deposit with the best mechanical properties). The tensile strength of the deposit was evaluated as a function of preferred crystallographic orientation and crystallite size. It was suggested that addition of polyethylene glycol (PEG) and LiOH prevented the interaction of the partial processes, giving rise to deposits with better physical properties. Matsuoka and co-workers proposed that the PEG diminished the extent of adsorption of the

methylene glycolate anion. Crystallite elongation occurred as a consequence of the diminished adsorption.

4.3.2 The effects and action of additives to copper baths

The effect of organic additives as accelerators and stabilizers in electroless copper baths has been investigated (Schoenberg 1972, 1973). The additive 7-iodo- 8-hydroxyquinoline 5-sulphonic acid (HIQSA),



was found to accelerate deposition at intermediate concentrations and to suppress the deposition reaction at high concentration (Figure 4.10).

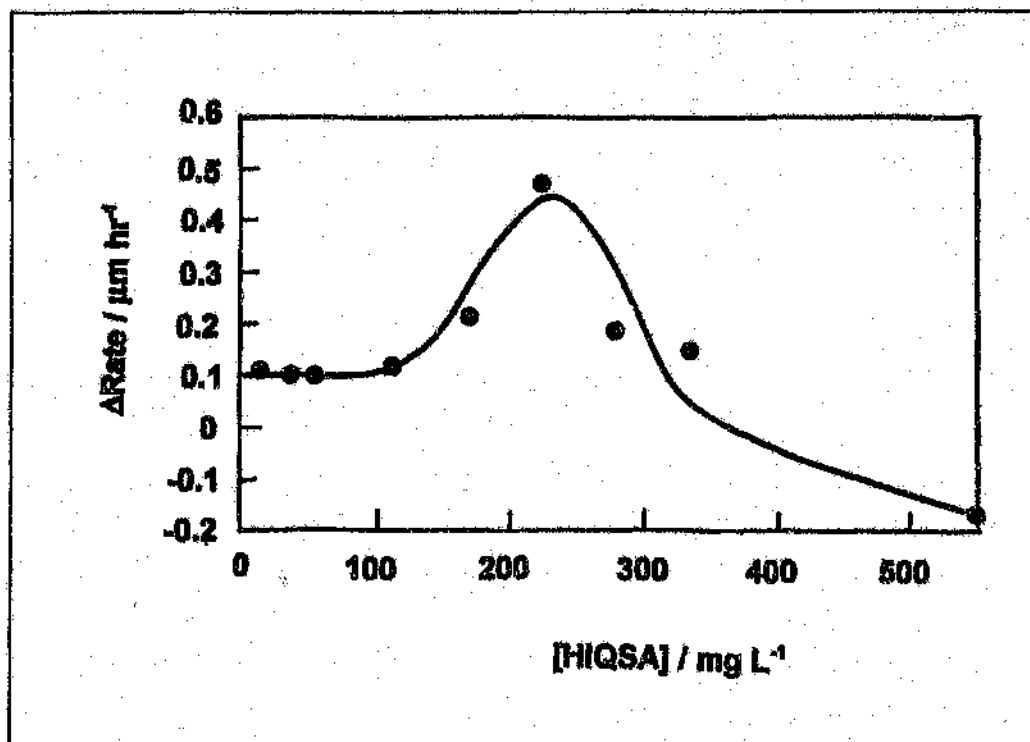


Figure 4.10 Change in plating rate (relative to a bath containing a given amount of HIQSA) as a function of [HIQSA]. Bath composition: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.02 mol L^{-1} , $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ 0.1 mol L^{-1} , HCHO 0.4 mol L^{-1} , [HIQSA] variable; pH 12.8, $\sim 25^\circ\text{C}$. Redrawn from Schoenberg (1972).

The adsorption of various quinoline sulphonic acids on catalytic surfaces, in conjunction with chelation by these species of Cu^{2+} ions, was shown to be a phenomenon which could be exploited in electroless copper bath formulation where formaldehyde was employed as the reducing agent (Figure 4.11).

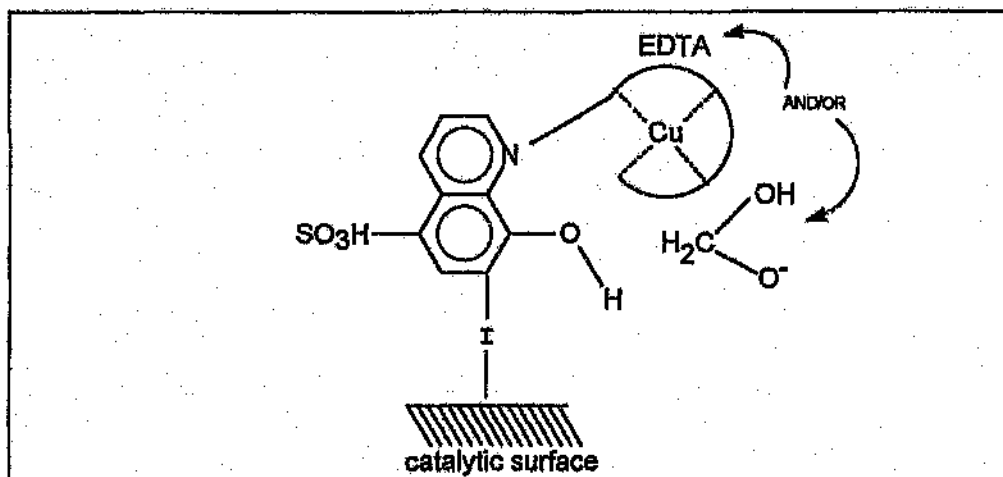
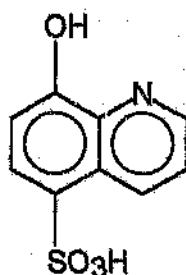


Figure 4.11 Adsorption of HIQSA to a copper surface, and chelation of aqueous copper complex (Schoenberg 1972).

Siegel and Hannemann (1981) and Hannemann and Siegel (1982) patented a method of controlling copper deposition rates by the addition of both HIQSA and 8-hydroxyquinoline sulphonic acid (HQSA):



Paunovic and Arndt (1983) used cyclic voltammetry and gravimetric plating rate determinations to define the effect of additives (adenine, guanine, saccharin and coumarin) on the kinetics of the partial processes in an electroless copper bath. The effect of these additives on the anodic dissolution of Cu in the absence of HCHO was also followed. Results were rationalised by considering the effect of delocalized π -electrons on the adsorption properties of the additives, and their effect on the metal solution

interphase. Duffy, Pearson and Paunovic (1983), investigating autocatalytic copper deposition, considered the influence of pH on the metal solution interphase conditions during electroless copper plating. Adsorption, potential of zero charge, structure of the double layer, structure of the copper species in solution and ionic strength of the solution were affected by the pH, and these factors, in turn, influenced the rate of metal deposition.

Hung (1985) published a study on the effects of thiourea and guanidine hydrochloride (GH) on electroless copper plating. In this work, the effect of the additives was examined in order to determine the reasons for bath stabilization with concomitant plating rate reduction. Thiourea was shown to stabilize the bath by virtue of a stronger chelation effect with Cu^+ than with Cu^{2+} , and reduced the plating rate (when in high concentration) by adsorption on to the catalytic surface, as a catalyst poison (Figure 4.12). Cu^+ was implicated as being a key species responsible for bath decomposition. A plating rate enhancement was seen with low concentrations of GH, and this phenomenon was attributed to the effect of delocalized π -electrons as described by Paunovic and Arndt (1983). In a subsequent paper, Hung (1986) used Auger electron spectroscopy, scanning electron microscopy and the construction of polarisation curves (potential vs. $\log(\text{current})$ plots) to investigate further the effects of GH. The rate enhancement at low concentrations was attributed to a roughened morphology of the copper plate in the presence of this additive. It was also noted that the plating potential was shifted to a more cathodic value in the presence of GH, and it was stated that this implied that GH caused the oxidation of formaldehyde to occur more readily.

A microdensitometric technique and weight gain method was used by Piatti and Podestá (1989) to observe the stabilizing effects of a number of additives to an electroless copper bath. Among the additives investigated were 2-mercaptobenzothiazole (2MBT) and potassium cyanide. The latter compound was found to have the following effects:

- (a) reduction of available active sites by adsorption on the plating surface;
- (b) enhancement of the plating rate as a consequence of interaction of the delocalized π -electrons of additive with the plating surface;
- (c) in common with CN^- , 2MBT has a stronger complexing ability with Cu^+ than with Cu^{2+} . Thus the formation of Cu_2O was prevented in the presence of these ligands. This species disproportionated in the presence of water to form Cu and Cu^{2+} . The presence of finely dispersed elemental copper resulted in the electroless process taking place in the solution bulk and not only on the substrate, which led to bath decomposition.

Van den Meerakker (1989) was able to show that the addition of a polyoxyethylene compound, $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ ($n = 13$ to $n = 500$), to an electroless copper bath could result in a ductile yet dense deposit. The additive was incorporated into the deposit. It was proposed that the presence of the additive compound resulted in a shift of the plating potential to a more negative value, and, consequently, the incorporation of hydrogen was diminished. This resulted in a less brittle deposit. The discovery that a cathodic shift of the plating potential resulted in less hydrogen incorporation was reconciled by considering the treatment of surface coverage of hydrogen on copper as given by Gottesfeld

et al. (1986). These workers reassessed van den Meerakker's (1981a) treatment of the kinetics of recombination of adsorbed hydrogen, and showed that on copper the surface coverage of atomic hydrogen did indeed decrease with potential shifts in the cathodic direction.

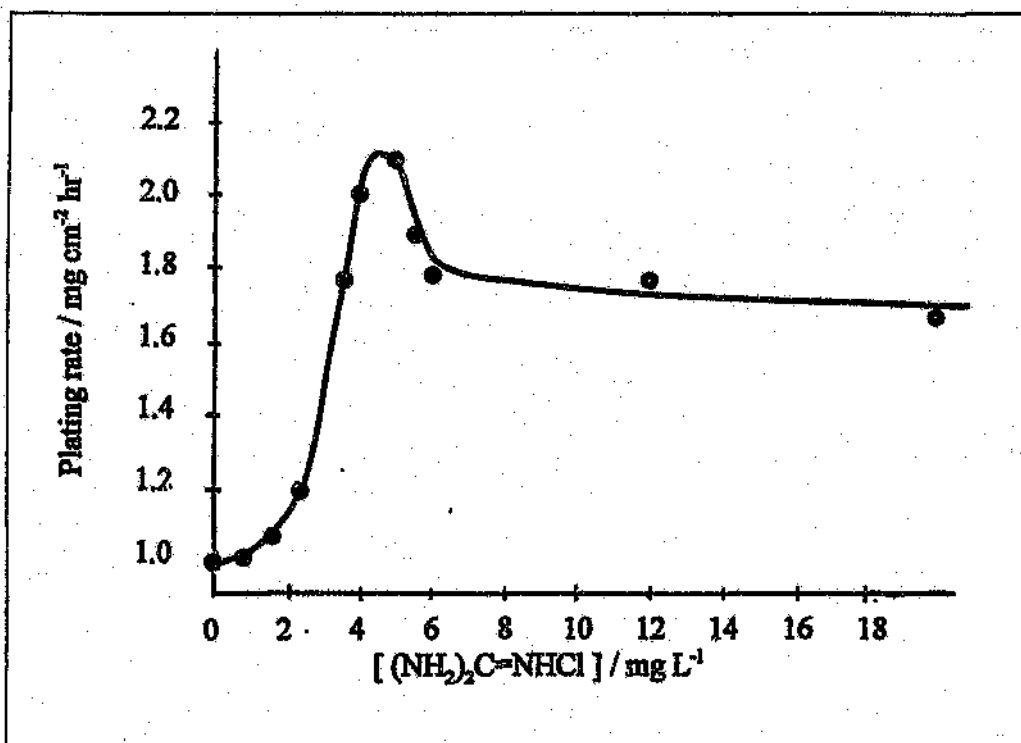


Figure 4.12 The effect of guanidine hydrochloride concentration on plating rate in an electroless copper plating bath (Hung 1985).

Junginger (1988) found that significant bath stabilization was achieved when air or oxygen was bubbled through an electroless copper plating bath. While additives, particularly ligands for copper(I), were also investigated as stabilizers in this work, Junginger proposed that O_2 oxidises metallic copper nuclei responsible for nodule formation and bath decomposition.

The works cited in the previous paragraphs have almost always attributed the spontaneous decomposition of electroless copper baths to the formation of Cu_2O . Baumgartner (1989) attempted to break away from the common practice of introduction of additives to counteract the decomposition problem, by slow, controlled addition of HCHO to a copper plating bath. He showed that the copper deposit so produced was more dense, of higher purity and lower electrical resistivity than those produced by baths with additives. It must be noted, however, that this work was done only on very small scale apparatus. Baumgartner's description of the action of CN^- on electroless Cu deposition was in agreement with the interpretation of Piatti and Podestá (1989). This stabilizing agent gave a Cu deposit of higher purity than found with other additives.

CHAPTER 5

INSTRUMENTATION AND PROCEDURES

CHAPTER 5 INSTRUMENTATION AND PROCEDURES

5.1 APPARATUS OF THE QUARTZ MICROBALANCE ELECTRODE

5.1.1 The quartz microbalance

A block diagram of the electrochemical and electronic equipment is given in Figure 5.1.

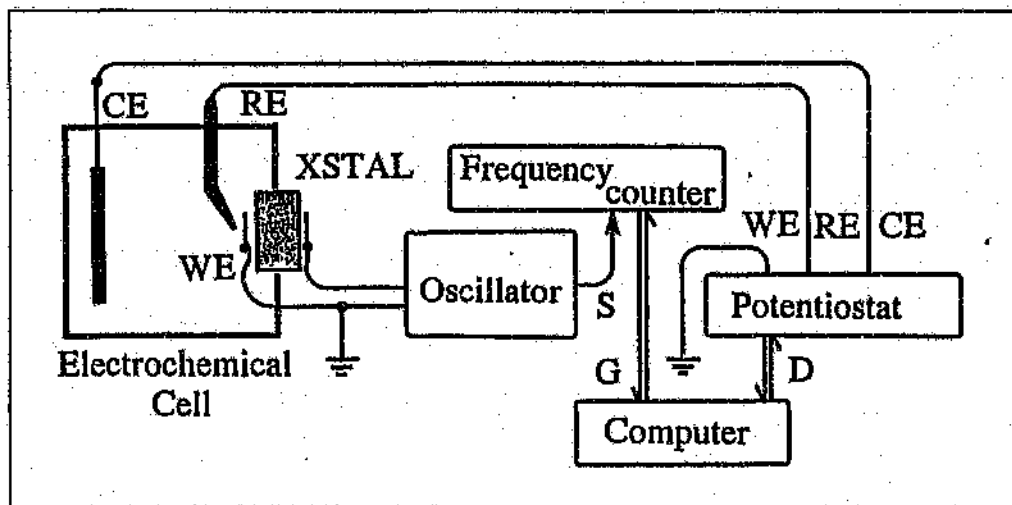


Figure 5.1 Block diagram of QME apparatus. WE, RE, CE are working, reference and counter electrodes respectively, D = analogue/digital interface, G = IEEE GPIB 488 interface, S = oscillator signal and XSTAL = 5 MHz AT-cut quartz crystal.

The quartz wafers used were planar, AT-cut blanks of 13.7 mm diameter lapped by the manufacturer (STC Components) to resonate at approximately 5.00 MHz. On the face of the wafer to be exposed to solution (front face), an electrode was formed by successively evaporating layers of chromium, palladium and gold (the

latter being 80 to 100 nm thick) in the conventional "keyhole" pattern as shown in Figure 5.2. Chromium was present to improve adhesion of electrode material and palladium to prevent diffusion of chromium to the current-carrying, electrochemically active gold surface. On the reverse face of the crystal, a gold electrode about 100 nm thick, was used without under-layers. The piezoelectric area was determined by the rear electrode diameter (5.5 mm), which was smaller than the front electrode diameter (6.6 mm). The surface area of the WE was 0.404 cm², as part of the connecting tab on the front face of the crystal was also exposed to solution.

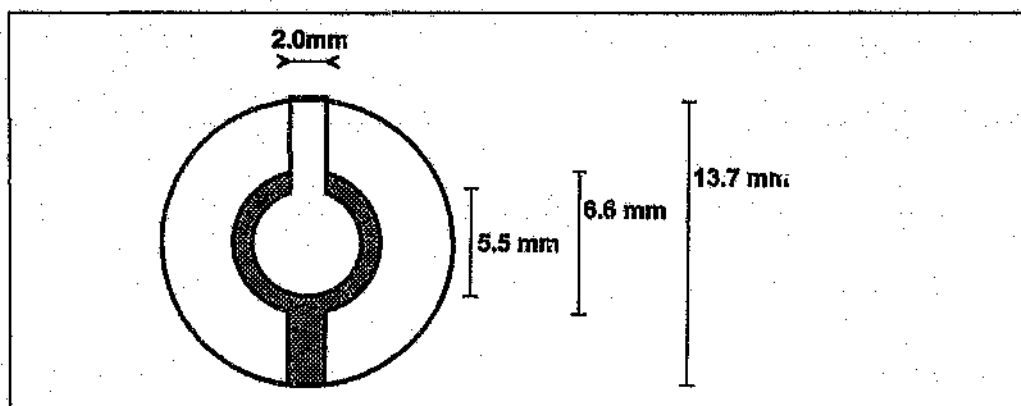


Figure 5.2 Electrode pattern on quartz crystal wafers. The shaded area shows the working electrode (plan view not to scale).

A modified version (Figure 5.3) of the Pierce-Miller oscillator used by Weil and co-workers (Benje et al. 1986) was built in-house and powered by a Philips PE1535 stabilised power supply. Frequency measurements were carried out by a Keithley 775A counter/timer. Data were logged using a Philips P3105 personal computer, via a General Purpose Interface Bus (National Instruments PC2A). The waveform of the oscillating crystal was monitored using a Philips PM3226 oscilloscope.

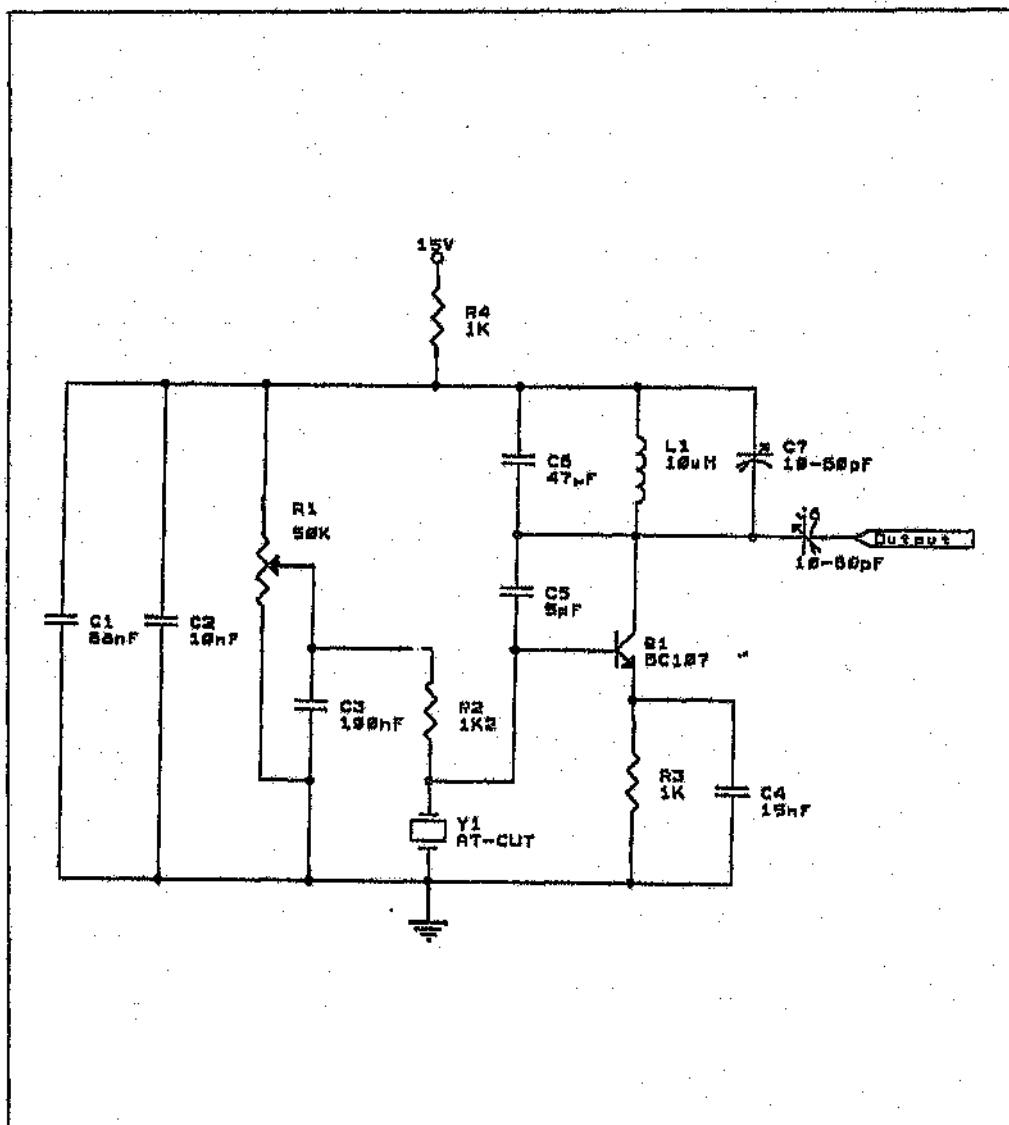


Figure 5.3 Modified Pierce-Miller oscillator circuit.

5.1.2 Electrochemistry

Electrochemistry was carried out in a Metrohm water-jacketed Pyrex cell (maximum capacity 100 mL), thermostatted by a MGW/Lauda RC3 circulator. This unit was capable of maintaining temperature to $\pm 0.1^\circ\text{C}$. All

electrodes and the gas sparge (glass frit) were designed to fit the Metrohm cell top. A Mintek-designed potentiostat with a grounded working electrode (WE), built in house, was used. Two 10 mH inductors were connected in series with the working electrode and reference electrode (RE). The WE current was monitored by a 12-bit analogue/digital card (IBM-DACA) fitted to the computer. The counter electrode (CE) used depended on the experimental context. Reference to the counter electrodes is made in the Experimental Procedures section. In every case, the counter electrode was parallel to and about 1.5 cm away from the WE. The reference electrode (RE) was a Metrohm saturated calomel electrode (SCE) fitted with a Luggin tip, situated about 0.5 cm from the WE. The Luggin tip was filled with 1 mol L⁻¹ KCl solution unless otherwise specified. All electrode potentials quoted in this Chapter, and in those dealing with the results of the experimentation (Chapters 6, 7 and 8), are relative to the SCE. A Metrohm E549 magnetic stirrer and stand supported the cell. Constant, moderate stirring was used throughout all experiments.

A list of chemicals used in this work is given in Appendix I.

Glassware was cleaned before use with a detergent solution and ethanolic sodium hydroxide, or in a mixture of equal proportions of concentrated sulphuric acid and nitric acid. For the preparation of solutions and rinsing of glassware, water from a Buchi Fontvapor 285 distillation column coupled to a Millipore Milli-Q unit was used. The resistivity of this water was 12 - 15 M Ω cm⁻¹.

5.1.3 Computer software

Computer software was written in either GW-BASIC (program in Appendix IIa) or in IBM Compiled BASIC (program in Appendix IIb) and run using the IBM Compiled BASIC software (version 2.00). Device drivers for the interface cards were the manufacturers' proprietary software as supplied. These programmes allowed the user to control the frequency counter front panel, and to set up and run experiments using the QME. The experiments could be designed such that frequency, electrode potential and current could be monitored for a selected duration or until the electrode potential reached a chosen value. The program in Appendix IIb incorporates a routine whereby the above-mentioned data are plotted versus time on the graphics monitor, directly after having been saved to disk. This allowed an immediate assessment of the experiment results.

It was also possible to calibrate the analogue/digital conversion by attaching a dummy cell to the potentiostat leads as shown in Figure 5.4. A known potential was applied to the A/D converter. One hundred readings were taken at each of ten such potentials. Each set of one hundred readings was averaged, a least squares straight line was fitted to the resulting ten data points, and the slope and intercept were used to calculate potentials read by the card during actual data collection. This procedure was performed prior to each set of experiments.

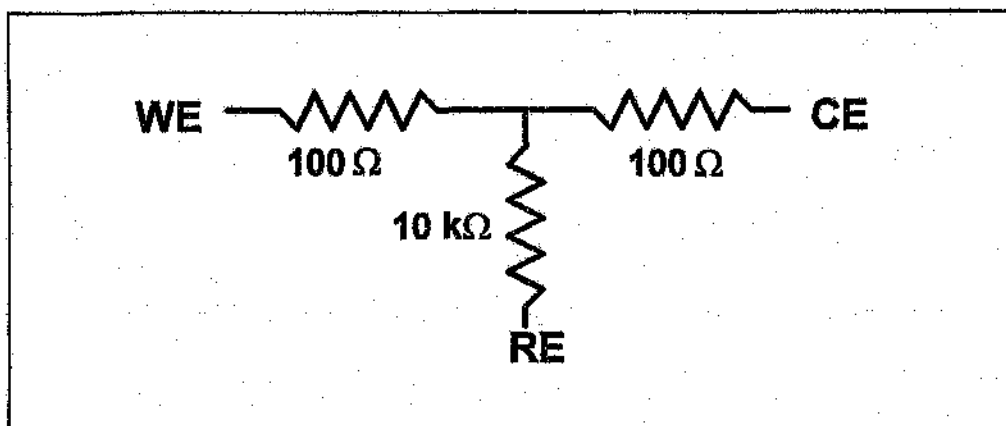


Figure 5.4 Dummy cell resistor network. RE = reference electrode, CE = counter electrode, WE = working electrode.

5.2 QUARTZ MICROBALANCE ELECTRODE PREPARATION

Blank crystals were cleaned in a mixture of sulphuric and nitric acids, rinsed successively in water and acetone, and dried. Using adhesive tape (3M "Magic Tape") or adhesive vinyl (Grafitack) as masking material, the blanks were attached to Perspex sheets in batches of 6 or 8 at a time. Gold coating of the rear faces of the crystals was done before coating the front, working face. After masking the front faces of the crystals, the plastic mount was affixed to a motor driven turntable in a Balzers ultrahigh vacuum coating unit. Two tungsten boats (coiled wire) held chromium and palladium pellets which would evaporate to coat the crystals. Prior to coating, the system was out-gassed for at least 24 hours. At the time of commencing metal evaporation the pressure was approximately 4×10^{-6} mbar. The thickness of the electrode under-layers was estimated to be in the range 10-30 nm.

Gold coating of reverse and current carrying electrodes was performed in a Polaron scanning electron microscopy coating unit. Copper leads were attached to the crystal

electrodes with silver epoxy adhesive (Demetron). Co-axial cable (30 cm) from the oscillator was soldered to these leads.

5.3 QUARTZ MICROBALANCE ELECTRODE HOLDERS

Three different holders were used during the course of this work. These Teflon holders were designed and built according to the cross section diagrams in Figure 5.5, Figure 5.6 and Figure 5.7. All of the holders used were designed to fit into 50 or 100 mL Metrohm cells, and to allow for convenient replacement of the crystal. The holder shown in Figure 5.7 was the most compact and the easiest to use of the three.

Silicone gaskets (Blue RTV Gasket Maker, Loctite Corp.) were made to seal the crystal. These proved to be better than commercial "Viton" or similar o-rings because of their softer, more yielding texture.

Photographs of the quartz microbalance electrode holder assembly are shown in Figure 5.8.

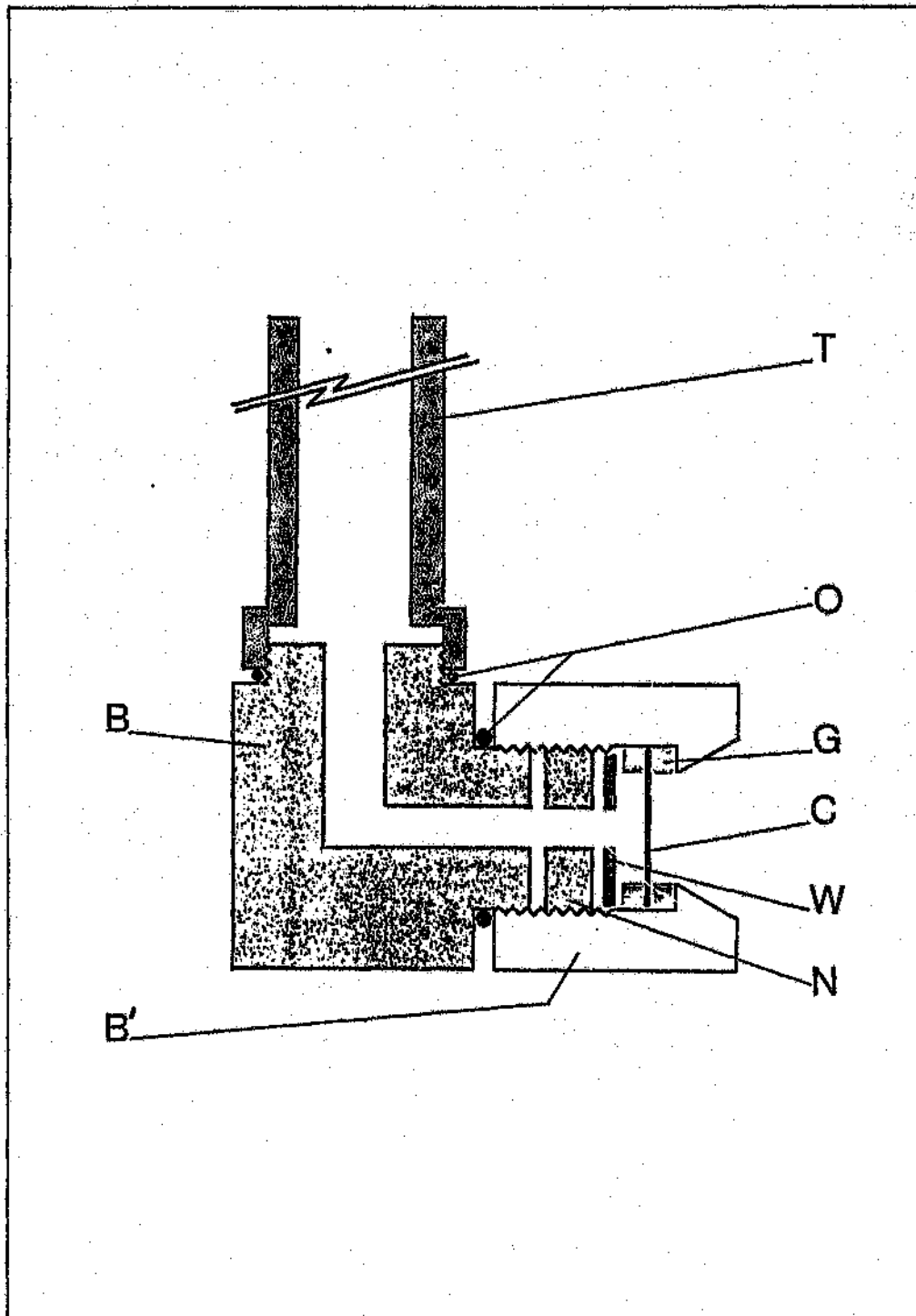


Figure 5.5 QME holder 1. T = glass tube, O = o-ring, G = silicone gasket, C = crystal, W = washer, N = nut, B; B' = Teflon body parts.

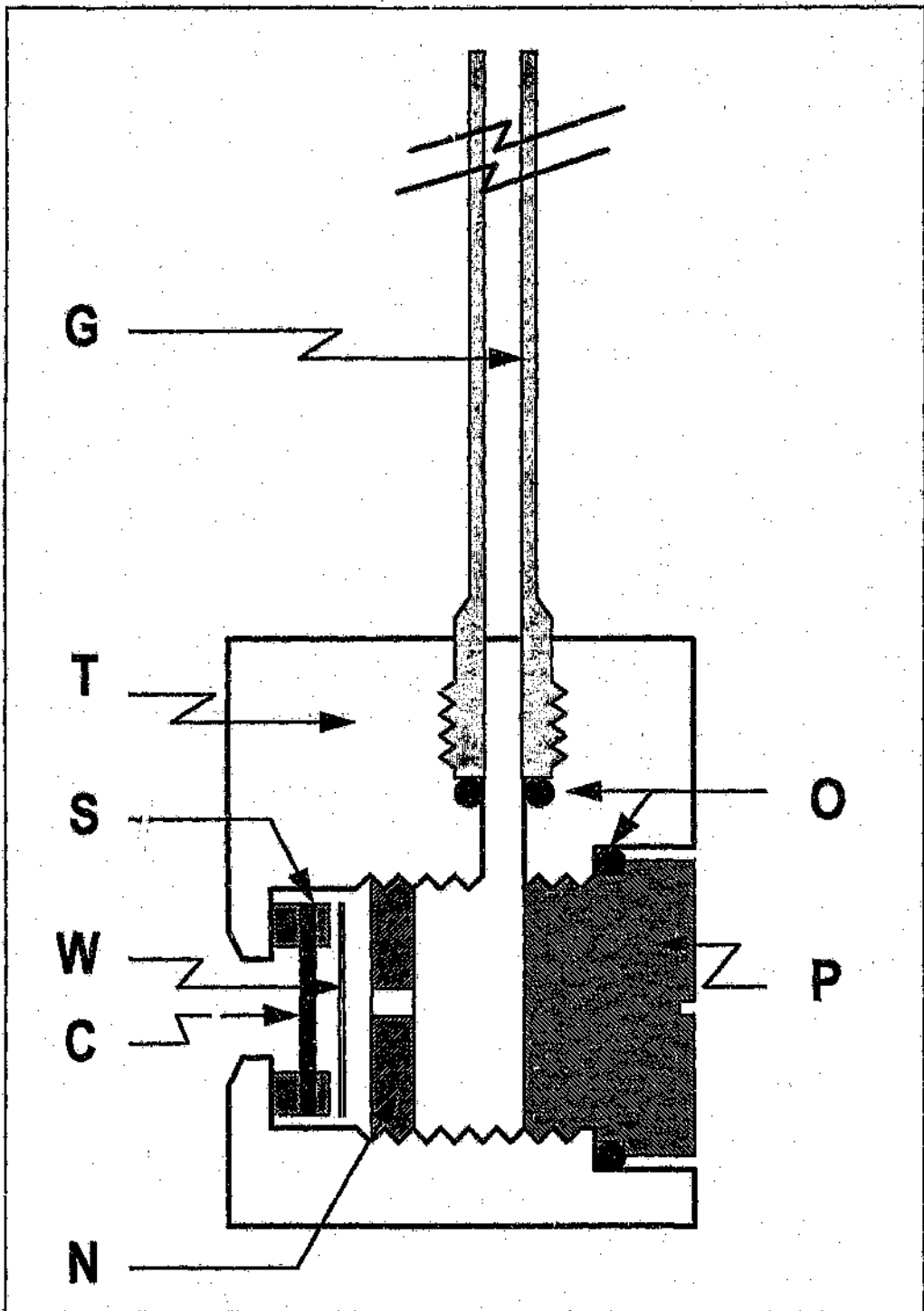


Figure 5.6 QME holder 2. T = Teflon body, O = o-ring, S = silicone gasket, C = crystal, W = washer, N = Perspex nut, G = glass tube, P = sealing plug.

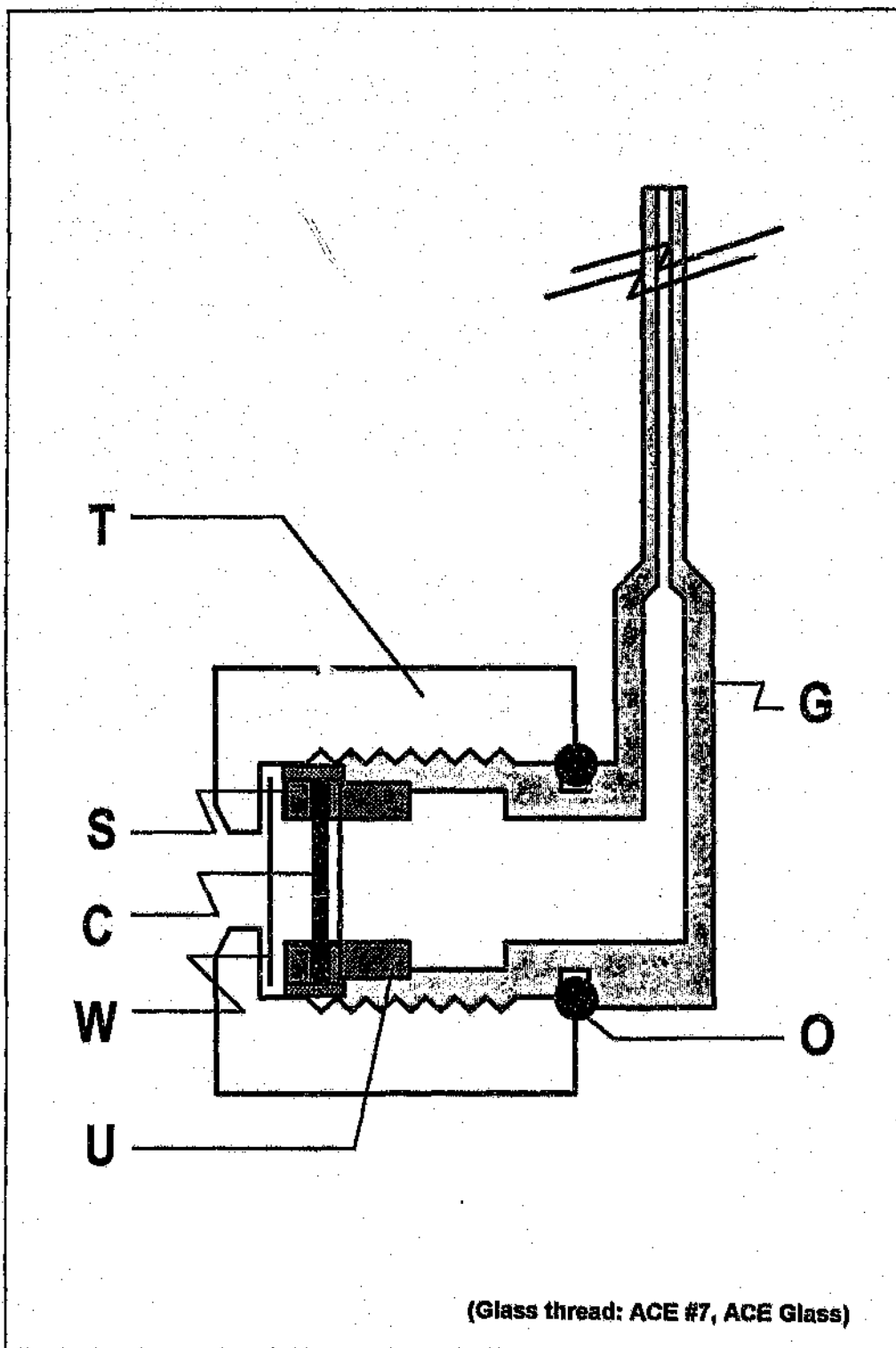


Figure 5.7 QME holder 3. G = glass tube, O = o-ring, S = silicone gasket, C = crystal, U = Teflon cup, W = Teflon washer.

