EVALUATION OF THE COVERAGE BY KINETICALLY INVOLVED 11 INTERMEDIATES DURING THE HYDROGEN EVOLUTION REACTION

by

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To Mom and Kimberley
PREFACE

For clarity it will be very useful to describe here how the present manuscript is structured. Six chapters and an appendix are used to present the background information, and to discuss the new results and related topics of interest in a way that is as clear and logical as possible.

Chapter 1 is an introductory review on previous works and discusses not only the role of adsorbed intermediates in electrocatalysis, e.g. H in the H$_2$ evolution reaction, but also some of the problems involved in the evaluation of their coverage. Chapter 2 describes the experimental techniques and electrochemical systems used in the present exploratory work. In Chapter 3 are discussed the principles behind a.c. impedance and the potential decay treatments. Chapter 4 is concerned with all the experimental results except those obtained by a.c. impedance which are discussed in Chapter 5. All results are then discussed comparatively in Chapter 6 in which final conclusions are drawn. The Appendix presents some of the programs used to derive useful quantities such as the interfacial capacitance at the metal-solution interface.

Some of the work presented in this thesis is under in the course of preparation for publication or is in submission for publication. The titles of the papers are as follows:

1. Behaviour of Overpotential-deposited Intermediates in Faradaic Reactions: Results for initial potential decay rates and overall potential relaxation.


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ABSTRACT

Electrocatalytic studies on the hydrogen evolution reaction require information on the potential dependence of coverage by the kinetically involved intermediate, chemisorbed H. Hitherto little information on this matter has been available, especially for the reaction at some of the alloys studied in this thesis.

The present research project deals mainly with the study and mechanistic behavior of the cathodic hydrogen evolution reaction (h.e.r.) at bulk phase alloys of Ni and W, and of Ni and Mo having various compositions, at electroplated alloys of Ni and V, Ni and W and, at pure Ni metal.

Also, introduced here, for the first time is a newly developed method for characterizing the pseudo-capacitance, $C_\phi$, associated with potential-dependence of H coverage. This is a new method of analysis, based on curve fitting of digitally recorded potential relaxation (potential decay) transients following interruption of cathodic polarizing currents, and enables the initial rate of potential decay at time zero, to be reliably determined. This method was applied for the examination of the kinetics of H$_2$ evolution and for the evaluation of the H adsorption behaviour at each of the electrode materials mentioned above.

On these same electrode materials, the Tafel slope behavior for the h.e.r. under controlled conditions, as well as the a.c. impedance, has also been determined in order to evaluate the adsorption behaviour of the "overpotential-deposited" (o.p.d.) H generated as an intermediate in the h.e.r. at appreciable currents.

The results of the work indicate appreciable H coverage by chemisorbed H that arise during the course of the reaction at substantial current densities, with $C_\phi$ declining from high values for the H$_2$/H$_2$O, OH$^-$ reversible potential to much lower values at appreciable overpotentials for all the systems investigated in this programme of research.
With the experimental evaluation of the adsorption behaviour and potential dependence of coverage by the electroactive adsorbed intermediates involved, a fuller understanding of the kinetics of multistep electrode processes can be achieved.

Also an attempt to rationalize the frequency dispersion in the impedance spectra is presented in the light of the experimentally observed dependence of this phenomenon on the size of the anions in solution, presumably reflecting their different adsorbabilities at the electrode interfaces studied.
CHAPTER 1

INTRODUCTION

1.1 The relation of electrocatalysis to heterogeneous catalysis

First the general point should be noted that electrode reactions are always heterogeneously catalyzed since charge-transfer normally requires a metal, metal oxide or semiconductor interface.

It is therefore necessary to define here the term "electrocatalysis," which is the phenomenon manifested when it is found that the electrochemical rate constant, for an electrode process, standardized with respect to some reference potential, depends on the chemical nature of the electrode metal, the physical state of the electrode surface, the crystal orientation of single-crystal surfaces, or on e.g. alloying effects.

It is also found that such factors can greatly affect the reaction mechanism, e.g. in electrochemical reductions of ketones or alkyl halides, or electrochemical oxidation of aliphatic acids (the Kolbe and Hofer-Moest reactions).

Catalysts are frequently used in chemical reactions to increase the rate of formation of products. Catalysts play the major role of reducing the energy barrier encountered in the conversion of reactants to products, which can be translated to diminished activation polarization and lower electrical power demands in the case of electrode processes.

Electrocatalysts, i.e. catalysts for electrochemical reactions, are defined here through a comparison with heterogeneous catalysts. Heterogeneous catalysts and electrocatalysts behave similarly in various aspects: both have the main purpose of altering the rates of the reaction concerned, without themselves being either consumed or generated in the process. Heterogeneous catalysts optimize reaction rates in chemical reactions, such as the
hydrogenation of organic compounds, by promoting the union of the reactants through the adsorption of intermediates which often arise from the reactants by dissociative adsorption processes. Similarly, an electrocatalyst involves the adsorption of chemisorbed species and/or, in some cases, the adsorption of the reactant(s) which accounts for the dependence of the electrochemical reaction’s rate constant on the chemical nature of the electrode material and sometimes on its physical state. The most significant difference between chemical catalysis and electrocatalysis is based on the fact that the electrocatalytic reaction’s rate is dependent on potential ($\Delta \phi$), while a chemical catalytic rate cannot be so affected.

The Arrhenius equation \(^1\) represents the catalytic rate of an heterogeneous reaction according to

$$v = c \frac{kT}{h} \exp\left[-\frac{\Delta G^0}{RT}\right]$$ (1a)

or

$$v = c(1 - \theta) \frac{kT}{h} \exp\left[-\frac{\Delta G^0}{RT}\right]$$ (1b)

or more generally

$$v = c f(\theta) \frac{kT}{h} \exp\left[-\frac{\Delta G^0}{RT}\right]$$ (1c)

whereas the rate of an electrocatalytic process \(^2\) is given by

$$v = \frac{i}{nF} = \left(c f(\theta) \frac{kT}{h} \exp\left[-\frac{\Delta G^0}{RT}\right]\right) \exp\left[-\frac{\beta \Delta \phi F}{RT}\right]$$ (2)

where $\beta$ is a barrier symmetry coefficient for the charge-transfer process, analogous to Brønsted’s coefficient, $\alpha$. Both of these rates, $v$, contain in their expression a reactant concentration term, $c$, a factor $f(\theta)$, representing some function of the coverage of the electrode surface by adsorbed intermediates, Boltzmann’s constant, $k$, Planck’s constant, $h$, the gas constant, $R$, and the standard Gibbs chemical energy of activation, $\Delta G^0$, at zero single metal/solution potential difference, $\Delta \phi$. Both expressions involve a dependence on temperature (T) but only the electrochemical reaction rate expression involves a potential-dependent term, in which $F$ represents Faraday’s constant and $\Delta \phi$ represents the
absolute metal-solution potential difference at the electrode/solution interface.

1.2 **Electrocatalysis and adsorbed intermediates**

Electrocatalytic processes always involve at least one adsorbed intermediate, or sometimes an adsorbed reactant, in their sequence of reaction steps. Sometimes these adsorbed intermediates are initially formed in a dissociative, or associative, chemisorption step as with H₂, CH₃OH, C₂H₄ oxidation, or O₂ reduction, and are subsequently involved in electrochemical charge-transfer steps. In other types of mechanisms, these chemisorbed intermediates are first produced in a charge-transfer step and are subsequently involved in the formation of a stable molecule (e.g. H₂, O₂ or Cl₂) through a desorption step involving a recombinative process, e.g. 2H_{ads} → H₂. No matter what is the order of involvement by chemisorbed species, the electrocatalytic activity will necessarily depend on the nature of the electrode material. In the case of single-step redox reactions such as

\[
\text{Fe}^{+++} + e_{M} \rightarrow \text{Fe}^{++}
\]  

"electrocatalysis" arises only if one or other, or both of the redox reactants are specifically adsorbed at the metal, so that a significant dependence of the rate on the nature of the electrode substrate is observed. In this type of reaction, the electrode normally only acts as an electron source or sink, with no adsorption of adsorbed intermediates or of the reactant and product ions. Adsorbed intermediates are usually involved in multistep electrode processes except in the cases where a stable intermediate is formed which may dissolve into the solution as with some electro-organic reactions.

The extent and Gibbs energy of adsorption by reaction intermediates is often a useful indication of the electrocatalytic activity of the electrode metal. Hence, the rate expression, where applicable, will contain one or more coverage terms which take into account the adsorption of the kinetically involved intermediates. (This matter will be fully described in a subsequent section).
1.3 **Early theoretical derivations of electrochemical rate equations**

Following the seminal paper of Butler\(^6\) in 1924 on the kinetic basis of Nernst equilibrium potentials, a first attempt at deriving theoretical rate equations for heterogeneous electrochemical processes was made by Gurney\(^3\). In his work, Gurney indicated the essential quantum-mechanical aspects of electron charge-transfer in electrode reactions. Since electrode processes are radiationless, electron tunneling through a potential-energy barrier was shown to occur significantly only if the energy at the Fermi level of the metal was equal to the energy of the lowest unoccupied (or highest occupied) orbital of the reactant, depending on the direction of charge-transfer. At finite temperature, there is a small but significant distribution of electron energy states around the Fermi level from which, or to which, electron transfer can occur. Figs. 1.1a and 1.1b show schematic representations of Gurney’s model for electron transfer from a metal to an ion in vacuum and in solution, respectively.

Conditions for ionization of these reactants in vacuum and solution are given below:

\[
\text{Vacuum: } \Phi \pm e\Delta\phi = I \\
\text{Solution: } \Phi \pm e\Delta\phi + \Delta S = I
\]

where \(I\) is the ionization potential of the reactant in the reduced form, \(\Delta S\) is the change of solvation energy upon electron transfer, \(\Delta\phi\) is the voltage applied to change the Fermi level of the electrons in the metal.

Gurney’s theory gave a correct qualitative account of the potential-dependence of the rates of reaction since it could be simplified to the form of Tafel’s empirical relation\(^4\), i.e. \(\eta = a + b \log i\) where \(\eta\) is the overpotential required to drive the reaction at a net current-density \(i\). However, much better and more refined rate equations were still to be developed in the works of Volmer\(^5\), Butler\(^6\) and others.
Fig. 1.1 Energetics of ion neutralization at an electrode surface after Gurney [3]:
   a) in a vacuum;  b) in solution involving an ion.
1.4 Kinetic aspects of electrode processes

Generally the reaction velocity, \( v \), of an electrochemical process having a rate-controlling discharge step, can be expressed in the following way:

\[
i = nFv = k_i nF(c_R)_s (1 - \theta)
\]

where \( k_i \), the electrochemical rate constant, according to "absolute rate theory"\(^7\), is given by

\[
k_i = \tau (kT/h) \exp[- \Delta G^o /RT]
\]

and \( \tau \) is the transmission coefficient (taken as approximately unity), \( k \) Boltzmann's constant, \( T \) the temperature in Kelvins, \( h \) Planck's constant and \( \Delta G^o \), is an electrochemical standard Gibbs energy of activation; \( nF \) is the number of Coulombs involved (expressed in terms of Faradays) in the overall reaction proceeding at the rate \( v \) in mol s\(^{-1}\) cm\(^{-2}\); \( (c_R)_s \) is the concentration of the reactant molecule or ion at the outer Helmholtz plane and \( \theta \) is the steady-state coverage of any intermediates that are adsorbed on the surface at a given potential as a result of the discharge of the reactant \( R \). The Gibbs energy of activation is potential-dependent according to

\[
\Delta G^o = \Delta G^o + \beta F\Delta \phi
\]

This equation is a relation between the electrochemical standard Gibbs energy of activation, \( \Delta G^o \), and the chemical free energy of activation, \( \Delta G^o \), plus an additional term which is the electrical energy factor assisting the reaction. In eqn (8), \( \Delta \phi \) represents the absolute metal-solution potential difference at the electrode and \( \eta \) is the overpotential required to drive the reaction at a net current-density \( i \) beyond the reversible rate (net rate zero) at the reversible potential, \( \Delta \phi_r \), i.e. \( \eta = \Delta \phi - \Delta \phi_r \); \( \beta \) is a barrier symmetry factor for the charge-transfer process analogous to Brønsted's coefficient \( \alpha \) in "linear free-energy relations", e.g. for proton transfer processes, as referred to already on p. 2.

For a simple discharge process, eqns (6), (7) and (8) can be combined to give a
general expression for the net current-density, \( i \), in the form of the so-called Butler-Volmer equation taking account of both the backward and forward components of the reaction rate (current-density):

\[
i = i_f - i_b
\]

= \( i_0 \left[ \exp(\beta F\eta/RT) - \exp[-(1-\beta) F\eta/RT] \right] \) (9b)

where \( i_f \), \( i_b \) represent the current-densities of the forward and backward reactions, respectively, and \( i_0 \) is the so-called exchange current-density for \( \eta = 0 \) which dynamically characterizes the reversibility of the reaction. In the case where the discharge step is rate-determining, the exchange current-density is given by the following equations:

\[
i_0 = Fk_f c_i (1-\theta) \exp(\beta F\phi_i/RT)
\]

= \( Fk_b c_j \theta \exp[-(1-\beta)F\phi_i/RT] \) (11)

where \( c_i \) and \( c_j \) are the concentrations of the reactants of the forward and backward steps with potential-independent rate constants \((k_f, k_b')\). The fractional coverage by adsorbed intermediates and free site availability are represented by \( \theta \) and \( 1-\theta \) respectively. At high values of overpotential \( \eta \), viz. \( \beta F\eta/RT \gg 1 \), eqn (9) becomes

\[
i = i_0 \exp(\beta F\eta/RT)
\]

or

\[
\eta = (RT/\beta F) \ln i - (RT/\beta F) \ln i_0
\]

This is a form of the well-known Tafel\(^4\) equation commonly represented as:

\[
\eta = a - b \log i
\]

where \( a \) and \( b \) are given by

\[
b = 2.303RT/\beta F
\]

and

\[
a = -(RT/\beta F)\ln i_0
\]

by comparison with eqn. (13).
At low values of overpotential $\eta$, viz. when $\beta F \eta / RT \ll 1$, equation 9b can be written, taking into consideration only the first term of the series expansion of the exponential:

$$i = i_0 \eta F / RT$$

(16)

Ohm's law allows us then to define a Faradaic charge-transfer resistance, $R_F$, as

$$R_F = RT / i_0 F$$

(17)

which is important in the analysis of the impedance behaviour of electrode reactions, to be considered later in this thesis.

The Tafel slope, $b$, and the exchange current-density, $i_0$, are the two fundamental parameters characterizing steady-state electrochemical polarization behaviour of an electrode reaction. Ideally, a combination of high $i_0$ and low $b$ values is the condition required for optimizing cathode or anode performance i.e., to minimize polarization at appreciable current-densities and provide "good electrocatalysis" in the process.

This is not always possible because $i_0$ and $b$ values for a given multistep process are usually mutually dependent quantities, e.g. both are closely related to the adsorption behaviour of the reaction intermediates adsorbed on the electrode surface. The kinetically involved intermediates influence the exchange current-density of the process through their standard Gibbs energy of adsorption, and the Tafel slope through the potential-dependence of their coverage (see below).

1.5 **The hydrogen evolution reaction**

One of the most extensively studied reactions in electrochemistry has been the hydrogen evolution reaction (to be abbreviated henceforth as h.e.r.). Cathodic $H_2$ evolution can take place from acid or alkaline aqueous solutions. The overall reaction in acid solution is

$$2H_3O^+ + 2e \rightarrow H_2 + 2H_2O$$

(18)
and in alkaline solutions, it is

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \]  \hspace{1cm} (19)

The h.e.r. is of great technological as well as fundamental interest because, not only is the electrolytic evolution of hydrogen a standard method for producing the gas in high purity, but it is of close relevance to many other electrode process as a "prototype reaction"\(^8\).

Several reaction pathways are possible for the h.e.r. but on account of the previous work of many electrochemists, e.g. Butler, Frumkin, Bockris, Horiuti, Conway and Parsons, only two reaction paths are regarded now as likely to be involved even though, at the beginning of this century, a variety of reaction steps had been proposed as part of the overall process\(^4,9-11\), including e.g. nucleation of bubbles.

In acidic solution, the reaction involves first the discharge of an hydrated proton at the electrode surface with formation of an adsorbed H atom at some site on the metal electrode surface lattice:

\[
\text{M(e)} + \text{H}_3\text{O}^+ \xrightarrow{k_{f,1}} \frac{k_{b,1}}{k_{b,1}} \text{MH}_{\text{ads}} + \text{H}_2\text{O} \] \hspace{1cm} (20)

The above step is common to all currently considered reaction paths and it represents the process by which H is initially deposited onto an electrode surface.

The adsorption step must be followed by either an electrochemical-desorption step:

\[
\text{MH}_{\text{ads}} + \text{M(e)} + \text{H}_3\text{O}^+ \xrightarrow{k_{f,2}} \frac{k_{b,2}}{k_{b,2}} \text{H}_2 + \text{H}_2\text{O} + 2\text{M} \] \hspace{1cm} (21)

or by an heterogeneous chemical recombination step:

\[
\text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} \xrightarrow{k_{f,3}} \frac{k_{b,3}}{k_{b,3}} \text{H}_2 + 2\text{M} \] \hspace{1cm} (22)

The steps (21) and (22) are alternative desorption paths.

In alkaline solution, the mechanism is similar except that the proton donor is a water molecule rather than \(\text{H}_3\text{O}^+\) and the conjugate base product is \(\text{OH}^-\) instead of \(\text{H}_2\text{O}\):

\[
\text{M(e)} + \text{H}_2\text{O} \xrightarrow{k_{f,1}} \frac{k_{b,1}}{k_{b,1}} \text{MH}_{\text{ads}} + \text{H}_1\text{O} \] \hspace{1cm} (20)
In the present research project, we shall be concerned only with the last series of steps because the experiments were carried out in alkaline solutions. It has been noted in the literature, for alkaline solutions, that the activation energy of the steps (23) or (24) will not generally be the same, respectively, as those for (20) or (21), so that the mechanism in terms of which step is rate determining of the h.e.r. in acidic and alkaline solution at a given metal will not generally be the same.

As can be seen from the two series of equations above, a multistep reaction is involved, for which it is assumed that there is always a "rate-determining step" (r.d.s.) which characterizes the kinetic behavior of the reaction. A rate-determining step in a reaction sequence is the step having the smaller or smallest rate constant or, correspondingly, the highest Gibbs energy barrier. Often the rate-determining step is incorrectly referred to as the "slow step" in the reaction but, in the steady state, all steps are proceeding at the same velocity. Through information obtained by means of the Tafel slope behavior\textsuperscript{8-12}, coupled with results from the new potential-decay methods*, and with a.c. impedance measurements, information on the adsorption behavior of the overpotential-deposited (o.p.d.) H can be obtained and the rate-determining step more easily identified.

*Here we refer to two different treatments of potential relaxation curves which will be fully described in a following section.
1.6 Parameters determining the exchange-current density

The electrochemical hydrogen evolution reaction has been one of the first electrochemical reactions to be studied\textsuperscript{12} in a detailed kinetic way. This reaction has been extensively examined in hope of gaining a better understanding of electrode processes in general. Since most mechanistic studies of electrochemical reactions have been limited to relatively few metals, except for work on the h.e.r., one should not be surprised to find published works predominantly concerned with the correlation between metal properties and the h.e.r. exchange-current\textsuperscript{13-20} densities.

The dependence of the strength of H adsorption on the metal, i.e. the H adsorption energy, on the rate of the h.e.r., as measured by its $i_0$ value, was first demonstrated by Horiuti and Polanyi\textsuperscript{21}, and examined quantitatively by Conway\textsuperscript{22}, Parsons and Bockris\textsuperscript{23}, and by Parsons\textsuperscript{16}. In 1966, Kita\textsuperscript{17} pointed out that the exchange current density for the h.e.r. at various metals in acidic solutions is represented by a periodic function of the atomic number within the three long transition periods. Considering the electronic configuration of the outer shells of the elements in their ground states, he observed that log $i_0$ first increases with increasing numbers of d-electrons up to the d\textsuperscript{8} electronic configuration. After this maximum, a sharp decrease of the catalytic activity is observed, as represented in Fig. 1.2.

In a more recent examination of this matter, Trasatti\textsuperscript{19} demonstrated that when log $i_0$ is plotted against the work function, $\Phi_M$ (using an updated set of critically-selected $\Phi_M$ values), d- and sp-metals exhibit two distinct linear relationships (see Fig. 1.3). However, such correlations should not directly arise since the potential-dependent reaction rate constants cannot depend on $\Phi_M$ due to the fact that the terms in $\Phi_M$ cancel out around the interfaces of the measuring circuit when the potential is referred to the potential of a reference electrode. Conway and Bockris\textsuperscript{24} demonstrated in one of their publications that it
Fig. 1.2 Observed $\log i_o$ on various metals in acidic solutions. The full and dotted lines indicate the periodic variation of $\log i_o$ with the atomic number [17].
Fig. 1.3 Log $i_0$ vs work function ($\Phi$) of electrode metals. Values of $\Phi$ are quoted from ref. 19. Dotted lines represent Trasatti’s relation.
must be the dependence of the energy of adsorption of H at the metal on $\Phi_M$ that gives rise to the work function dependence of $\log i_0$.