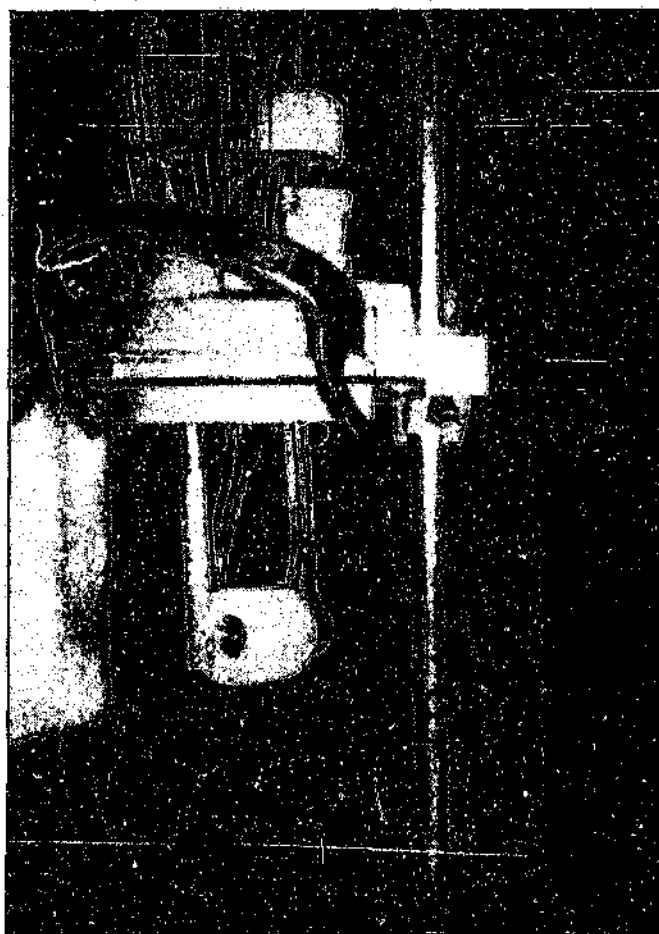
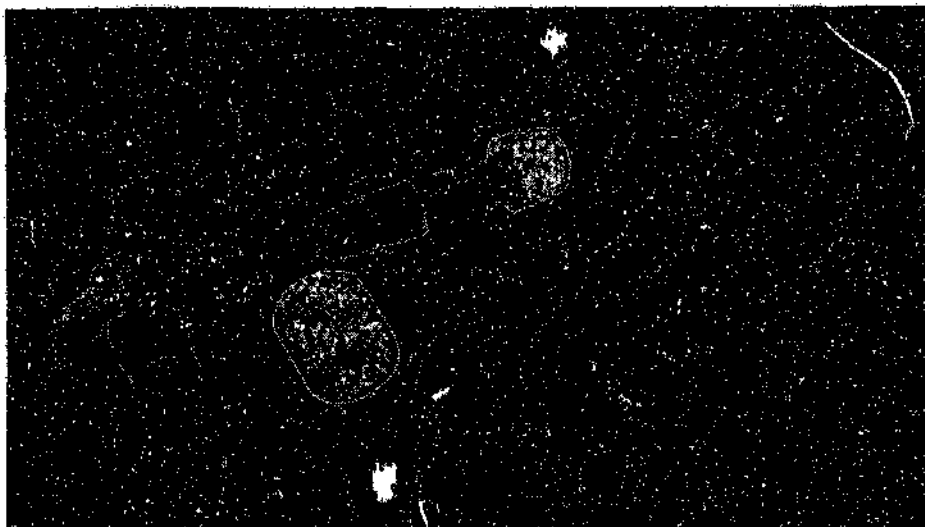


Figure 5.8 Photographs of the QME holder (holder 3, Figure 5.7) and the assembly of the electrochemical cell top.

5.4 GLASSY CARBON ELECTRODES AND HOLDERS

Glassy carbon discs of 12 mm diameter were cut from a 2 mm thick sheet (Sigridur "G", Sigri). Copper wire was attached to the rear face with conducting silver epoxy (Demetron). The wire was fed through the holder (Figure 5.9) and the discs were sealed to the glass by means of silicone gasket maker (Blue RTV Gasket Maker, Loctite Corp.). The amount of adhesive used was minimal, so that removal of the disc was possible after use. The working face of the discs was prepared by polishing to a matt finish on 600 grit water paper (Leco) followed by ultrasonication in pure water for 30 s.

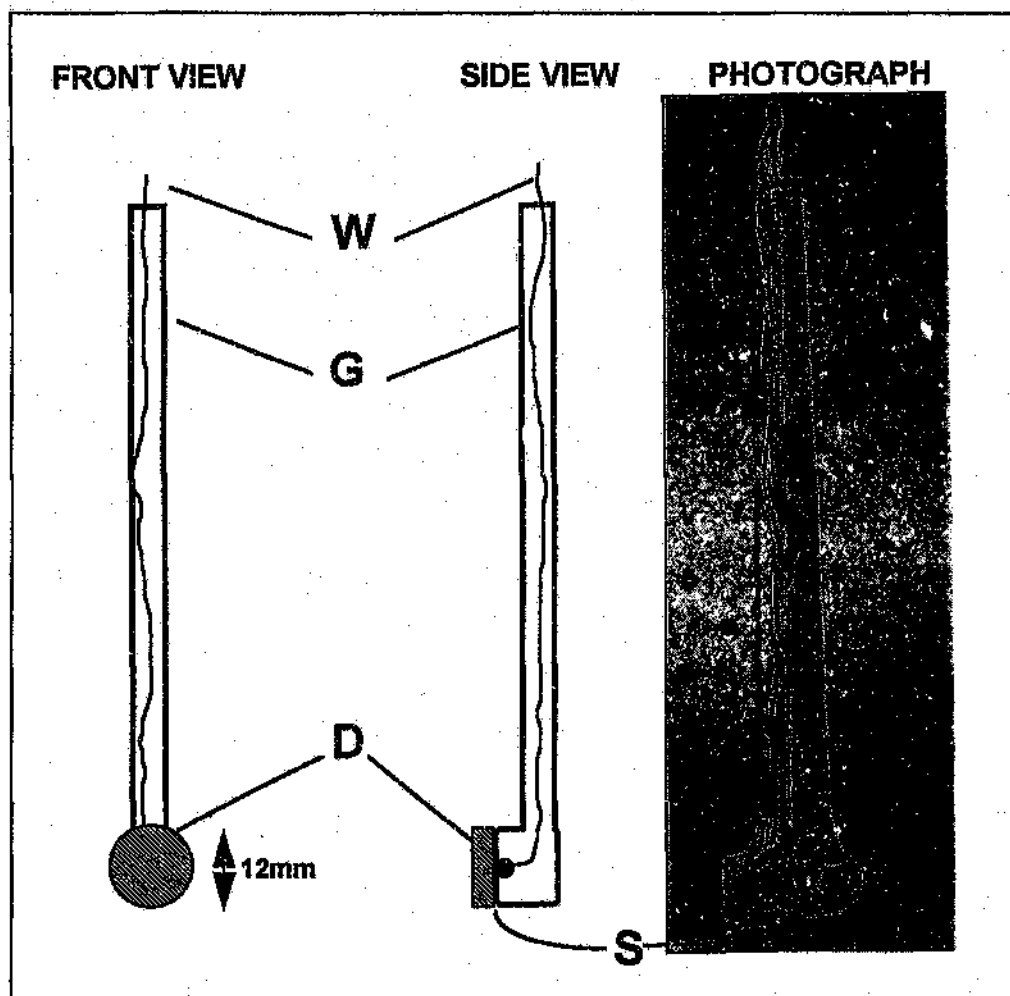


Figure 5.9 Glassy carbon electrode holder. G = glass elbow, D = G.C. disc, S = silicone adhesive, W = multi-strand copper wire.

5.5 ELECTROLESS PLATING BATH FORMULATIONS

5.5.1 Low temperature electroless nickel

Two bath formulations, almost identical to those proposed by Feldstein (1970) were studied. Their compositions are given in Table 5.1.

Table 5.1 Bath formulations (figures are concentrations in mol L⁻¹).

Reagent	Bath 1	Bath 2
Ni ₂ SO ₄ ·6H ₂ O	0.095	0.095
Na ₄ P ₂ O ₇ ·10H ₂ O	0.110	0.110
NH ₃ (to pH 10.8)	~0.34	~0.34
NaH ₂ PO ₂ ·H ₂ O	0.280	---
(CH ₃) ₂ NH·BH ₃ *	---	0.051
KCl **	1.00	1.00

* Dimethylamine borane (DMAB)
 ** supporting electrolyte

The compositions of the two baths differ only in respect of the reducing agent. Potassium chloride, a component not part of the original formulation, serves as a supporting electrolyte and reduces any uncompensated solution resistance. It has been found that KCl has minimal effect on the plating rate of the hypophosphite-reduced bath (Orchard 1988b). As a consequence of the presence of a supporting electrolyte, the exact positioning of the Luggin tip was not critical.

Two stock solutions were prepared at double the concentrations required for the final baths, so that when equal volumes were combined, the correct concentrations were attained. Stock solution "A" contained the nickel ions (Ni^{2+}) and complexing agents while solution "B" contained the reducing agent (R.A.) and the supporting electrolyte. Fresh solutions were prepared for each experiment.

5.5.2 High temperature electroless nickel

This work was done in collaboration with Douglas Mughogho (1993). A nickel bath (Bath 3) operating at acidic pH (4.6) and high temperature ($85 \pm 1^\circ\text{C}$) was used for QME studies and the half-reaction current density curves thus obtained were compared to those obtained using a RDE.

Table 5.2 High temperature electroless nickel plating bath (Bath 3). Concentrations are in mol L^{-1} unless otherwise specified.

Reagent	Concentration
$\text{Ni}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	0.0871
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	0.189
$\text{NaC}_2\text{H}_3\text{O}_2$ (sodium acetate)	0.0207
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ (lead acetate)	15 ppm
KCl	1

5.5.3 Copper - triethanolamine bath

Table 5.3 gives the composition of the copper bath used to study the effect of triethanolamine (TEA, triethyl-2,2,2-trihydroxyamine) on the rate of copper deposition, and for electrochemical studies. The concentration of TEA was varied from approximately 0.06 mol L^{-1} to approximately 0.60 mol L^{-1} . This bath (Bath 4) was used at 60°C .

Table 5.3 Composition for Copper - Triethanolamine bath, Bath 4 (concentrations in mol L^{-1} unless otherwise specified).

Reagent	Concentration
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.060
HCHO (added as 35% solution)	0.220
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	35 ppm
2,2' - Dipyridyl	10 ppm
TEA	0.060 - 0.600
NaOH to pH 12.5 at 25°C	

5.5.4 Copper bath with hydroxyquinoline sulphonic acid additives

A copper bath with composition similar to one used by Schoenberg (1972) was used in the determination of the effect of two additives,

8-hydroxy-7-iodo-5-quinolinesulphonic acid (HIQSA), and σ -hydroxyquinoline-5-sulphonic acid (HQSA).

The additives were used separately in the various experiments. Bath composition is given in Table 5.4. Concentrations of the additives are given in mg L^{-1} in keeping with the quantity calculus used in Schoenberg's work. This bath (Bath 5) was used at 30°C .

Table 5.4 Composition of electroless copper bath (Bath 5) using HIQSA or HQSA as additive. Concentrations in mol L⁻¹ unless otherwise specified.

Reagent	Concentration
CuSO ₄ .5H ₂ O	0.020
Na ₂ EDTA*	0.100
HCHO (added as paraformaldehyde)	0.400
HIQSA	0 - 620 mg L ⁻¹
HQSA	0 - 420 mg L ⁻¹
NaOH to pH 12.4 at 25°C	

* ethylenediaminetetraacetic acid, disodium salt

5.6 MISCELLANEOUS SOLUTIONS

5.6.1 Copper plating solution for calibration of the QME and stripping of copper deposits

For purposes of assessment of the accuracy and precision of the QME, and for removal of copper deposits from the microbalance electrode, a copper sulphate solution consisting CuSO₄.5H₂O (0.16 mol L⁻¹) and H₂SO₄ (0.020 mol L⁻¹) was used. In some cases the copper sulphate concentration was 0.721 mol L⁻¹, with the H₂SO₄ concentration of 0.036 mol L⁻¹.

5.6.2 Stripping solution

A solution for the stripping of plated nickel from the QME consisted of Na_2SO_4 (0.10 mol L^{-1}) and H_2SO_4 (0.20 mol L^{-1}).

5.6.3 Plating bath modifications for low temperature nickel baths

As required by the particular experiment, substitutes for the usual solutions of "A" or "B" were prepared. As a substitute for Ni^{2+} , solution A (modified) contained 0.095 mol L^{-1} zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) instead of nickel sulphate ($\text{NiSO}_4 \cdot \text{H}_2\text{O}$). Where reducing agent was required to be omitted from the bath, a KCl solution (1.00 mol L^{-1}) was used instead of Solution "B".

5.6.4 Sodium acetate solution

Sodium acetate solution (1.2 mol L^{-1}) was prepared for addition to low temperature nickel plating baths.

5.6.5 Concentrated sodium hypophosphite solution

Sodium hypophosphite (2.84 mol L^{-1}) was prepared for addition to Bath 2.

5.6.6 Copper plating solution for use as substrate in Bath 1

An electroless copper plating bath was prepared to produce a copper substrate for study in Bath 1. This bath followed the composition presented by Kondo *et al.* (1991). The bath consisted of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.060 mol L^{-1}), HCHO (0.22 mol L^{-1}), added as paraformaldehyde, EDTA (disodium salt) (0.080 mol L^{-1}) and NaOH to pH 12.5. This bath was used at 60°C . Initiation of electroless copper plating on the gold electrodes was spontaneous, and 3 minutes plating produced a coherent pink deposit.

5.6.7 Palladium chloride solution

A solution of PdCl_2 ($1.41 \times 10^{-3} \text{ mol L}^{-1}$) and HCl (2.5 mL L^{-1}) was applied to the electrode of a crystal which had previously been coated with copper (Section 5.6.6 above). Three to four applications were made, keeping the solution from the non-metallized area of the crystal.

5.6.8 Solution for electrolytic deposition of Ni-P alloy

An alloy of nickel and phosphorus was produced using the solution given in Table 5.5. This plating solution was originally used by Cargill (1979) and later by Benje *et al* (1988).

Table 5.5 Composition of plating bath for electrodeposition of Ni-P alloy. The bath operated at 70°C at a current density of 20 mA cm⁻². Concentrations in mol L⁻¹ unless otherwise specified.

Reagent	Concentration
NiSO ₄ ·6H ₂ O	0.857
NiCl ₂ ·H ₂ O	0.300
H ₃ PO ₃ (25%)	48.0 g L ⁻¹
H ₃ PO ₄ (85%)	58.3 g L ⁻¹
NiCO ₃ ·2Ni(OH) ₂ ·4H ₂ O	0.131

5.7 EXPERIMENTAL PROCEDURES

5.7.1 Calibration of the quartz microbalance electrode

To verify that the constructed QME was responding satisfactorily to mass changes, the following procedure was followed. The copper plating solution (section 5.6.1) with a plating efficiency known to be very close to 100% was used as an electrolyte, with a copper CE (20 x 25 mm). The cell top with electrodes was attached to the cell and the solution stirred at a constant rate. Resistor R1 and capacitor C7 (Figure 5.3) were adjusted to tune the circuit to obtain the optimum waveform on the oscilloscope. By running the computer program, the frequency counter was set up with the required gate time and trigger level. These were typically 1.0 s and +0.1 V respectively. In addition, the counter was set to trigger on the downward side of the signal wave (this was done because this side of the signal appeared to be more sinusoidal). Alternating

current (a.c.) coupling was used throughout. By electrolytically plating copper on to the QME at a known current for a set period of time, an expected mass change could be calculated. The quotients of the measured frequency changes, Δf , divided by the mass changes expected using Faraday's law, provided the experimental ratios. These ratios were determined for a number of expected mass values and compared to the theoretical ratio for a 5.00 MHz crystal, using the first-read frequency as f_0 in the calculation.

5.7.2 Determination of rates of electroless deposition

Steady state deposition rates of electroless plating baths were determined by monitoring the frequency of the QME for an appropriate time period. Solutions were thermostatted and moderately stirred. In most cases, measurements were taken for 200 s, after allowing at least 120 s for a steady state condition to be reached. Since these measurements were made without the application of a potential, no counter electrode was used. The computer program monitored the electrode potential as well as frequency during plating, so the reference electrode was present for these measurements.

5.7.3 Stripping nickel alloys from the QME

Large amounts of deposited material are deleterious to the operation of the QME. This was revealed by the distorted waveform seen on the oscilloscope (the extreme case was a total failure of the system to oscillate). In addition to this, lateral growth of the

working electrode was observed, changing the electrochemically active area. To avoid the obvious problems resulting from either of these situations, periodic stripping of the deposit was required. This was achieved by placing the WE in the stripping solution and sweeping the potential anodically from a value of -200 mV to $+200\text{ mV}$ at a rate of 5 mV s^{-1} . If, at the end of this sweep, a clean gold surface was not observed, the potential was held at the final value of $+200\text{ mV}$ until this criterion was met.

5.7.4 Derivation of the half-reaction current densities in the complete low temperature nickel baths

A fresh, complete bath, was prepared from stock solutions. This was thermostatted to the required temperature. The QME was assembled as in Section 5.7.1, using the nickel CE (coiled wire, surface area $\sim 7.6\text{ cm}^2$).

In order to initiate nickel plating over the gold electrode, a potential of -1.00 V was briefly applied to the QME. A subsequent open circuit potential of about -0.94 V (hypophosphite bath) or -1.02 V (DMAB bath) was evidence of successful initiation.

Prior to the commencement of readings, the potential of the WE was stepped to the required value. After allowing the interfacial conditions at the WE to reach a steady state (a period of time less than 60 s), the computer was activated to read the electrode current and resonance frequency. By visually monitoring the current and frequency change on the computer monitor,

it was possible to determine whether or not a steady current and constant rate of mass change was being exhibited. In this type of experiment, these two criteria were required to be met. Data collection continued for a period of 60 to 200 s. Frequency deviations from the initial reading were converted to mass changes per unit area, using the Sauerbrey equation (3.1). The value used for f_0 was the first frequency value of the data set. For each experiment, three data files were saved. The first contained the current values corresponding to the time of reading (i.e., time from start of data logging). The second contained the frequencies and cumulative mass changes per unit area, and the third contained the measured electrode potential.

These data were manipulated after the completed experiment, to produce the current densities. The cell current measured at the WE was divided by the working electrode area to obtain the net current density, j_{net} . In order to obtain the cathodic current density, j_c , the rate of mass change per unit area, R_q , was calculated from the mass change/time data using the linear least squares method. Then, following the relationship of rate of an electrode reaction to charge flux given in Equation 2.8, the cathodic current density corresponding to R_q can be determined. The basis of the calculation is given in Appendix III.

For the H_2PO_2^- reduced bath, 1 HPO_3^{2-} is the product of hypophosphite oxidation, for a composition of 95.8 atom % Ni, 4.2 atom % P, then $1 \text{ mg cm}^{-2} \text{ hr}^{-1}$ corresponded to $j_c = -0.983 \text{ mA cm}^{-2}$ (Orchard 1988b). The alloy composition may vary slightly with small changes in concentrations and plating temperature, but the quoted

conversion factor was used for all calculations involving the Ni-P alloy from Bath 1.

Similarly, for the DMAB reduced bath, the composition of the nickel - boron alloy was taken as 99.5% Ni, 0.5% B (Feldstein 1970). Assuming elemental boron in the alloy and two- and three electron reductions for nickel and boron respectively, $1 \text{ mg cm}^{-2} \text{ hr}^{-1}$ corresponded to $j_c = -0.946 \text{ mA cm}^{-2}$, the negative sign of j_c indicating a cathodic process.

Equation 2.30 was used to calculate the anodic current density, j_a . This is a lower limit for the anodic current density since hydrogen evolution and any other possible reduction side-reactions were not taken into account.

By plotting potential as the abscissa and current density as the ordinate, with j_{net} , j_c and j_a on the same set of axes, the anodic and cathodic current-potential relationships were generated. The mixed potential (plating potential) of the electroless process is theoretically the value of the abscissa where $j_{\text{net}} = 0$.

5.7.5 Derivation of the current density - potential relationships for nickel baths of different composition

Apart from the altered composition of the baths, the procedure differed from the above only in respect of the method of electrode pre-treatment. When the modification to the bath was such that there was no metal deposition taking place, but only the anodic

process(es), it was necessary to provide an initial electroless nickel film over the gold QME. A complete plating bath was used for this purpose. The QME was allowed to plate electrolessly in the complete bath until a uniform deposit formed. The electrode assembly was briefly rinsed in pure water and transferred to the modified bath without delay. Measurements were then carried out as previously described.

When the modification was the removal of the reducing agent, an initial electrolytic layer was formed *in situ* prior to the first set of readings. Since an electrolytic nickel film was formed and continuously renewed throughout the experiment, there was no need to preplate the electrode with an electroless film.

5.7.6 Derivation of the half-reaction current densities on various surfaces in nickel baths

In this series of experiments, the objective was to determine the influence of the initial surface condition on the rates of the anodic and cathodic partial processes. Bath 1 was used both to produce electroless nickel substrates for further study and (in either modified or unmodified form) as the solution for studies of the initiation process.

Anodic stripping of electroless nickel deposits was carried out at $25 \pm 2^\circ\text{C}$ in a moderately stirred solution of Na_2SO_4 (0.040 mol L^{-1}) and H_2SO_4 (0.200 mol L^{-1}). Electrolytic nickel deposits were obtained by cathodically plating nickel from a bath of the same

composition as the electroless bath above, except that the sodium hypophosphite was omitted.

For stripping, an anodic-going potential sweep was employed, starting at the open circuit potential (which was between -0.370 V and -0.336 V) and ending at either 0.045 V (for partial stripping) or 0.300 V (for complete stripping), at a rate of 2.5 mV s^{-1} . Electroless nickel substrates which were not to be stripped at all were held at -0.336 V in the acidified Na_2SO_4 for a time equivalent to the sweep time of partial stripping. The electrodes were rinsed in water after removal from the stripping solution. Spontaneous initiation of electroless plating on the different substrates was studied by immersing the QME in the plating bath at open circuit, and monitoring the electrode potential and mass change with time. Potentiostatic studies of the early stages of electroless plating were performed by immersing the QME in the plating bath, under potential control by a potentiostat (at either -1.025 , -0.950 or -0.875 V), and monitoring the electrode current and the mass change with time. A period of 3-4 s was allowed prior to commencement of the data logging. A magnetic stirrer bar provided moderate stirring during all plating studies. None of the solutions were deaerated.

5.7.7 Preparation of electrolytic Ni-P deposits

Electrolytic nickel deposits rich in phosphorus were prepared on the QME after the method of Cargill (1979). These deposits were used as prepared, or were partially stripped as was done for the electroless nickel

deposit. Electrolytic Ni-P deposits were prepared for comparison to those produced by autocatalytic plating.

5.7.8 Derivation of the half-reaction current densities for copper baths

The experimental procedure follows that for current density determinations in the low temperature nickel baths. The counter electrode employed was a copper rod (99.9%, Johnson Matthey), 15 mm long with a diameter of 6.35 mm. This was cleaned in dilute nitric acid and de-ionised water prior to use. During experimentation with the TEA bath, the Luggin capillary was filled with 0.06 mol L⁻¹ Na₂SO₄·10H₂O. For the baths with the HIQSA and HQSA additives, the reference electrode was separated from the working solution by an agar bridge (4% agar gel, 1.0 mol L⁻¹ KCl).

The calculation of the cathodic current density from mass change per unit area data was accomplished by treating the deposition of copper as the only cause for mass change on the crystal and as the only significant cathodic partial process.

Since Bath 4 required very low concentrations of 2,2'-dipyridyl (DIPY) and potassium ferrocyanide, a 200.0 mL stock solution of these components was prepared, containing 35.0 mg potassium ferrocyanide and 20.0 mg DIPY. A 10.0 mL aliquot of this solution in a total volume of 100.0 mL working solution yielded the correct concentrations of the compounds.

5.7.9 Activation energy measurements

By allowing the QME to be electrolessly plated with the nickel alloy, at various temperatures, the activation energy (E_a) of the electroless plating process could be determined.

The rate of the reaction, or deposition rate, R_d , has been defined as the rate of mass change (per unit area) of the QME. This may be related to the activation energy by Equation 5.1.

$$R_d = A \times \exp \left(\frac{-E_a}{RT} \right) \quad (5.1)$$

$$\text{therefore } \ln(R_d) = \ln(A) + \left(\frac{-E_a}{RT} \right) \quad (5.2)$$

A is the pre-exponential factor, R the gas constant and T the temperature. Plotting $\ln(R_d)$ vs. T^{-1} gives a line with a slope equal to $(-E_a/R)$. Hence

$$E_a = -R \times (\text{slope}) \quad (5.3)$$

5.7.10 Plating on glassy carbon substrates

Glassy carbon (G.C.) discs (Sigridur G), were used as substrates for analysis of nickel-containing deposits by energy dispersive analysis by x-rays (EDAX) and for some electrochemical studies.

By holding a G.C. electrode in Bath 1 at -1.050 V for 30 s, sufficient Ni-P alloy was deposited for continued electroless deposition. After 10 minutes of electroless

deposition, the alloy was stripped off at 0.300 V in the acidified sodium sulphate solution. This process served to condition the electrode for the deposition of the substrate of interest. The deposition process was repeated to yield the experimental substrate. This substrate was then replaced in Bath 1, or partially stripped as described above prior to replacement in Bath 1. The appropriate measurements of electrode potential were then made.

5.7.11 Spectrophotometry

5.7.11.1 Nickel, Bath 1

Determinations of the effect of reducing agent and oxidation reaction product on the metal complexes in solution in the low temperature nickel baths were qualitatively made by spectrophotometry. A Hitachi U2000 spectrophotometer was used, which operated in the ultraviolet and visible ranges. This instrument had the facility to calculate a baseline for any reference sample, so it was possible, for example, to use a complete nickel bath solution in the reference beam and obtain absorption spectra relative to this. In each case, the instrument was initially set up to create a baseline using the reference beam sample. Spectra were obtained at room temperature.

A solution of sodium phosphite (Na_2HPO_3) was prepared by reacting 15.00 mL phosphorous acid (H_3PO_3) (25% w/v) with excess sodium hydroxide to reach a final pH of 10.85 and a concentration of Na_2HPO_3 of 0.51 mol L^{-1} .

This solution was used in equal proportion to Solution "A" (Section 5.5.1).

Solutions for which spectra were obtained:

- * Bath 1, without R.A.

- * Bath 1

- * Bath 2

(reference solution: 1 mol L⁻¹ KCl)

- * Bath 1, without KCl; pH 10.65

- * Bath 1, without KCl and with H₂PO₂⁻ anion substituted with phosphite anion of equal concentration, i.e., 0.26 mol L⁻¹; pH 10.85

(reference solution: pure water)

- * Bath 1, without KCl and with H₂PO₂⁻ anion substituted with phosphite anion of equal concentration i.e. 0.26 mol L⁻¹; pH 10.85

(reference solution: Bath 1, without KCl; pH 10.65)

5.7.11.2 Copper, Bath 5, with HIQSA and HQSA

Using the same instrumentation as described in the previous section, spectra in the range 350 to 700 nm were obtained for the following solutions:

- * Bath 5 (without HCHO)

- * Bath 5 (without HCHO) and with HIQSA (208 mg L⁻¹)

- * Bath 5 (without HCHO) and with HQSA (200 mg L⁻¹)

These solutions were prepared by first making up the quinoline sulphonic additive solutions at alkaline pH (approx. pH 12.8), and then using these as stocks to prepare the solutions containing copper sulphate and EDTA. In this manner, it was possible to use the quinoline sulphonic acid additive solutions as blanks in both spectrophotometry and cyclic voltammetry.

5.7.12 Addition of acetate anion to plating baths

Both Baths 1 and 2 were investigated. A Gilson 20 μL Pipettman was used to add small volumes of sodium acetate solution to the baths while the electroless plating was occurring on the QME. Baths were thermostatted at 20°C for these experiments. Plating rate was determined as a function of acetate anion concentration. Dilution of the bath with addition of the small aliquots was considered to be negligible. A period of 60 s was allowed before rate measurements were taken after each addition of acetate solution.

5.7.13 Effect of addition of H_2PO_2^- to Bath 2

The effect of H_2PO_2^- on the plating rate of Bath 2 was determined by adding aliquots of the concentrated sodium hypophosphite solution to a bath plating electrolessly at 20°C. The dilution effect due to addition was considered negligible. The experiment was also performed using solution "B" (Section 5.5.1) of Bath 1 as the added component. The first addition of sodium hypophosphite solution was preceded by 290 s of uninterrupted measurement of R_p . A grade A 1.00 mL pipette was used to discharge the solution into the bath. Electronic circuitry and measurement devices were not interrupted. Measurement continued for 300 s, the final rate being determined over the last 200 s. Subsequent aliquots were added prior to 100 s measurement periods.

5.7.14 Effect of sparging the hypophosphite bath with oxygen

The plating rate of a deoxygenated hypophosphite bath was determined. Thereafter, oxygen was bubbled through the bath and the effect on plating rate noted.

5.7.15 Cyclic Voltammetry

A CV27 voltammograph (Bioanalytical Systems) connected to a PCB-386 personal computer was used in cyclic voltammetry of Bath 5 and the various modifications thereof, as described in Section 5.7.11.2 above. The computer was equipped with a National Instruments PC-LabCard 12-bit A/D converter and PC-LabDriver ver. 1 software. The cyclic voltammetry data acquisition program was developed by John Marsh (Marsh 1993). Solutions were thermostatted to 30°C using a MGW Thermotemp water circulator. A copper disc electrode, (2.0 mm diameter, 99.9% Johnson Matthey) set in epoxy, served as the working electrode. A Pt flag (Metrohm 6.035.000) was the counter electrode and the reference was a calomel electrode with salt bridge as described in Section 5.7.8. The working electrode was polished to a 1 μm finish with alumina (Buehler) and cloth (Hyprocel, Engis Ltd.) prior to each scan.

After allowing the solution to become quiescent, a potential of -0.30 V was applied to the WE for 30 s. Following this, the CV was started with the cathodic-going scan at 50 mV s⁻¹.

5.7.16 X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy

An x-ray photoelectron spectrometer comprising of the following systems was used for x-ray photoelectron spectroscopy (XPS). Vacuum chamber: Vacuum Generator "Solar 300" (base pressure 4×10^{-10} bar); x-ray and electron source: VG "CLAM 100", with standard (Mg/Al) water cooled anode and LEG61 electron gun. The sources shared a 150° spherical detector analyser and channeltron detector.

Nickel phosphorus and nickel boron alloys on G.C. substrates were examined. Samples were scanned in the relevant binding energy ranges in the as-produced state, and after argon ion ablation.

A JSM 840 scanning electron microscope (SEM) was used to examine G.C. and quartz microbalance electrodes, and to perform energy dispersive analysis by x-rays (EDAX) on Ni-P and Ni-B deposits on these substrates. For SEM studies, the samples were examined as produced without further coating. Semi-quantitative EDAX analysis was performed by ZAF-4 computer programs.

CHAPTER 6

RESULTS AND DISCUSSION -

THE QUARTZ MICROBALANCE ELECTRODE

CHAPTER 6 RESULTS AND DISCUSSION - THE QUARTZ MICROBALANCE ELECTRODE

6.1 APPARATUS

The utility of the quartz microbalance in electrochemical applications has been shown by numerous researchers as described in the literature survey (Chapter 3). In the present work, the QME and related circuitry which were constructed were found to be of an acceptable standard in terms of response to mass change, robustness and compatibility with the instrumentation described.

During the course of the development of the QME used in this work, experimentation with crystals and circuitry revealed a number of important facts.

6.1.1 Crystal

The technique of application of electrode material to the crystal surface determined, to a large degree, the success of the device. Gold did not adhere sufficiently strongly to the quartz surface to stand up to the harsh conditions of gas evolution and surface stress during electrolytic or electroless plating. The use of a chromium underlayer was required. A silane compound has been used as a molecular adhesive for gold on SiO_2 (Goss, Charych and Majda 1991). These authors applied (3-mercaptopropyl) trimethoxysilane to a clean surface prior to gold coating, for ultimate use in an

electrochemical environment (the silane moieties bind covalently to the oxide surface through siloxane bonds, while the thiol groups engage in strong binding to gold). The adhesive layer is thus monomolecular. If adopted for QME preparation, this method would allow for easier recycling of crystals, since the difficult step of removal of a tenacious and passive Cr layer would be avoided. A problem which could be encountered, however, is that for autocatalytic plating, nucleation may occur on the silanized surface not within the bounds of the actual electrode. Spurious results would then be obtained as a result of radial growth of the electrode.

It was found that if the thickness of the gold electrodes was below a minimum value, oscillation was sustained in the gas phase (i.e. air) but ceased when one crystal face was in contact with liquid. In order to quantify the required film thickness, a four-point probe (Smits 1958) was constructed, but was found to be superfluous; a minimum coating time in the Polaron coating unit of 55 minutes was found to consistently produce suitable films. The connection of the wire lead to the WE was best achieved by a small amount of silver epoxy adhesive. Attempts to incorporate a wrap-around of gold from the coating procedure were unsuccessful. The best arrangement obtained was the attachment of the WE current collector (i.e., copper wire) to the front face of the crystal, ensuring that the Cu and conducting epoxy did not protrude from the silicone o-ring after assembly. Thus a wrap-around of conducting epoxy was avoided, although this technique was used in the earlier experiments in this work. Bending the wire around the edge of the crystal was a distinct improvement in methodology, because an epoxy

wrap-around proved to be difficult to remove during recycling of the crystals.

Possible improvements to the coating procedure include a masking technique which does not employ adhesive tape, a modified mask which allows a tab of gold to be deposited on the reverse face where the wrap-around of conducting epoxy would be applied, and simplification of the procedure to allow coating of all required metals of the WE in one unit. An o-ring allowing for sealed contact of leads without the necessity of silver paint as adhesive would expedite the recycling of crystals after use in experiments, as well as rapid replacement of crystals during experimentation. One particularly useful design was recently developed at IBM Research Labs., San Jose (Hessami, Armstrong and Kanazawa 1992), whereby the crystal was sealed to an o-ring by the action of a vacuum pump. Spring loaded pins served as contacts to the electrodes. This arrangement is more feasible for large diameter crystals (i.e., about 25 mm dia.), than for the smaller sizes (i.e., 13-14 mm dia.). Interestingly, this design allowed the QME to be used as a wall-jet electrode.

6.1.2 Circuitry and instrumentation

Numerous oscillator circuits were built and tested during the course of this work. These included the Clapp, dual input NAND gate and 74LS320 based oscillators already mentioned in Chapter 3, as well as an oscillator of unknown circuit design loaned from STC Components. The latter was found to have sufficient pullability and power to sustain oscillation for the QME but could not be used without considerable contribution to potential and/or current at the WE. The

former three oscillators did not sustain oscillation for the loaded QME. The oscillator based on the Pierce-Miller design described in Chapter 5 was the most successful circuit, as it exhibited pullability, sustained oscillation in liquid, maintained one crystal face at ground potential, and was found to be stable when a sealed test crystal was connected in place of the microbalance crystal.

A modification of the Pierce-Miller oscillator circuit to allow for operation at higher harmonics of the crystal was implemented by Beck, Pittermann and Weil (1992). Operating the crystal at harmonics extends the sensitivity of the microbalance. These workers utilised the amplifying properties of a field effect transistor, and other minor changes, to achieve the desired effect. In the present case, however, operation at 5 MHz was found to be sufficient, and acceptable precision and accuracy were obtained.

A Bioanalytical Systems CV27 Voltammograph was used in initial tests. This potentiostat was found to be unsuitable because the internal arrangement is such that the reference electrode, and not working electrode, is at ground potential. Thus the use of the equipment and circuitry as listed in the Instrumentation and Methods section (Chapter 5) was shown to be the best available for this study. The use of earthing leads between all instruments, and a metal box to house the oscillator circuit was found to be necessary, in order to minimise the effects of electrical noise. Fine tuning of the oscillator circuit for each crystal was required.

The final version of the computer program allowed for measurement of frequency, cell current and potential up

to three times per second, including averaging of the latter two parameters. By user specification, this could be done for a pre-defined time, or until a specific potential was measured (e.g., for LSV). After recording the data on disc, all three quantities were plotted simultaneously on the monitor on separate, annotated scales. This provided for immediate assessment of the results of the experiment.

6.2 SENSITIVITY AND ACCURACY

The following results led to the conclusion that a reliable QME had been constructed.

6.2.1 Theoretical and observed sensitivity

The QME was shown to exhibit a linear response to mass change occurring at a constant rate. This is illustrated in Figure 6.1 and Figure 6.2. The current was seen to be steady during the potentiostatic electrolytic deposition. Thus, the measured mass change rate did not vary with time for low loading of the crystal.

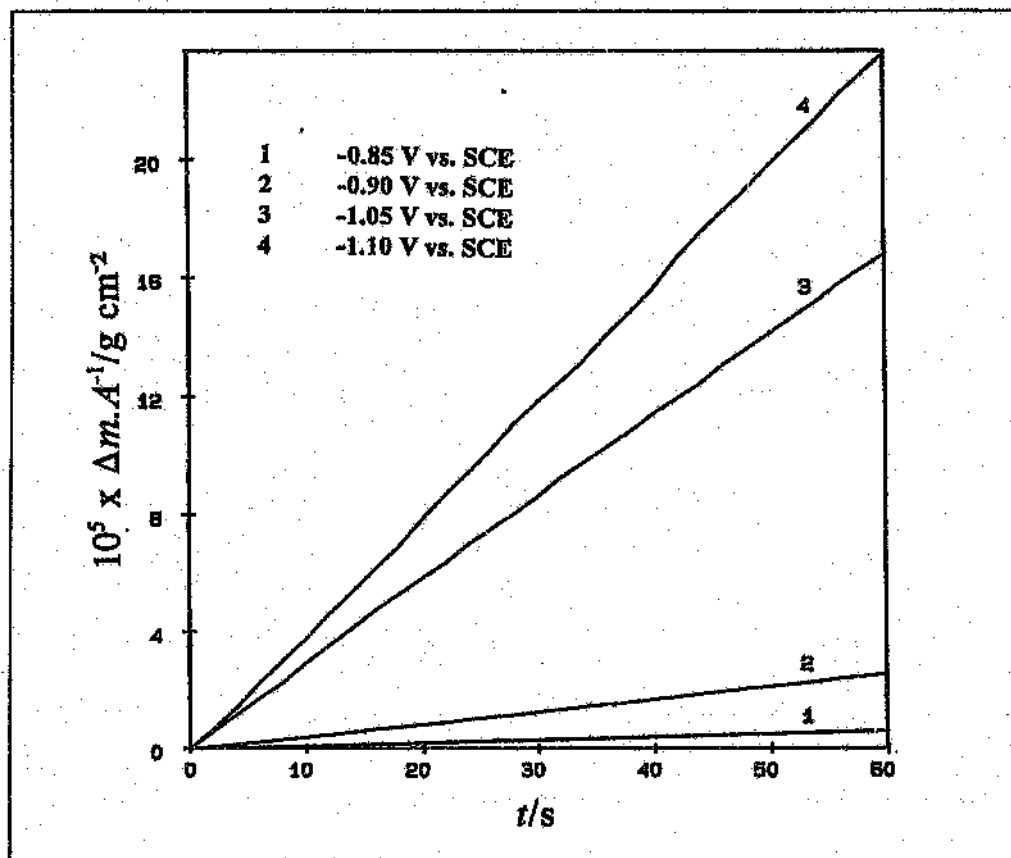


Figure 6.1 Response of the QME to electrolytic deposition of nickel at various potentials. Electrolyte: Bath 1. Temperature 35°C.

For a crystal with a resonance frequency of exactly 5.00 MHz, the theoretical sensitivity is 5.66×10^7 Hz cm² g⁻¹, according to Equation 3.2. The sensitivity calibration described in Section 5.7.1 (Chapter 5) yielded the results given in Table 6.1. In this table Δm_0 represents the mass change per unit area predicted from the faradaic current. The last column, containing the ratio of frequency change to mass change, represents the sensitivity. The average sensitivity obtained was 5.328×10^7 Hz cm² g⁻¹, with a standard deviation of 0.443×10^7 Hz cm² g⁻¹.

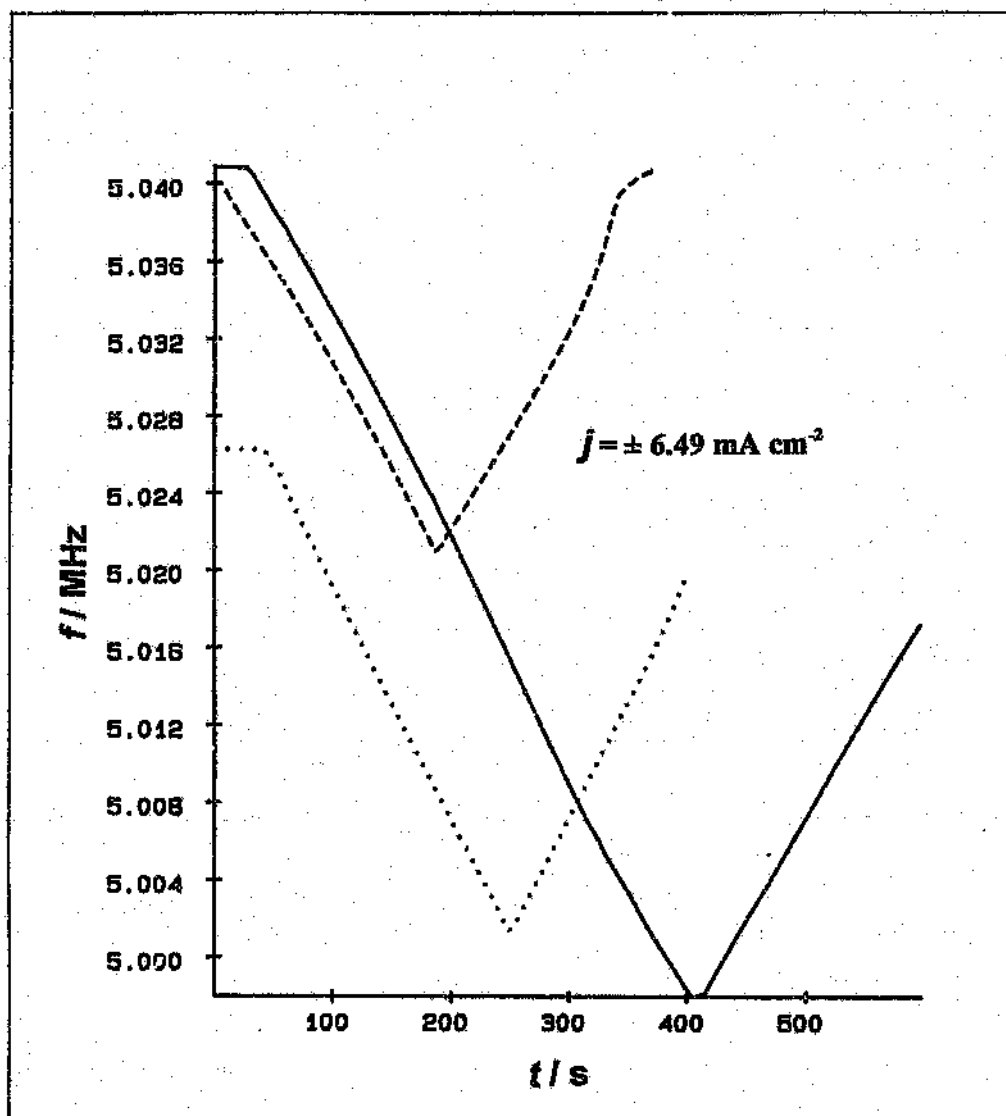


Figure 6.2 Resonance frequency as a function of time during galvanostatic deposition of copper. Electrolyte: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.721 mol L^{-1}), 98% H_2SO_4 (0.036 mol L^{-1}). Temperature 30°C . Moderate stirring.

Examination of the box-and-whisker plot (Figure 6.3) confirms that the measured sensitivities were evenly spread around the median value, with no outliers. Thus the mean value, closely corresponding to that expected for a 5.00 MHz crystal, was not obtained by virtue of fortuitous outlying data. Box-and-whisker plots are described in Appendix V.

Table 6.1 Calibration of the QME by galvanostatic deposition of copper from acidic copper sulphate (0.16 mol L^{-1}) solution.

I /mA	t /s	F_o /Hz	F_t /Hz	$10^4 \times \Delta m_Q$ /g $\text{cm}^{-2} *$	$10^{-7} \times \Delta F / \Delta m_Q$ /Hz $\text{cm}^2 \text{g}^{-1}$
-2.50	100	5033706	5019152	2.74	5.31
2.50	90	5019728	5030424	-2.03	5.27
-2.50	150	5034376	5013160	4.12	5.15
2.50	60	5013044	5020957	-1.65	4.80
2.50	20	5021242	5023753	-0.55	4.57
-2.50	30	5021971	5017560	0.83	5.30
-3.50	30	5017490	5011752	1.15	4.98
-2.50	100	5010906	4998682	1.65	6.00
2.50	24	5007824	5010238	-0.402	4.9
-2.50	43	5010696	5005945	0.703	5.5
-1.51	158	5010903	4999227	1.57	5.99
-2.52	400	5010141	4961266	6.64	5.95
-2.51	327	4960472	4997693	5.41	5.56

* minus sign implies mass loss

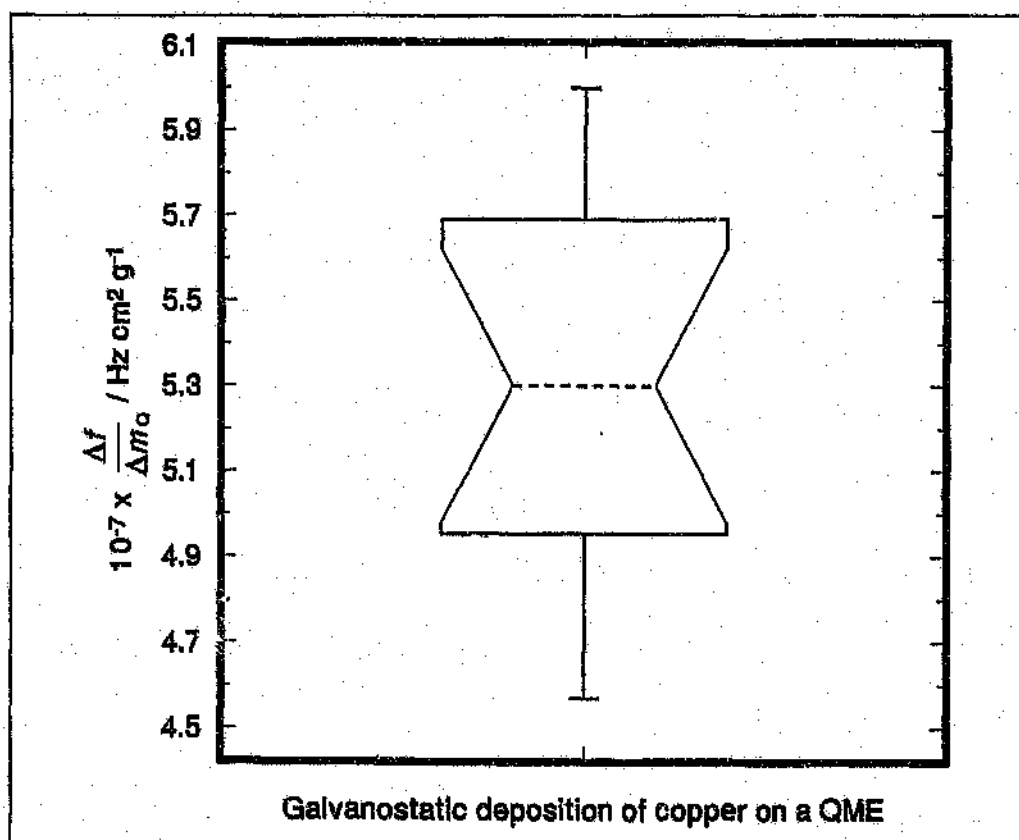


Figure 6.3 Box-and-whisker plot of the sensitivity data for the QME, presented in Table 6.1.

The results given in Table 6.1 are plotted along with some of the results of Stöckel and Schumacher (1987), for purposes of comparison (Figure 6.4). Results obtained in a nickel plating bath yielded sensitivities between 4.8×10^7 and 5.2×10^7 Hz cm² g⁻¹.

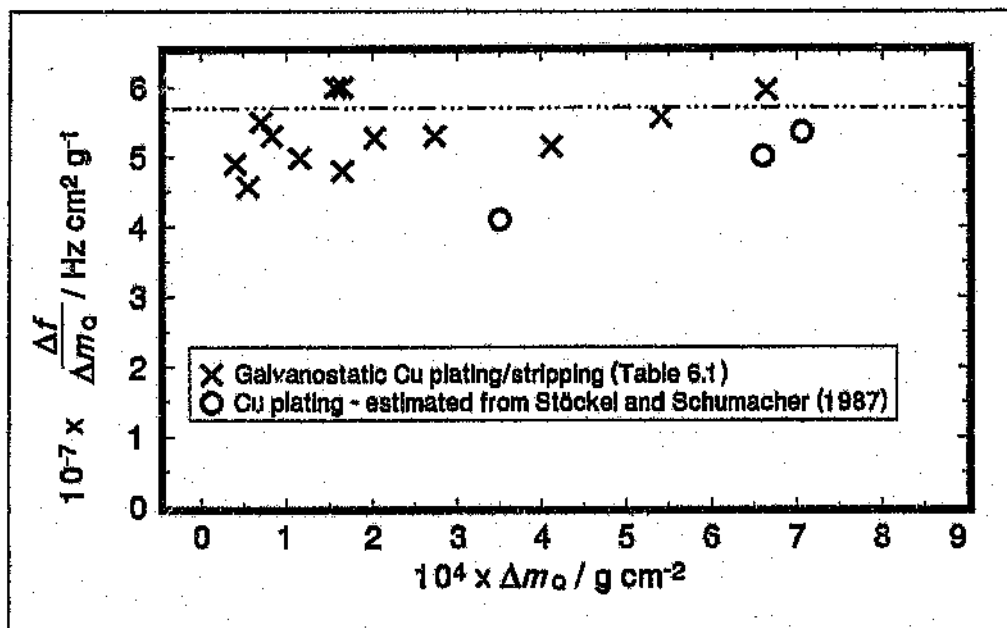


Figure 6.4 Sensitivity of the QME.

It was concluded that the average sensitivity obtained in the present study was consistent with values expected for crystals operating at fundamental frequencies near 5.00 MHz. The device was considered to be reliable for further electrochemical work.

6.2.2 Comparison to previous results

Curves illustrating the relationship between current densities and potential (CD curves) for Bath 1, obtained with the QME (Figure 6.5), were compared with those obtained with an RDE (Figure 6.6) (Orchard 1988b). The CD curves compared very favourably, although a minor difference was noted. The point where

the three curves converge to zero current was found to be at about -0.6 V vs. SCE (all potentials hereinafter are referenced to the saturated calomel electrode) for the QME whereas it was at about -0.8 V for the RDE. The discrepancy could well be attributed to the different hydrodynamic conditions at the QME as compared to the RDE, which would affect the relative mass transfer rates at the two electrodes. A similar phenomenon was noted by Chandler and co-workers (Chandler et al. 1991), who used a QME and an RDE in corrosion studies of thin films. Discrepancies in polarisation curves obtained with the two types of electrode were explained in terms of the different hydrodynamic conditions at the two electrodes.

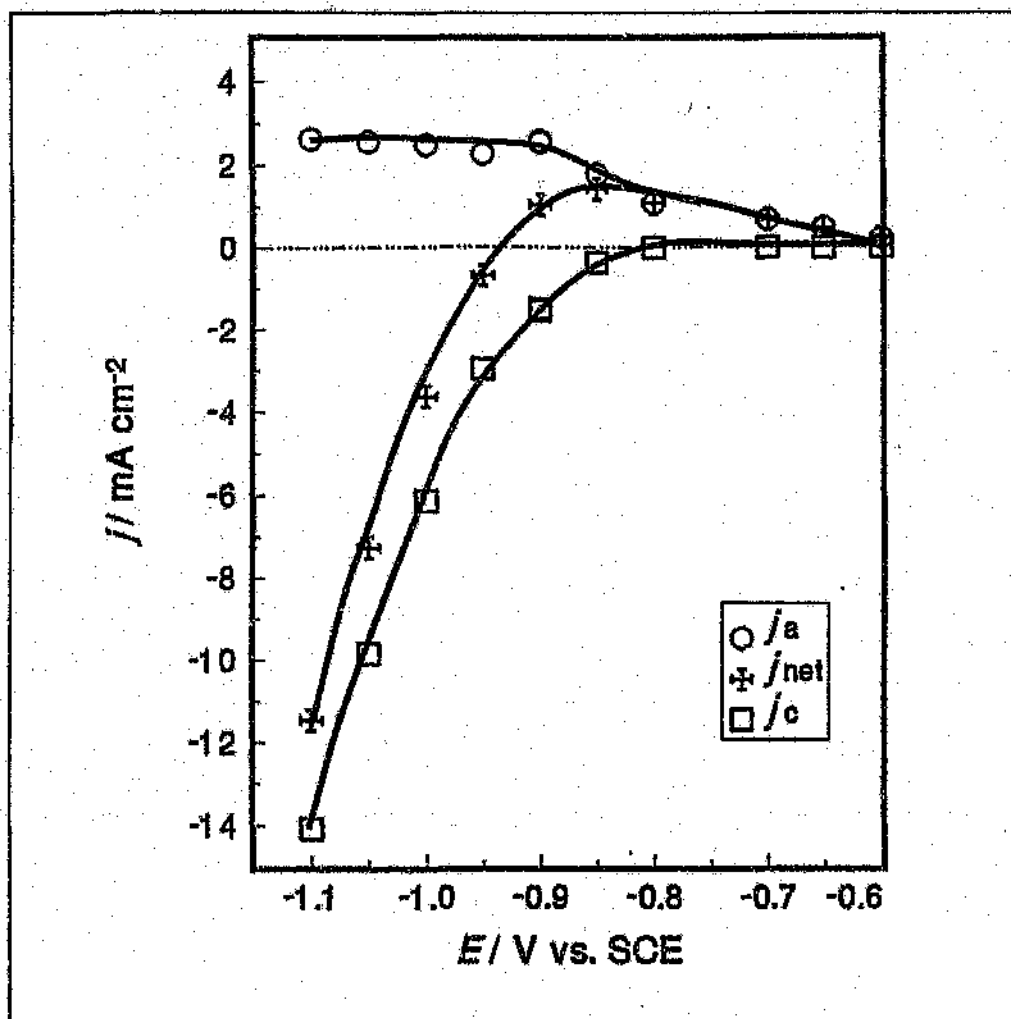


Figure 6.5 Partial CD curves for Bath 1 at 35°C obtained using the QME.

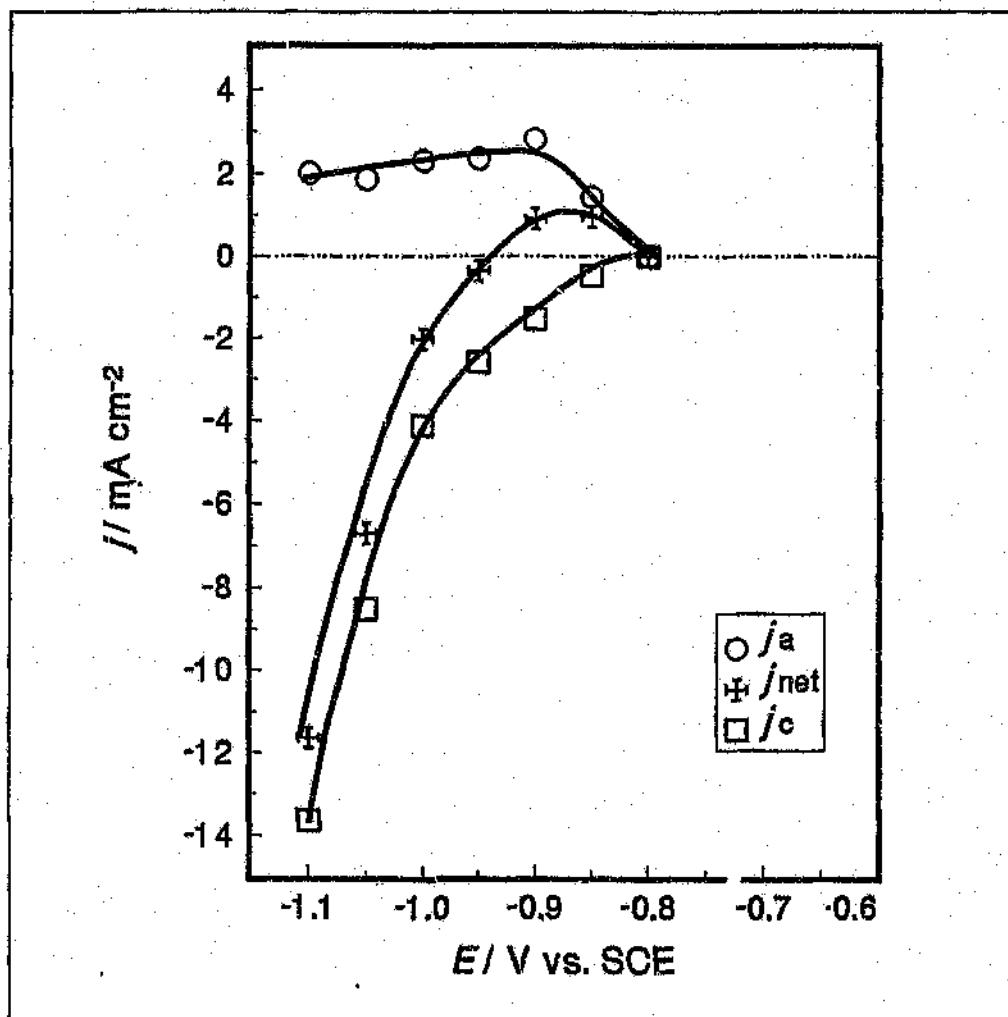


Figure 6.6 Partial CD curves for Bath 1 at 35°C obtained using the RDE (Orchard 1988b).

6.2.3 Use of the QME in corrosion studies of aluminium

The quartz microbalance equipment constructed for this project was also successfully used in potentiodynamic corrosion studies of evaporated Al films (Gnoinski 1993). The various validation procedures described in the present work, as well as others specific to the Al system, were employed, and the results found to be entirely satisfactory.

6.2.4 Reproducibility of experimental results

Replicate experiments performed during the course of this work were found to be in good agreement with one another. Some examples of replicate experiments are illustrated in Appendix IV.

CHAPTER 7

AUTOCATALYTIC NICKEL DEPOSITION

CHAPTER 7 RESULTS AND DISCUSSION -

AUTOCATALYTIC NICKEL DEPOSITION

7.1 EFFECT OF OXYGEN ON NICKEL PLATING RATE

It was possible to pass nitrogen through the solutions during all types of measurements performed in this work. This deaeration technique was avoided, since the resulting depletion of ammonia from the baths would change the bath compositions and pH. In order to verify the assumption that deaeration was not required, a previously deaerated and actively plating bath was sparged with O_2 . No significant effect on plating rate was noted. None of the electroless baths investigated in this work were deoxygenated.

7.2 ANODIC STRIPPING OF ELECTROLESS NICKEL FILMS

When thin ($0.2 - 0.3 \mu m$) electroless nickel deposits on glassy carbon or gold substrates are anodically stripped (see Section 5.7.6), voltammograms such as that of Figure 7.1 are observed. The QME response, expressed as the first derivative, is superimposed on a stripping voltammogram to illustrate the mass change of the electrode associated with the current response (Figure 7.2).

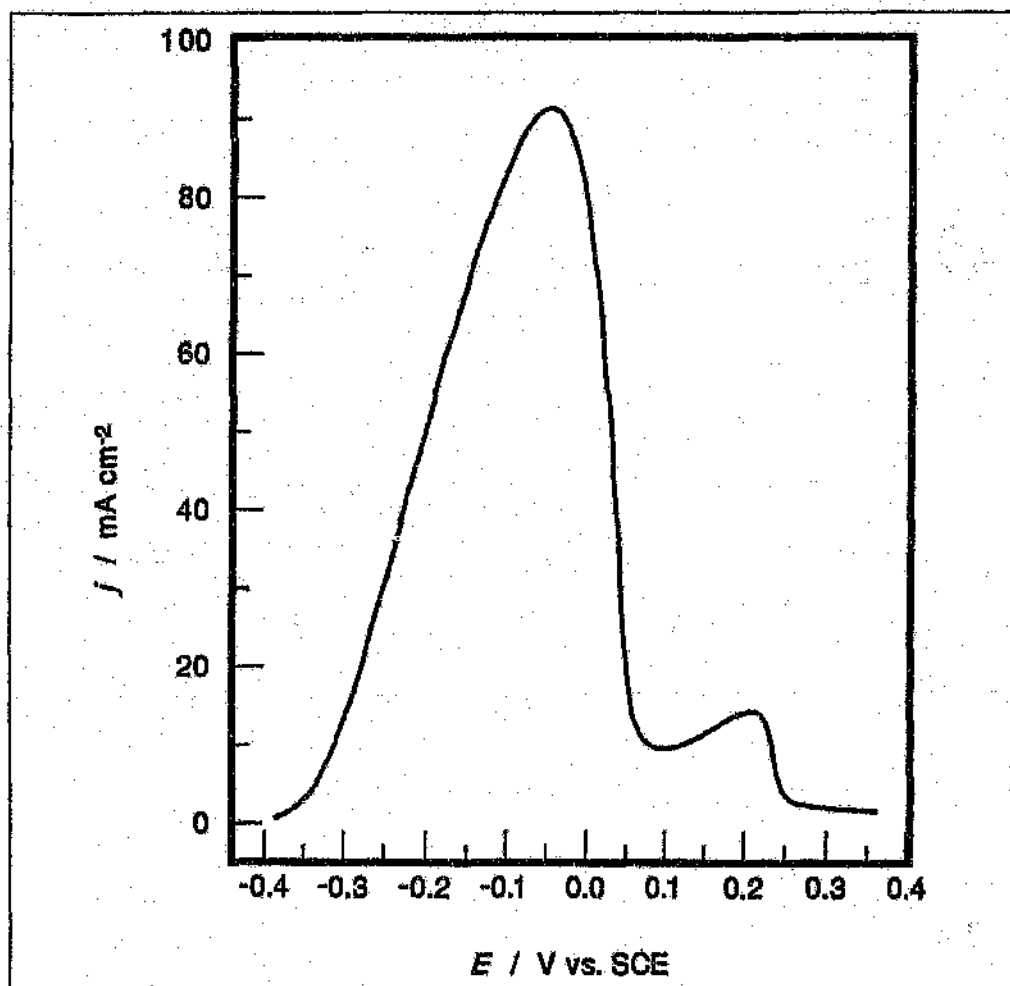


Figure 7.1 Anodic stripping voltammogram of electroless Ni-P deposit in acidified Na_2SO_4 solution, on glassy carbon. Sweep rate 2.5 mV s^{-1} , temperature 26.5°C .

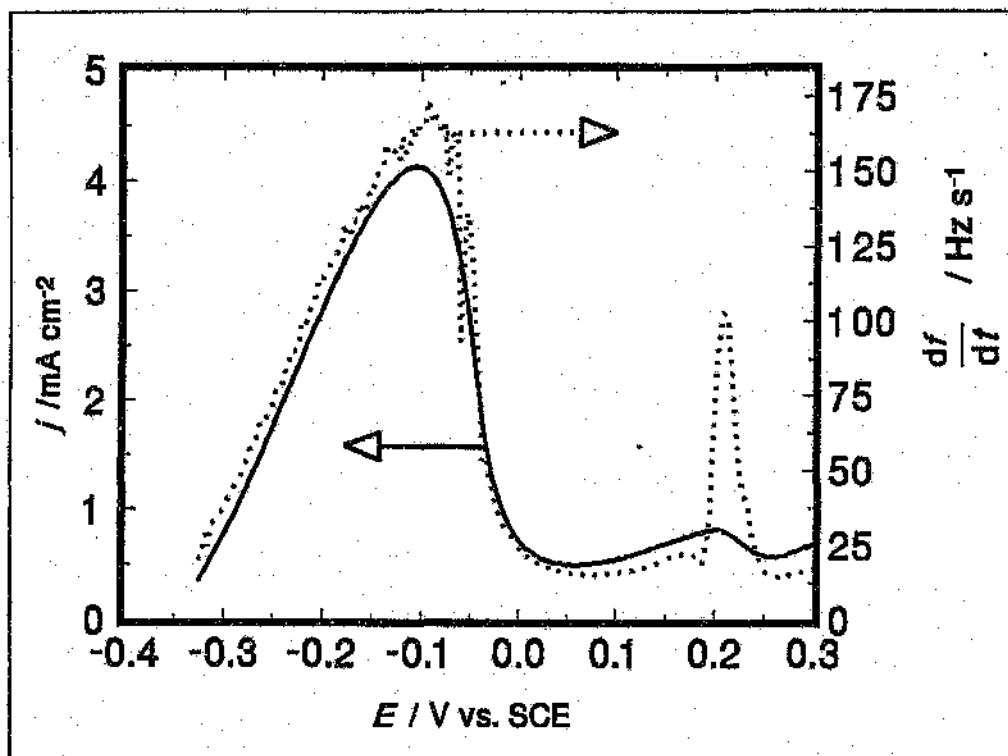
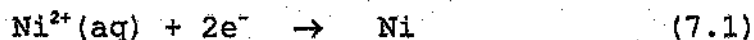


Figure 7.2 Superimposed traces of current response and rate of frequency change for a QME undergoing anodic stripping of a nickel-phosphorus alloy film. Sweep rate 2.5 mV s^{-1} , temperature 23°C .

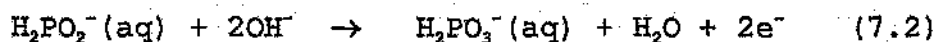
The two peaks of the voltammogram are very similar in form to those reported by Benje and co-workers (1988) who stripped thin, electrolytic nickel-phosphorus (Ni-P) deposits under similar conditions. The potential sweep of Figure 7.1 results in complete stripping of electroless nickel deposits from the substrate. However, if the sweep is stopped at 0.045 V , incomplete stripping occurs, leaving a residual deposit which is highly enriched in phosphorus. The residue has a matt black appearance, in contrast to the electroless nickel film which looks much like bulk nickel. Table 7.1 shows results of EDAX analyses of such deposits, along with analyses of the original electroless nickel and a pure, electrolytic nickel deposit. In keeping with the findings of Benje and co-workers, it appears that the first stripping peak is due to a nickel-rich phase, and

the second peak to a phosphorus-rich phase. Benje et al. (1988) used electron diffraction to characterise the two phases, reporting that the less noble phase is fcc nickel, supersaturated in phosphorus, while the more noble phase is amorphous Ni-P. In the present work, it was found that the deposits were too thin to yield useful x-ray diffraction patterns, and it has been assumed that the two phases observed in this study are essentially the same as those reported by Benje et al. (1988), and Weil and Hofmann (1990).

During steady state nickel plating, the two half-reactions of primary interest here are



and



Here $\text{Ni}^{2+}(\text{aq})$ represents the complexed nickel ion. Additional electron transfer reactions produce hydrogen gas, and phosphorus in the solid deposit. However, since reaction (7.1) accounts for almost the entire mass of the deposit (Table 7.1), the mass change measurements made with the QME essentially reflect the rate of this process.

Table 7.1 EDAX analysis of nickel-containing deposits originating from Bath 1* or modifications thereof.

	Type of Deposit		
	Full electroless nickel	Partially stripped electroless nickel	Electrolytic nickel
Atom % Ni	94±1	52±1	>99.5
Atom % P	6±1	48±1	<0.5

7.3 ACTIVATION ENERGY DETERMINATIONS

The Arrhenius activation energy for the hypophosphite based bath (Bath 1) was found to be 66.4 kJ mol^{-1} , using the QME, compared to Feldstein's value of $59 \pm 2 \text{ kJ mol}^{-1}$, and Orchard's (1988b) value of $58 \pm 2 \text{ kJ mol}^{-1}$. A graph of the data used for the activation energy determination of Bath 1 is illustrated in Figure 7.3.

The Arrhenius activation energy for the DMAB bath (Bath 2) was found to be approximately 57 kJ mol^{-1} (Figure 7.4). Feldstein (1970) obtained a value of $36 \pm 2 \text{ kJ mol}^{-1}$.

While the values of the activation energy obtained with the QME were higher than those obtained by Feldstein, particularly for the DMAB bath, the data obtained in the present work showed little scatter as evidenced by the 95% confidence bounds on Figure 7.3 and Figure 7.4. It is not clear why the QME gave a value of activation

* Bath compositions are given in Chapter 5, Section 5.5.

energy 68% greater than that presented by Feldstein. The difference between the data for the H_2PO_4^- bath was lower, and it was concluded that small variations in bath composition and pH were responsible for the inconsistencies. This source of error may be magnified since the QME obtains data over a short period of time whereas *ex situ* gravimetric methods require longer plating times. Changes in pH and bath composition may then occur. In this regard, Feldstein presented data showing a strong dependence of plating rate on the concentration of DMAB when the concentration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was 25 g L^{-1} , equivalent to that used in the present work.

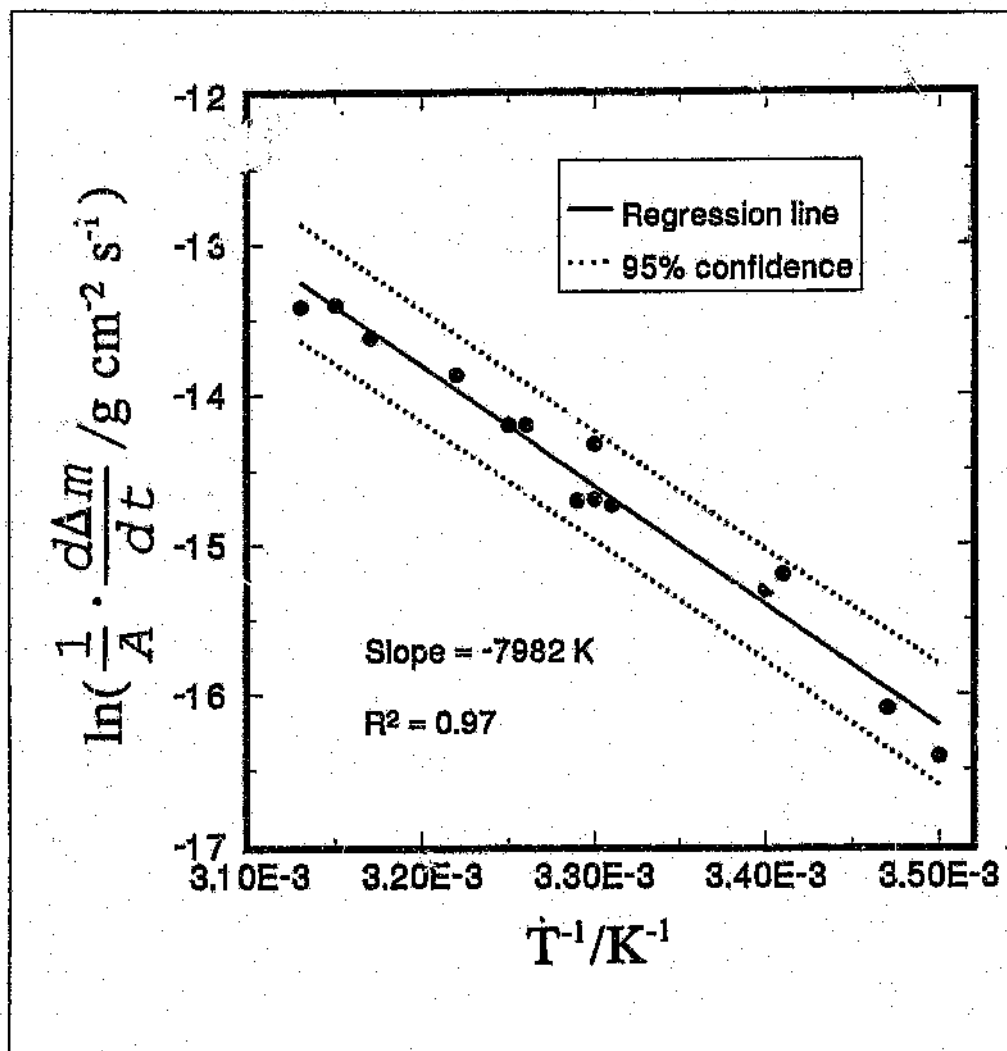


Figure 7.3 Arrhenius plot of the rate data for the hypophosphite based bath.