Parsons$^{16}$ derived theoretically a general relation between the exchange current density for the h.e.r. and the standard Gibbs energy ($\Delta G_H^\circ$) for the chemisorption of H at the metal for different assumed forms of the equilibrium adsorption isotherm for the overall reaction. His results, shown in Figure 1.4, reveal a maximum when $\Delta G_H^\circ$ is zero in the plot of $\log i_0$ versus $\Delta G_H^\circ$. Essentially similar conclusions were reached independently by Gerisher$^{25}$. These Baladin-type volcano relationships seem to arise no matter what is the mechanism because $\ln i_o$ is dependent on the coverage product, $\theta_H^{\alpha}(1-\theta_H)^{1-\alpha}$, that is determined by $\Delta G_H^\circ$ (a maximum is reached when $\theta = 0.5$, taking $\alpha (=\beta) = 0.5$).

A plot of $\log i_{0,H}$ against the heat of adsorption of hydrogen on metals, as derived by Krishtalik$^{26}$, from experimental data on the h.e.r., revealed another volcano-like dependence (Fig. 1.5). Clear evidence of electrocatalysis is revealed here since the electrochemistry is affected by the nature of the electrode metals. It is also important to point out that maximum exchange current-densities are observed at metals with intermediate heats of adsorption of hydrogen, as predicted by Sabatier's catalysis principle$^{27}$. Another theoretical explanation for an optimal ($d^8$) electronic configuration has been deduced in a joint work of Conway and Bockris$^{13}$. In their paper, it was demonstrated that a decrease in the heat of adsorption of hydrogen, $\Delta H_{\text{ads}}$, is related to an increase in the percentage d-character* (see Fig. 1.6). This implies that metals which have a lower percentage d-character, i.e. more unpaired electrons or 'holes' in the d-band, interact strongly with electron-donating adatoms, and hence adsorb hydrogen strongly.

*The "percentage d-character" is a concept introduced by Pauling$^{28}$ to represent the extent of participation of d-electrons in the dsp hybrid bonding in d-metals or alloys.
Fig. 1.4 Parsons h.e.r. Volcano curve [16], where the logarithm of the exchange current densities at various metals is plotted against the standard Gibbs energies of adsorption for H ($\beta = 0.5$).
Exchange current densities for electrolytic hydrogen evolution vs bonding adsorption strength of intermediate metal-hydrogen (M-H) bond formed during the electrode reaction itself (Trasatti [19] with E(M-H) from Krishtalik [26]).
Plot of the heat of adsorption of hydrogen on the metal ($\Delta H_{\text{ads}, H}$) vs percentage d-band character for several metals (Conway and Bockris, [13]).
1.7 Electrochemical reduction of hydroxides (HER) in light of the Brewer-Engel theory

The need to replace precious metals as catalysts by cheaper and more available metals and alloys having improved electrode polarization behaviour has led to the investigation of the electrocatalytic features of composite transition metal catalysts for the hydrogen evolution reaction. Westrip pointed out that alloyed zinc-copper cathodes are more electroactive for the HER than electrodes consisting of either individual metal. A similar behaviour for zinc-cobalt alloys was also observed by Znamenskii et al. Mo-Co alloyed composites revealed enhanced polarization characteristics, better than those of any of the platinum group of metals. These and other experimental observations have been examined in terms of the Brewer-Engel valence-bond model for bonding in metals and intermetallic phases. The Brewer intermetallic bonding model is based on the Lewis acid-base reaction concept. If metals on the left half of the transition series, having empty or half-filled d-orbitals, are alloyed with metals of the right half of the transition series, having internally paired d-electrons not available for bonding in the pure metal, an "internal charge transfer" will tend to occur. Brewer-Engel theory is concerned with the prediction of the particular mix of d and p electrons, which should be such that a configuration of lowest Gibbs energy is achieved for the metal or alloy. Therefore, the Brewer-Engel model predicts the crystal structure of the metallic system under study, since the organization of the crystal lattice is related to the metal electronic configuration, e.g. the body-centred cubic (bcc) structure is obtained for alkali metals with an electronic configuration approximating...
the \( d^{n-1}s \) (\( n \) is the total number of valence ((\( d + s + p \))-electrons), while a \( d^{n-2}sp \) valence shell state corresponds to the hexagonal close-packed (hcp) unit-cell structure observed in aluminium.

The Brewer-Engel theory also predicts most of the structures and composition ranges of the various alloying systems, in accordance with the Hume-Rothery prediction where the particular structure is being determined by the ratio of the p- and s- electrons, but it also predicts cohesive bonding forces at transition metal surfaces in which d electrons play a predominant role. With increasing nuclear charge from the first to the third transition series, the d-orbitals become more exposed relative to the s and p orbitals and thence stronger bonding due to better overlap and sharing of d-orbitals for metals of the higher transition series. The Brewer-Engel theory suggests that the following list of alloys MoCo\(_3\), MoNi\(_3\), UNi\(_3\), HfPd\(_3\), ZrPt\(_3\) and LaNi\(_5\), should exhibit an enhanced electrocatalytic activity for the h.e.r which could surpass the individual catalytic activities of the metals by themselves or in combination (the synergism condition). The total percentage of d-orbital participation in dsp-hybrid-bond orbitals must be low in order to obtain strong cohesive bonding energy (here reflected in terms of H adsorption)\(^{41-47}\). However, in terms of the theory of the volcano relation (Fig. 1.4 and ref. 16), too strong an H adsorption energy is undesirable since then the \( \theta_H^\alpha (1-\theta_H)^{1-\alpha} \) product will be small, leading to low \( i_0 \) values. It is interesting to point out that Jaksic tried to relate the polarization properties for the h.e.r. across the phase diagrams for some of the above mentioned alloy systems, as depicted in Fig. 1.7. The relative electrocatalytic activities used in his relations, are taken as relative current density changes at constant overvoltage, for the h.e.r. at the various composition of the investigated electrodeposited binary alloys.
Fig. 1.7 Relative electrocatalytic activities of a) Ni-W and b) Ni-Mo coatings upon Ni substrate for the h.e.r. along the phase diagrams taken as relative current density changes at constant over-potential (Jaksic, [48]).
Fig. 1.7c Relative electrocatalytic activity of a Fe-Mo coating upon a Ni substrate for the h.e.r. along the phase diagrams, taken as relative current density changes at constant overpotential (Jaksic, [48]).
1.8 The relationship between the Tafel slope, b, and the isotherm for adsorption of an intermediate such as H

Besides affecting the exchange current density, H adsorption is a determining factor in the value of the Tafel slope, b, through an adsorption isotherm factor. This is because (cf. eqns. 21 to 24) the rate equation for the rate-determining step normally involves a function of coverage, f(θ), of the adsorbed intermediate. The reciprocal of the Tafel slope, b⁻¹, can be expressed as follows:

\[
\frac{1}{b} = \frac{d \log i}{d \eta} \text{ Reciprocal of the Tafel slope} = \frac{d \log f(\theta_H)}{d \eta} \text{ Adsorption isotherm factor} + \frac{2.3036F}{RT} \text{ charge-transfer factor}
\] (25)

This equation reveals that the dependence of log[rate] on electrode potential is inversely related to both the adsorption isotherm factor and the charge-transfer factor which includes β. For electrode processes in which there is no adsorption of intermediates and where the electrode simply acts as source or sink of electrons, as e.g. ionic redox reactions, the reciprocal of the Tafel slope is only dependent on the charge-transfer factor. This type of electrochemical process has only one reaction step and no intermediate, as in the \( V_{aq.}^{3+/2+} \) redox reaction.

For electrode processes in which there is adsorption of intermediates (e.g. chemisorbed H in the h.e.r.), the reciprocal of the Tafel slope is dependent on both the charge-transfer factor and the adsorption factor as in eqn. (25). The function of the H coverage that is used in eqn. 25 depends on which step controls the overall rate (see reaction equations 21, 22, 23 and 24). If the rate-determining step is discharge, electrochemical-desorption or heterogeneous chemical-recombination, the function, f(θ_H), of the H coverage for the adsorption isotherm factor will explicitly contain the term \( 1-\theta, \theta \) or \( \theta^2 \), respectively. It is also important to indicate here that eqn. (25) offers also the
possibility of a dual Tafel slope polarization behaviour for the same rate-determining step, i.e. if the adsorption isotherm factor becomes appreciable and constant in one particular potential range, or if it tends to zero in another, then two Tafel slopes can be observed for the same rate-determining step depending on whether \( d \log f(\theta_H)/d\eta \) is \(< 1 \) or \( \rightarrow 1 \).

For reaction mechanism studies, the importance of the Tafel slope and its dependence on the adsorption of intermediates has been emphasised in various works of Bockris,\textsuperscript{49-54,61-62} Parsons,\textsuperscript{54-57} Despic,\textsuperscript{58-59} and Conway.\textsuperscript{60-64}

When the proton-discharge step is rate-determining and \( \theta_H < 1 \), the reciprocal of the Tafel slope is determined mainly by the charge-transfer factor in eqn (25). This situation is found to arise at mercury and also gold for the hydrogen evolution reaction\textsuperscript{54,65-66} since an experimental Tafel slope of 0.118 V is obtained, as expected theoretically, taking \( \beta = 0.5 \) at 298 K. However, when either of the desorption steps control the overall rate, e.g. (24) or (22) in alkaline and (21) or (22) in acidic solutions, \( \theta_H \) can be appreciable and potential dependent. It is seen that a significant value of the adsorption isotherm factor must lead to reduced values of the Tafel slope; this is of great importance for electrocatalysis and is exemplified experimentally (0.030 V) at Pt for the h.e.r.\textsuperscript{51,67-70} Hence, proper elucidation of the rate-determining step and characterization of the electrocatalysis requires reliable experimental evaluation of the adsorption behaviour of the o.p.d. H in relation to Tafel slopes.

1.9 Treatment for consecutive and alternative processes

Reaction mechanisms involving adsorbed intermediates always involve at least two reaction steps. In such multistep processes, it is not surprising to observe more than one Tafel slope, since a step which is rate-controlling at one potential may not be the kinetically limiting step at another potential.\textsuperscript{57,71} In consecutive reactions, it is always the step with the
smallest rate constant that is rate-determining. For consecutive rate-determining reaction steps, a lower Tafel slope at low currents followed by a higher b value at larger currents will be observed. An opposite sequence of the Tafel slope magnitudes will be observed for alternative rate-determining steps as depicted in Figure 1.8b. This relation arises since it is the path which proceeds with the greatest velocity that characterizes the kinetics in alternative rate-determining pathways.