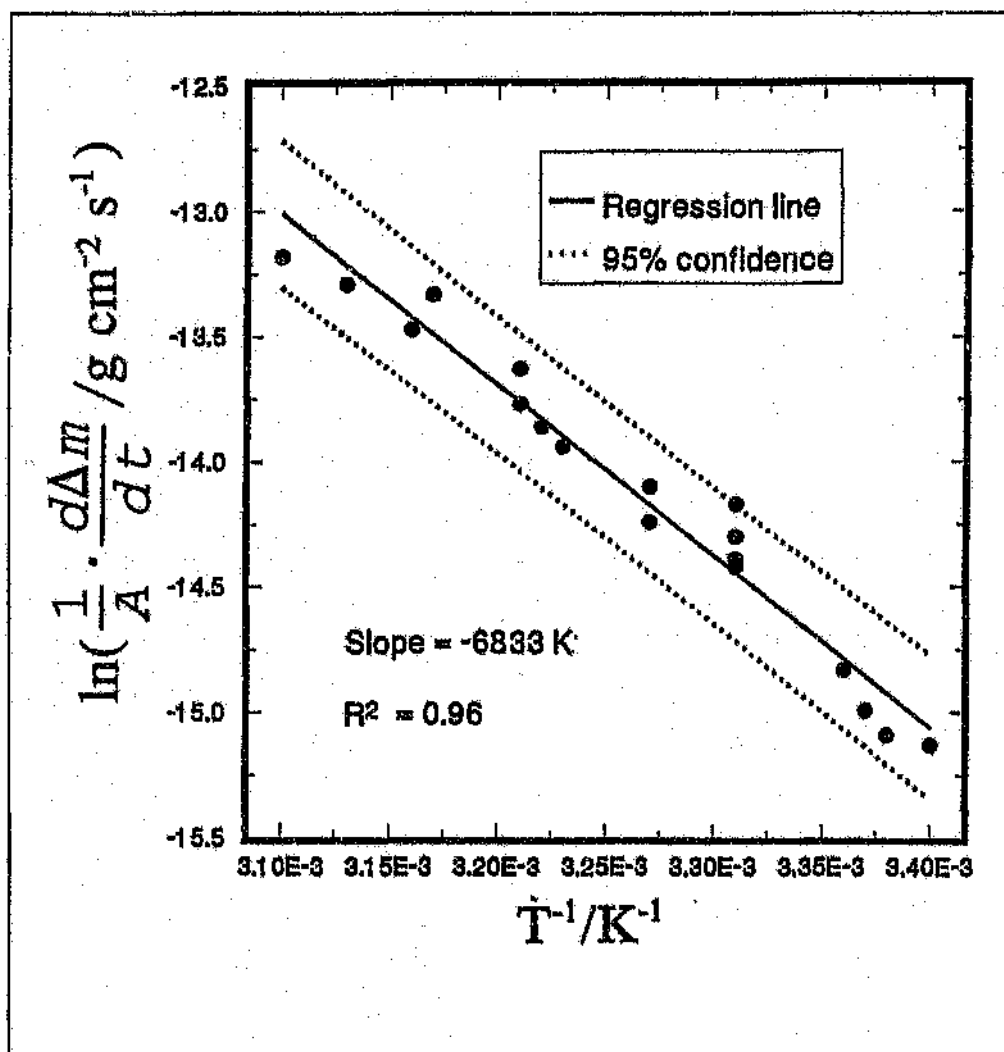


Figure 7.4 Arrhenius plot of the rate data for the DMAB based bath.

7.4 PARTIAL CURRENT DENSITY CURVES AT STEADY STATE

7.4.1 Low temperature electroless nickel baths

Figure 7.5 and Figure 7.6 show plots of j_{net} , j_c and j_a vs. E , obtained for the two electroless baths at 20°C. All potentials quoted are with respect to a saturated calomel electrode. While the general forms of the two figures are similar, there are important detailed differences. With reference to Figure 7.5, it can be noted that for Bath 1, j_a shows little dependence on potential near the plating potential. The overall rate is thus under anodic control. In contrast, Figure 7.6 shows that for the DMAB bath, both partial processes depend markedly on potential near the plating potential. The overall rate is under joint cathodic and anodic control. A further difference can be seen in the shapes of the j_a plots. When DMAB is being oxidised, the rate of this half-reaction reaches a maximum at about -0.8 V. The plating rate, however, is not affected by this local maximum of the anodic rate, and in fact plating is scarcely occurring. In the hypophosphite bath, no similar maximum in the rate of the anodic process was noted.

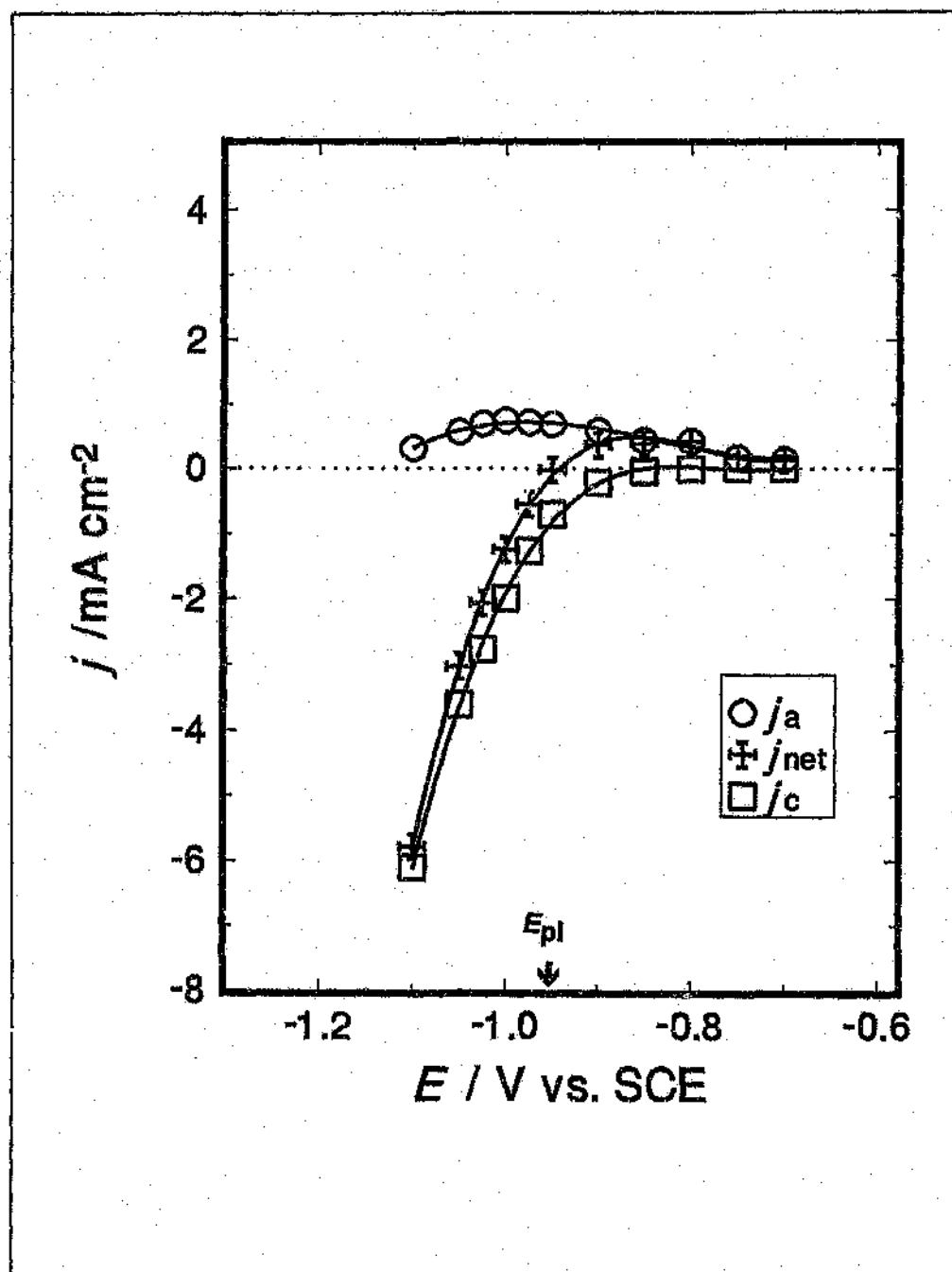


Figure 7.5 Plots of net current density (j_{net}), and cathodic and anodic partial current densities (j_c and j_a) vs. potential (E) for the hypophosphite bath (Bath 1) at 20°C . E_{pl} = open circuit plating potential.

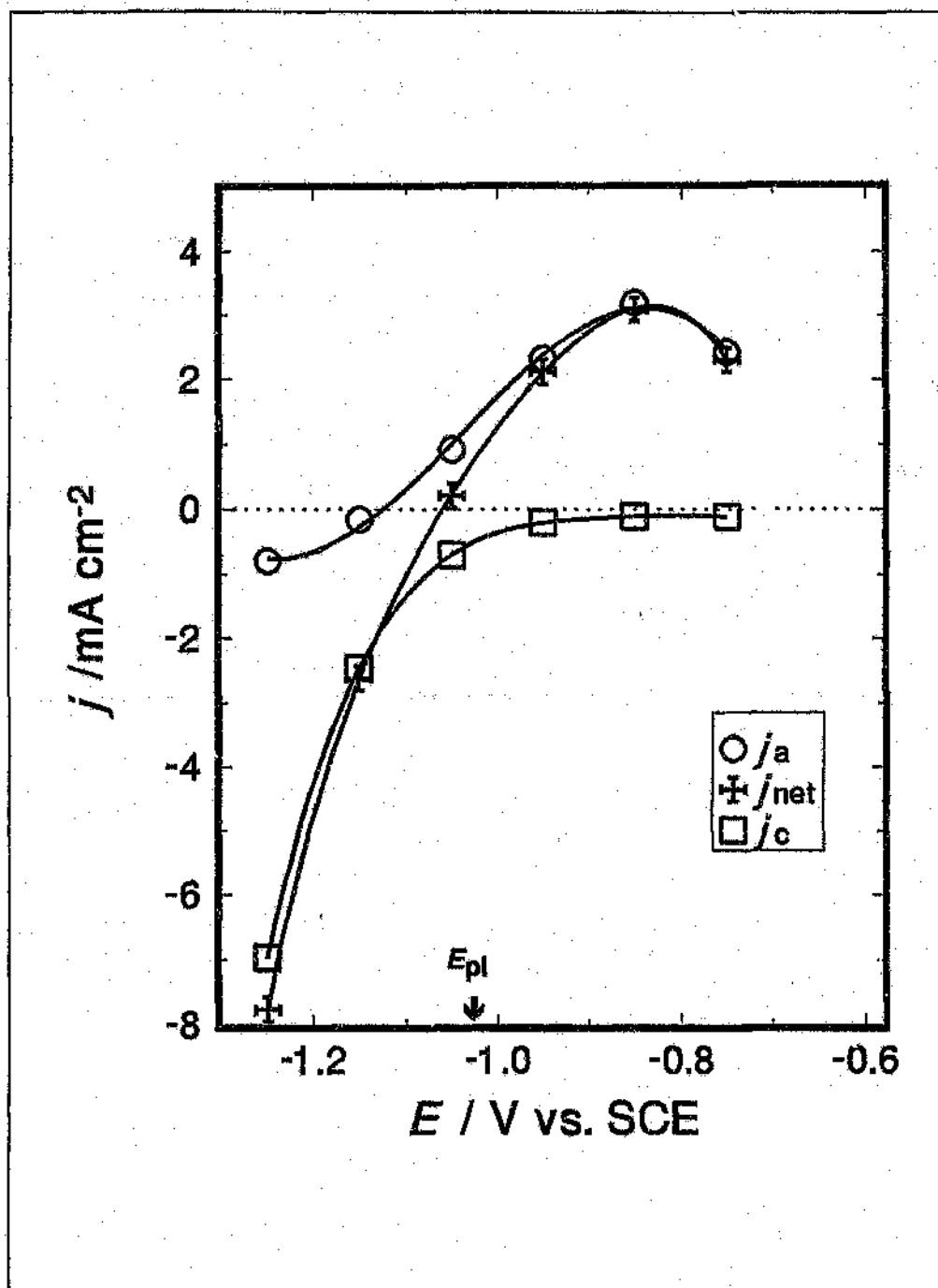


Figure 7.6 Plots of net current density (j_{net}), and cathodic and anodic partial current densities (j_c and j_a) vs. potential (E) for the DMAB bath (Bath 2) at 20°C. E_{pl} = open circuit plating potential.

The similarity between the results obtained using the QME and RDE at 35°C for the hypophosphite bath has been mentioned in Section 6.2.2. Since the current density curves are similar under significantly different hydrodynamic conditions, it is clear that the anodic and cathodic half-reactions are not under mass transport control. In support of this, Feldstein and Amodio (1969) and Orchard (1988a) found that agitation had little effect on the plating rate for a similar bath composition.

The substitution of zinc ions for nickel ions in either the hypophosphite or DMAB bath gives rise to a situation where the most significant faradaic response in the potential range under study is oxidation of the reducing agent. In such situations, oxidation of the latter species is made to occur without the simultaneous reduction of metal. For both baths, the rate of oxidation is decreased when compared to the complete baths at the corresponding potentials (at the extreme cathodic potentials, solvent reduction does occur, as evidenced by the detection of a small cathodic current in the absence of nickel(II), for example, Figure 7.7). The anodic current densities for modified and complete baths are shown in Figure 7.7.

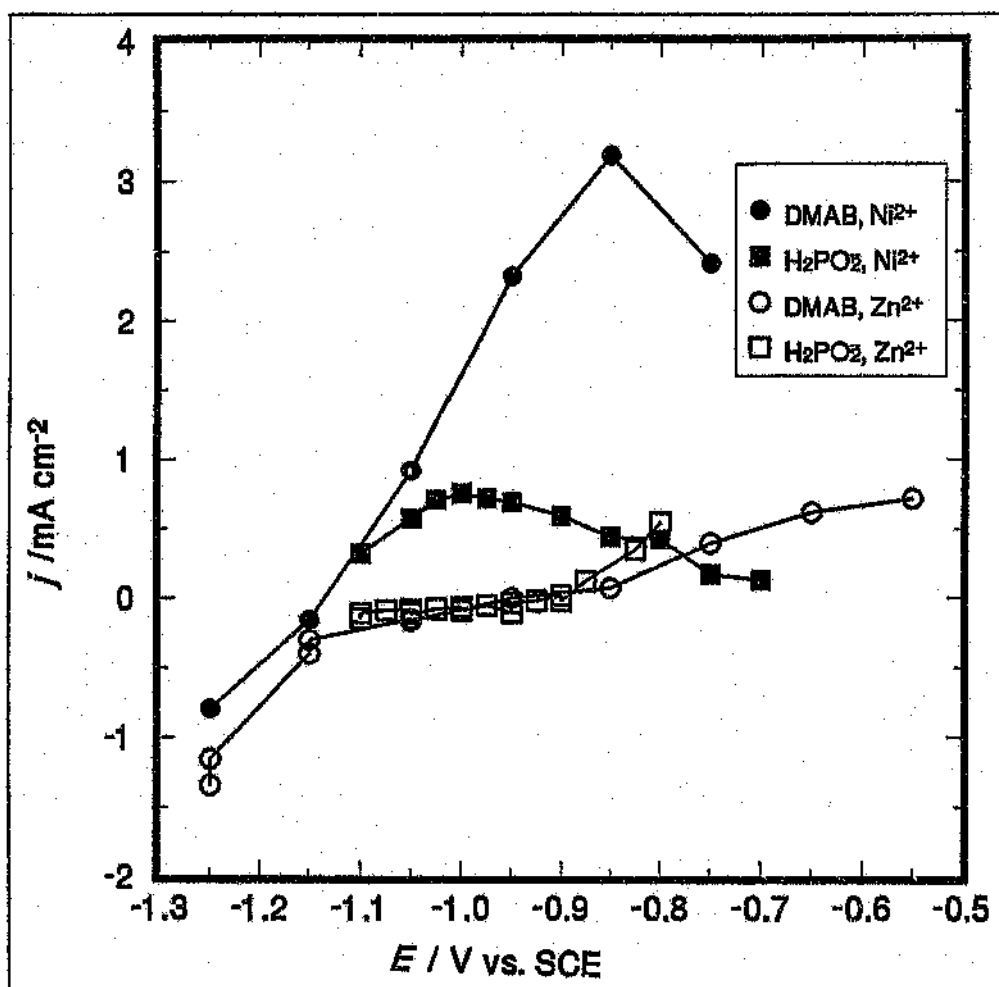


Figure 7.7 Plots of the anodic current density (j_a) vs. applied potential (E) for Baths 1 and 2, and these baths containing Zn^{2+} instead of Ni^{2+} . All measurements were made at 20°C.

Since the anodic current densities differ from those when simultaneous metal reduction takes place, it is suggested that the anodic and cathodic half-reactions are interdependent. This point was further illustrated by results obtained when the reducing agent was omitted from the baths. It was found that the deposition of nickel occurred over the relevant potential range, but at a rate different to that noted when simultaneous oxidation of reducing agent was taking place, at corresponding potentials. These results are illustrated in Figure 7.8, and in semi-logarithmic form in Figure

7.9. The data for j_c in the absence of reducing agent were derived from QME frequency changes. If j_c was derived from the observed current, the data would only be about 1 mA cm^{-2} more cathodic, at potentials more negative of about 1 V.

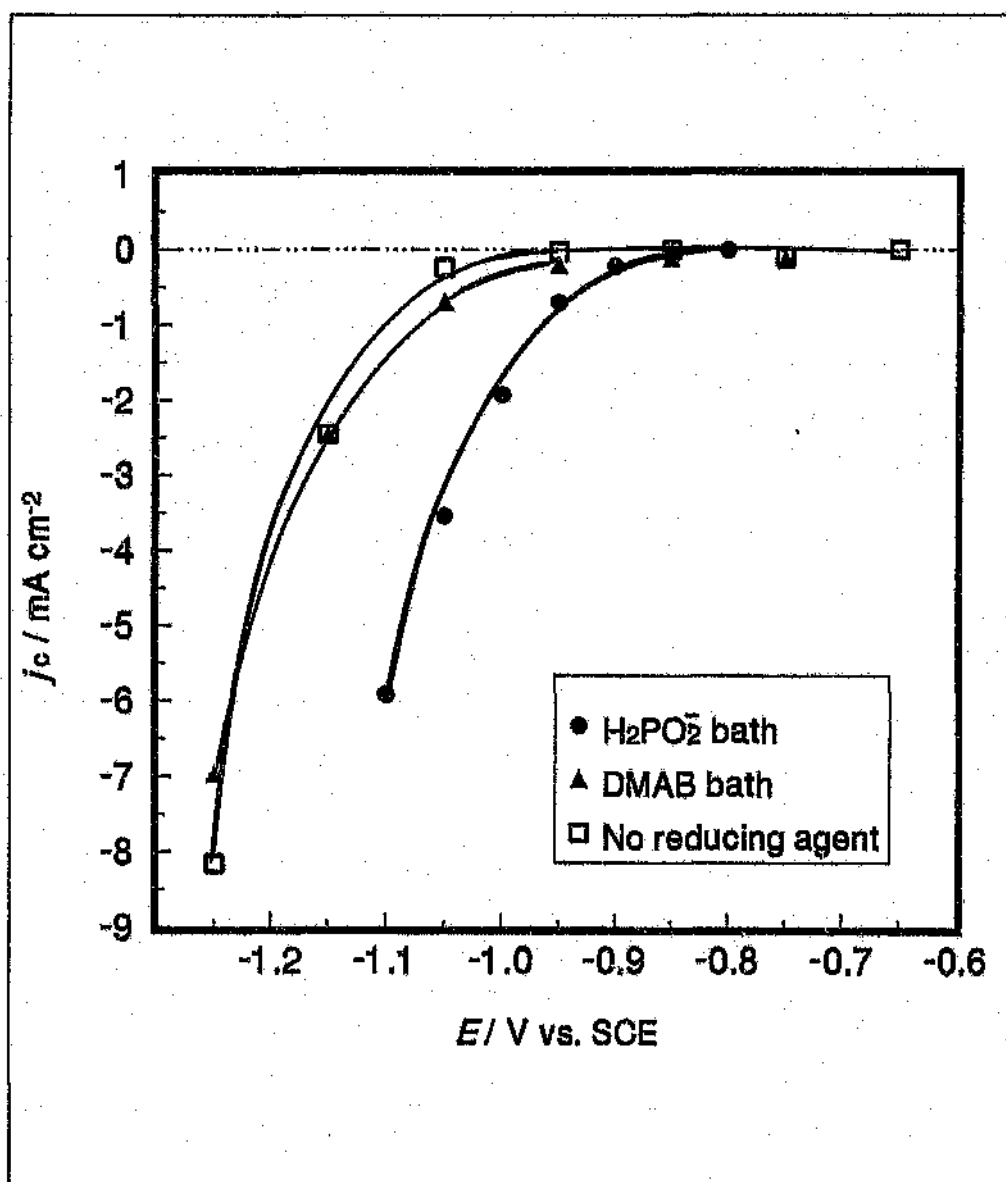


Figure 7.8 Plots of cathodic current densities (j_c) for Bath 1, Bath 2 (from Figure 7.5 and Figure 7.6) and for a bath containing no reducing agent. All data obtained at 20°C .

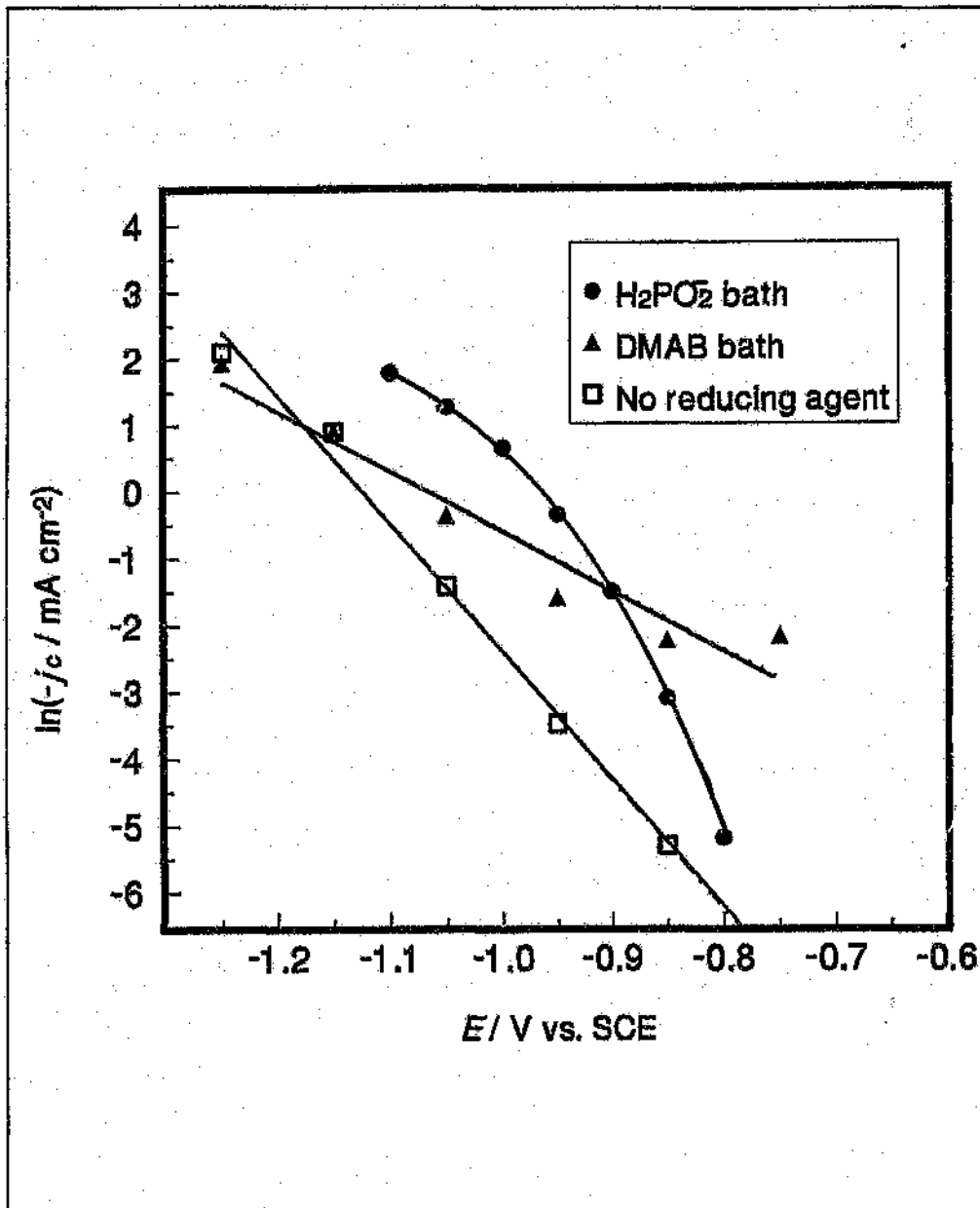


Figure 7.9 Plots of $\ln j_c$ vs. E for data of Figure 7.8.

Reduction of nickel at a given potential is notably higher in the presence of hypophosphite oxidation than with DMAB or no reductant. At -0.95 V, for example, the relative cathodic rates (hypophosphite : DMAB : no reductant) are in the approximate ratio 22 : 7 : 1.

In addition to the differing rates, the different slopes and curvature in Figure 7.9 clearly indicate

that the two half-reactions occur at rates depending on the nature and presence of the reducing agent.

The shapes of the curves in Figure 7.7 can be compared with two of the curves presented in the model of Ohno (1991), which has been represented by Figure 4.2, Chapter 4, in so far as a maximum value of j_a is achieved at an intermediate potential (in Ohno's model the curves are presented as $\ln(j_a)$ vs. E). The hypophosphite oxidation current density curve (in the presence of Ni^{2+}) exhibits a local maximum at about -1.01 V, much like the volcano plot of Ohno. The shape of the current density curve (for the oxidation of H_2PO_2^-) is consistent with results cited by Ohno, and in addition, strongly supports the possibility of the existence of an oxide film on the Ni-P alloy. Similarly, in the presence of nickel(II) ions, the oxidation of DMAB shows a maximum rate, at about -0.86 V. In contrast, the current density curves of the oxidation of both reducing agents in the presence of Zn^{2+} are considerably more plateau-like at intermediate potentials (curve 2, Figure 4.2). The range of electrode potential investigated in the present work did not extend to the anodic value of +0.3 V vs. SCE as in the work cited by Ohno, thus it is not possible to be certain that the j_a curve for DMAB oxidation does not exhibit volcano-type behaviour in this region. It may be, that an extension of the range of measurement of the current density for DMAB in Figure 7.7 to even more anodic potentials would reveal volcano-type behaviour as presented in the review by Ohno. Similarly for the oxidation of H_2PO_2^- in the presence of Zn^{2+} in place of Ni^{2+} .

The results of current density measurements for complete and modified baths (given above) indicate

substantial mechanistic differences between the systems. The reduction partial process in both baths is strongly dependent on potential. Thus the possibility of chemical (non-electrolytic) mechanisms, in which a direct electron transfer reaction between surface-bound species takes place, can be eliminated. This type of mechanism has been observed in the corrosion of steel and titanium alloys (Mansfeld and Kenkel 1976). In their corrosion study, polarisation resistances determined from physical dimension changes of substrates differed from those obtained by electrochemical methods. Dissolution rates were found to be almost independent of applied potential in the cathodic region, in contrast to the more commonly observed exponential relationship.

Another possible interaction which could lead to the observed interdependence of the two partial reactions is one between the metal ion and either the reducing agent or a product (or intermediate product) of its oxidation. The effect of an adsorbed species on plating rate has been noted (de Minjer and Brenner 1957, Schoenberg 1972, Donahue et al. 1982, and Paunovic and Arndt 1983). For the hypophosphite-reduced system, a number of species have been suggested as being responsible for the reduction of the metal ions. The conversion of hypophosphite given in Figure 4.6, is one possible mechanistic starting point. The tautomeric form, involving three-valent phosphorus, is another possibility (Figure 7.10).

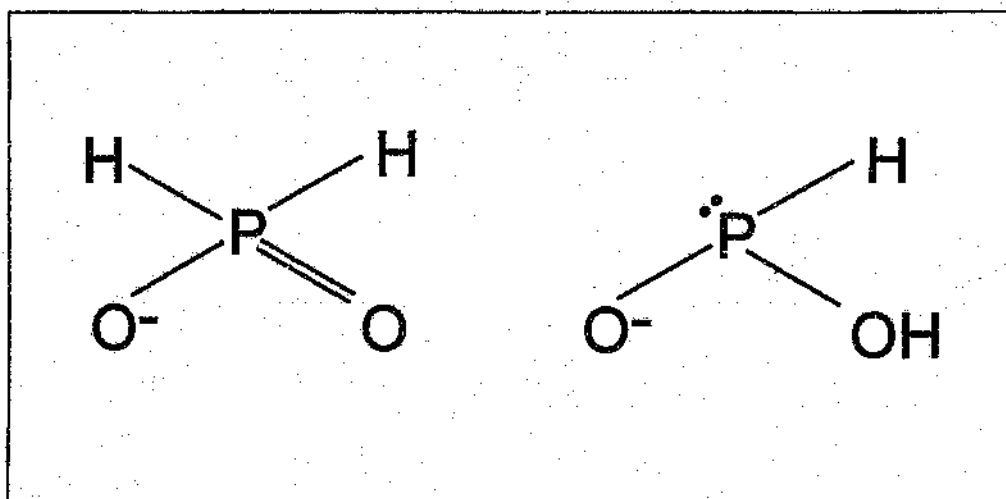


Figure 7.10 Tautomeric forms of the H_2PO_2^- anion.

The three-valent tautomer shown in Figure 7.10 has been proposed as being the more readily oxidizable (Hickling and Johnson 1967), and can also act as a bridging ligand (Figure 7.11).

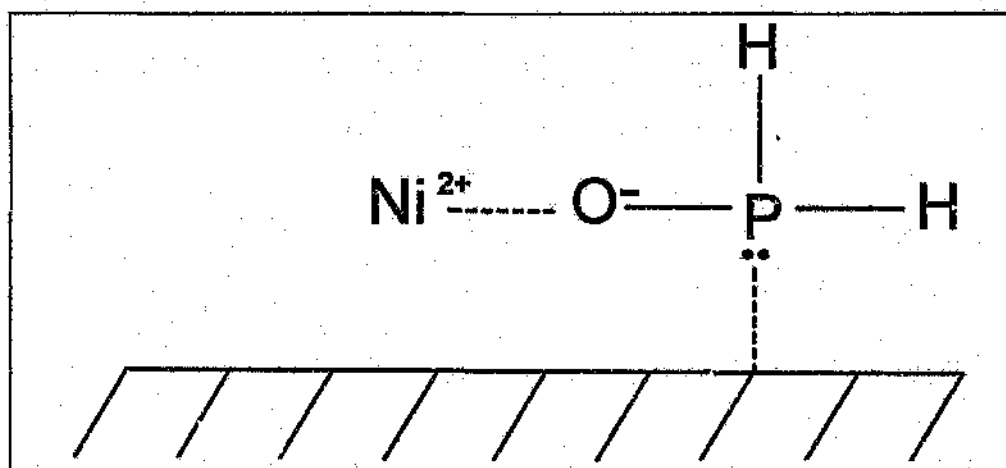


Figure 7.11 Three-valent phosphorus tautomer of H_2PO_2^- acting as a bridging ligand for Ni^{2+} .

Schoenberg (1972) speculated that the action of the accelerator/stabilizer, HIQSA, is via a similar bridging mechanism (this is discussed further in Chapter 8, Sections 8.5 and 8.6). It was stated (Chapter 4, Section 4.3.1) that the results of Wiese and Weil (1987) suggested that direct adsorption of copper on the surface was not part of the mechanism of

the process in that particular study. Further corroboration of the bridging ligand requirement may be inferred from the observations of Feldman and Melroy (1989), where significant differences in cathodic partial current density curves were noted in the presence and absence of the reducing agent (formaldehyde). It was hypothesized that a Cu^{2+} -(EDTA)-formaldehyde complex formed, and was adsorbed on the electrode surface. A concerted reduction of the Cu^{2+} and oxidation of the reducing agent was then suggested as a possible mechanism. The possible importance of bridging ligands is illustrated by these examples, and this mode of interaction of the reacting species cannot be dismissed.

The possibility of interaction in the bulk solution between metal ions and some species related to the reducing agent also exists. The spectrophotometric experiments were performed to identify any such interactions. Feldstein (1970) reported that the presence of reducing agent had no effect on the nature of the complexes present in solution. The results of this work (Figure 7.12, Figure 7.13 and Figure 7.14) corroborate those of Feldstein.

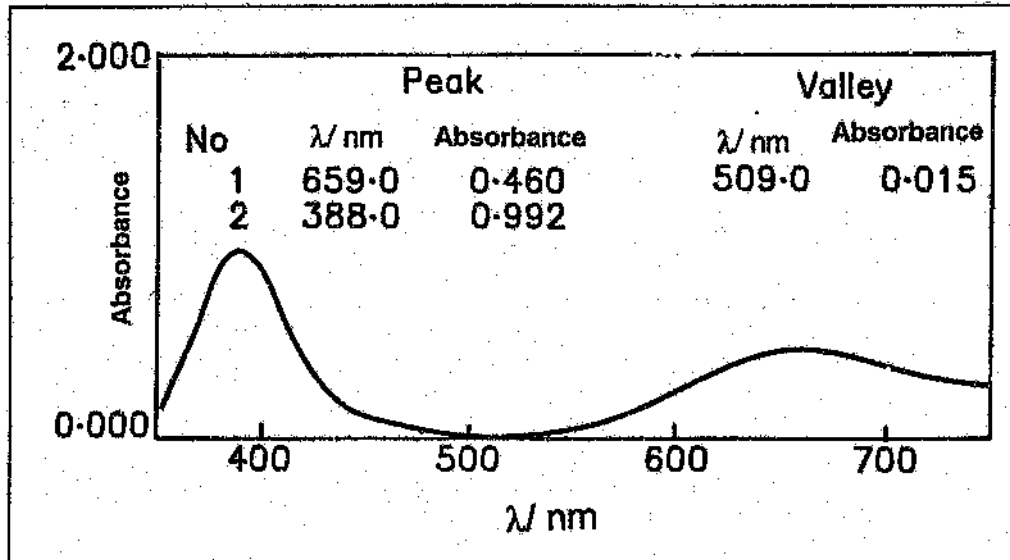


Figure 7.12 Absorption spectrum of Baths 1 and 2 without reducing agent, at 23°C.

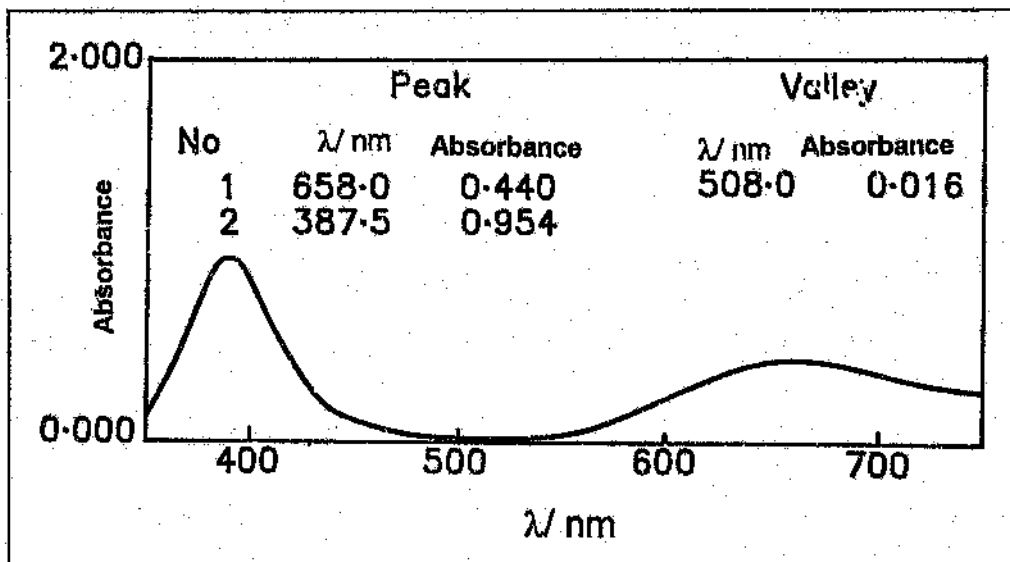


Figure 7.13 Absorption spectrum of Bath 1 at 23°C.

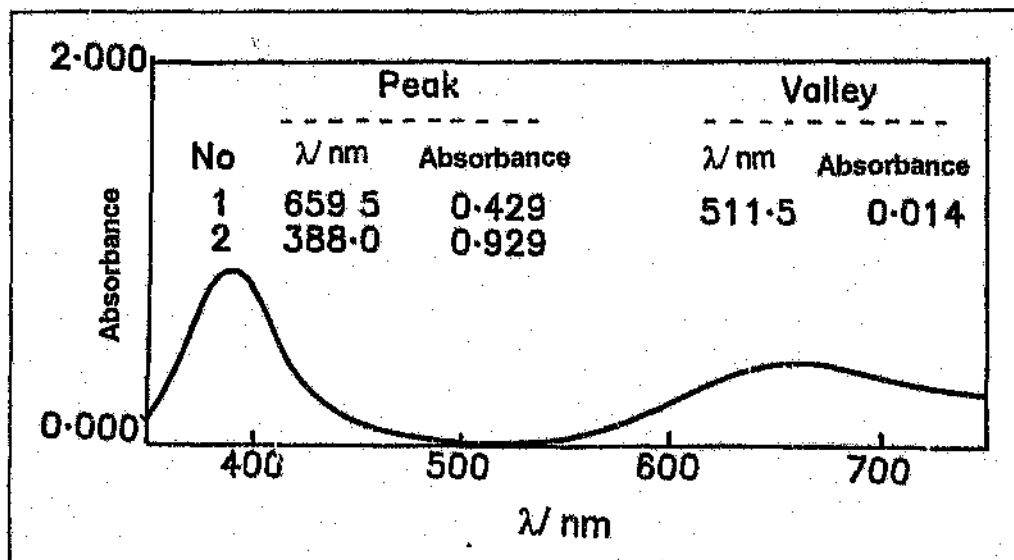


Figure 7.14 Absorption spectrum of Bath 2 at 23°C.