1.10 Adsorption isotherms

The potential dependence of the coverage by the chemisorbed H intermediate is normally represented by an electrochemical adsorption isotherm for the so-called "electrosorption process". The first adsorption isotherm considered here is that corresponding to Langmuir's relation^{72-74}. It represents the adsorption behaviour of chemisorbed intermediates which randomly occupy sites on the lattice without energetic preference. The isotherm is only concerned with species adsorbing on a homogeneous surface where the lateral-interactions are also negligible. It is represented by the following equation:

\[
\frac{\theta}{(1-\theta)} = K_c \exp(VF/RT)
\]

where K is the adsorption equilibrium constant, and \(c\) is a concentration of adsorbate in solution or in the gas phase.

The Frumkin adsorption isotherm is also frequently used in the field of electrochemistry. Here, the pairwise lateral-interactions between the adsorbing species are taken into account in the adsorption equilibrium constant as shown below:
Current-potential relation for consecutive and alternative electrode processes with exchange currents $i_{0,1}$ and $i_{0,II}$ and Tafel slopes $b_1$ and $b_2$. In (a), reaction I is slower than II, but its rate is more potential-dependent than that of II. II becomes rate determining at high potentials even though $i_{0,II} > i_{0,1}$. In (b), if I and II are alternative, I passes more current than II even though $i_{0,1} < i_{0,II}$. (After Parsons [57]; Conway [71]).
\[ K' = K \exp \left( -\frac{2a\theta}{RT} \right) \]  
\[ = K \exp (-g\theta) \]  
(27)  
(28)

where the two pairwise repulsions, with an interaction parameter \( a \), affect exponentially the adsorption equilibrium constant \( K' \). This equation indicates that the adsorption equilibrium constant \( K' \) will decrease with increasing coverage for the positive \( a \) or \( g \) values. This latter observation is related to the fact that the standard Gibbs energy of adsorption varies linearly with coverage:

\[ \Delta G_\theta^0 = \Delta G_\theta^{0=0} + g\theta/RT \]  
(29)

The Frumkin isotherm is therefore importantly different from the Langmuir isotherm since it contains the \( g \) or \( a \) parameter characterizing lateral interactions in 2-dimensions in the ad-layer\(^{72}\) as shown below:

Frumkin: \[ \frac{\theta}{1-\theta} = Kc \exp(-g\theta) \exp[\eta F/RT] \]  
(30)

The Temkin isotherm\(^{70}\) is another representation of adsorption behaviour that takes into account the heterogeneity of surface sites with regard to decreasing energy of adsorption with increasing coverage; a distribution function for the number of sites having various energies of adsorption is introduced. However, the Temkin differs from the Frumkin isotherm in the development of its potential-dependent coverage expression.

For intermediate values of coverage (0.2 < \( \theta < 0.8 \)), it is possible to assume as an approximation that \( \theta = 1-\theta \). So eqn. (30) can be rearranged to:

\[ K \exp (-g\theta) c_{H^+} \exp(\eta F/RT) = 1 \]  
(31)

or in a logarithmic form

\[ \ln K - g\theta + \eta F/RT + \ln c_{H^+} = 0 \]  
(32)

with \( c_{H^+} \) being the concentration of reacting \( H^+ \) ion at the outer-Helmholtz plane.

The important difference of this equation from the Langmuir one (eqn. 26) is that \( \theta \) is linearly related to \( \eta \) while for the Langmuir case \( \theta/1-\theta \) (or limitingly \( \theta \) when \( \theta \ll 1 \)) is
exponentially related to $\eta$.

A charge $Q$ is required to electrochemically adsorb a number of H atoms up to a coverage $\theta_H$ which depends on the applied overpotential $\eta$; hence the adsorbed species give rise to an adsorption pseudo-capacitance, $C_\phi$, which can be defined as

$$C_\phi = \frac{dQ}{d\eta} = \frac{q_1 d\theta}{d\eta}$$  \hspace{1cm} (33)

where $q_1$ is the charge required for development of a full monolayer of the chemisorbed intermediate.

If the coverage potential vs $\eta$ relationship for chemisorbed H follows a Langmuir isotherm, $C_\phi$ can be easily derived, as in equation (34):

$$C_\phi = \frac{q_1 F}{RT} \left[ \frac{K_1(c_{H^+}) \exp(F\eta/RT)}{[1 + K_1(c_{H^+}) \exp(F\eta/RT)]^2} \right]$$  \hspace{1cm} (34)

By similar operations, a different relation can be derived for Temkin adsorption where, since $\theta$ is linearly related to $\eta$, a potential-independent pseudocapacity arises, determined by the letter $g$ in eqn. (32).

When the Frumkin isotherm (Eqn. 30) applies, $\theta_H$ cannot be written as an explicit function of $\eta$ and so $C_\phi$ can be expressed only as a function of $\theta_H$:

$$C_\phi = q_1 \frac{F}{RT} \left[ \frac{\theta_H(1 - \theta_H)}{1 + g \theta_H(1 - \theta)} \right]$$  \hspace{1cm} (35)

which can, of course, be numerically evaluated as a function of $\eta$ by means of a computer.$^{73}$

1.11 The electrode capacitance

It is well known that the metal solution interphase behaves electrically as a condenser, involving very high fields ($10^7$-$10^8$ V cm$^{-1}$) between the separated charges on the metal and, as ions, in the solution.

The charge separation due to ion charges on the solution side of an electrode interface together with electron charges or holes on the electrode side, leads to what is called the
Fig. 1.9 Schematic diagram of the double-layer interphasical region at an electrode across which the microscopic processes of proton and electron transfer occur in cathodic $\text{H}_2$ evolution with the assistance of the potential drop over the inner, compact layer region of the ionic charge and solvent ($\text{H}_2\text{O}$) dipole distribution. Positive, $\oplus$, represents $\text{H}_3\text{O}^+$. 
"double-layer" capacitance, $C_{dl}$. Helmholtz$^{77}$ provided a first simple model where charges on the surface and those in solution are simulated by a plane charge distribution on a paralleled-plate condenser. Later Gouy$^{78}$, Chapman$^{79}$, Stern$^{80}$, Grahame$^{81-84}$ and Mott and Watts-Tobin$^{85}$ developed more detailed models of the double layer. For example, they considered a sheet of solvated ions, the first layer of water molecules on the electrode surface, the diffuse ionic-atmosphere layer and the contact adsorption of negative ions and neutral molecules, as depicted in Fig. 1.9.

The magnitude of the double layer capacitance, $C_{dl}$, is measurable by modulation or transient techniques since the charge on the capacitance is related to the applied potential across the double-layer. Double-layer charging is a non-Faradaic process, while electron-charge transfer through the double-layer, i.e. when $C_{dl}$ behaves as a leaky condenser, is a Faradaic process. Normally the magnitude of $C_{dl}$ is about $20 \sim 40 \mu F \ cm^{-2}$ and can noticeably vary with applied potential.

The pseudocapacitance, $C_{\Phi}$, arising from the deposition of adsorbed intermediates on electrodes, is, wherever applicable, unavoidably measured simultaneously with the $C_{dl}$ by electrochemical techniques. The pseudocapacitance has been found experimentally to be potential-dependent, as represented in eqn (34), and of much larger magnitude than $C_{dl}$ except as $\theta$ or $1-\theta \rightarrow 1$. This is a useful feature of the $C_{\Phi}$ behaviour.

The present research project introduces, amongst other things, a new treatment for analysis of potential-relaxation curves in order to measure the high-frequency component of the electrode's capacitance consisting primarily of the $C_{dl}$ contribution, under some conditions with a pseudocapacitance contribution, depending on potential and electrochemical system, as will be described later.

The electrode's capacitance, as also measured by a.c. impedance and by a potential decay technique developed in this laboratory, enables the coverage by the intermediates
involved in the kinetics of the h.e.r. at different metals, to be determined as a function of
overpotential, $\eta$.

1.12 Distinction between u.p.d. and o.p.d. adsorbed species

At potentials more negative than the hydrogen reversible potential, adsorbed H
intermediates are involved kinetically in the electrolytic $H_2$ evolution reaction. Species
adsorbing at these potentials are referred to as the "overpotential deposited" H (o.p.d.). The
coverage, $\theta_H$, of the o.p.d. H can be evaluated as a function of overpotential, by integration of
the $C_\phi$ vs $\eta$ profile.

In other words, equation (33) is integrated as

$$ q_1 \int_{\theta_H,\eta=0}^{\theta_H,\eta=\eta} d\theta_H = \int_{0}^{\eta} C_\phi d\eta $$

(36)
giving

$$ \theta_H = \frac{1}{q_1} \int_{0}^{\eta} C_\phi d\eta + \theta_{H,\eta=0} $$

(37)

where $q_1$ is the charge required to establish full coverage of the adsorbed intermediate. The
o.p.d. H species are deposited in excess of any coverage by strongly chemisorbed species
that may already be present at the reversible potential, $\theta_{H,\eta}=0$. So-called "underpotential
deposition" (u.p.d.) of H adatoms occurs by direct Faradaic reaction from solution, at more
anodic potentials than the h.e.r. $E_{H_2/H^+}$ reversible potential. The coverage of these strongly
bonded u.p.d. adatoms can be measured experimentally at noble metals by means of charging
curve, a.c. impedance, or cyclic-voltammetry methods. Several theoretical works on u.p.d. H have indicated the probability that the
underpotential-deposited adatoms are not necessarily the species that participate as
intermediates in the kinetics of h.e.r. since a full monolayer of chemisorbed H is already found to be present on platinum at the reversible potential. Since there is no interference by large currents of a continuous Faradaic process in the case of u.p.d., i.e. positive to the reversible potential in the case of H, not only the small currents associated with the formation of u.p.d. H can be easily be detected and quantitatively measured, but also various peaks due to multiple-state adsorption at electrodes can be resolved (see Fig. 1.10) with excellent sensitivity.

No u.p.d. H determination on the investigated base metal alloys has been attempted in the present research project, since onset of surface-oxidation already occurs at these metals either near to, or already at, the H₂ reversible potential in alkaline solution.

1.13 Problems in the evaluation of o.p.d. H coverage

The coverage by o.p.d. H species can only be evaluated with considerable difficulty since large currents of the continuous Faradaic process interfere with the small current densities associated with deposition or desorption of monolayer arrays (see Fig. 1.10). Until recently, virtually no satisfactory methods existed for reliable quantitative evaluation of o.p.d. H. Hence, apart from new work done in this laboratory in the last few years, and a significant a.c. impedance paper of Gerischer and Mehl in 1955, very little experimental information has been available on how θ_H varies with potential during the continuous Faradaic production of H₂ in the h.e.r., or of corresponding intermediates in other reactions, e.g. O₂ or Cl₂ production in anodic reactions.