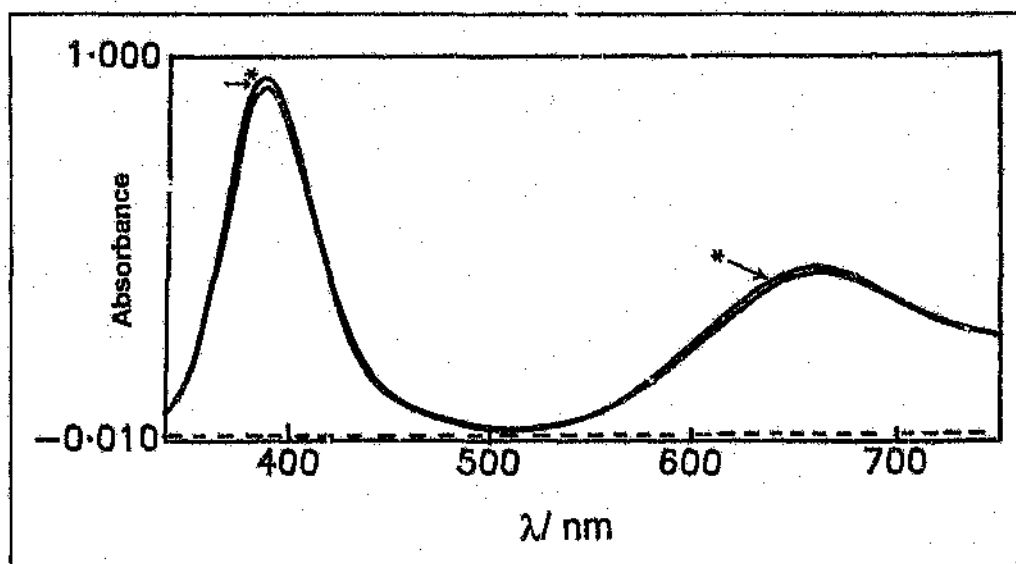


Figure 7.15 Absorption spectra of Bath 1, and Bath 1 modified to contain phosphite instead of hypophosphite anions. Modified solution trace indicated by (*).

No evidence of any significant influence on the solution complexes by the reducing agent could be inferred from the above spectra.

To explore the possibility of an interaction between the metal ion complexes and the phosphite anion (HPO_3^{2-}), a product of H_2PO_2^- oxidation, spectra were obtained by substituting phosphite for hypophosphite in Bath 1. A marginal difference was observed (Figure 7.15) which was more clearly defined when the reference beam contained a sample of Bath 1 (Figure 7.16). This difference was not, however, much greater than the small differences noted when DMAB or H_2PO_2^- was added to the bath (see absorbance at 388 nm, Figure 7.12 and Figure 7.14), and it has been noted that Feldstein could not detect a significant effect of either reducing agent on the absorption spectra. The effect of phosphite on the nature and concentration of complexes in Bath 1 can therefore be seen to be within experimental error. However, if the concentration of the phosphite anion near the interface builds up to significant levels during electroless plating, a pH change may occur, and this would affect the distribution of the various Ni^{2+} complexes with ammonia and pyrophosphate (Feldstein 1970). There does not appear to be a direct effect on the distribution of complexes brought about by phosphite when the pH remains constant.

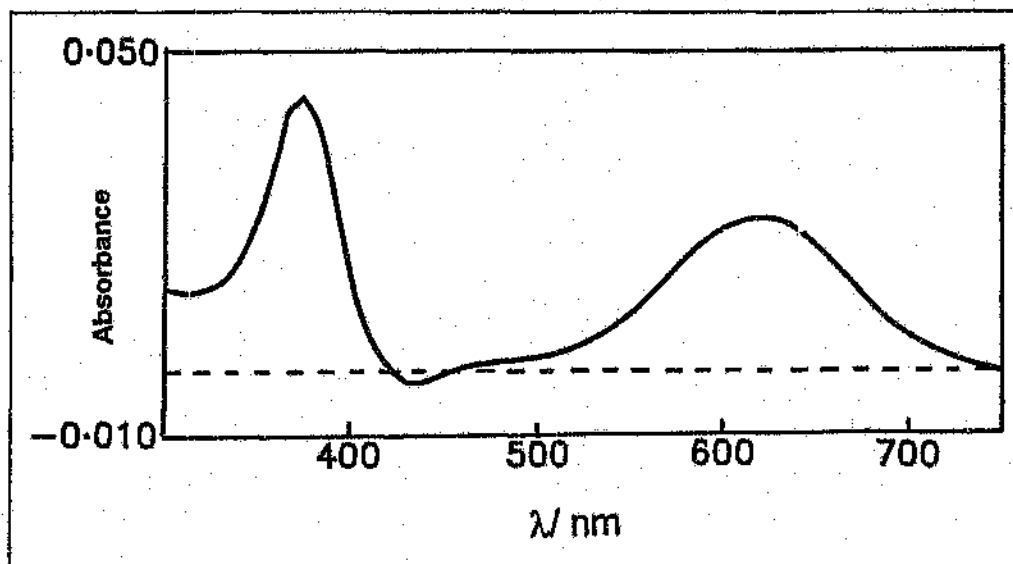


Figure 7.16 Absorption spectrum of phosphite-containing solution with Bath 1 as reference.

No further data were obtained regarding interactions in the bulk solution. Studies using *in situ* spectrophotometric methods would be helpful in detecting the presence of interactions near the surface, involving surface bound species.

Since the rate of nickel deposition at any given potential increased in the presence of the hypophosphite anion, it was of interest to determine the effect of H_2PO_2^- on the plating rate of the DMAB bath. The results of an experiment with a combination of reducing agents could illustrate the nature of the control on deposition rate and further highlight the different effects of the reducing agents on the cathodic half-reaction. Effects on plating potential and deposition rate were noted when the concentrated sodium hypophosphite solution was added to an actively plating DMAB bath (at 20°C). The plating potential became slightly more positive (from -1.01 V to -0.94 V) and the deposition rate dropped to 80% of the value measured prior to addition of hypophosphite, with H_2PO_2^-

concentration of about 60% of that of Bath 1. In a mixed potential system, the observed rate would be governed by the rates of only two partial processes (Section 2.2.1, Chapter 2). The presence of a reagent which does not participate in either of the two partial processes should not affect the measured rate.

In the present case, an inhibition of nickel deposition was observed, when H_2PO_2^- was added to the active DMAB bath. Lelental (1974) showed that the rate of nickel deposition in baths containing amine borane type reducing agents proceeded via a mechanism involving catalytic dissociative adsorption of the reducing agent on the plating surface. Hence the presence of hypophosphite, which must also adsorb to the surface, lowers the plating rate, indicating either competition for active surface sites by the reducing agent species, or interference by some other means. It is important to note that the combination of reducing agents resulted in a decrease in plating rate and not an increase. Further study in regard of the mechanism involving the combined effect was not carried out, but experimentation with mixed reducing agents could be of significance in future research.

7.4.2 Quartz microbalance electrode study of a high temperature electroless nickel bath

A rotating disc electrode has been used to study the partial current density curves of Bath 3 (Mughogho and Orchard, 1993), which was operated at a higher temperature (80°C) than the room temperature baths 1 and 2. During the course of Mughogho's study, it was noted that the cathodic and anodic current densities

were relatively independent of potential, over a wide range spanning the plating potential (Figure 7.17).

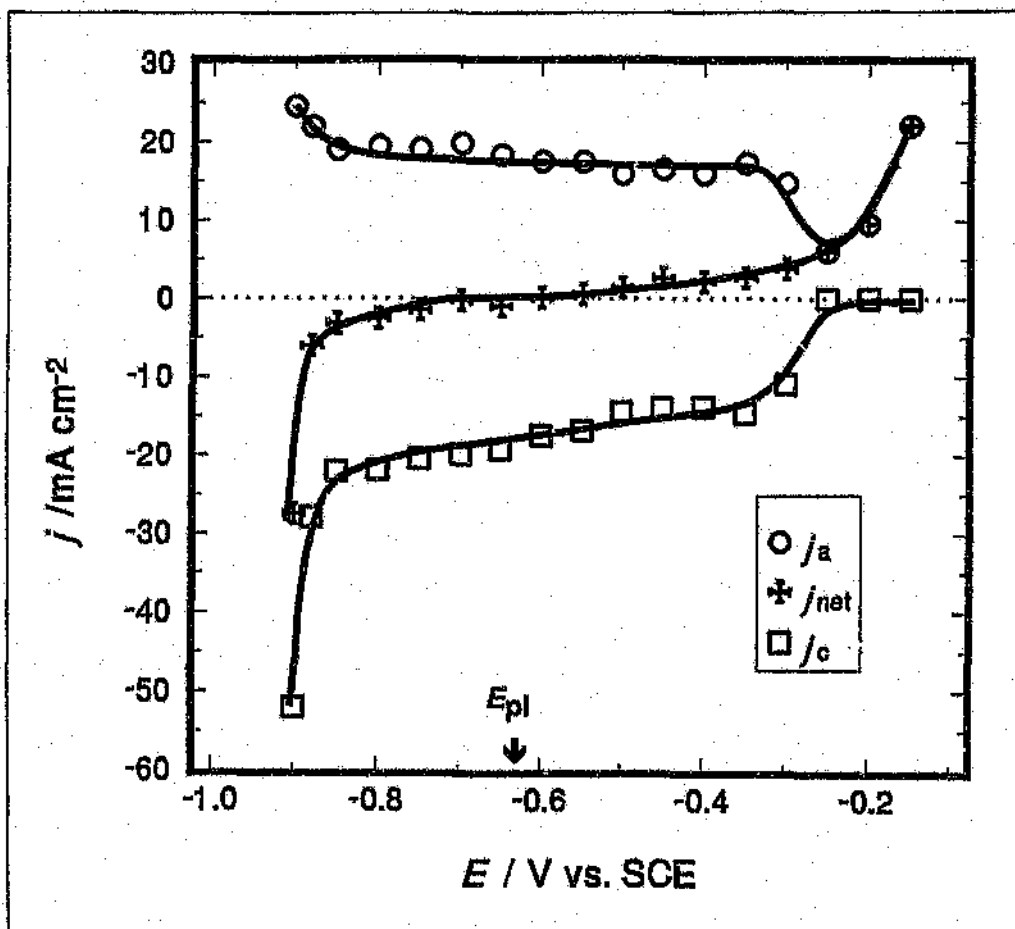


Figure 7.17 Partial current density curves for Bath 3, obtained using a rotating disc electrode (Mughogho and Orchard 1993).

Since it is rather unusual for both the anodic and cathodic partial processes to exhibit such potential independence, the QME was used to obtain current density curves over a much shorter period of time, in an only gently stirred solution. The current density curves thus obtained (Figure 7.18) are similar to those obtained using the RDE. This work was done in collaboration with Mughogho (1993b).

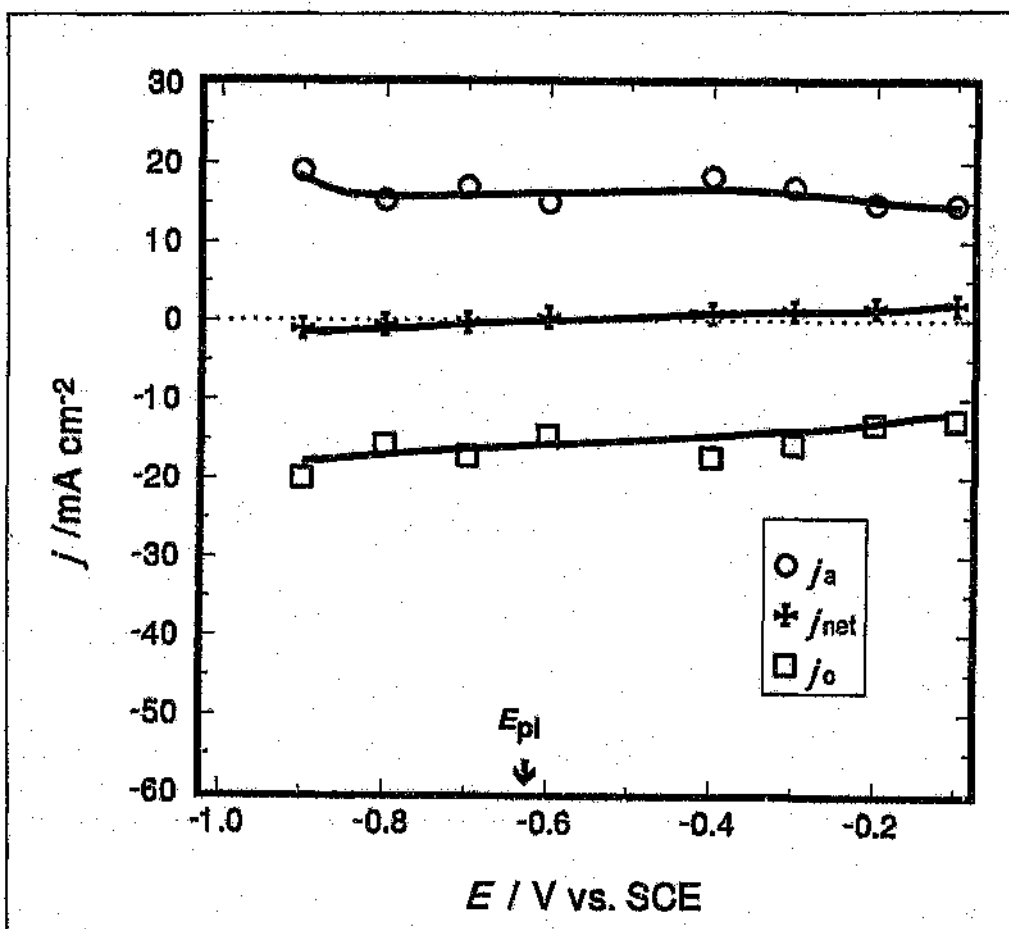


Figure 7.18 Partial current density curves for Bath 3, obtained using a quartz microbalance electrode.

Further investigation with the QME is required for the study of the behaviour of this bath. The results presented here confirm the finding that in many cases, the rate of the electroless process is insensitive to solution agitation (Section 7.4.1; Ohno 1991, *op cit.*). Thus the rates of the partial processes of Bath 3 appear to be limited by a non-electrochemical step. The dramatic effect of additives on the plating rate of this bath observed by Mughogho suggests that interfacial dynamics, rearrangement of reducing agent or metal ion complex are of prime importance in the mechanism of this bath.

7.4.3 Addition of sodium acetate to Bath 1 and Bath 2

Acetate has been reported to affect electroless plating rates (Pearlstein 1973). The effect of addition of acetate to both of the above electroless baths was marginal or beyond the detection limit of the QME as used in the experiment. Further experiments with this compound were not undertaken.

7.5 ELECTROCATALYTIC ACTIVITY OF Ni-P AND Ni-B DEPOSITS

7.5.1 The Ni-P alloy

7.5.1.1 Electrochemical studies

In this section, the influence of different nickel-containing substrates on the rates of electroless nickel plating and its constituent half-reactions is reported (Gafin and Orchard 1993). Low temperature (35°C) nickel baths were employed, since catalytic effects would be expected to be more prominent and readily detectable under such conditions. The useful properties of Ni-P alloys have attracted considerable research into their structures, as well as their mechanisms of formation (Hofmann and Weil 1990, Diegle et al. 1988, Hefland et al. 1992, Zeller III and Landau 1992).

When QMEs with surface coatings of either electroless nickel or the partially stripped electroless nickel were rinsed in water and returned to the electroless plating solution at open circuit, the typical potential-time and mass-time behaviour was as shown in Figure 7.19 and Figure 7.20, respectively. Normal electroless plating is evidenced by a potential of -0.92 V and a constant rate of increase in mass of about $7.5 \times 10^{-7} \text{ g cm}^{-2} \text{ s}^{-1}$.

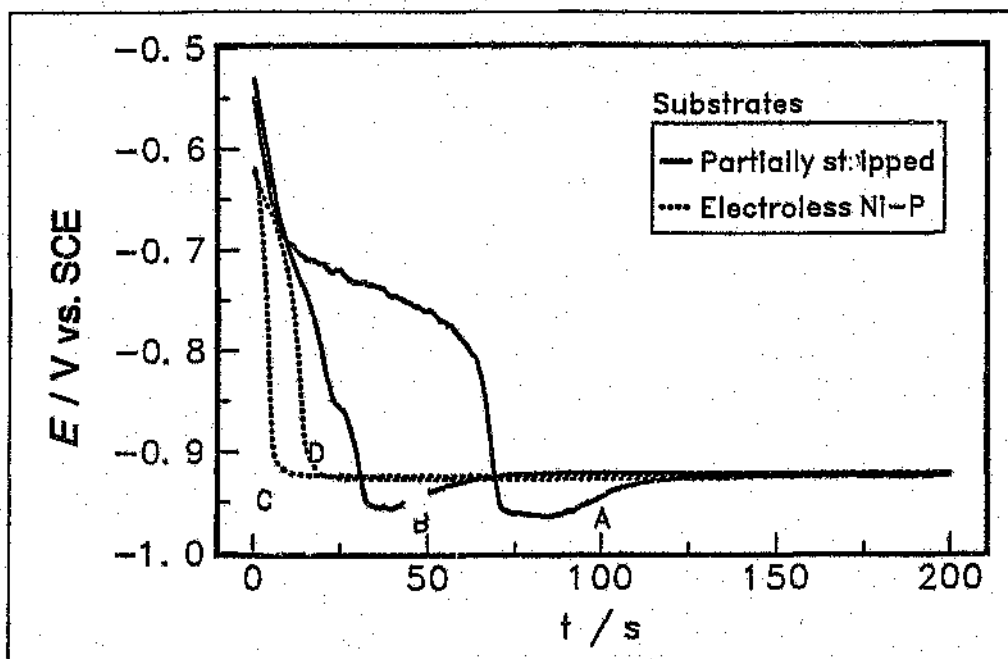


Figure 7.19 Potential vs. time behaviour during open circuit re-initiation of autocatalytic deposition at 35°C on partially stripped deposit (A, B) and non-stripped electroless deposit (C, D) (see also Figure 7.20).

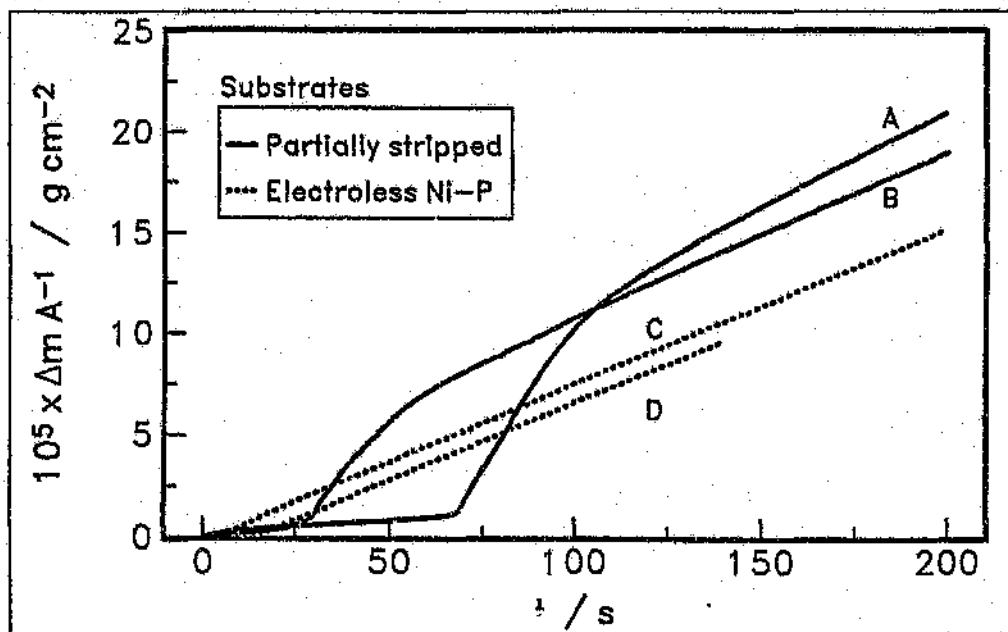


Figure 7.20 Mass change per unit area vs. time behaviour during open circuit re-initiation of autocatalytic deposition at 35°C on partially stripped deposit (A, B) and non-stripped electroless deposit (C, D). (Same experiments as in Figure 7.19).

Electroless nickel substrates initiated fairly quickly (< 20 s), while the partially stripped deposits displayed longer initiation times (over 120 s in one of the cases shown). The initiation times were irreproducible, as indicated in the Figures. More significantly, the phosphorus-rich deposits showed potential excursions (overshoots) during the initiation process, to more negative potentials, before returning to the normal plating potential; during the overshoot, the plating rate was substantially higher than during steady state plating. The potential-time behaviour described above was also seen on similarly treated glassy carbon substrates.

The electrode potential was also followed during initiation of autocatalytic deposition from Bath 1 on other substrates, including copper treated with Pd, copper, and Ni-B. The results of these measurements are presented in Figure 7.21. It can be seen that Pd, a well known catalyst for electroless Ni, also caused a potential overshoot, accompanied by a steeper slope in the frequency change vs. time curve during this time period (10-20 s). This phenomenon is typical of a system of coupled simultaneous electrochemical reactions where the mixed potential is determined by the rates of the reactions. The mixed potential value is closest to the equilibrium potential of the faster reaction (Smyrl 1981). The effect of a good electrocatalyst serves to increase the rate of at least one electrode reaction, and this may be achieved by lowering the activation overpotential. On a highly active electrocatalyst, one possible consequence would be a shift in the mixed potential to a more cathodic value. Since the deposit covers the substrate, the effect will be observed only in the initial stages of deposition. It was concluded that the partially

stripped Ni-P deposit exhibits electrocatalytic activity different to that of the mother material.

Because of the surprisingly high activity of the partially stripped deposits, it was decided to examine the early stages of the plating process in more detail. In view of the erratic initiation times at open circuit, a potentiostatic method for studying the initiation process was chosen.

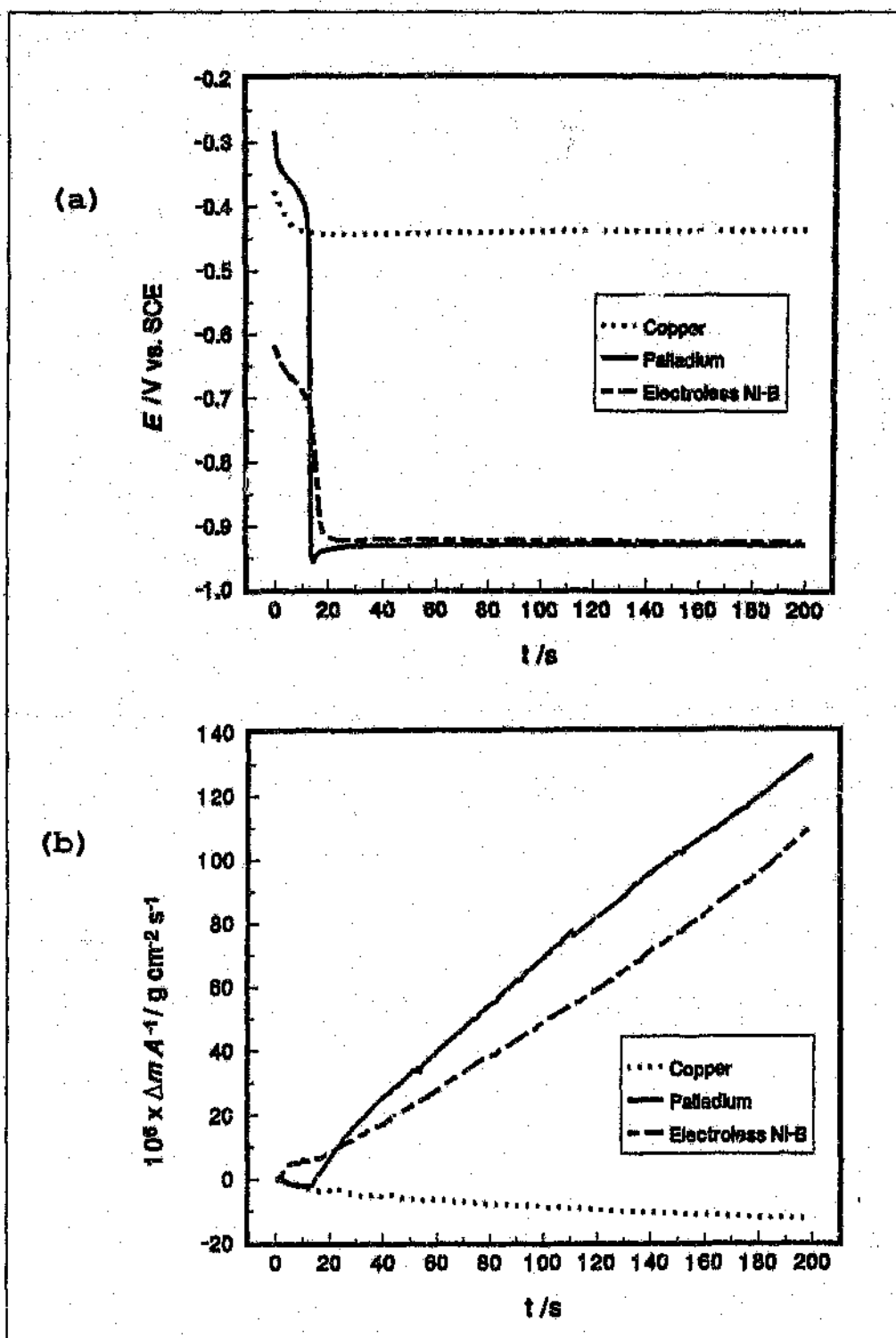


Figure 7.21 Initiation of electroless plating on various substrates: (a) electrode potential and (b) mass change per unit area vs. time.

Three types of substrate nickel film were studied under potentiostatic conditions:

- (a) electroless nickel (S1),
- (b) partially stripped electroless nickel (S2), and
- (c) pure electrolytic nickel (S3).

When QMEs coated with such deposits were placed into the electroless plating solution and related solutions, under potentiostatic control, current-time and mass-time curves such as those shown in Figure 7.22 and Figure 7.23 were obtained. In order to investigate the behaviour of the contributing half-reactions both in combination and in isolation, studies were carried out in

- (i) the full plating bath (B1),
- (ii) a bath without hypophosphite (B2), and
- (iii) a bath lacking in nickel ions (B3).

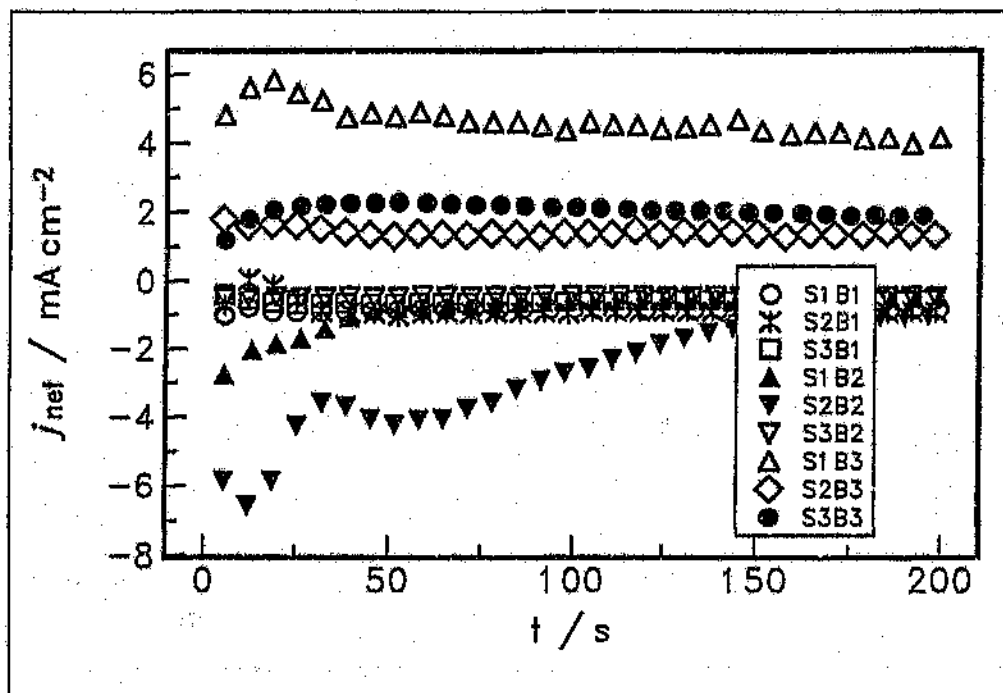


Figure 7.22 Current-time behaviour of various surfaces in different solutions during the early stages of potentiostatic deposition at -0.950 V. Key to surface, solution combinations: S1, S2, S3 are electroless Ni-P, partially stripped Ni-P and electrolytic Ni, respectively. B1, B2, B3 are complete electroless bath, the bath without H_2PO_4^- and the bath without Ni^{2+} , respectively. For clarity, plotting symbols show only every 10th datum.

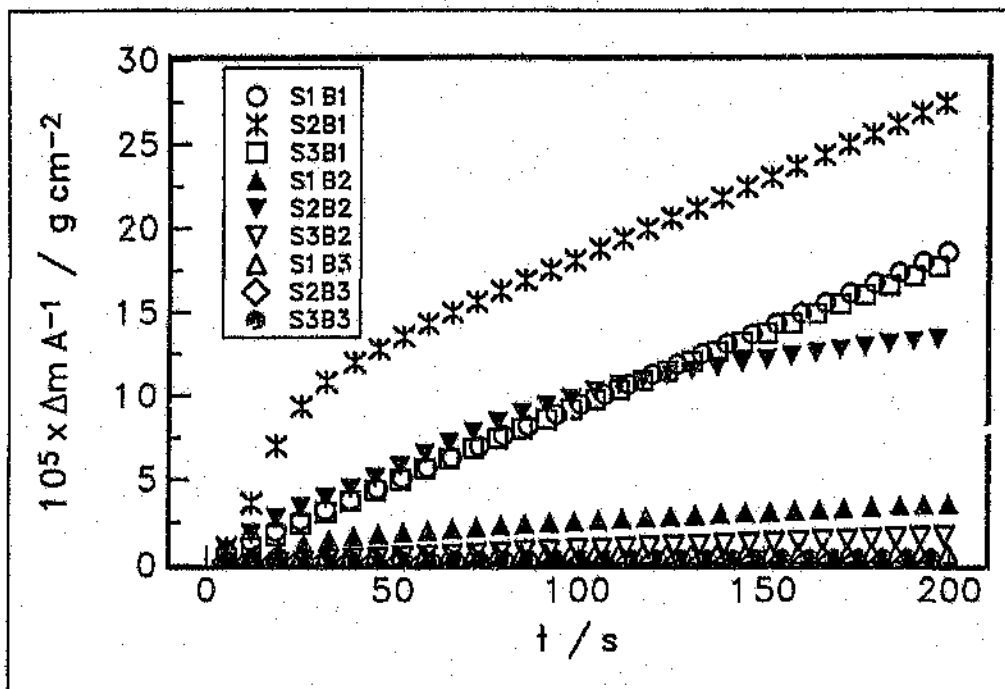


Figure 7.23 Mass change per unit area vs. time behaviour of various surfaces during the early stages of deposition at -0.950 V. For key to surface:solution combinations, see Figure 7.22. For clarity, plotting symbols show only every 10th datum.

For most combinations of substrate, solution and potential, a steady state was re-established within 100 s, as indicated by the measured current and plating rate. In keeping with its unusual activity at open circuit (Figure 7.19 and Figure 7.20) the phosphorus-rich substrate initially gave substantially higher plating rates than the other surfaces, when placed in the electroless nickel bath.

The mass change data of Figure 7.23 are readily transformed into partial cathodic current densities for the plating process, j_c , by means of finding the slope of a fitted curve, described as follows. Where the data were found to be linear, the partial cathodic current density was taken as the slope of the line over the full range multiplied by an appropriate conversion

factor (as described in Section 5.7.4; Orchard 1988b). Where an initially non-linear response was seen, a polynomial was fitted over the appropriate range, with the first derivative being used to calculate the current density. A linear fit was performed on the remaining data in the set, and the slope treated as described above to yield the steady state partial current density. (No physical interpretation was made in connection with the polynomial; it was used simply to enable calculation of the current density.) Data regarding rates of deposition are presented in Table 7.2.

Table 7.2 Cathodic current densities at 20 and 200 s after immersion in Bath 1, the electroless nickel plating bath, for the data presented in Figure 7.24.

Potential /V vs. SCE	Substrate	j_c /mA cm ⁻²	
		t = 20 s	t = 200 s
-0.875	Partially stripped	-9.8	-1.44
	Normal Ni-P	-0.99	-0.99
-0.95	Partially stripped	-12.9	-3.3
	Normal Ni-P	-3.2	-3.2
-1.025	Partially stripped	-9.0	-5.3
	Normal Ni-P	-5.2	-5.2

With reference to Table 7.2, the effect of the fresh partially stripped surface on j_c can be readily seen. However, at -0.875 V a difference can be noted between the value of $j_c(200\text{ s})$ on the two substrates. Since this result appeared to be in conflict with the other observations, the differences in frequency change with time (from which j_c is ultimately calculated) for both substrates were compared.

The difference in frequency between subsequent readings was calculated for the data in the linear regions of the respective data sets (see Figure 7.24a and d). Mean and variance, as well as pooled variance were calculated for these data, and the means were compared at the 5% level. The results are presented in Table 7.3. It was found that the means of these frequency differences did not differ significantly from one another, and thus it was concluded that the small variation noted was due to the internal variance of the measured frequency change at this potential. At -0.875 V, very little deposition is occurring at 35°C , and frequency variation from surface relaxation may be large in comparison to that brought about by deposition.

Table 7.3 Hypothesis test to determine the significance of the difference noted in j_a values on Ni-P and partially stripped Ni-P during steady state deposition.

Statistic for frequency change in the linear region	Ni-P (1)	Partially stripped Ni-P (2)
Number of observations	287	199
Mean *	-11.031	-16.367
Median	-11.000	-16.000
Variance (s)	26.233	56.546
Pooled variance (s_p) **	41.409	
H_0 : mean(1) = mean(2)		
H_A : mean(1) < mean(2)		
Confidence level:	95%	
Degrees of freedom:	484	
t ***	1.40	
Critical value:	1.70	
The null hypothesis is thus accepted.		

* mean(1) = $\bar{X}_1$ similarly mean(2) = $\bar{X}_2$

$$** \quad s_p^2 = \frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1 + n_2 - 2} \quad (7.3)$$

$$*** \quad t = [\bar{X}_1 - \bar{X}_2] / s_p \sqrt{1/n_1 + 1/n_2} \quad (7.4)$$

Neglecting other cathodic processes occurring simultaneously with reaction (7.1), application of Equation (2.30) permits calculation of j_a , the partial anodic current density. (The true value of j_a , the rate of reaction 7.2, would actually be greater than the value calculated in this way since cathodic processes not leading to mass change on the electrode would contribute to the cathodic partial current, and this increment must be accounted for in the anodic partial current according to Equation 2.30. However, in this

work, interpretation of the data focuses primarily on j_c , the rate of the cathodic deposition of nickel, and is therefore not compromised.) Selected plots of j_{net} , j_c and j_a versus time are shown in Figure 7.24(a-f), when the potential was held at the values indicated. These data span potentials on either side of the normal plating potential which is close to -0.92 V. Again the unusual behaviour of the partially stripped surface in the early stages of plating is evident. By 100 s however, most memory of the original surface has been erased, and the different substrates are behaving similarly. During the initial stages of plating, the cathodic partial current density is greater in magnitude on the partially stripped residue than on a normal electroless nickel substrate. A complete set of current density curves for the various combinations of substrate, bath composition and potential is given in Figure 7.26 to Figure 7.33. (Figures 7.24 and 7.25 contain data selected from Figures 7.26 - 7.28.)

Although some small artefacts of the data work-up can be observed in the final form, it is felt that that this does not detract from the qualitative interpretation of the results. For example, the polynomial fit and linear fit sections of j_c and j_a do not meet exactly at about 60 s, in Figure 7.24(e and f).

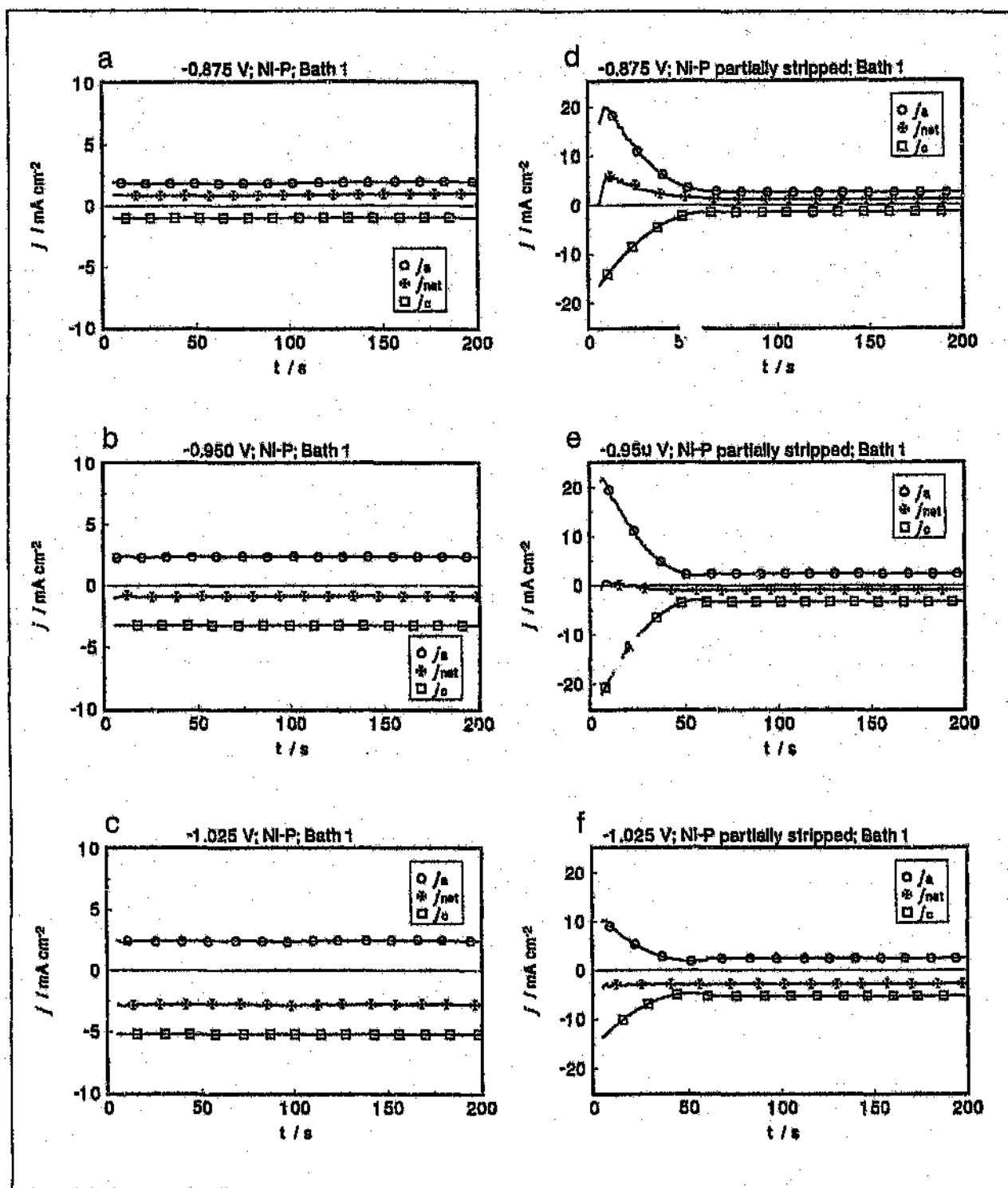


Figure 7.24 Selected current density vs. time curves at three potentials on the electroless and the partially stripped deposit, respectively. Moderately stirred solutions at 35°C. For clarity, plotting symbols show only every 20th datum.