1.14 O.p.d. H measurement

So far, only electrochemical experimental techniques have been reliably demonstrated as being able to quantify the o.p.d. H coverage in situ.
Fig. 1.10 Schematic representations contrasting the behaviour of the u.p.d. H and o.p.d. H in faradaic reactions.
In an earlier section, we pointed out the fact that adsorbed intermediates deposited on electrodes tend to behave electrically as a pseudocapacitance, \( C_\phi \). However, nothing was mentioned about the possibility of indirectly evaluating the coverage of the o.p.d. H through such capacitance measurements.

The pseudocapacitance, just like a normal capacitance, can be measured by modulation or transient techniques. The principal methods available for the indirect determination of the surface coverage by o.p.d. H are:

1) Rapid galvanostatic charging\(^{104-105}\);
2) Open-circuit potential decay\(^{70,106-109}\);
3) Potentiostatic step charging\(^{110-113}\) and
4) A.c. impedance\(^{114-116}\).

However, problems are encountered in some of these methods, as will be discussed later. Recently\(^ {132}\), it has been claimed that an i.r. absorption band, anoxidated with o.p.d. H on Pt, can be observed near the reversible \( H_2/H^+ \) potential but coverage in function is not provided by such measurements.

The rapid galvanostatic-charging method consists in recording charging curves, i.e. the potential \( \Delta \eta \) is measured as a function of time at constant current \( i \), during the continuous Faradaic deposition of o.p.d. H. The amount of charge, \( \Delta q \), passed in time \( t \) is accompanied by a change of potential \( \Delta \eta \). As the charge \( \Delta q \) is passed in time \( t \), a change in potential \( \Delta \eta \) is recorded. The total electrode capacitance, which is a combination of the double-layer capacitance, \( C_{dl} \), and the pseudo-capacitance, \( C_\phi \), can be evaluated according to the following equation:

\[
C = \frac{\Delta q}{\Delta \eta} \quad (38a)
\]

\[
= \frac{d(i dt)}{d\eta} \quad (38b)
\]
Double-layer charging

\[ i_2 \text{ at } \eta_2 \theta_2 \equiv \theta_1 = 0 \]

\[ i_1 \text{ at } \eta_1 \theta_1 = 0 \]

D.L. charging and change of \( \theta \)

\[ i_2 \text{ at } \eta_2, \theta_2 (> \theta_1) \]

\[ i_1 \text{ at } \eta_1, \theta_1 \]

Fig. 1.11 Potential-step transient current response where: a) there are no adsorbed intermediates and b) where there is a detectable coverage by chemisorbed species.
In the charging-curve method where an anodic current is used to strip the surface of adsorbed $\text{H}^{104}$, unfortunately, oxidation of the metal electrode surface, reoxidation of previously generated $\text{H}_2$ in solution and/or desorption of some strongly bound u.p.d. H, can seriously affect the experimental values of the o.p.d. H coverage measured by this technique, depending on the metal, as discussed by Breiter et al.\textsuperscript{117-118}.

Another experimental technique for o.p.d. H determination is the potentiostatic-step charging method\textsuperscript{110-113}, carried out in the cathodic direction. This technique involves stepping the overpotential from $\eta_1$ to $\eta_2$, by means of a fast potentiostat, which gives rise to some current response function in time which must be analyzed. The steady-state current is changed from $i_o \exp \eta_1/b$ to $i_o \exp \eta_2/b$. Changing the metal-solution potential difference will also give rise to an instantaneous non-Faradaic current flow to charge or discharge the interphasial capacitance over the potential range $\eta_2 - \eta_1$. In the case where no chemisorbed species are involved, the capacitance can be calculated simply according to equation (38) where the change of charge, $\Delta q$, is represented graphically as the area under the peak observed in the potential-step transient current response, as depicted in Fig. 1.11a.

When, however, the electrode process involves a deposited intermediate, such as H in $\text{H}_2$ evolution, the transient of current in response to the step modulation is more complex, as shown in Fig. 1.11b. In this case, some complex mathematical interpretation of the transient current response is required due to the change of coverage which additionally occurs and is the quantity that is desired to measure. Conway, Sattar and Gilroy\textsuperscript{119} have made a mathematical derivation for interpretation of the results from the potential-step method during the oxygen evolution reaction, but no detailed treatment for the h.e.r. has yet been proposed; however, the mathematics will be similar.
Another powerful procedure for o.p.d. H adsorption measurements involves application of a sinusoidal modulation signal to an electrode. This method, referred to as a.c. impedance spectroscopy, is one of the most useful procedures, but the collected experimental results (often expressed in terms of complex-plane plots of the imaginary versus the real component of the impedance, or by Bode plots) are not always easy to interpret, and simulation of the behaviour of equivalent circuits is sometimes resorted to, although a less arbitrary kinetic analysis is also possible and is to be preferred. Early reliable impedance measurements were made by Gerischer and Mehl at mercury, silver and copper electrodes. Also, for the h.e.r., Armstrong and Bell made impedance studies at rotating W and WC electrodes, at which they observed, at appreciable overpotentials, single distorted semi-circles in the complex-plane plots, with corresponding large capacitance values most likely associated with adsorption pseudo-capacitance. Impedance spectra were also recorded at activated Pt in alkaline solutions, and at unactivated Pt in acid and alkaline solutions in works of Bai, Harrington and Conway. In their impedance interpretation, they used a kinetic-analysis treatment, based on Armstrong and Henderson's analysis for interpretation of the impedance components in terms of Faradaic resistance and pseudocapacitance in equivalent circuits, to simulate numerically the observed a.c. behaviour through evaluation of rate constants for each step.

In order to ease the analysis of complex impedance spectroscopy results, Macdonald and Potter have recently developed a very general and flexible complex, nonlinear least-squares fitting program, which can be applied to simulate the impedance behaviour of a wide variety of equivalent circuits.

Evaluation of the open-circuit overpotential decay behaviour of a previously polarized electrode is another useful way of examining the adsorption behaviour of reaction intermediates in the electrode process. A full theoretical description of this method, which
has been used in the present research project, will be given later. Early potential decay
measurements, using an analogue oscilloscope, were made by Butler and Armstrong\textsuperscript{122} at
Hg, and by Conway and Bourgault\textsuperscript{123} at nickel oxide electrodes. Works of Matsuda and
Ohmori\textsuperscript{124}, and of Past and Jofa\textsuperscript{125,126}, on nickel electrodes, indicated different capacitances
for two different potential-decay treatments using either the initial rate of decay of potential
\[(d\eta/dt)_{t=0},\] or the rate of decay, \(d\eta/dt,\) read from the decay curve at any \(\eta(t)\) value. Not
much experimental work had been done up to that time, and it was only after Kobussen\textsuperscript{175},
Tilak and Conway\textsuperscript{127-128} proposed a general treatment of potential-relaxation behaviour, that
the o.p.d. H coverage started to be more extensively evaluated by the decay method. Recent
works by Conway et al.\textsuperscript{70,106-109,129,130} have provided much of the present information on the
coverage by the kinetically-involved intermediates at various metals, e.g. Pt, Au, Ni, Ni-Mo
alloys, and Pd. Non-electrochemical techniques to evaluate reliably the coverage by o.p.d. H
have still to be discovered. However, it should be mentioned that \textit{in situ} I.R. spectroscopy
has helped understand the behaviour of the adsorbed intermediates in the ammonia
synthesis\textsuperscript{131} and \textit{in situ} applications have been made in recent years by Bewick\textsuperscript{132} to
electrode interfaces.

1.15 \textbf{Aims of the present work}

Any electrocatalytic reaction involves the adsorption of kinetically involved
intermediates with coverages dependent on the nature of the electrode material and the
overpotential. The coverage of such chemisorbed species, e.g. H in the h.e.r., normally
appears explicitly in the expression for the reaction rates and needs to be evaluated in any
proper kinetic studies of electrocatalysis. Also, o.p.d. H coverages have hitherto been
measured only at very few metals, even though the h.e.r. reaction has been one of the most
extensively studied electrochemical reactions. This is probably due to the fact that no
appropriate, convenient or unambiguous method has, until recently, been available to evaluate the coverage by the kinetically involved H intermediate, although one impedance study of the h.e.r. had been reported in 1955 by Gerischer and Mehl\textsuperscript{120}, as mentioned earlier. The present work described in the thesis is concerned with the evaluation of coverage behaviour of these H adatoms through indirect electrical measurements of the capacitance at the interface of various metallic substrates in alkaline solutions, e.g. Ni, Mo and various nickel-based alloys.

Some of the electrochemical experimental techniques used in this work to quantify the o.p.d. H have been mentioned in Section 1.14 and are already well documented in the literature, e.g. open-circuit potential decay\textsuperscript{70,106-109} and a.c. impedance spectroscopy\textsuperscript{114-116}. Unfortunately, as was mentioned earlier, results obtained by the latter technique are not always easy to interpret. At Ni and Ni-Mo alloys, for the potential range under study, depressed semi-circles are observed in their complex-plane impedance plots. This is not only typical of these electrochemical systems since such a phenomenon has been observed at other metals and electrode processes. An attempt is made in the present work to rationalize this somewhat puzzling behaviour by measuring the impedance spectra at Hg and Au for the h.e.r. over a wide range of potentials, e.g. -50 to -500 mV on the hydrogen reference electrode scale.

Also, it is felt that determination of the interfacial capacitance behaviour should be made by some other complementary method. Therefore, for the first time, we introduce in the present work, a new treatment for analysis of digitally recorded potential relaxation curves, developed to evaluate the interphasial capacitance at an electrode during a continuous faradaic process, i.e. here, H\textsubscript{2} evolution, over a wide range of overpotentials and corresponding current-densities.
CHAPTER 2

EXPERIMENTAL

2.1 Electrochemical systems

2.1.1 Electrodes

i) Mercury electrodes

A Hg pool electrode was used and consisted of a silanized pyrex glass cup containing pure liquid Hg (Aldrich Gold Label, 99.99 %), giving an area of close to 0.393 cm². Electrical connection was made by contact of a Pt wire with the Hg at the bottom of the pool, furthest away from the working electrode’s surface.