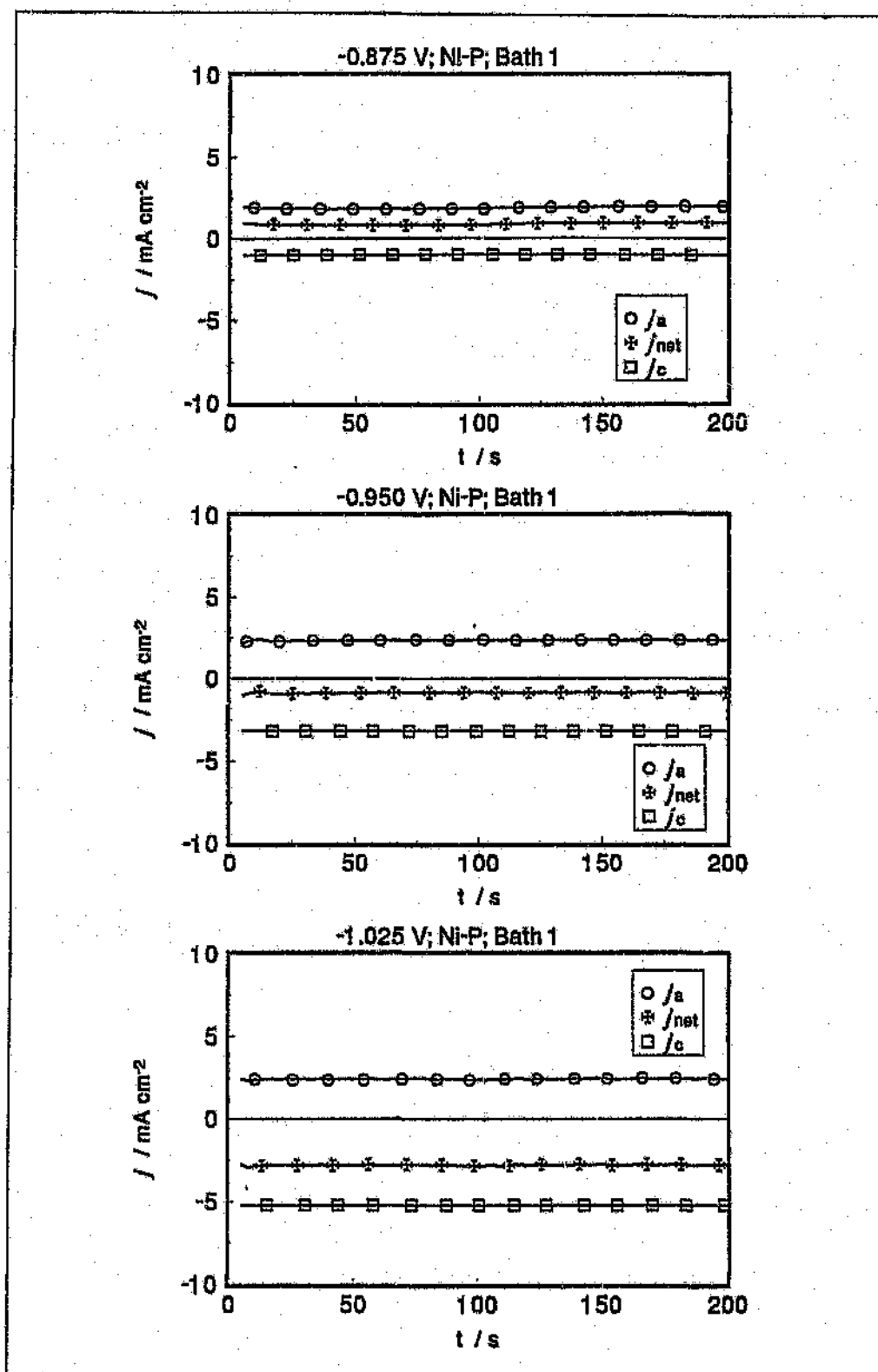


Figure 7.25 Current density curves over a period of 200 s, at potentials -0.875 V, -0.950 V and -1.025 V in the complete Bath 1, using an electroless Ni-P substrate (Ni-P). For clarity, plotting points show every 20th datum.

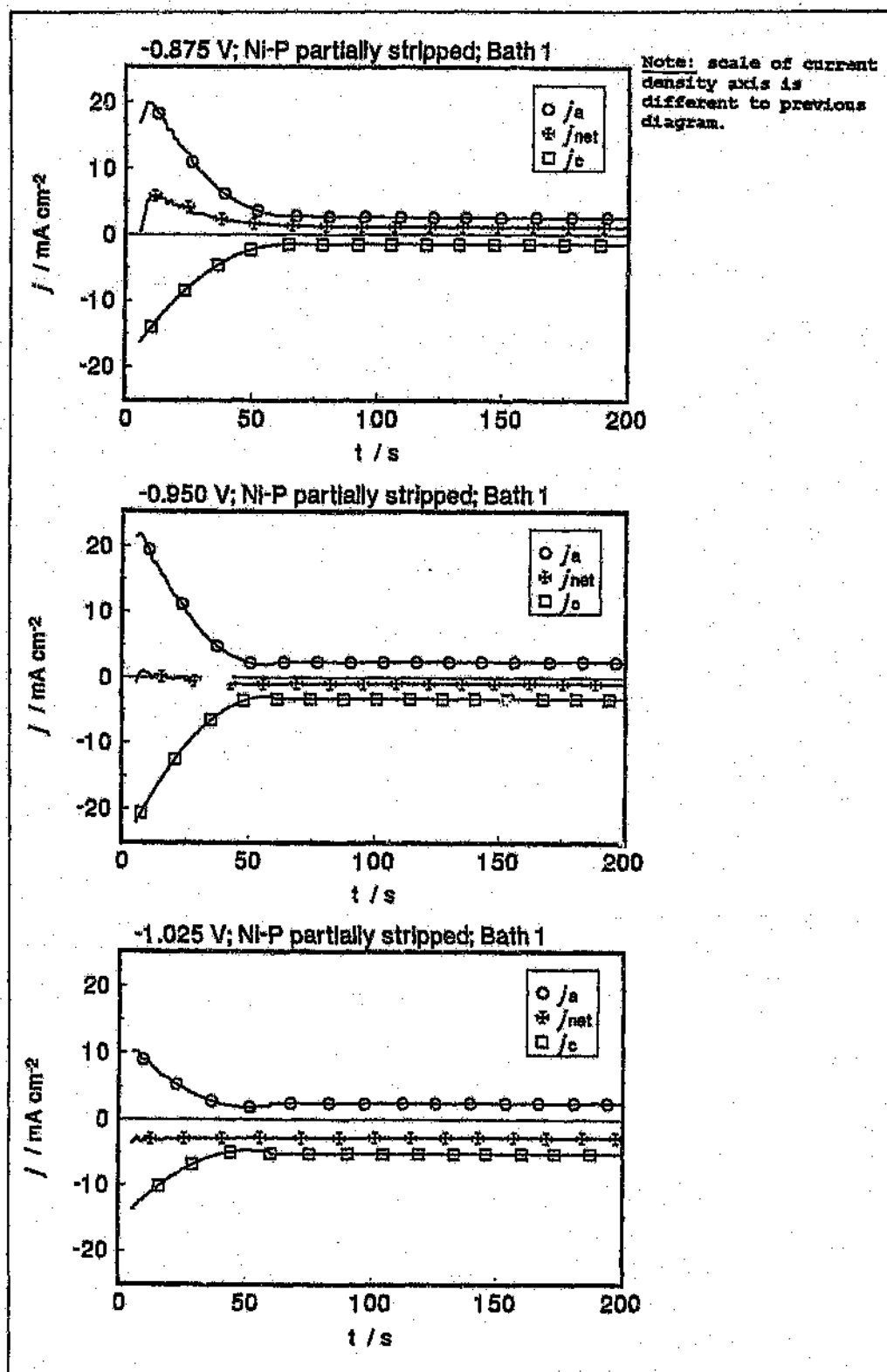


Figure 7.26 Current density curves over a period of 200 s, at potentials -0.875 V, -0.950 V and -1.025 V in the complete Bath 1, using a partially stripped electroless Ni-P deposit as substrate. For clarity, plotting points show every 20th datum.

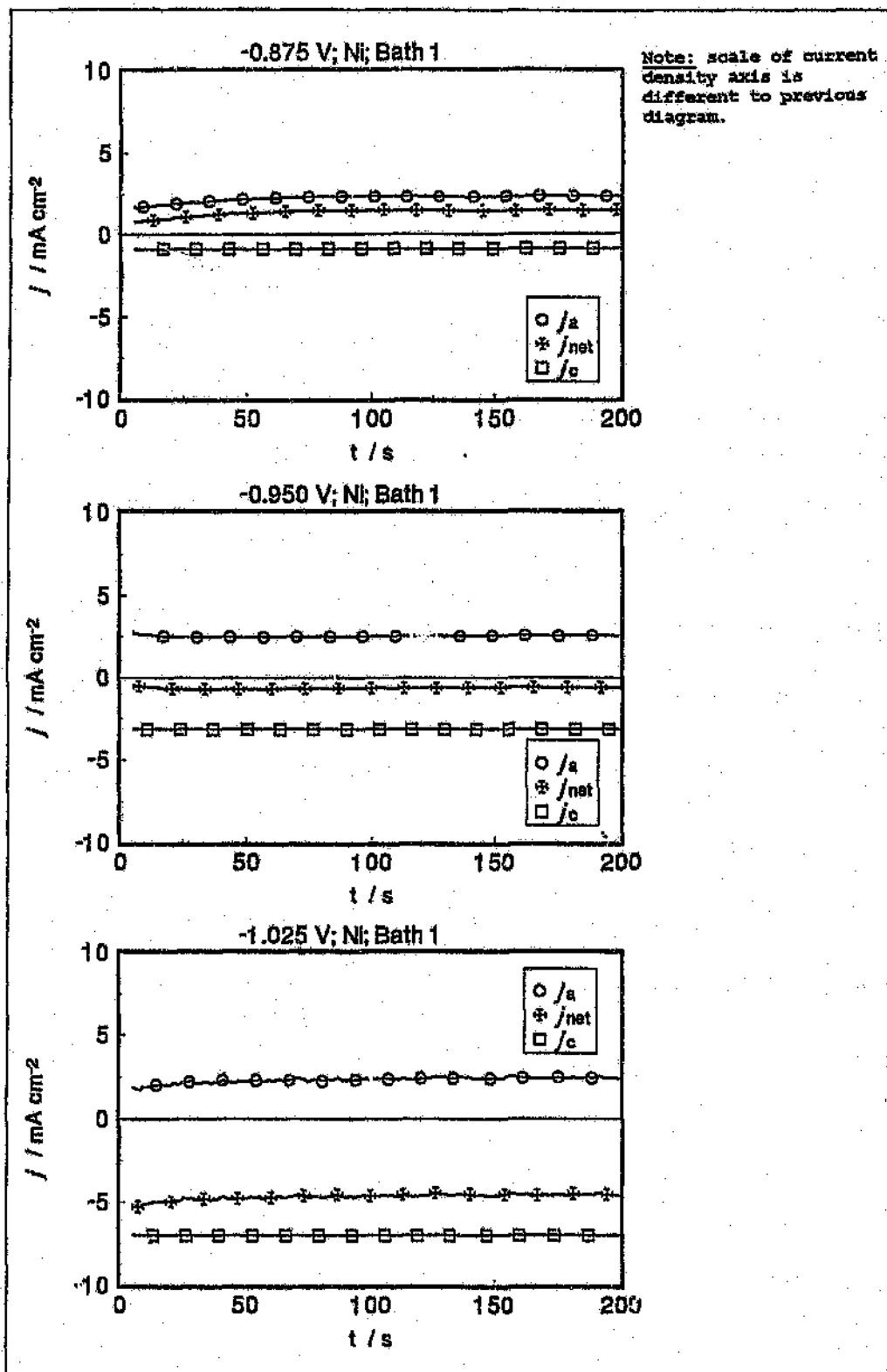


Figure 7.27 Current density curves over a period of 200 s , at potentials -0.875 V , -0.950 V and -1.025 V in the complete Bath 1, using an electrolytically deposited pure nickel substrate (Ni). For clarity, plotting points show every 20th datum.

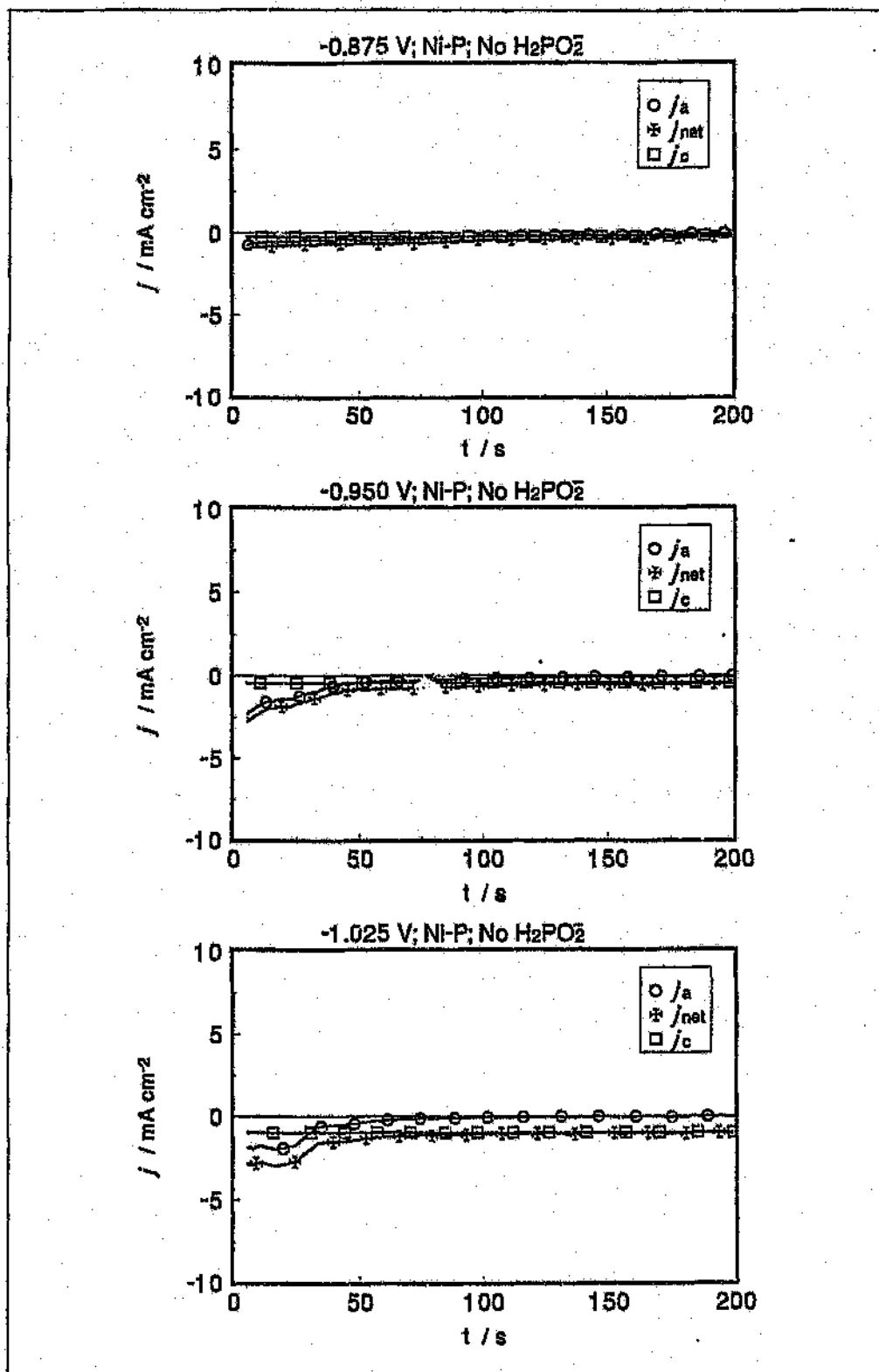


Figure 7.28 Current density curves over a period of 200 s, at potentials -0.875 V , -0.950 V and -1.025 V in Bath 1 lacking in H_2PO_2^- , using an electroless Ni-P substrate (Ni-P). For clarity, plotting points show every 20th datum.

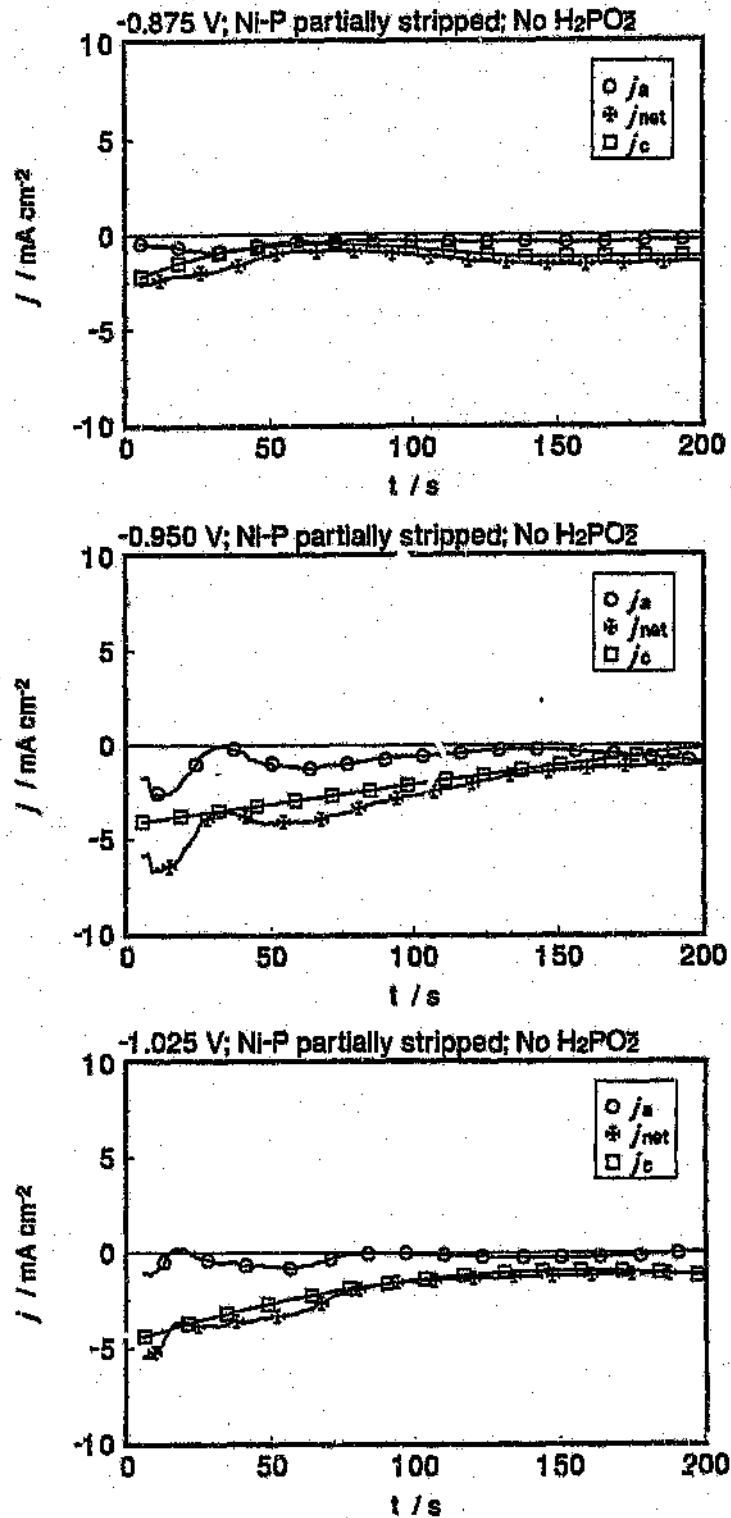


Figure 7.29 Current density curves over a period of 200 s, at potentials -0.875 V , -0.950 V and -1.025 V in Bath 1 lacking in H_2PO_2^- , using a partially stripped electroless Ni-P deposit as substrate. For clarity, plotting points show every 20th datum.

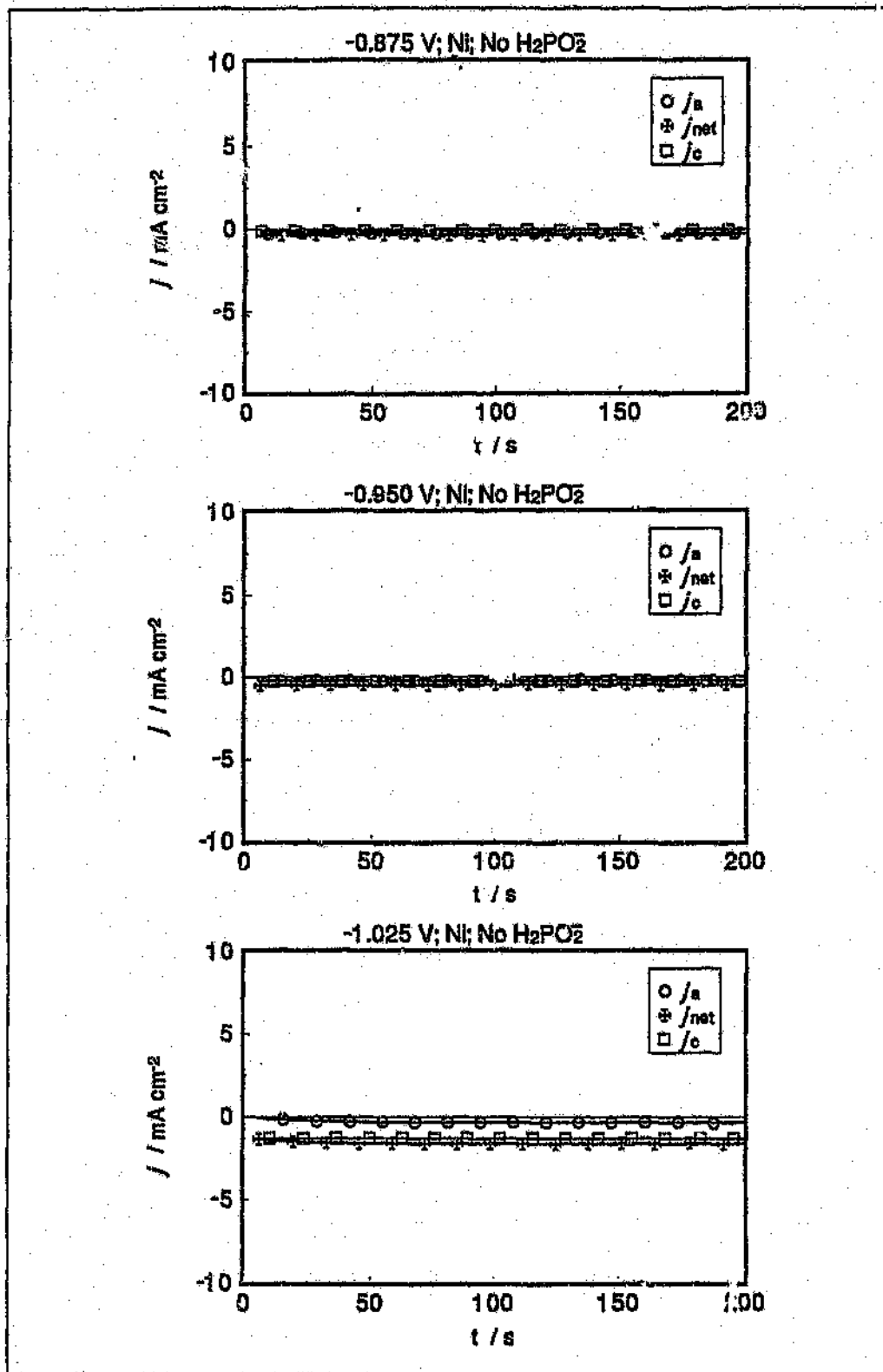


Figure 7.30 Current density curves over a period of 200 s, at potentials -0.875 V, -0.950 V and -1.025 V in Bath 1 lacking in H_2PO_2^- , using an electrolytically deposited pure nickel substrate (Ni). For clarity, plotting points show every 20th datum.

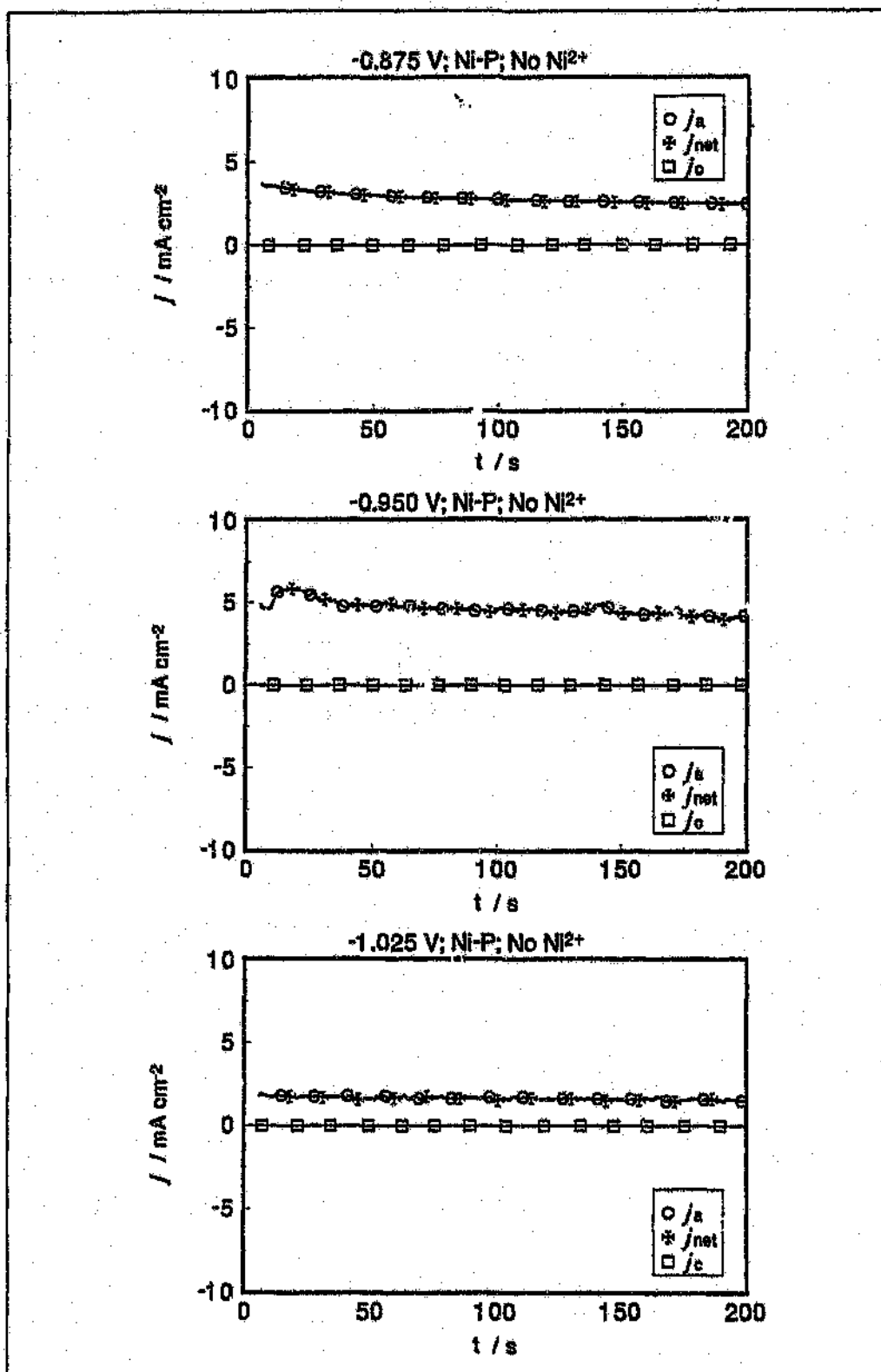


Figure 7.31 Current density curves over a period of 200 s, at potentials -0.875 V, -0.950 V and -1.025 V in Bath 1 lacking in Ni^{2+} , using an electroless Ni-P substrate (Ni-P). For clarity, plotting points show every 20th datum.

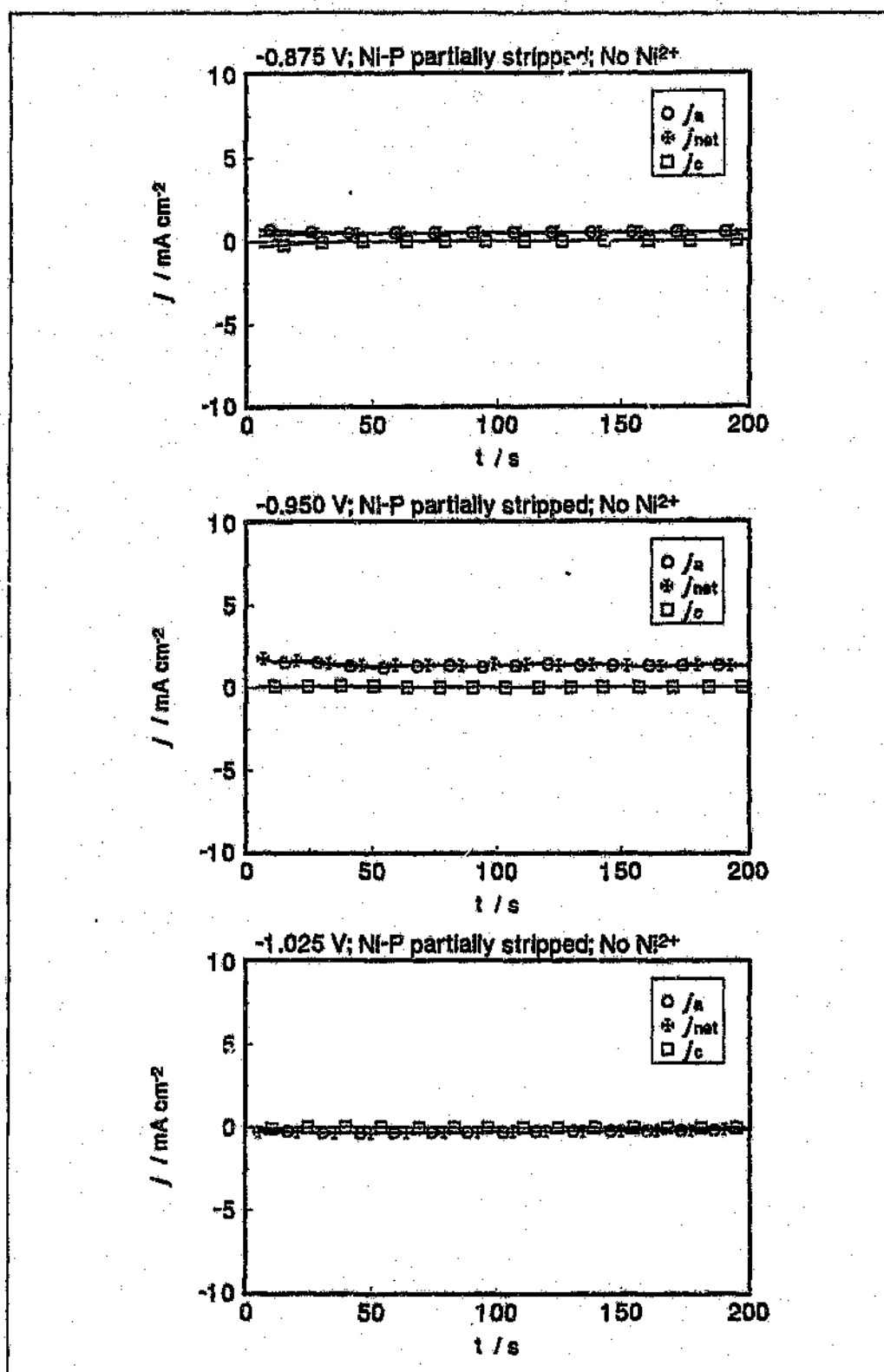


Figure 7.32 Current density curves over a period of 200 s, at potentials -0.875 V , -0.950 V and -1.025 V in Bath 1 lacking in Ni^{2+} , using a partially stripped electroless Ni-P deposit as substrate. For clarity, plotting points show every 20th datum.

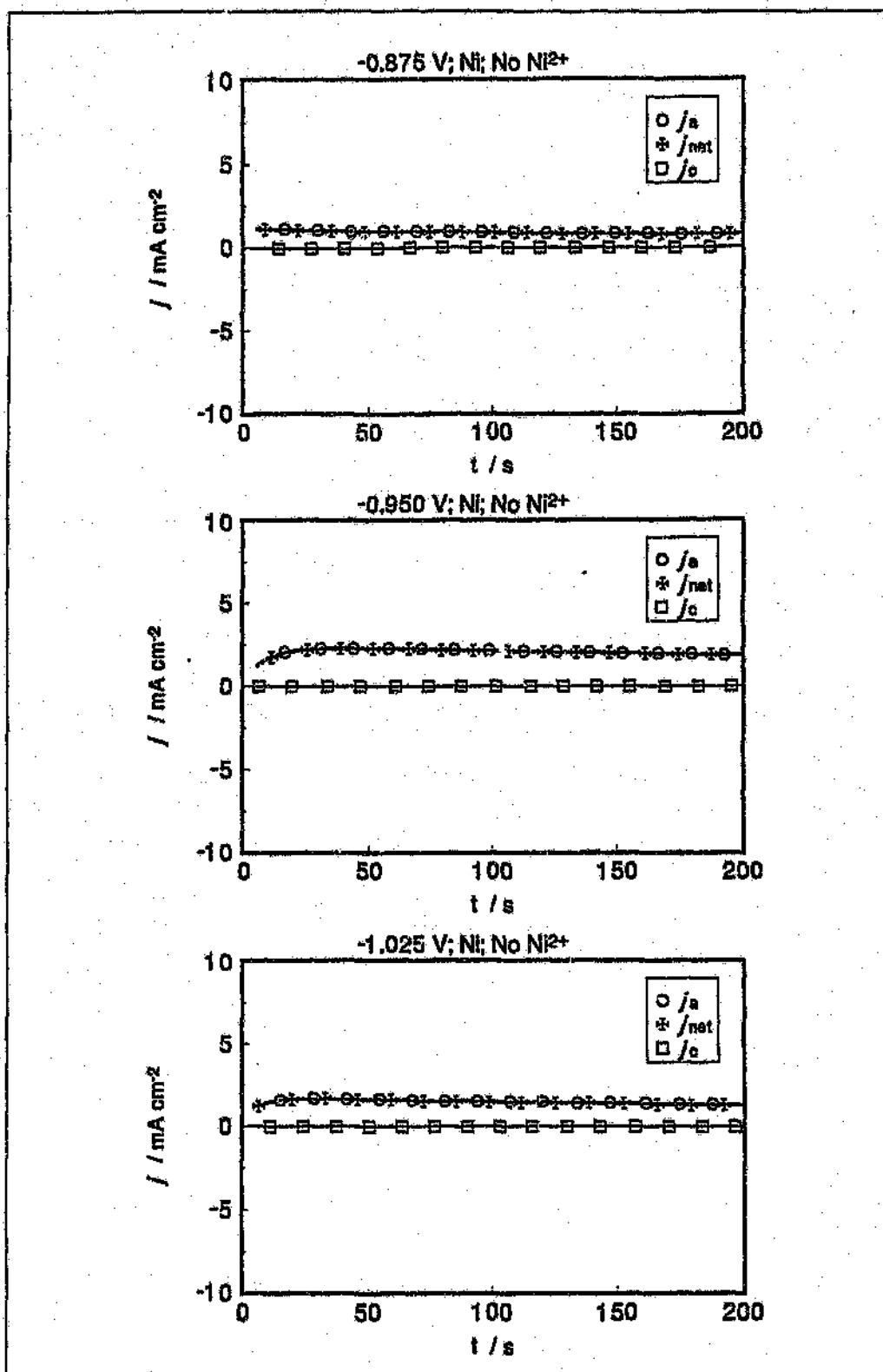


Figure 7.33 Current density curves over a period of 200 s, at potentials -0.875 V , -0.950 V and -1.025 V in Bath 1 lacking in Ni^{2+} , using an electrolytically deposited pure nickel substrate (Ni). For clarity, plotting points show every 20th datum.

Three possible different factors might be expected to influence the initial rate measured on the partially stripped surface as compared with normal electroless nickel. These are, firstly, a change in surface area; secondly, a change in the specific catalytic activity of the surface, and, thirdly, the contribution of a specifically adsorbed species produced during stripping.

As a result of the removal of the less noble crystalline phase from the amorphous matrix, partial stripping might be expected to produce a rougher surface of greater active area. Since the piezoelectrically sensitive area, which is governed by the rear electrode of the crystal, would remain constant, this could lead to an erroneously high plating rate measurement. In this connection, it should be noted that the deposition rate of this electroless plating solution is insensitive to the rate of stirring (Feldstein and Amodio 1969) or rotation of the electrode (Orchard 1988a). Since the plating rate is not under mass transfer control, an increase in the micro-roughness of the surface would lead to a greater measured plating rate. Another roughness-dependent effect is the coupling of electrolyte solution to the shear oscillation of the electrode surface (Beck, Pittermann and Weil 1992). As the plating process displaces solution from low spots and smoothes out the surface, the measured mass change would be less than the actual mass of the deposit formed, since the mass of coupled solution will decrease. This effect would oppose the primary surface area effect, but would probably be insufficient to cancel it entirely. To explain rate enhancements as great as that seen on the partially stripped surface at -0.875 V (Table 7.2) would require that the active surface area is actually

about ten times the superficial area. An examination of electron micrographs (Figure 7.34 - Figure 7.36) of the various surfaces suggests that this is highly improbable, since the surface morphology does not significantly change during plating, partial stripping and recoating.

Quite apart from such considerations, it is difficult to fully explain the potential overshoots at open circuit (Figure 7.19) and the concurrent higher deposition rates (Figure 7.20) in terms of a simple physical surface area effect. Enhanced surface catalytic activity provides an alternative explanation of these observations. Studies of the electrochemistry of this plating bath have shown that there is a significant mutual interaction between reactions (7.1) and (7.2); they are both faster in the full electroless bath than in isolation under otherwise identical conditions (Figure 7.7 and Figure 7.8, Section 7.4.1, Orchard 1988b). Furthermore, j_a in the full electroless bath depends exponentially on potential over a substantial range around the mixed potential; in contrast, the derived j_c value is virtually independent of potential (Figure 6.5, Section 6.2.2, Figure 7.5, Section 7.4.1, Gafin and Orchard 1992, Orchard 1988b). Thus the anodic process is rate-controlling, and the observed plating rate increase during the negative potential excursion (Figure 7.19 and Figure 7.20) is to be expected.

It therefore appears that in the presence of the full plating solution, the phosphorus-rich, partially stripped surface is a better catalyst for the oxidation of hypophosphite ions than is electroless nickel itself. This will lead to a higher nickel deposition rate in two ways: through the interaction between the

processes and through the negative shift in the plating potential. Based on the earlier measurement of the dependence of the plating rate on potential (Section 7.4, Orchard 1988b), the maximum potential overshoot shown in Figure 7.19, -0.040 V, would by itself give rise to an increase in j_c by a factor of 1.9. However, the maximum rate increase derived from the slopes of the curves in Figure 7.20 is about 3.3 times, confirming that a second effect (the interaction between the half-reactions) is probably operating.

Alternatively, if the potential overshoot and rate increase are entirely the result of a higher substrate area, the implication is that the nickel deposition process, reaction (7.1), is moving into a region of mass transfer control, giving rise to a concentration overpotential.

It is therefore proposed that an enhanced catalytic activity, rather than any change in actual surface area, is primarily responsible for the effects noted on the partially stripped electroless nickel surface. The sharp positive excursion of the net current seen in at short times in Figure 7.24(d) also supports the suggestion of a particularly reactive combination of catalytic surface and reagents. A similar investigation of reinitiation behaviour, using phosphorus-rich electrolytic Ni-P deposits (produced after the method of Cargill (1979)) as substrates, did not exhibit either the potential overshoot or the initial rate enhancement.

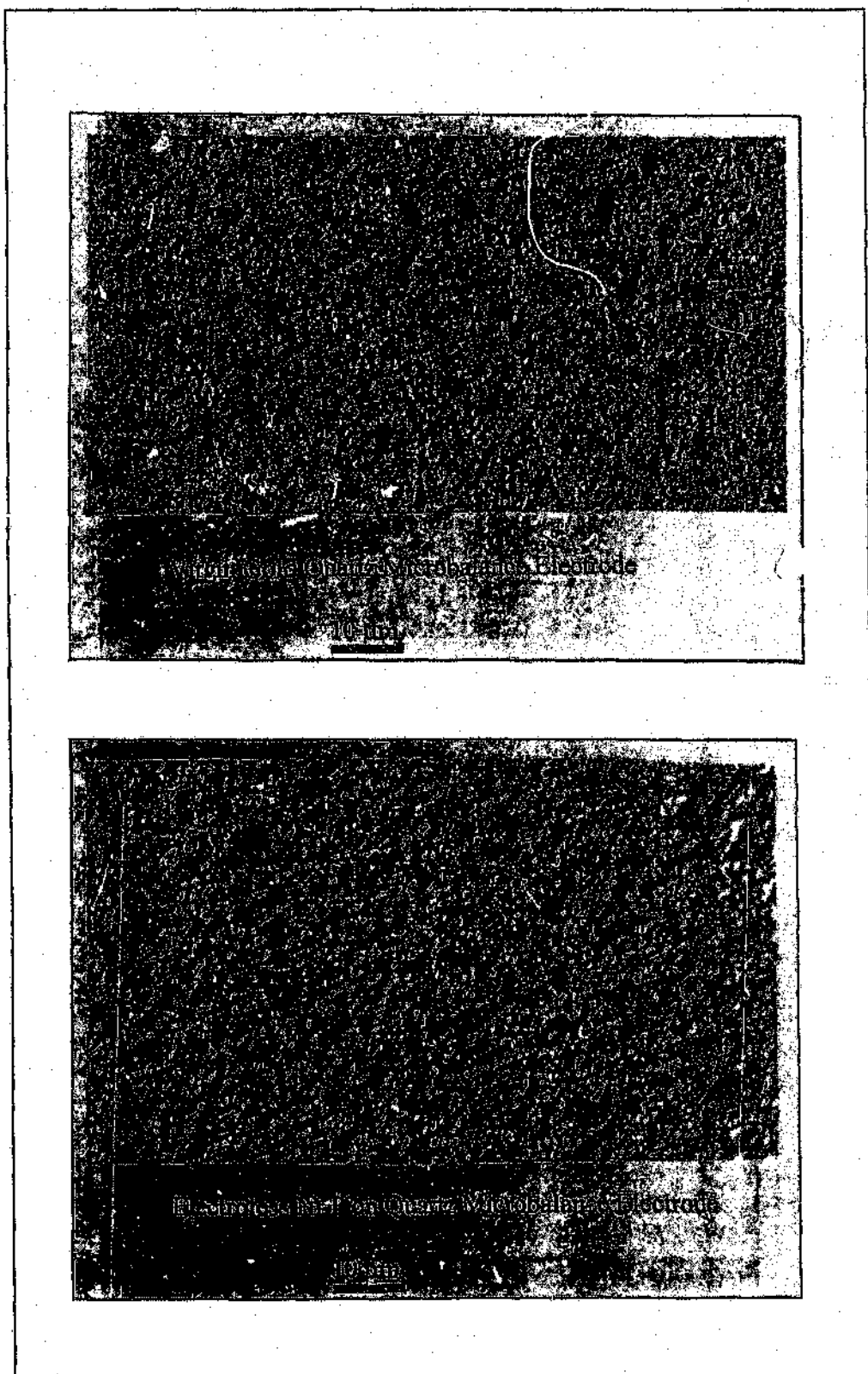


Figure 7.34 Electron micrographs of virgin gold, and electroless Ni-P deposit on quartz microbalance electrodes.

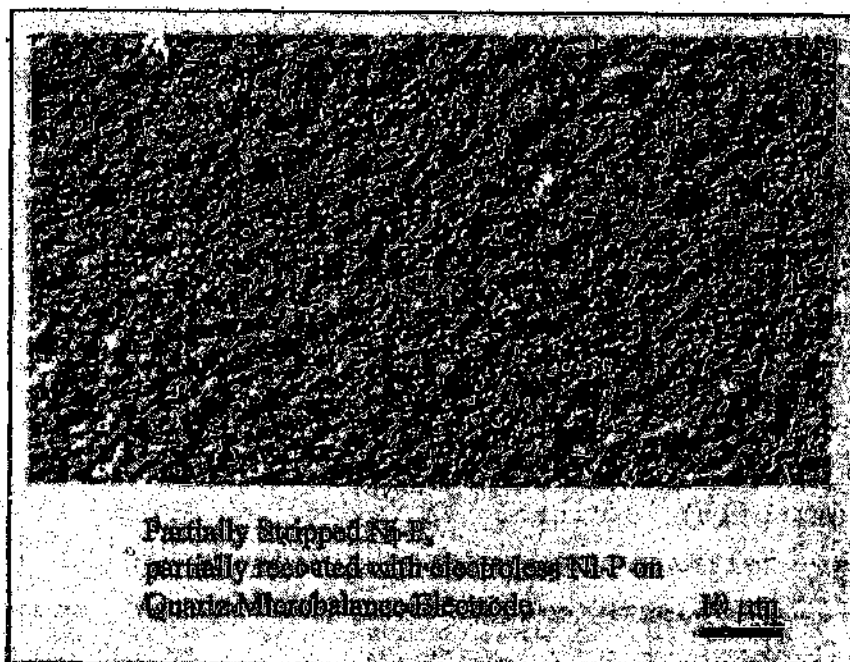


Figure 7.35 Electron micrographs of electroless Ni-P deposits on quartz microbalance electrodes. The partially recoated deposit was plating at an enhanced rate when removed from solution.

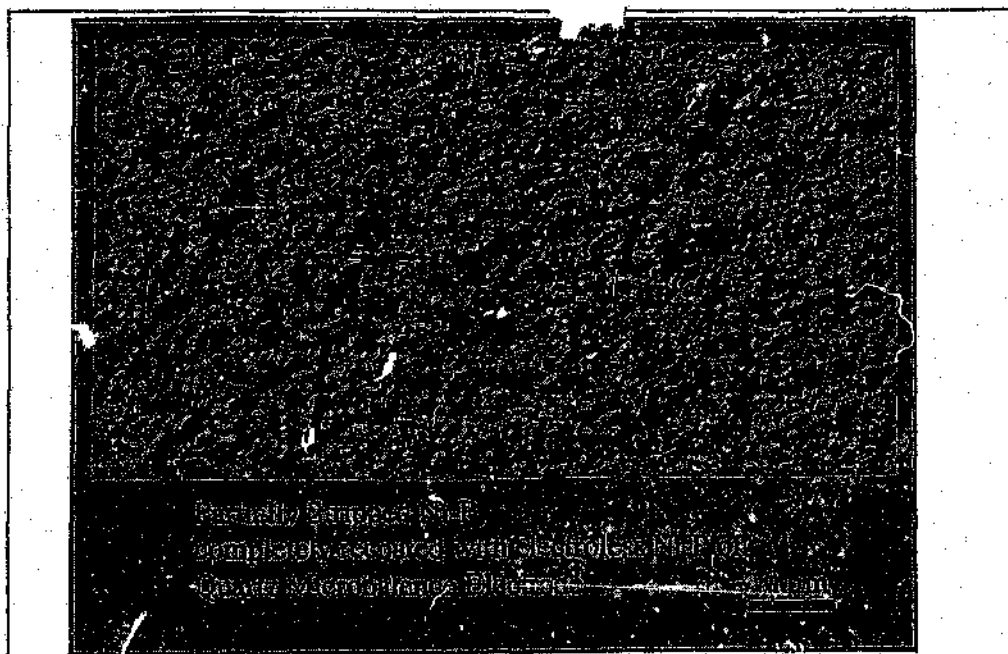


Figure 7.36 Electron micrograph of electroless Ni-P on a quartz microbalance electrode. The deposit was partially stripped, then recoated with electroless Ni-P until the steady state deposition rate was observed.

7.5.1.2 XPS characterisation of deposits

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state of the surfaces of the nickel and Ni-P alloys. In the characterisation of electrode surfaces, the XPS spectra should be obtained with as short a delay as possible following the electrode process(es). Furthermore, transfer of the electrode to the ultrahigh vacuum chamber should be performed in an inert atmosphere. This facility was not available in the instrument used for the present work. It remained possible, however, to obtain useful information about the nature of the electroless deposits, by performing argon ion ablation of the surface layer.

XPS spectra of the electroless Ni-P deposit (as produced and partially stripped), and an electrolytically formed Ni deposit are given in Figures 7.35 to 7.39. The Ni(2p $3/2$) and P(2p $3/2$, 2p $1/2$) regions are shown. All spectra were corrected according to the offset of the C(1s $1/2$) peak, which has a binding energy of 284.5 eV. The XPS spectra obtained for the various nickel-containing deposits were noisy prior to the argon ion ablation, a common phenomenon when surfaces are oxidised or contaminated. Following the ablation treatment, the relevant peaks were more clearly defined. Literature values of peak positions were obtained from Wagner (1990) pp. 599-608, and Diegle et al. 1988). These are presented in Table 7.4.

Table 7.4 Binding energies of Ni and P, and some of their alloys and compounds (Diegle et al. 1988).

Element or compound	Ni 2p	P 2p	Comments
Ni	852.3	-	Pure crystalline
P	-	129.8	Amorphous red
Ni	852.3	-	Metallic Ni-20P
P	-	129.2	Elemental Ni-20P
Ni ₂ P	857.0	133.4	Powder
NaH ₂ PO ₂	-	132.4	Powder
H ₃ PO ₃	-	134.0	Powder
Na ₂ HPO ₄	-	133.3	Powder
KH ₂ PO ₄	-	133.5	Powder
NiPO ₄	856.6	133.3	Powder
NiSO ₄	857.4	-	Powder
NiCl ₂	856.5	-	Powder
NiO	854.1	-	Powder
NiO	854.3	-	Oxidised Ni
NiO	853.8	-	not specified
NiO	854.2	-	Powder
Ni ₂ O ₃	855.5	-	Powder
Ni ₂ O ₃	855.7	-	Oxidised NiO
Ni ₂ O ₃	855.6	-	O bombarded Ni
Ni(OH) ₂	855.9	-	Powder
Ni(OH) ₂	856.4	-	not specified
Ni(OH) ₂	855.7	-	Powder
Ni(OH) ₂	855.8	-	Powder
α-Ni(OH) ₂	855.9	-	On Pt electrode
β-Ni(OH) ₂	855.8	-	On Pt electrode

Table 7.5 XPS peak positions for Ni and Ni-P deposits on Glassy Carbon. All values were obtained from kinetic energy raw data, and corrected to the carbon (1s 1/2) peak position.

Spectrum	Treatment	Peak	Binding Energy /eV	Possible Chemical State
Electroless Ni-P				
Ni (2p 3/2) Figure 7.35	Untreated	1	852.8	Ni; Ni-xP
		2	856.8	Ni ₂ P; NiPO ₄ ; Ni ₂ O ₃
	Argon ion ablation	1	852.6	Ni; Ni-xP
		2	859.5	Ni ₂ P
P (2p 3/2 and 1/2) Figure 7.38	Untreated	1	129.7	elemental P
		2	133.6	Ni ₂ P; KH ₂ PO ₄
	Argon ion ablation	1	130.2	elemental Ni-xP
Partially stripped Ni-P				
Ni (2p 3/2) Figure 7.36	Untreated	1	853.6	NiO; Ni-xP
		2	857.1	Ni ₂ P; Ni(OH) ₂
	First argon ion ablation	1	853.4	Ni; Ni-xP
		Third argon ion ablation	1	853.5
P (2p 3/2 and 1/2) Figure 7.39	Untreated	1	129.8	P; Ni-xP
		2	133.4	Ni ₂ P; NaH ₂ PO ₂ ; NiPO ₄
	First argon ion ablation	1	129.8	P; Ni-xP
		2	133.8	Ni ₂ P
	Third argon ion ablation	1	129.8	P; Ni-xP
		2	134 broad	Ni ₂ P
Electrolytic Ni				
Ni (2p 3/2) Figure 7.37	Untreated	1	852.5	Pure crystalline Ni
		2	856.3	Ni(OH) ₂ ; Ni ₂ O ₃
	Argon ion ablation	1	853.0	Pure crystalline Ni
		2	858.4	Ni(II)

The changes observed in the spectra (viz. peak positions, relative intensities) brought about as a consequence of argon ion ablation of the full electroless and partially stripped deposits are of prime interest. Peak positions of the spectra obtained in this work are listed in Table 7.5.

In the unspattered sample of as-produced electroless Ni-P (Figure 7.37), the Ni (2p 3/2) region shows two peaks, indicating that nickel is present in both metallic and oxidised form. The peak toward the higher binding energy is due to oxidised nickel, either a compound of Ni and P, or a nickel oxide or hydroxide. The signal to noise ratio in the unspattered samples made exact determination of the peak positions difficult. A broad peak 6 - 8 eV higher than the nickel(II) peak may be a shake-up satellite, further confirmation of the presence of nickel(II) (Briggs and Rivière 1990 pp. 130-131). Argon ion sputtering results in an enhancement of the lower binding energy peak (about 852 eV) which arises from metallic nickel. An oxidised form of nickel was still present after ablation (about 858 eV). Subsequent sputtering did not alter the form of the spectrum.

Two forms of phosphorus may be identified in the spectrum of unspattered electroless Ni-P (Figure 7.40). Elemental P gives rise to a peak at around 130 eV, but the signal at this position is not significantly greater than the noise. A peak arising from an oxidised form of phosphorus is noted at 132 - 136 eV in the unspattered sample but it is not possible to identify the species. [The P peaks are doublets in this region (Briggs and Seah 1990 p. 641) and are not resolved in these spectra.] After ablation the strongest peak is at lower binding energy, i.e. about 130 eV.

The spectra obtained with the partially stripped deposit (Figure 7.38 and Figure 7.41) exhibited peaks at the binding energies expected for both oxidised and reduced forms of nickel and phosphorus. Successive ablation, however, had a marked influence on the spectra of both nickel and phosphorus (2p) binding energy regions. In the case of nickel, the intensity of the metallic Ni peak increased with successive ablations relative to the peak expected from nickel(II). The higher binding energy peak of phosphorus was most intense on the untreated sample, with the lower binding energy peak becoming much more significant as the surface was exposed to argon ions. A peak at 132 eV was seen on the untreated sample but was not present, or could not be resolved, after ablation. This peak may be due to NaH_2PO_2 , according to Diegle et al. (1988).

The electrolytically produced nickel deposit consisted of oxidised and reduced nickel prior to ablation, with the metallic Ni peak becoming more pronounced with argon ion ablation. No phosphorus peak could be detected.

These results are in support of the findings of Diegle et al. (1988) as described in Chapter 4, Section 4.2, that anodic oxidation of Ni-P alloys results in a high concentration of oxidised phosphorus on the surface. The form of phosphorus present was proposed to be hypophosphite. This was subsequently confirmed by Hofmann and Weil (1993).

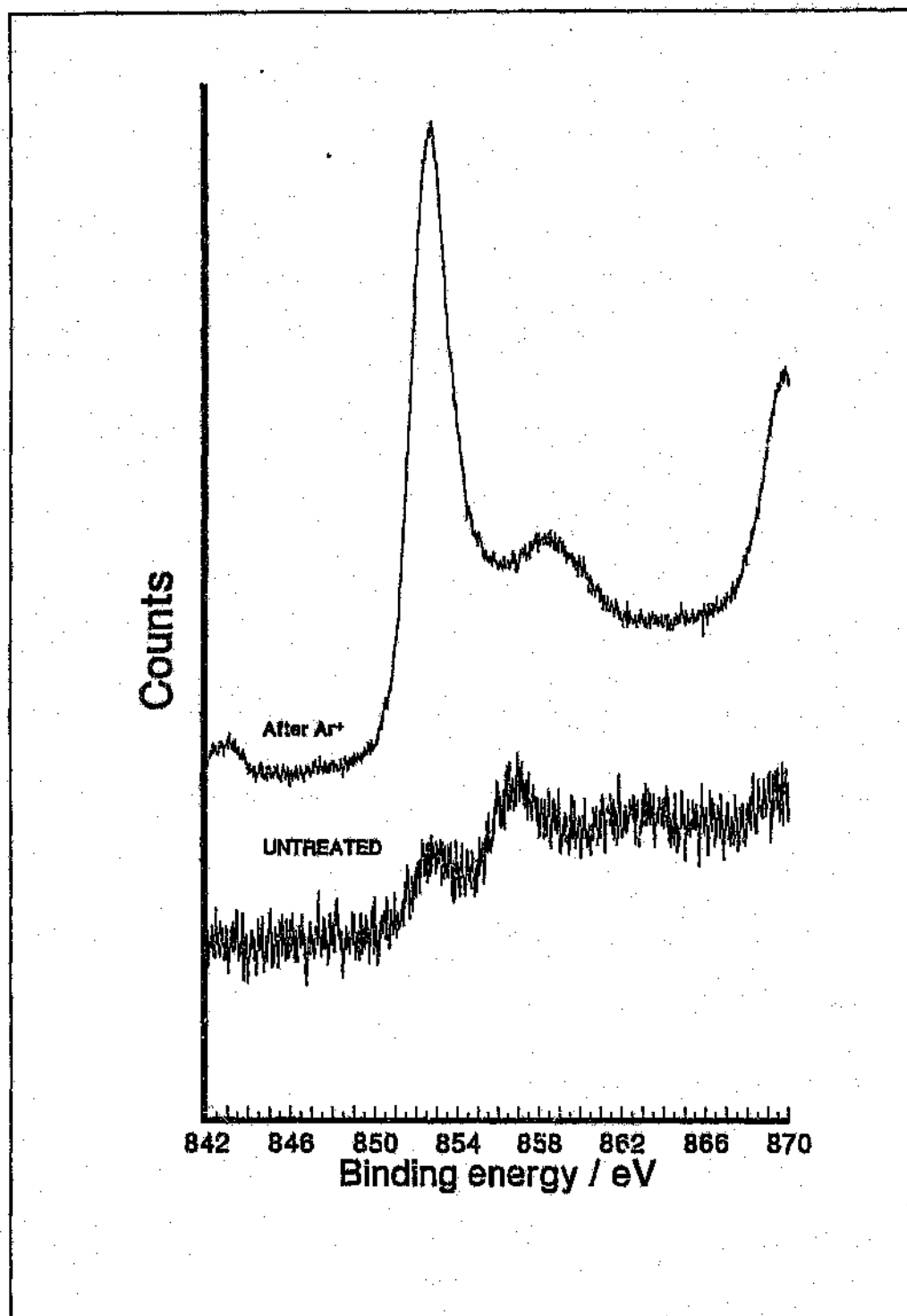


Figure 7.37 XPS spectra of electroless Ni-P, in the Ni (2p 3/2) region. Deposit produced in Bath 1 on a glassy carbon substrate.

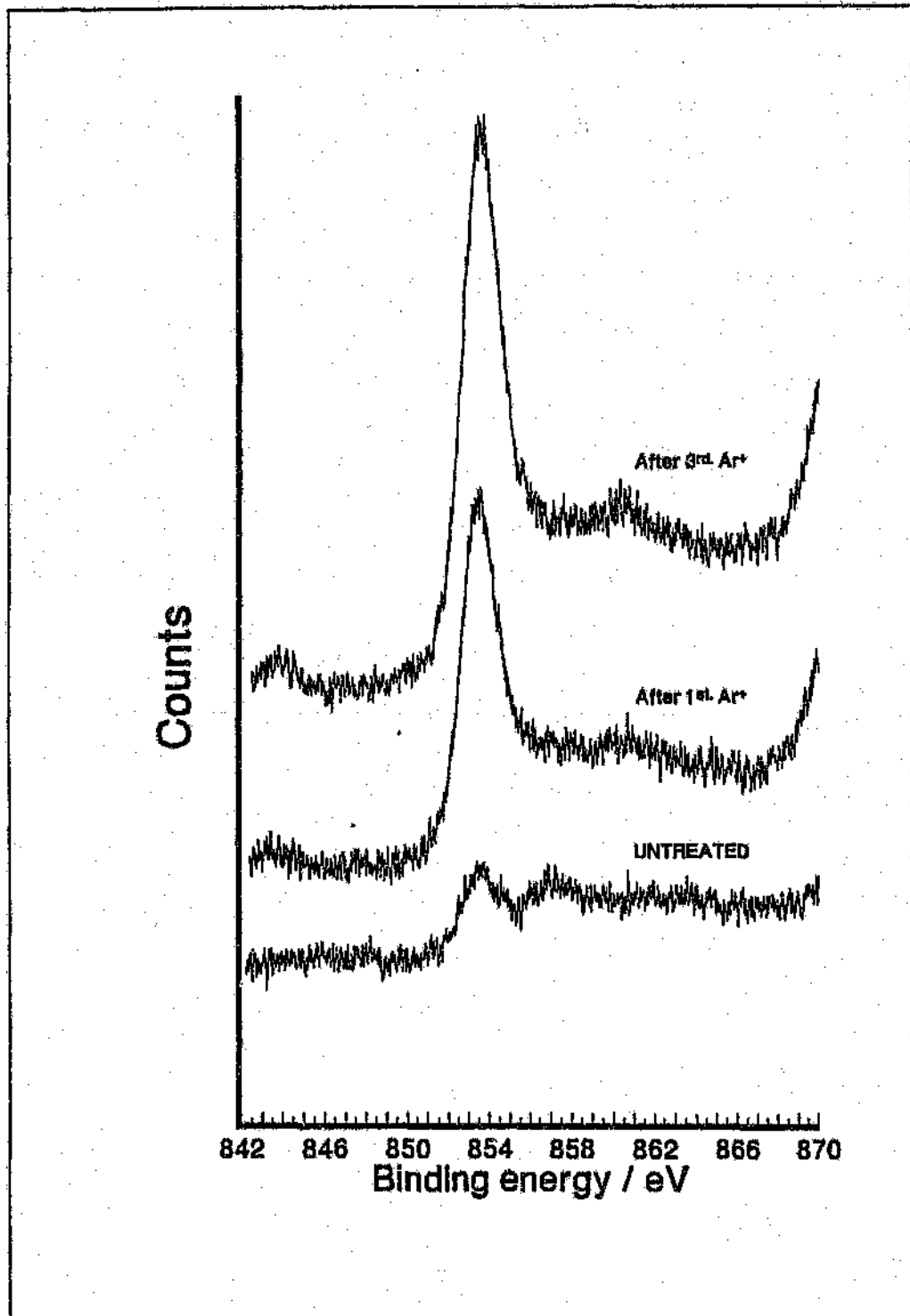


Figure 7.38 XPS spectra of partially stripped electroless Ni-P, in the Ni (2p 3/2) region. Deposit produced in Bath 1 on a glassy carbon substrate, and anodically stripped as described in the text.

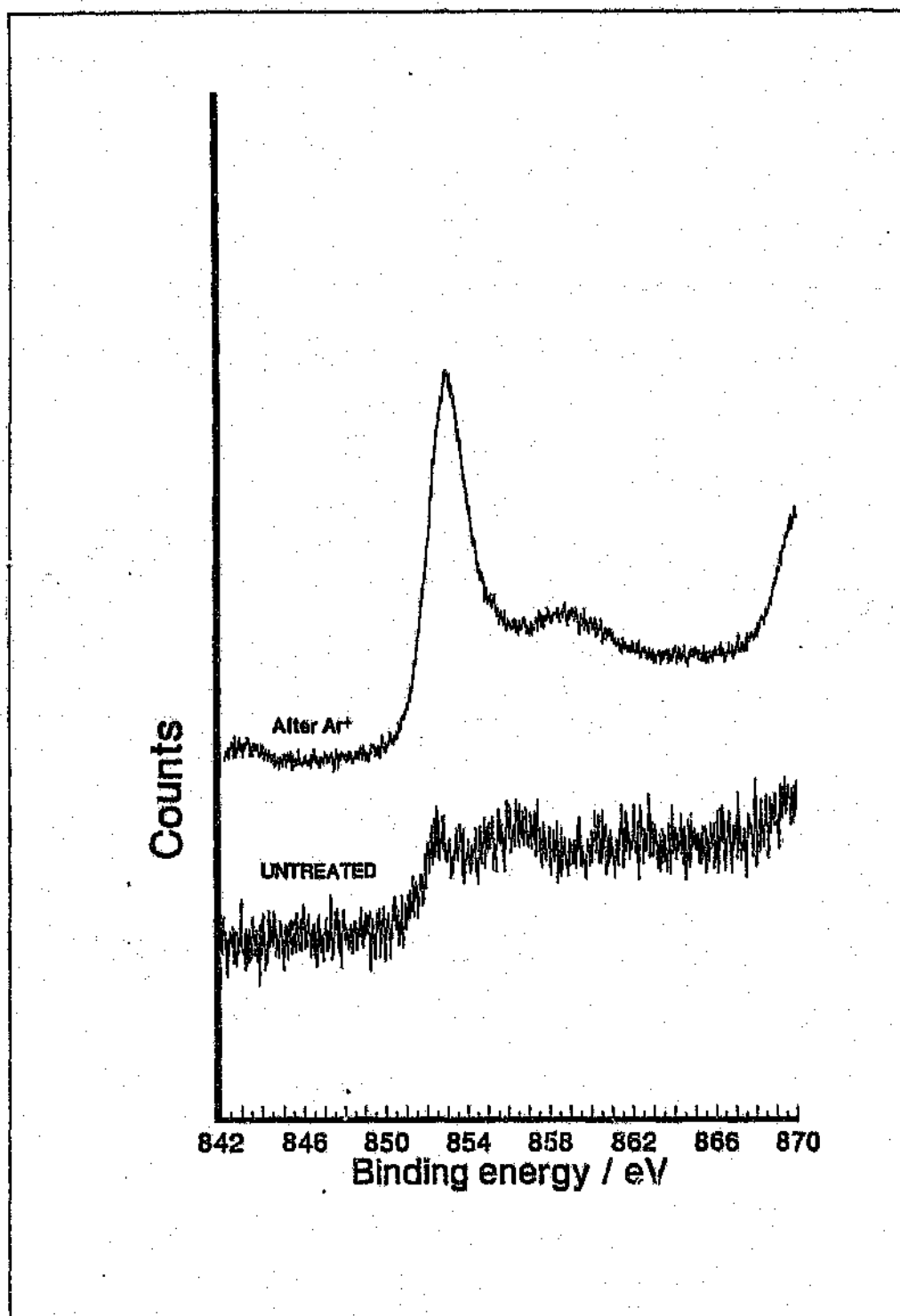


Figure 7.39 XPS spectra of electrolytic Ni in the Ni (2p 3/2) region. Deposit produced in Bath 1 (in absence of H_2PO_2^-), on a glassy carbon substrate.

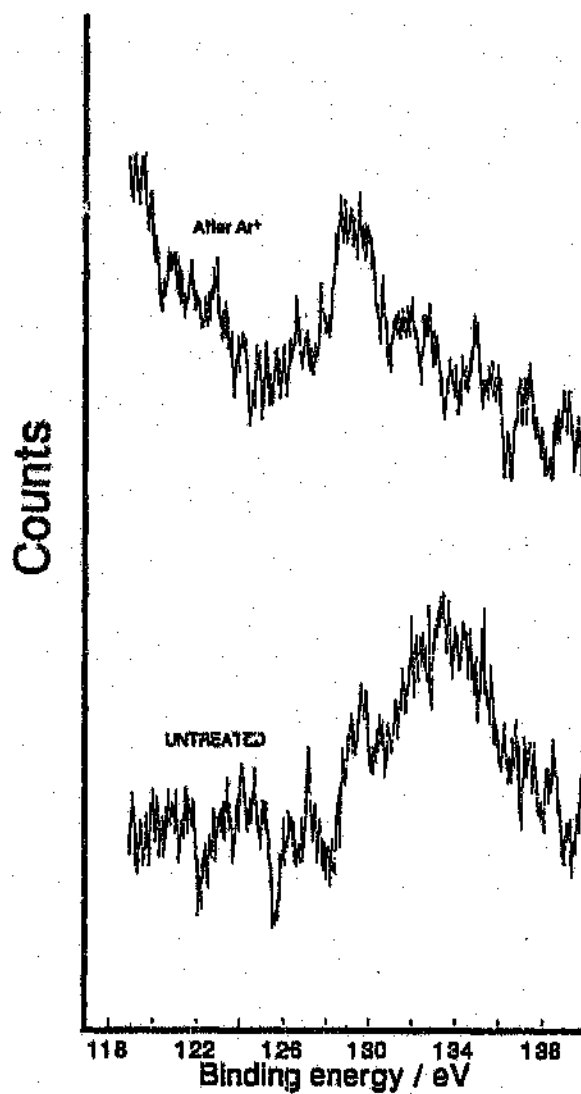


Figure 7.40 XPS spectra of electroless Ni-P, in the P ($2p\ 3/2$ and $2p\ 1/2$) region. Deposit produced in Bath 1 on a glassy carbon substrate.

Counts

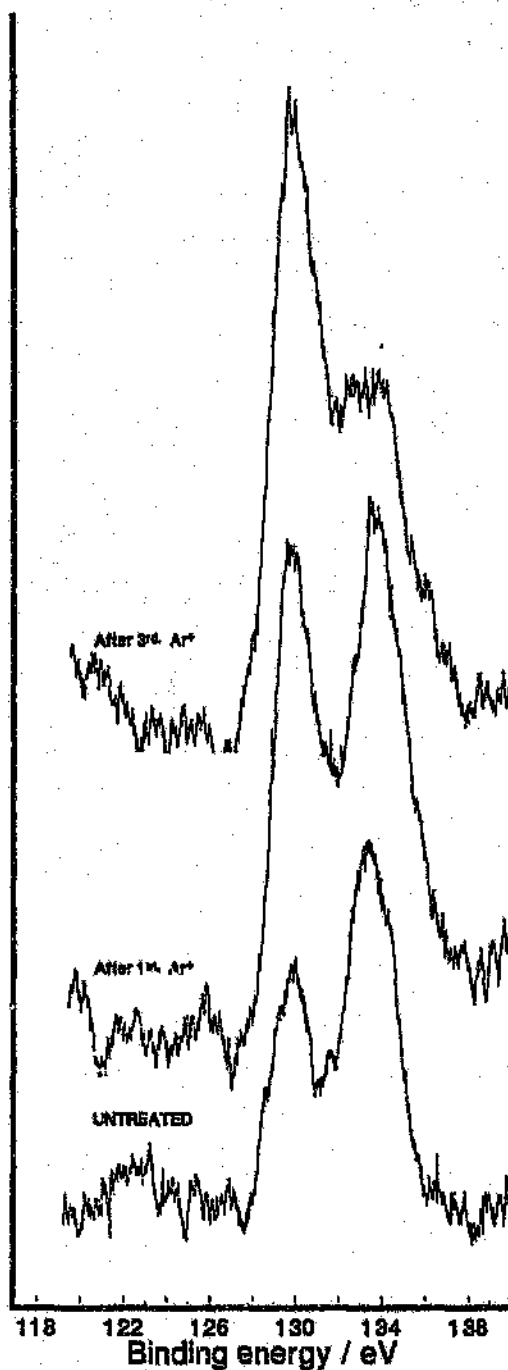
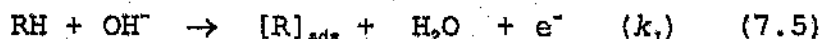


Figure 7.41 XPS spectra of partially stripped electroless Ni-P, in the P (2p 3/2 and 2p 1/2) region. Deposit produced in Bath 1 on a glassy carbon substrate and anodically stripped as described in the text.

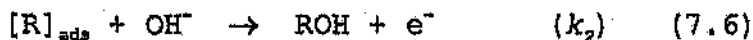
In the light of the mechanisms of Ni-P oxidation described by Diegle and co-workers (1988), and Hofmann and Weil (1993), it is conceivable that during the partial stripping of the alloy, adsorbed H_2PO_2^- (i.e., the P(I) species) is formed on the residual surface. This could then act as a bridging ligand for nickel. In this case it is clear that the rate of autocatalytic Ni-P deposition could be positively influenced, particularly if adsorption of H_2PO_2^- is the rate determining step. This process has been suggested as being rate determining under certain conditions (Ohno 1991).

The possibility that adsorption of H_2PO_2^- to the metal is rate determining is high. The computer simulation of the oxidation partial process described by Ohno (1991) showed how the rate of the adsorption (7.5) or OH⁻ attack (7.6) could, in certain circumstances, be rate determining. Ohno's generalised mechanism is presented below.

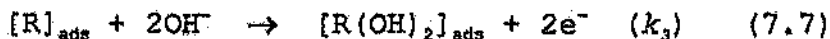
step 1:



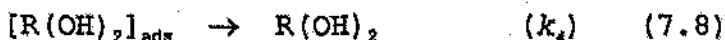
step 2:



step 3:



step 4:



(where k_n is the rate constant of step n.)

According to Homma et al. (1991), and Homma, Yamazaki and Osaka (1992), a complete electroless Ni-P film may have an average thickness of about 30 nm (i.e., growth is not always uniform). This is significantly higher than one monolayer of Ni or P, or a mixture of these two elements. Thus up to this thickness the original substrate may be exposed to the plating solution. In the present work, the enhanced plating rate of the partially stripped surface continues until a film thickness of about 100 nm has been formed, and adsorbed hypophosphite must still be exposed and active up to this average thickness. The value of 100 nm was estimated from the maximum mass deposited prior to the change of slope in Figure 7.20 (curve S2B1), using a density of 7.9 g cm^{-3} . Adsorbed hypophosphite is unlikely, therefore, to play a major part in the initial enhancement of the deposition rate of nickel on the partially stripped surface.