The most serious difficulty with the Hg electrode was the well known problem of creeping of the electrolyte solution between the Hg and glass. This changes the accessible surface of the electrode and can result in poor reproducibility of measurements and introduction of an apparent frequency-dependence of the double-layer capacitance. Creeping of the electrolyte was minimized by ensuring a clear, smooth glass surface and covering it with an hydrophobic silicone coating. The following silanisation procedure was used with success:

a) Immersion in 65 % nitric acid to remove Hg residues.

b) A rinse with distilled H₂O.

c) Immersion in a 50/50 HF:HCl solution for ca. 30 seconds.

d) A rinse with distilled H₂O.

e) Drying for 2 hours at 403 K - 413 K.

f) Repeated dipping in a solution of 6 % (CH₃)₂SiCl₂ in toluene.

g) Drying for 2 - 3 hours at 403 K - 413 K.
The Hg pool electrode was resilanized regularly to prevent solvent creep, and the Hg was replaced regularly to prevent any accumulation of impurities within or at the Hg surface.

ii) Au electrode

Electrodes were made from Au wires of 99.999% purity, using Johnson Matthey "Grade 1" Au. Appropriate lengths of these wires, of diameter 0.51 mm, were first degreased overnight in refluxing acetone in a Soxhlet extractor. After short lengths of Au were flame welded to much longer Ag electrical-contact wires, a droplet of softglass was melted onto the Au wire and sealed into the end of a soft-glass tube, leaving ca 3.3 cm of Au wire protruding beyond the end of the tube. Seals in Pyrex glass were found to be unreliable, giving occasional leaks.

iii) Ni electrodes

99.99% "Gold Label" nickel rods (Aldrich Chemical Company Inc.) were spot welded to platinum wires which were flame welded to much longer Ag electrical-contact wires. The nickel was then sealed in a glass tube with Struers Epoxy resin, 'Epofix', which was found not to contaminate the system in alkaline solution over the experimental time period (up to a few days). A flat face was then ground off with silicon carbide sand paper followed by a finer polishing done with 0.3 and 0.05 alumina powder on a selvyt polishing cloth. The geometrical area was found to be 0.408 cm$^2$ by physical measurement.

iv) Ni-Mo bulk alloy electrodes

Kinetic and mechanistic studies were also made at Ni-Mo alloys of various compositions, viz. 1, 6.2 and 12 atomic percent of Mo; the electrodes were prepared similarly to those of nickel, as above. These binary alloys were metallurgically prepared by Aremco Products Inc. in the composition range where only homogeneous solid solutions of the two elements are found, as depicted in their phase diagram (Fig. 1.7b). Work was also done on
Ni-Mo alloys in the non-homogeneous regions of the phase diagram, but phase segregation arising at these compositions made it impossible to obtain reproducibility in the experimental results. In Fig. 2.1, the S.E.M. pictures of various non-homogeneous Ni-Mo alloys clearly reveal phase segregation.

v) **Ni-W bulk alloy electrode**

Since Mo and W belong to the same group in the periodic table, the cathodic behaviour at a Ni-W (90:10) bulk alloy was also examined for comparison. This alloy is in the range of composition for which the phase diagram (Fig. 1.7a) indicates a continuous range of solid solutions and had been prepared especially for this work by Aremco Products Inc. For the electrochemical experiments, these electrodes were prepared similarly to those of Ni-Mo.

vi) **Electrodeposited Ni-V alloy**

The electrodeposition of this alloy was made in a plating solution containing NaCl, tartaric acid, NiCl$_2$ and NH$_4$VO$_3$. The alloy was electrodeposited onto a Fe wire in a plating bath agitated vigorously by ultrasound. The ultrasound was not only useful for microscopically stirring the solution but it also ensured minimum dendrite formation, which otherwise usually shed very easily. Ultrasonic stirring was used here also in the expectation of minimizing, as much as possible, the real surface area of the electrode in order to simplify the kinetic studies since otherwise diffusion could significantly affect the electrode polarization behaviour of the plated, catalytic porous material on account of passage of large currents. (See S.E.M. picture, Fig. 2.2).

vii) **Ni-W plated alloy electrodes:** Ni (92%) - W(8%) (atomic percent) composite electrodes were prepared by electrolytic codeposition of Ni and W onto an Fe wire, based on a patented procedure$^{135}$ which was modified for the preparation of high-activity electrocatalytic materials for H$_2$ evolution. The modifications introduced in the
Fig. 2.1a S.E.M. picture of a phase segregated Ni-Mo alloy (34.3 atomic percent of Mo) at a magnification scale of 4 μm.
Fig. 2.1b S.E.M. picture of a phase segregated Ni-Mo alloy (48.0 atomic percent of Mo) at a magnification scale of 2 μm.
Fig. 2.2a  S.E.M. pictures of an electrodeposited Ni-V alloy on an Fe wire (94.5% Ni, 5.5% V) at a magnification scale of 10 μm.
Fig. 2.2b S.E.M. pictures of an electrodeposited Ni-V alloy on an Fe wire (94.5% Ni, 5.5% V) at a magnification scale of 4 μm.
Fig. 2.2c  S.E.M. pictures of an electrodeposited Ni-V alloy on an Fe wire (94.5% Ni, 5.5% V) at a magnification scale of 1 µm.
Fig. 2.3  Phase diagram of the Ni-V binary alloy system [139].
procedure involved:

a) Using only the Watts bath, followed by an intermediate layer bath.
b) Omitting any salts involving cadmium (cf. ref. 135).
c) Replacing Na$_2$MoO$_4$.2H$_2$O by Na$_2$WO$_4$.2H$_2$O.
d) Plating while the system was being stirred ultrasonically.

The composition of the Ni-W electrocoated film was determined by X-ray emission analysis in a S.E.M. These electrodes, as with the Ni-Mo electroplated ones$^{136}$, had a nodular cauliflower-like appearance under the S.E.M. at moderate magnifications (Fig. 2.4). The structure is evidently porous with a real/apparent area ratio of ca. 60 determined by comparing the $C_{dl}$ of the porous electrode from capacitance measurements with that of a polished sample which was metallurgically prepared to a similar composition (see v above).

viii) Reference electrode

Potentials of the test electrodes were referred to that of a platinized Pt hydrogen reference electrode (RHE) immersed in the same solution as that under study. The Pt electrode was plated in 2% H$_2$PtCl$_6$ in 2 N HCl platinizing solution, and then thoroughly washed with distilled water before use. When not in use, the electrode was always kept in pyrodistilled water to prevent deactivation by dehydration or by adsorption of impurities. For convenience, throughout this thesis, cathodic overpotentials are taken with a positive sign, as mentioned earlier.

ix) Counter Electrode

A platinized platinum gauze having a large surface area was used as the counter electrode. The large surface area minimizes the Faradaic resistance of the oxygen evolution reaction occurring at the counter electrode and also reduces the polarization of this electrode which, if too important, could lead to some dissolution of Pt.
Fig. 2.4a S.E.M. pictures of an electrodeposited Ni-W (92:8) alloy on an Fe wire at a magnification scale of 10 μm.
Fig. 2.4b  S.E.M. pictures of an electrodeposited Ni-W (92:8) alloy on an Fe wire at a magnification scale of 4 μm.
Fig. 2.4c  S.E.M. pictures of an electrodeposited Ni-W (92:8) alloy on an Fe wire at a magnification scale of 1 μm.
2.1.2  **Cell**

The cell used for the electrochemical measurements was a conventional three-compartment Pyrex vessel. The reference-electrode compartment was connected to the working-electrode compartment via a Luggin capillary. Through the cell top, a temperature probe, a bubbler and the electrode under study were inserted into the working-electrode compartment which was isolated from the counter-electrode compartment by a glass stopcock which could be opened slightly as necessary. Such a cell is drawn in Fig. 2.5.

High-purity electrochemical procedure requires that the cell and its glass component parts be frequently immersed in recently prepared, concentrated chromic-sulphuric acid solution for cleaning for about 12 hours, then rinsed several times with doubly distilled water and finally soaked in doubly distilled water for at least 24 hours to remove residual chromate ions.

2.1.3  **Solutions**

The 0.5N alkaline solutions used were prepared with BDH "Aristar" potassium hydroxide with pyrodistilled water as solvent. Since high-purity reagents were used, it was found unnecessary to pre-electrolyze the solutions.

The H$_2$SO$_4$ and HClO$_4$ solutions were made up from the BDH "Aristar" grade acid which, in earlier work, had been found to be of sufficiently high purity as judged by sensitive cyclic-voltammetry results at Pt electrodes$^{137}$.

2.1.4  **Pyro-distilled water**

Pure water, free from organic and/or other surface-active contaminants, can be obtained by means of pyro-distillation$^{137}$. 
Fig. 2.5 A standard electrochemical three-compartment cell in which the reference compartment is connected to the working compartment via a Luggin capillary and a closeable, wetted stopcock. The sleeved stopcocks allow the whole cell to be partially immersed in a thermostat fluid without contamination.
The residual organic contaminants, commonly present in domestic and industrial water supplies, are often steam-volatile and hence not removed by a simple distillation. The sensitivity of electrochemical measurements to adsorption of impurities requires further purification of the regular Barnstead-distilled water, as demonstrated by Conway and co-workers\textsuperscript{137,138}. The principle involved is pyrolysis of organic impurities by passage of the steam through a column of silica at 1023 K in a stream of oxygen. The hot column contains a 90% Pt/Rh gauze which provides a zone for the efficient catalytic oxidation of organic impurities. The pyrodistillation apparatus is shown in Fig. 2.6. The pyrolysed steam is condensed and the resulting water recirculated for ca. 12 h.

2.1.5 Gases

Electrolytic grade hydrogen gas was passed through a conventional purification train consisting of a drying agent, molecular sieve, an oven containing Cu turnings and palladized asbestos at 623K, and finally charcoal traps maintained at liquid nitrogen temperature. Nitrogen was treated as above, except that only Cu turnings were used in the heated oven. A bright metallic state of the Cu turnings was maintained by periodic regeneration of the Cu by passage of H\textsubscript{2} through the oven (see Fig. 2.7).

2.2 Electrical circuit

The steady-state polarization and the potential decay measurements were made with the various instruments represented in the schematic electrical circuit of Fig. 2.8. The potential of the working electrode was controlled to within 1 mV using a Wenking HP72 potentiostat (small signal rise-time, < 10 $\mu$s). The potential between the working and the reference electrodes was applied through a high-impedance Tektronix AM501 operational amplifier, in cathode-follower configuration, to a multimeter and oscilloscope. The
Fig. 2.6 Pyrodistillation apparatus for water purification (oxidation of the organic impurities is achieved in the presence of O$_2$ at high temperature on a Pt-Rh catalyst located in the oven tube [137,138]).
Fig. 2.7 Gas line used in the purification of the gases, N₂ and H₂, used in the electrolysis experiments.
Fig. 2.8 Electrical circuit for steady-state polarization and potential decay measurements.
steady-state currents were measured by means of a Racal-Dana digital multimeter (range 0.01 μA to 200 mA) in the counter-electrode circuit.

Current interruption was done by means of a Clare vacuum relay (HGI2MT51231E00) and the resulting potential-relaxation curves were recorded by means of a Nicolet 2090 digital oscilloscope (4096 data points per curve with a maximum collection speed of 0.5 μs per point).

2.3 Solution resistance compensation

The iR-drop corresponding to the solution resistance, Rs, between the Luggin capillary of the reference and working electrodes, was determined at various current densities by the current interruption method with digital recording of the potential versus time relaxation transients being made by means of a Nicolet digital oscilloscope, Model 2090. Currents were interrupted by means of the Clare vacuum mercury relay, mentioned above, controlled by a suitably debounced micro-switch which gave a clear interruption of current with no ringing or spike in the potential transient. Using the fastest horizontal sweep mode of the oscilloscope (horizontal sweep rate of the oscilloscope), that is to say, the scale of 0.5 - 1 μs per point the difference in potential between the last point before and first point after the interruption of current was recorded for various current densities, i, and this gave the iR drop for the current density i. This difference in overpotential, Δη (V = iR), was plotted versus current density, i, and always gave the expected straight line plot. From this plot, the slope gave the resistance, R, so that "iR" for any other i values could be determined. The solution resistance was also checked by means of a.c. impedance measurement using a Solartron Frequency Analyzer with values in agreement with those determined by the interruption method.
2.4 **Measurement techniques**

2.4.1 **Measurements**

Before any data acquisition, it was found necessary that the electrode be polarized for a few hours to reduce any thin oxide film at the electrode surface.

Since oxygen is chemically reactive with many substances and can be reduced electrochemically at cathodes, solutions were freed from oxygen, following usual practice, by bubbling nitrogen gas in the counter-electrode compartment and hydrogen gas in both reference and working compartments of the cell prior to, and during, the electrochemical measurements.

Other critical experimental conditions involved in the potential-decay and/or the Tafel-polarization measurements were as follows:

i) There should be no other reaction occurring during the course of the potential decay measurements besides the charge-transfer processes under investigation, involving the adsorption or desorption of reaction intermediate(s). This means that it must be ensured that there is no corrosion of the electrode, or no adsorption or desorption of impurities, or reduction of any impurities.

ii) In the case of the h.e.r. it is important that, constant H$_2$ pressure must be maintained since the potential of the electrode is also a function of H$_2$ gas pressure. This was achieved by bubbling H$_2$.

iii) The Tafel-polarization and potential-decay results must be almost exactly reproducible and the two types of measurements must be made under identical experimental conditions, one immediately following the other, so that no changes in the state of the electrode have time to arise.
2.4.2 Tafel polarization measurements

Measurements of the steady-state currents resulting from controlled but varied applied potentials provide the required information on the kinetics of the electrode process, e.g. the h.e.r.. It is well known that the general form of the so-called Tafel plot, i.e. the log i vs η relation, and its slope(s) can be diagnostic of the reaction mechanism(s) operative in the electrode process. Also the exchange current-densities derived from extrapolation of the Tafel plots are explicitly related to the rate constant(s) of the electrode process(es), as was indicated in Eqn. 10.

An automated data acquisition system was used for conveniently measuring the steady-state polarization behaviour by means of the hardware schematically represented in Fig. 2.9.

An HP217 computer-controlled HP-IB-compatible digital-to-analog converter (Kepco, model SN488-122) was used to supply the desired potential to the external control input of a potentiostat; this DA converter gave 13 bit resolution over ±1 V or ±10 V, which corresponds to a minimum potential increment of 0.2 mV and 2.4 mV, respectively (linearity error ± 1/2 LSB).

The current resulting from the applied potential was monitored by means of an HP-IB-compatible digital multimeter (DMM) (Keithley, model 195A); the autoranging feature provided by this instrument allowed for continuous measurements over the several decades in current of interest in the experiments, thus avoiding the need for controller-, or user-implemented sensitivity selection.

This computerized experimental setup allowed convenient use of staircase and rectangular potential programs for steady-state polarization measurements (see Fig. 2.10 for their schematic representation).
Fig. 2.9  Schematic diagram of an automated set-up in which a mini-computer controls the data acquisition during polarization measurements.
Fig. 2.10 A schematic representation of the various potential programmes applied during steady-state polarization measurements.
The positive deviation from the expected straight line of $\eta$ vs $\log i$, which usually appears at fairly high overpotentials, is due to the uncompensated solution resistance, $R_u$, between the tip of the Luggin capillary of the reference electrode and the working electrode surface. Since $R_u$ (assumed constant) is previously measured by the current interruption method, a minicomputer will easily calculate the $iR_u$ drop at various current densities; hence the actual applied overpotentials $\eta$, at the metal-solution interface in steady-state polarization measurements, are given by

$$\eta = \eta_{obs} - iR_u$$

(39)

where $\eta_{obs}$ is the observed overpotential. Converted $\eta$ values are then automatically computed for all $i$ values.

The determination of the coverage, $\theta$, of an electrode surface by some electroactive intermediate needs also to be evaluated in kinetic studies. The o.p.d. H coverage, indirectly evaluated from the pseudocapacitance characteristics of a covered electrode (see Eqn. 37), can yield important mechanistic information on the h.e.r. The various modulation techniques used in this work for capacitance determination, can only be briefly described here, but more detailed discussion is given in later sections.

2.4.3 Open-circuit potential decay

Open-circuit potential decay transients were recorded as soon as possible after recording the Tafel relation (2.4.2) in order that the same experimental conditions were maintained. Again, the Nicolet digital oscilloscope was used to record the potential versus time relaxation transients on floppy disks, the current interruption being made by means of the Clare vacuum mercury relay. In order to cover adequate time scales in the transients, two separate transient measurements were made as follows: first, the $\eta(t)$ data were acquired and stored using the faster range of time scales (0.5 - 100 $\mu$s per point). In this case, the circuit
needed to be "open" for less than a few seconds. With this small disturbance, the system came back easily to the controlled steady-state, which was indicated by both current and potential being almost identical with the respective values before interruption of current. Then a further acquisition and storage of $\eta(t)$ data was made using a slower x-axis sweep-speed (longer time scale) on the oscilloscope.

The resulting digitally acquired $\eta(t)$ data were then processed in an HP216/217 computer to join the two sets of data from the time scales from which the kinetic parameters of the h.e.r. and the adsorption behaviour of H were to be obtained. The quantity $d\eta/dt$ was calculated by a differentiating program, this derivative being required for the evaluation of the o.p.d. H pseudocapacitance according to Eqn. 40 in Section 3.2.

An advantageous aspect of this technique over other methods is that the capacitance behaviour can be determined for the whole potential range under study from only one set of joined decay curves covering a short time interval of a few seconds. Very clear $\eta$-time decay curves can be obtained by carefully grounding all instruments, together with the working electrode, and shielding the reference electrode, including the wires, as well as removing any significant a.c. noise source form the working area.

2.4.4 **Initial potential decay rate, $(d\eta/dt)_{t=0}$, following current interruption**

Here we introduce, for the first time, a new treatment based on the fitting of the potential-relaxation curves recorded on open-circuit following interruption of the polarizing current of an electrode reaction. This method has been developed in collaboration between Mr. Gu Ping in our laboratory and the present author, and can be used to obtain conveniently both the interfacial capacitance behaviour of the electrode and the uncompensated solution resistance arising in an electrochemical cell during a continuous Faradaic process.

The proposed technique has a number of advantages over previously published
methods for the evaluation of the capacitance at the electrode's interface. Here it may be noted that:

i) No assumptions need to be made about the form of the dependence of the capacitance on overpotential in the derivation of the fundamental equations employed in this method.

ii) Only the steady-state current passing prior to interruption of the current, and the subsequent potential-decay curve, recorded using the fastest sweep-speed, are required as the experimental data base.

iii) The capacitance is evaluated directly from an equation involving the current passing immediately prior to opening of the circuit \( t = 0 \), together with the derivative of the potential-decay curve fitting function (see below) at this \( t = 0 \).

The potential relaxation curves were collected in a similar manner as before (2.4.3), with the difference that only fast time-scales (0.5 - 5 \( \mu \text{s} \) per point) were used. This means that the circuit needs only to be opened for less than a second, with no apparent permanent disturbance to the electrochemical system (if the current would be interrupted for too long, open-circuit corrosion could ultimately occur since the electrode metal is no longer cathodically protected in an aqueous alkaline medium which is significantly corrosive for some base metals).

A curve fitting-procedure, to be described in section 3.3, was carried out using the University of Ottawa Main-Frame computer and employed a non-linear regression programme corresponding to a nonlinear representation of the time-course of \( \eta(t) \). The programming language used is normally abbreviated as SAS (Statistical Analysis Software), where the nonlinear regression subroutine (NLIN) was used to fit the \( \eta(t) \) curves by means of a Gauss-Newton iterative method. An example of a fitted \( \eta(t) \) curve is plotted in Fig. 2.11 and discussion of the significance of this procedure will be given in Section 3.3.
2.4.5 **A.C. impedance measurements**

The a.c. impedance method provides an approach that is complementary to the potential-decay methods just described. Here, a Solartron 1250 Frequency Response Analyser (FRA), equipped with a Solartron potentiostat (ECI 1286) which controlled the electrode system, were used for taking the measurements. The Solartron 1250 FRA consists basically of a programmable signal generator and an analyser which provides rapid and accurate measurements of frequency response at various input signals to the system under study. The generator provides an output signal of known amplitude \( A \) and frequency \( \omega \) which is in the form \( A \sin(\omega t) \). This signal is applied to the electrochemical system to be tested, through the potentiostat. The analyser accepts the electrochemical system’s response to the stimulus signal of the generator using a correlation procedure, resolving it in terms of resistance \( R \) and phase-angle, or evaluating the in-phase (real, \( Z' \)) and quadrature (imaginary, \( Z'' \)) components, i.e. in terms of their complex function relation in Cartesian coordinates \( (Z',Z'') \) as a \( f(\omega) \).

The analyser uses a digital integration procedure to give precise measurements of the system’s response in the presence of interfering noise and harmonics. The \( (Z',Z'') \) data are then analyzed and plotted on a graphics screen or a plotter, using an HP216 computer. For the systems studied, the impedances were measured at several cathode overpotentials, with frequencies ranging from 0.001 to 50,000 Hz, a \( 10^6 \) Hz band width!
Fig. 2.11  An example of a η(t) curve, fitted by a non-linear regression procedure using Eqn. (49).
CHAPTER 3

PROCEDURES OF MEASUREMENT AND DATA ANALYSIS

3.1 Measurement techniques for evaluation of the electrochemical capacitance

We have seen in the Introduction that the presence of chemisorbed intermediates on the electrode metal surface can give rise to a large differential pseudo-capacitance, $C_\phi$. This pseudocapacitance can be measured by various methods, e.g. rapid galvanostatic charging, potentiostatic-step charging, a.c. impedance, open-circuit potential decay, and our new treatment of initial potential decay rate. It was noted earlier in section 1.14, that not all of these methods can satisfactorily evaluate the coverage by the kinetically involved o.p.d. H in the h.e.r. This is one of the reasons why the present work was restricted to the last three mentioned methods in the determination of the fractional coverage by H adatoms.

In this Chapter, the principles of the a.c. impedance and the two potential-decay methods are described in relation to the quantitative experimental evaluation of the coverage by the kinetically involved adsorbed H intermediates in cathodic H$_2$ evolution.