It is most likely, therefore, that the effect seen on the partially stripped deposit is a consequence of the nature of the material, i.e., amorphous Ni-P, rather than simply the enriched P content. Rearrangement of the hypophosphite to its active form may be more rapid on the amorphous phase than on the crystalline phase. The possibility that the catalytic activity of Ni-P is different to that of Ni was considered by Jusys and co-workers (1992), but at that time no evidence in support of this had been noted. Flis and Duquette (1984) attributed differing induction ("incubation") times on Ni and Ni-P to differing rates of dissolution of surface oxides, the oxide on the latter being less protective. Haruyama and Ohno (1988) demonstrated that the oxidation of the reducing agent depends on prior dissolution of an oxide film which may cover the surface. The observation of finite yet erratic

induction periods in the present work is consistent with this proposal, since the stripping process may be expected to produce such an oxide on the surface (the XPS studies do not serve as sufficient confirmation because the electrodes were exposed to air before examination).

The strong potential dependence of the cathodic half-reaction (alloy deposition) and the relatively potential-independent rate of H_2PO_2^- oxidation (Section 7.4, Orchard 1988b) indicates that although these partial processes are not independent of each other, in this bath the interaction is not due to direct coupling. In other words, the electron transfer processes occur between ions and the electrode rather than directly between the adsorbed ions themselves. The present work confirms an interaction of the partial processes and in addition shows that the more noble, amorphous Ni-P glass is more catalytically active than the alloy comprising the glass and fcc nickel supersaturated in phosphorus. If it were possible to examine the catalytic activity of the less noble fcc nickel supersaturated in phosphorus in the absence of the amorphous glass, further identification of the catalytic mechanism could be expected.

As a logical consequence of these arguments, it is proposed that the amorphous phase contributes a disproportionately high fraction of the catalytic activity of the electroless nickel surface. Partial stripping of the electroless Ni-P results in adsorbed H_2PO_2^- , which can play a minor role in increasing the deposition rate in the initial stages. Further study should lead to a greater understanding of the catalytic activity of the amorphous Ni-P surface. In particular, it may prove to be a useful catalyst for processes

other than electroless nickel plating, such as hydrogenation reactions. Ni-P amorphous alloys have indeed been reported to be useful catalysts in styrene hydrogenation (Shen et al. 1993).

7.5.2 The Ni-B alloy

7.5.2.1 Electrochemical studies

During anodic stripping of the Ni-B alloy, only one current peak was observed. Partial stripping, such as in the case of the Ni-P alloy, was therefore not possible. In view of this, the approach adopted in the investigation of the catalytic property of the Ni-B alloy was to obtain current density diagrams on

- (a) the as-plated alloy, and
- (b) essentially pure nickel produced electrolytically in absence of reducing agent.

These substrates were investigated in

- (i) the full bath (Bath 2),
- (ii) the bath where Ni^{2+} had been omitted or
- (iii) the bath where DMAB had been omitted.

In the assessment of the results in this section, the partial current density curves of the complete bath (Bath 2) on the as-plated electroless Ni-B surface are used as reference. The potentials chosen for the investigation again spanned the mixed (plating) potential of Bath 2, which is -1.02 V.

Figure 7.42, Figure 7.43 and Figure 7.44 show the current density curves under the various conditions at the three potentials of interest. As would be expected,

j_a has a low magnitude at more cathodic potentials, and j_c has low magnitude at the more anodic potential for the full alloy in the full bath. This trend is followed, for the most part, when the pure Ni substrate is used in the full bath. The effect of the substrate on the rates of the partial processes was considerably more subtle than those observed on the partially stripped Ni-P alloy (Section 7.5.1) and, in order to identify significant features in the data, statistical techniques were employed.

Analysis of variance (ANOVA) was applied to the data of cathodic current density, and the average value of anodic current density determined in the periods 9 to 12 seconds, and 194 to 200 seconds. The values are presented in Table 7.6. A description of the ANOVA technique is given in Appendix V.

ANOVA for j_c was calculated only for the data from the full bath (Bath 2) and this bath containing no DMAB, and similarly, for the anodic partial current density ANOVA was calculated only for the full bath and for the bath containing no Ni^{2+} . The F-ratio was tested at the 95% level.

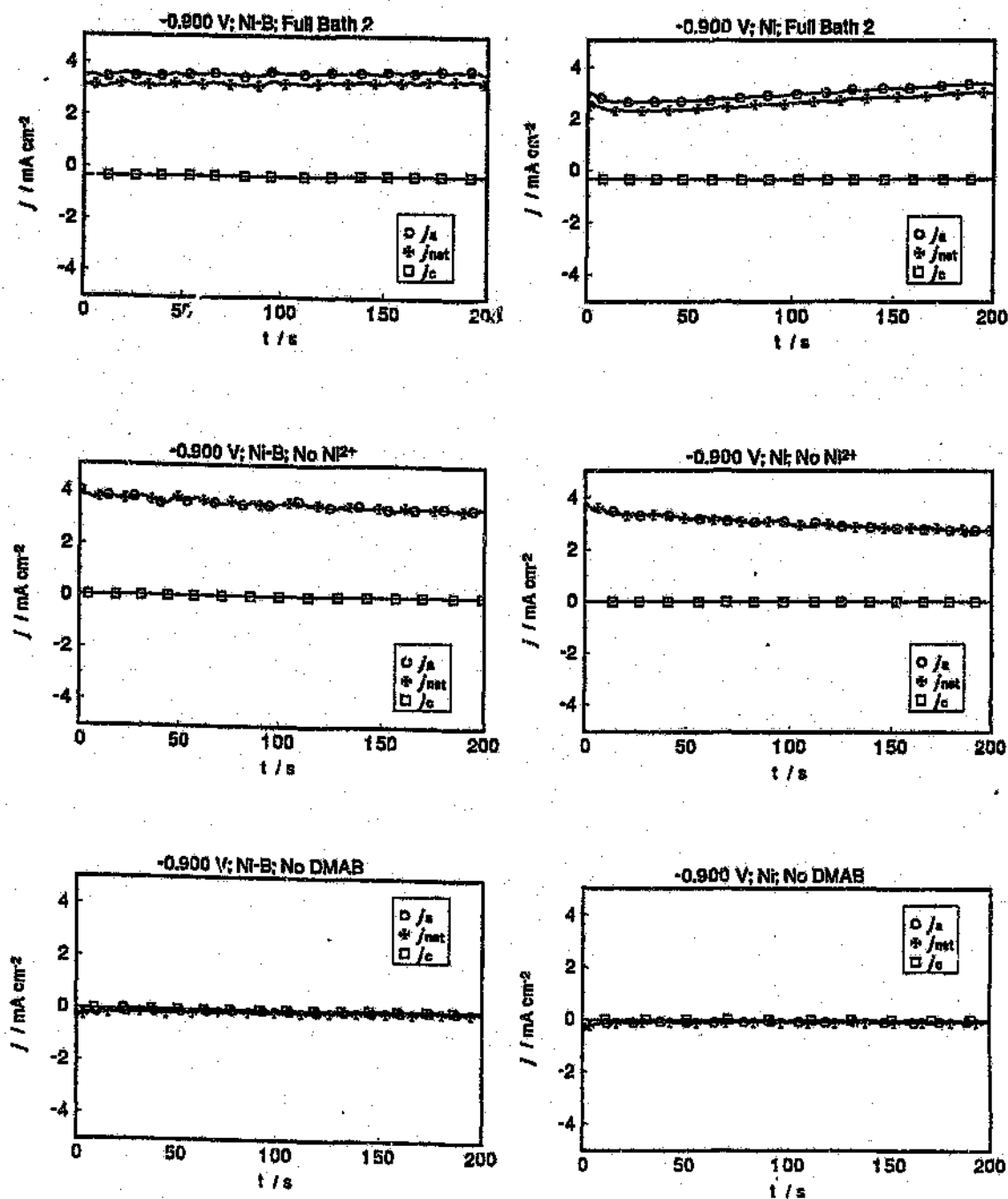


Figure 7.42 Partial current density curves for various substrates and compositions of Bath 2, electroless Ni-B. All results at -0.900 V . Top row: Full Bath 2. Middle row: Bath 2 without Ni^{2+} . Bottom row: Bath 2 without DMAB. Left column: Ni-B substrate. Right column: electrolytically deposited Ni substrate. For clarity, plotting points show every 20th datum.

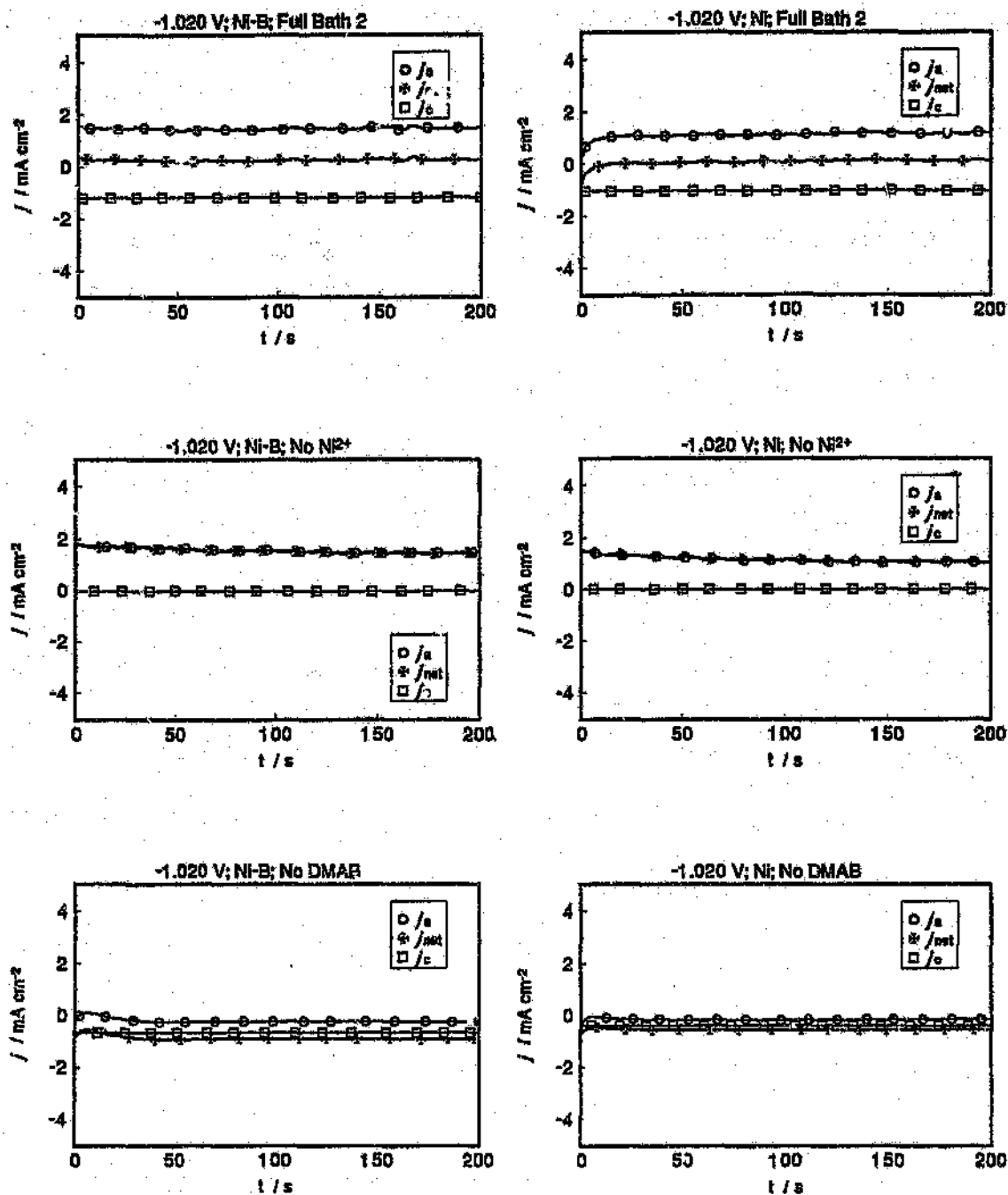


Figure 7.43 Partial current density curves for various substrates and compositions of Bath 2, electroless Ni-B. All results at -1.020 V. Top row: Full Bath 2. Middle row: Bath 2 without Ni^{2+} . Bottom row: Bath 2 without DMAB. Left column: Ni-B substrate. Right column: electrolytically deposited Ni substrate. For clarity, plotting points show every 20th datum.

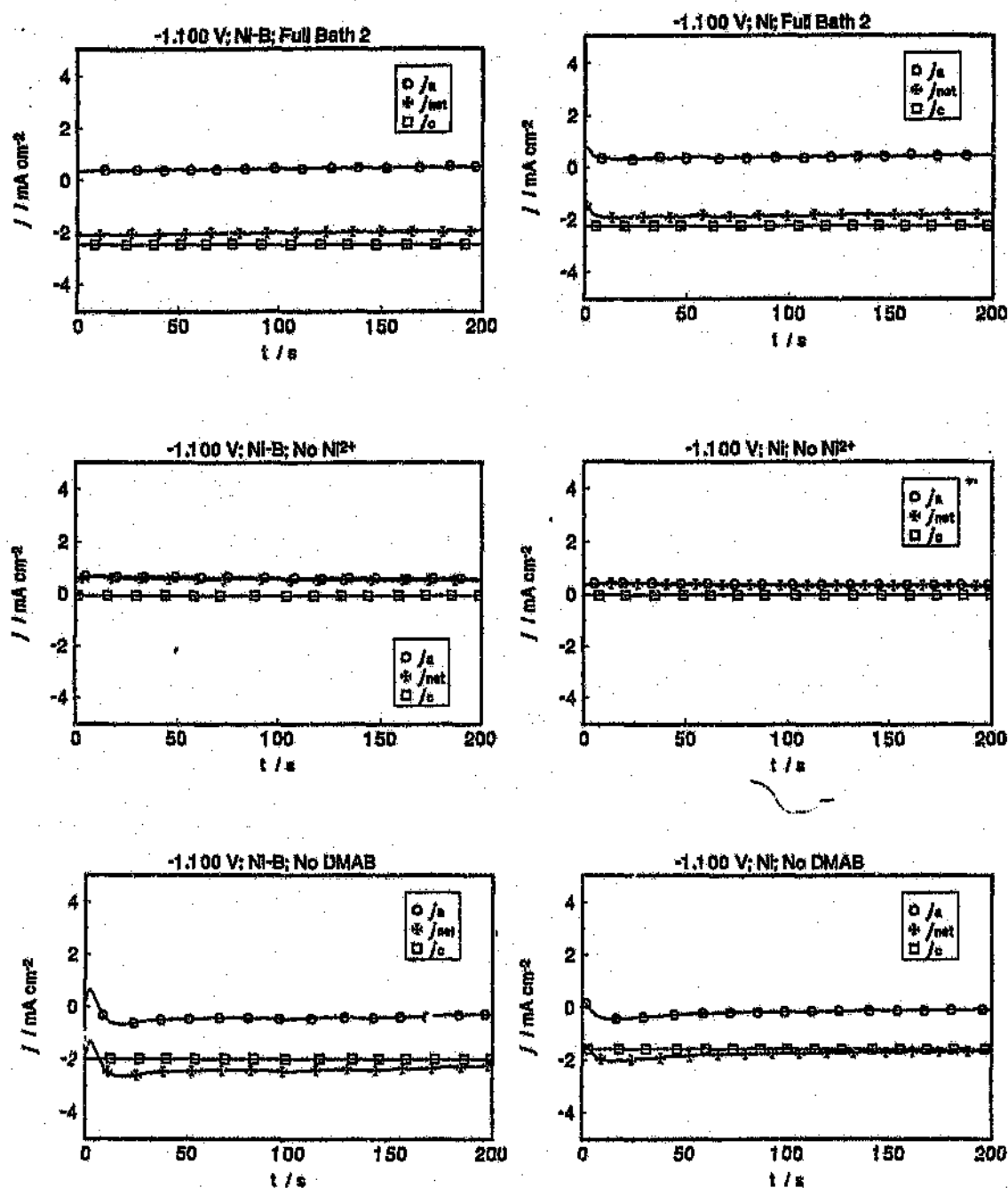


Figure 7.44 Partial current density curves for various substrates and compositions of Bath 2, electroless Ni-B. All results at -1.100 V. Top row: Full Bath 2. Middle row: Bath 2 without Ni^{2+} . Bottom row: Bath 2 without DMAB. Left column: Ni-B substrate. Right column: electrolytically deposited Ni substrate. For clarity, plotting points show every 20th datum.

Table 7.6 Data used in the ANOVA calculations for the anodic and cathodic partial current densities measured in Bath 2. The cathodic current density represents an average value over the entire period of measurement.

Applied potential /V vs. SCE	Bath *	Substrate	j_a 9-12 s /mA cm ⁻²	j_c /mA cm ⁻²	j_a 194-200 s /mA cm ⁻²
-0.900	Full	Ni-B	3.444	-0.374	3.661
-0.900	Full	Ni-B	3.289	-0.205	2.921
-0.900	Full	Ni	2.665	-0.341	3.355
-0.900	No Ni ²⁺	Ni-B	3.799	-0.002	3.386
-0.900	No Ni ²⁺	Ni	3.431	-0.015	2.738
-0.900	No DMAB	Ni-B	-0.178	-0.045	-0.104
-0.900	No DMAB	Ni	-0.139	-0.023	-0.106
-1.020	Full	Ni-B	1.351	-1.092	1.257
-1.020	Full	Ni-B	1.371	-0.905	1.147
-1.020	Full	Ni-B	1.437	-1.200	1.454
-1.020	Full	Ni	1.017	-1.044	1.179
-1.020	No Ni ²⁺	Ni-B	1.771	-0.018	1.470
-1.020	No Ni ²⁺	Ni-B	1.721	-0.025	1.464
-1.020	No Ni ²⁺	Ni	1.334	0.018	1.033
-1.020	No Ni ²⁺	Ni	1.392	0.014	1.056
-1.020	No DMAB	Ni-B	0.013	-0.676	-0.259
-1.020	No DMAB	Ni	-0.103	-0.401	-0.147
-1.100	Full	Ni-B	0.391	-2.470	0.513
-1.100	Full	Ni-B	0.284	-2.071	0.429
-1.100	Full	Ni	0.331	-2.292	0.496
-1.100	Full	Ni	0.331	-2.243	0.461
-1.100	No Ni ²⁺	Ni-B	0.702	-0.064	0.575
-1.100	No Ni ²⁺	Ni	0.436	-0.029	0.329
-1.100	No DMAB	Ni-B	-0.554	-1.986	-0.263
-1.100	No DMAB	Ni	-0.425	-1.601	-0.078

* Bath 2, complete or in the absence of Ni²⁺ or in the absence of DMAB.

ANOVA for the cathodic partial current density (Table 7.7) indicated that only two effects were significant

at the 95% level (i.e., where the p-value is less than 0.05). These were potential (as would be expected) and bath composition. The latter significance is further confirmation of the interaction between the anodic and cathodic partial processes in Bath 2 and is illustrated in Figure 7.45. In this Figure, it is clear that the mean cathodic current density has a larger magnitude in the full bath than in the bath containing no DMAB. While the magnitude of j_c is greater on Ni-B than on Ni, this effect is not significant at the 95% level. Thus at this significance level it cannot be stated that Ni-B is more catalytically active for the reduction of nickel(II) than is Ni.

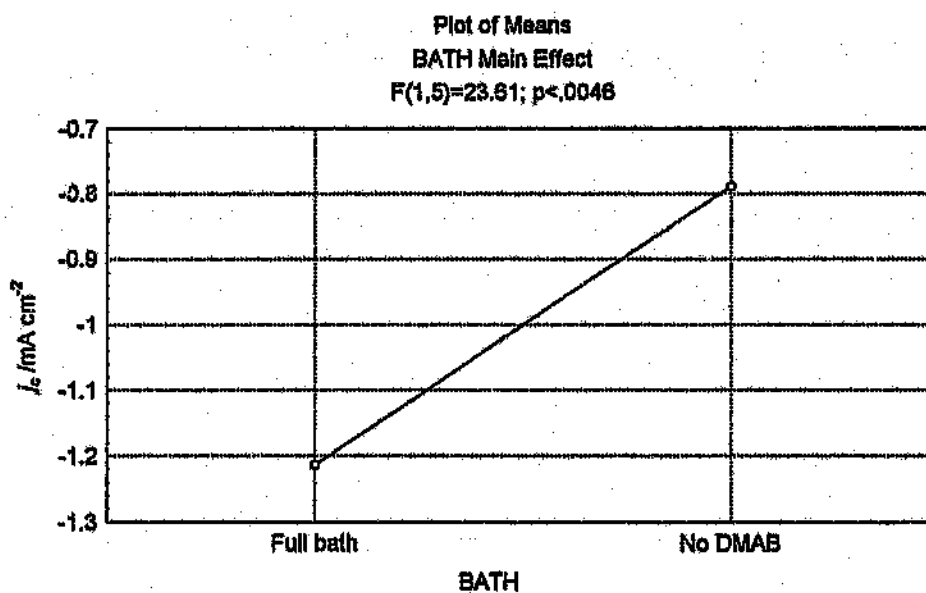
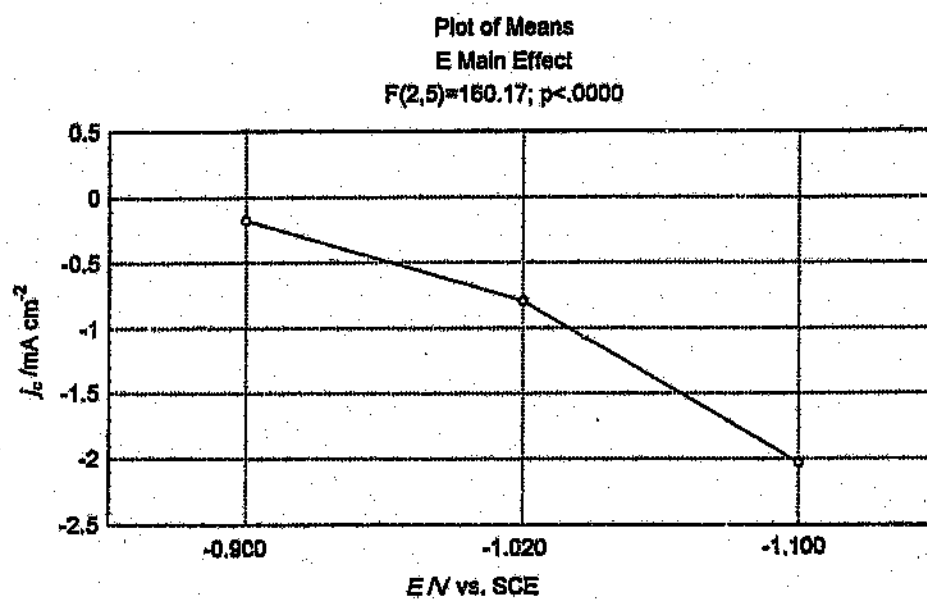


Figure 7.45 Means plots for the effect of applied potential and bath composition on j_c in Bath 2 and in this bath containing no DMAB.

The ANOVA calculations for the anodic current density are summarised in Table 7.8 and Table 7.9. At the early stage of measurement (9-12 s), the bath composition, the nature of the substrate, as well as applied potential, are significant effects. A three-way interaction was shown and is presented in Figure 7.46. This interaction shows the complex ensemble of catalytic activity and interaction of partial processes leading to electroless nickel plating and oxidation of DMAB.

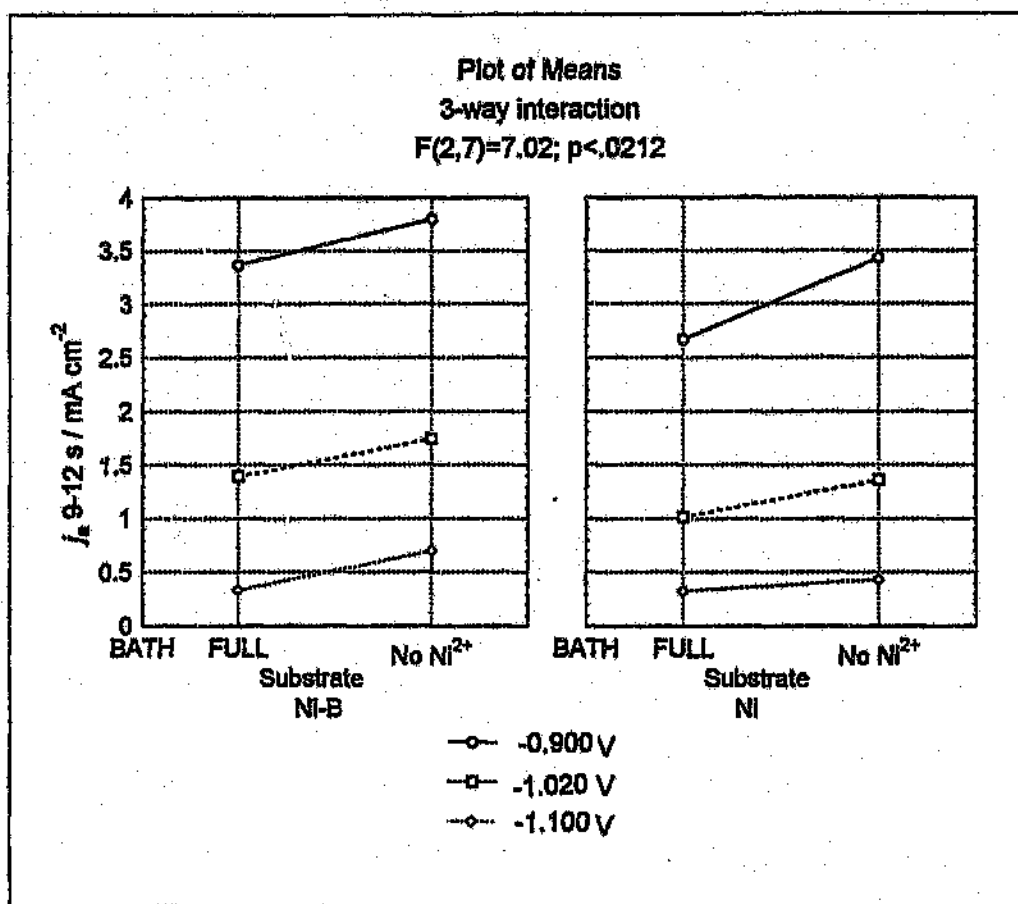


Figure 7.46 Three-way interaction of applied potential, bath composition and nature of the substrate on j_a during the 9-12 s period of measurement in Bath 2 and in this bath containing no Ni^{2+} .

It was found that the residuals for j_a (194-200 s) exhibited a fan shape when plotted against applied

potential or predicted values, indicating that a data transform was necessary. Thus the natural logarithm of j_a (194-200 s) was used for ANOVA calculations (Table 7.9). Besides applied potential (where, as expected, j_a decreased in magnitude as potential was made more cathodic), the effect of substrate was found to be significant. The mean value of j_a (or $\ln j_a$) was lower on pure Ni than on Ni-B after 194 s of measurement when all potentials were considered. In addition, a two-way interaction was noted, namely between bath composition and nature of substrate. This interaction is illustrated in Figure 7.47. The logarithm of j_a was almost unaffected by substrate in the full bath, but strongly affected by substrate when nickel(II) was absent from the solution. That is, the magnitude of the anodic current density during the later stages of measurement was lower on Ni than on Ni-B, particularly in the latter bath. An interpretation of these effects can most easily attribute the stability of j_a in the full bath to generation of a Ni-B surface, whereas in the bath lacking in nickel ions, the pure Ni substrate was initially less active to electrocatalytic oxidation of DMAB, and remained so throughout the measurement period.

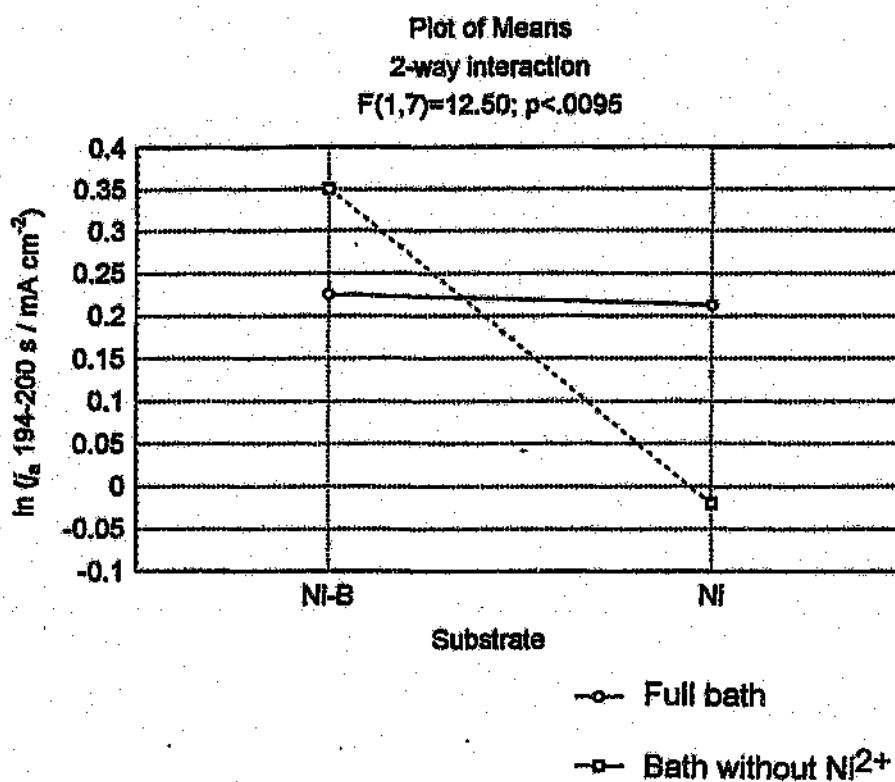


Figure 7.47 Two-way interaction effect between the bath composition and the nature of the substrate on j_a (194-200 s) in Bath 2 and in this bath containing no Ni^{2+} .

Table 7.7 ANOVA summary of all effects on the cathodic current density in Bath 2 and this bath containing no DMAB.

Effects: 1=Potential; 2=Bath composition; 3=Substrate * indicates significance at 95% level						
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1*	2	4.4731	5	0.02793	160.173	0.000029
2*	1	0.6593	5	0.02793	23.6076	0.004638
3	1	0.0437	5	0.02793	1.5631	0.266538
12	2	0.0185	5	0.02793	0.6621	0.555772
13	2	0.0145	5	0.02793	0.5173	0.624897
23	1	0.0511	5	0.02793	1.8296	0.234120
123	2	0.00734	5	0.02793	0.2628	0.778871

Table 7.8 ANOVA summary of all effects on the anodic current density (9-12 seconds) in Bath 2 and in this bath containing no Ni^{2+} .

Effects: 1=Potential; 2=Bath composition; 3=Substrate * indicates significance at 95% level						
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1*	2	10.4075	7	0.00386	2696.94	0.000000
2*	1	0.63427	7	0.00386	164.360	0.000004
3*	1	0.49972	7	0.00386	129.495	0.000009
12*	2	0.04233	7	0.00386	10.969	0.006962
13*	2	0.05064	7	0.00386	13.124	0.004282
23	1	0.00051	7	0.00386	0.132	0.727397
123*	2	0.02711	7	0.00386	7.024	0.021211

Table 7.9 ANOVA summary of all effects on the natural logarithm of the anodic current density (194-200 seconds) in Bath 2, and in this bath containing no Ni^{2+} .

Effects: 1=Potential; 2=Bath composition; 3=Substrate * indicates significance at 95% level						
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1*	2	4.67919	7	0.01043	448.553	0.000000
2	1	0.01185	7	0.01043	1.1360	0.321884
3*	1	0.14914	7	0.01043	14.2971	0.006882
12	2	0.00432	7	0.01043	0.4145	0.675871
13	2	0.00981	7	0.01043	0.9405	0.434720
23*	1	0.13038	7	0.01043	12.4979	0.009531
123	2	0.01223	7	0.01043	1.1723	0.363805

Thus, it has been shown that the Ni-B alloy enhances the anodic partial process (i.e., acts as an electrocatalyst), and may enhance the rate of nickel deposition. The results presented in this Section are indicative of a situation where the continued regeneration of Ni-B alloy surface is partly responsible for the enhancement of the rates, and it is not simply the contemporaneous reduction and oxidation partial processes which causes the observed enhancement. The deposition of Ni does, however, occur by a different mechanism when DMAB is being oxidised, as opposed to electrodeposition in the absence of this reducing agent (c.f. Figure 7.9 and associated discussion).

7.5.2.2 XPS characterisation of deposits

XPS investigation of the Ni-B deposit from Bath 2 yielded less information about the Ni-B alloy than was obtained in respect of the Ni-P alloy. The detection limits of the XPS instrument are such that at atom percentages less than 1-2%, depending on conditions, peaks due to the relevant species may not be noted. Boron was detected only prior to argon ion sputtering of the surface. A reference peak for NiB has a binding energy of 853.2 eV, which is very close to that of the Ni (2p $3/2$) (852.3 - 852.7 eV) and a peak for NiO (853.8 - 854.2 eV) (Wagner 1990 pp. 607-608, Diegle et al. 1988). This proximity of peaks likely to be seen in the deposit may have obscured the NiB peak.

7.5.2.3 Catalysis by the Ni-B alloy

Interaction of the partial processes, namely, oxidation of DMAB and reduction of nickel(II), has been noted (Figure 7.8, Figure 7.9 and Section 7.5.2.1). The enhanced catalytic activity of Ni-B over Ni has been shown to contribute to the rate of the oxidation partial process (Section 7.5.2.1).

Lelental (1975) observed that a Ni-Cu alloy enhanced the deposition rate in an electroless bath containing nickel(II), copper(II) and DMAB. This effect was attributed to the promotion of weak chemisorption of hydrogen on copper, or, more generally, on the Ni-Cu alloy. Lelental, who could not detect boron by Auger electron spectroscopy, found that the boron content of the alloy could not exceed 1%. Lelental thus did not attribute catalytic enhancement to the presence of

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boron, but to the presence of copper in the deposit. The results of this thesis, however, clearly show that the presence of boron does contribute to the catalytic activity of the alloy. Boron acts as a promoter of the catalytic process. The interaction of the partial processes is separate to this effect, resulting in the enhanced deposition rate of nickel in the presence of DMAB. This is a consequence of the mechanism leading to electroless nickel deposition. Further mechanistic studies are required to identify the cause of the mutual enhancement of the partial processes.

7.6 CONCLUDING REMARKS

The activation energies of the electroless reaction in the two low temperature baths (Baths 1 and 2) were determined using the quartz microbalance electrode. These results differed from literature values. There was no clear reason for these differences, but these results were not felt to detract from the validity of other electrochemical data obtained using the QME.

Current density curves of the partial processes in the low temperature electroless baths were obtained using a quartz microbalance electrode. The result thus obtained for a bath employing H_2PO_2^- as reducing agent was compared to that obtained with the aid of a rotating disc electrode. These results were seen to be similar, eliminating the possibility of mass transport control in the mechanism of this bath. Semi-logarithmic plots of the cathodic current densities ($\ln |j|$ vs. E) of the low temperature baths in the presence and absence of reducing agents were significantly different. This is indicative of mechanistic differences in the deposition of nickel under the various conditions. No bulk

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interaction of the metal complexes and the reducing agent was noted by visible range spectrophotometry. Little interaction, if any, between phosphite (an oxidation product of H_2PO_2^-) and the aqueous Ni^{2+} complexes was observed in the absorption spectrum.

The electroless Ni-P alloy was seen to be a two-phase deposit, by virtue of two peaks on an anodic stripping voltammogram. Partial stripping of the alloy yielded a phosphorus-rich residue. This residue catalysed electroless nickel deposition from the H_2PO_2^- reduced bath at a rate greater than that observed under steady state conditions on the virgin, or as-deposited Ni-P alloy. XPS results indicated that oxidised P exists on the surface to a greater extent after partial stripping than on the virgin electroless deposit. It is likely that this phosphorus is present as H_2PO_2^- .

The initially enhanced deposition rate on the partially stripped surface may be attributed to higher electrocatalytic activity of the partially stripped P-rich residue, or to the presence of adsorbed H_2PO_2^- , a product of oxidation of the alloy. The presence of this adsorbed species may temporarily enhance the rate of deposition until the surface regains a steady state condition, if adsorption of the reducing agent is rate determining. The adsorption process will then be unnecessary and OH^- attack (Equation 7.6) can take place, followed by the remaining steps of electrocatalytic oxidation, and consequential reduction of Ni^{2+} . This effect is, however, considered to be less likely than a catalytic effect brought about by the altered surface composition and structure. Rearrangement of H_2PO_2^- to a more reactive form, or OH^- attack may be enhanced on the more active surface.

The Ni-B deposit was investigated in a similar manner as the Ni-P alloy. Since only one stripping peak was seen in an anodic sweep on this substrate, it was not possible to examine catalytic activity of any phase other than that of the bulk deposit.

The Ni-B alloy was seen to have a promoting effect on the rate of DMAB oxidation, over pure nickel. An increased rate of nickel deposition was observed in the presence of DMAB. The partial current density of the oxidation of DMAB was positively affected by the presence of trace amounts of B in the deposit. The well known catalytic phenomena of synergism and spill-over appear to be applicable to the Ni-B deposit, in that the boron can modify the surface conditions sufficiently to enhance catalytic activity. Since the boron is only present in small amounts, catalytically active centres on the surface can initiate the oxidation process, with reduction occurring some distance away by virtue of spill-over effects. XPS studies on the Ni-B alloy did not give any evidence of a significant concentration of an NiB species, this being below the detection limits of the instrument. It is acknowledged that no accurate determination of the boron content of the alloy has been presented. Analysis by inductively coupled plasma - optical emission spectroscopy is recommended.

CHAPTER 8

AUTOCATALYTIC COPPER BATHS