3.2 Open-circuit potential decay

As indicated earlier, the current-density, $i(\eta)$, for an electrode process can be expressed as a function of overpotential, $\eta$, according to the following equation:

$$i = i_0 \exp (\alpha \eta F/RT)$$

which is the Tafel equation in exponential form and where $i_0$ is the exchange current-density.

The transient response following interruption of current, $i$, initially passing at an overpotential, $\eta$, is represented by
\[- C \frac{dn}{dt} = i(\eta) \quad (40a)\]
\[= i_0 \exp \left( \frac{\alpha F \eta}{RT} \right) \quad (40b)\]

where \( C \) is the total capacitance corresponding to a non-steady-state response of the electrode process. \( C \) is a combination of an electrostatic double-layer capacitance \( (C_{dl}) \) and, more importantly here, a pseudocapacitance, \( C_\phi \), corresponding to the potential-dependence of coverage, \( \theta \), by reaction intermediates. Thus

\[ C = C_{dl} + C_\phi \quad (41a) \]
\[ = C_{dl} + q_1 (d\theta_H/d\eta) \quad (41b) \]

where \( q_1 \) is the charge for formation or desorption of a monolayer of the electroactive intermediate (here \( H \) for which \( q_1 = \text{ca.} \ 210 \mu \text{C cm}^{-2} \)). The quantity \( d\theta_H/d\eta \) is the differential electrochemical adsorption isotherm for \( H \) chemisorption at the electrode for steady-state conditions.

Rearranging Eqn. 40 gives:

\[ \eta = 2.3 \frac{RT}{\alpha F} \log \left( \frac{i_0}{C} \right) + 2.3 \frac{RT}{\alpha F} \log \left( -\frac{dn}{dt} \right) \quad (42) \]

In the limiting case where \( C \neq f(\eta) \), a rearranged form of Eqn. 40b can be integrated to

\[ \eta(t) = a \ b \log (t + \tau) \quad (43) \]

where

\[ a = -b \log \left( 2.3 \frac{i_0}{bC} \right), \quad (44a) \]
\[ b = 2.3 \frac{RT}{\alpha F} \quad \text{(Tafel slope)} \quad (44b) \]

and

\[ \tau = bC/2.3 \ i_{(t=0)} \quad (44c) \]

where \( \tau \) is a constant resulting from the integration of Eqn. 40b.

Therefore, both \( \log (t + \tau) \) (Eqn. 43) and \( \log (-dn/dt) \) (Eqn. 42) should be linear functions of \( \eta \) as is found experimentally, and the slopes should have the same absolute
values as the Tafel slope, \( b \), when the condition \( C \neq f(\eta) \) is maintained, i.e. mainly when \( C_\phi \ll C_{dl} \), although it is well known that \( C_{dl} \) may also vary significantly with potential, especially around the potential of zero charge\(^{81-84} \).

Since the actual \( i(\eta) \) data are experimentally determined in the steady-state polarization measurements and \( d\eta/dt \) can be accurately evaluated from the digitally recorded transient curves by means of a minicomputer, the electrode interface capacitance\(^{70,106,108} \) as a function of \( \eta \) can be determined. In this way, \( i(\eta) \) and \( d\eta/dt \) from separate experimental measurements can be combined to evaluate the interfacial capacitance behaviour as follows:

\[
C_\phi + C_{dl} = C(\eta) = \frac{i(\eta)}{(-d\eta/dt)} \tag{45a}
\]

or

\[
\log(C_\phi + C_{dl}) = \log i(\eta) \log \left(-\frac{d\eta}{dt}\right) \tag{45b}
\]

This last approach is most useful since, besides the assumption that \( i(\eta)_{\text{steady-state}} = i(\eta)_{\text{transient}} \), nothing needs to be assumed about the form of the potential dependence of the interfacial capacitance.

When the surface is appreciably, but not fully covered by reaction intermediates, e.g. \( H, C_\phi \gg C_{dl} \).

The desorption of these \( H \) adatoms during self-discharge of the polarized interface must proceed through coupled anodic and cathodic reactions since, on open-circuit, \( i = 0 \). These processes are represented by the following two electrochemical equations for the h.e.r. in alkaline solution:

\[
\text{OH}^- + \text{MH}_{\text{ads}} \rightarrow \text{M} + \text{H}_2\text{O} + e \quad \text{(anodic)} \tag{46}
\]

\[
\text{MH}_{\text{ads}} + \text{H}_2\text{O} + e \rightarrow \text{H}_2 + \text{OH}^- \quad \text{(cathodic)} \tag{47}
\]

which are chemically equivalent to desorption of 2\( H \) atoms, giving \( \text{H}_2 \). Processes (46) and (47) occur together with decreasing \( \theta_H \) according to the electrochemical isotherm for adsorption of the o.p.d. \( H \) relating \( \theta_H \) to \( \eta \).
3.3 **Open-circuit potential decay at \( t = 0 \); method of the "fitting function"

Alternatively, the potential-decay rate immediately after interruption of the polarization current, \( i(\eta)_{t=0} \), is determined by the potential-relaxation relation\(^{125,126}\)

\[
C = \frac{i(\eta)_{t=0}}{-\frac{d\eta}{dt}}_{t=0} \tag{48}
\]

where \( C \) is the total interfacial capacitance, \( C_0 + C_{dl} \), which may or may not be potential dependent. Here, it is proposed that evaluation of \( C \) be made using an appropriate fitting function to the potential-decay curve, \( \eta(t) \), followed by a numerical evaluation of the derivative, \( \frac{d\eta}{dt} \), with respect to time, of this function limitingly at \( t = 0 \). It was found that the potential-decay curves can be very well fitted by the function below*, for both the hydrogen and chlorine evolution reactions, with a standard derivation, of \( \pm 0.1 \text{ mV} \), which is less than the experimental error (see Fig. 2.11):

\[
\eta(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 + a_6 t^6 + a_7 \ln(t + a_8) \tag{49}
\]

where \( \eta(t) \) is the potential at the electrode's interface at a certain time, \( t \), after current interruption and the \( a_n \) values are fitting constants. This fitting function consists of two main parts: the first seven terms simply correspond to a polynomial of degree 6, while the final term, \( a_7 \ln(t + a_8) \), accounts for the possible but, not necessarily, exponential dependence of the capacitance on potential that is observed in some experiments. In practice only terms up to the 4th order are required, together with the \( \ln \) term**. The significance of the last

---

* Other trivial functions could have also been employed to fit the potential relaxation curves with time. Eqn. 49 has no fundamental significance in relation to the mechanism of potential relaxation.

** It must be emphasized that no assumptions are made here about the form of the capacitance behaviour with respect to its dependence on potential. Only a possible exponential term representing dependence of the capacitance on overpotential needs to be
taken into account in Eqn. 49, so that when such C dependence arises, proper fitting can be achieved with the minimum number of fitting parameters. For most purposes, a polynomial (Eqn. 49) of order less than 6 will suffice, together with the logarithmic term.
logarithmic term of Eqn. 49 is rationalized, using the following approach: if C is an exponential function of \( \eta \), then

\[
-C_0 \exp(\eta/d) d\eta/dt = i_0 \exp(\eta/b)
\]

(50)

where \( d^{-1} \) represents the dependence of \( \ln C \) on \( \eta \). Then, separating the \( \eta \) and \( t \) terms and integrating, gives an equation of the form

\[
\eta = a_0' + a_7 \ln(t + a_8)
\]

(51)

The initial potential-decay slope, \( (d\eta/dt)_{t=0} \), can be evaluated by means of Eqn. 49 simply by taking the derivative of the fitting function (49) for the condition \( t = 0 \), which gives:

\[
C = \frac{i(\eta)_{t=0}}{-(a_1 + a_7/a_8)}
\]

(52)

An advantageous aspect of this technique over other methods is that the capacitance, at a certain applied d.c. potential, can be evaluated directly from the above equation, involving only the current passing immediately prior to opening of the circuit \( t = 0 \), together with the derivative of the potential-decay curve fitting function at \( t = 0 \). The capacitance behaviour of an electrode can be determined for the whole potential range under study, if for a succession of \( \eta \) values, clear noise-free \( \eta \)-time decay curves are recorded along with their respective initial currents passing immediately prior to opening of the circuit.

As will be discussed later in Chapter 4, it is a matter of some interest to compare the values of \( \text{C}_\Phi \) determined at \( t = 0 \) for various initial \( \eta \) values with values derived from the whole decay curve over the same range of \( \eta \) values.

Additionally, it is interesting to point out that fitting of potential relaxation curves recorded on open-circuit, following interruption of a polarizing current of an electrode reaction, also offers the possibility of evaluating \( (\eta)_{t=0} \), from which the uncompensated solution resistance can be evaluated. With \( t = 0 \), Eqn. 49 becomes

\[
\eta_{t=0} = a_0 + a_7 \ln(a_8)
\]

(53)
This approach offers the possibility of a better solution resistance determination, since \( \eta_{i=0} \) can be reliably evaluated using Eqn. (53).

However, the new procedure used in this work can only provide satisfactory results if good noise-free \( \eta(t) \) transients are fitted. Under most conditions, such transients were obtained in nearly all the experiments conducted in this work.

3.4 **A.c. impedance spectroscopy**

Information about the "overpotential-deposited" ad atom species can also be obtained by means of a.c. impedance measurements at controlled potentials. Impedance studies of the h.e.r. in the overpotential region, although relatively few, have been made at several metals, e.g. Gerisher and Mehl\textsuperscript{120} made impedance studies of the h.e.r. at mercury, silver and copper electrodes. Brug et al.\textsuperscript{140} recorded impedance spectra at Au, where no significant adsorption of the kinetically-involved chemisorbed H could be detected during electrolytic \( \text{H}_2 \) evolution. Other experimental impedance studies of the h.e.r. have been reported by Armstrong and Bell\textsuperscript{141}, Breiter, Knorr and Völkl\textsuperscript{88,117}, Durand\textsuperscript{142}, Frumkin et al.\textsuperscript{143}, and Sluyters-Rehbach and Sluyters\textsuperscript{144}. However, the complexity of measurements of impedance during passage of net current in electrode processes, e.g. the h.e.r., requires, frequently, that the experimental data obtained from such experiments be analysed in terms of an "equivalent circuit", i.e. an electrical circuit which is considered to model correctly the electrical behaviour of the electrode interface when its calculated impedance, as a function of frequency, agrees with the experimentally-determined impedance behaviour.

An "ideally polarized" electrode, e.g. Hg in an aqueous acid solution from ca. +0.25 to -1.0 V on the \( \text{H}_2/\text{H}^+ \) scale, has the simplest equivalent circuit since it involves only a
double-layer capacitance and a series solution resistance $R_s$; thus:

\[ \frac{1}{C} \parallel R \]

Since a continuous Faradaic process, such as cathodic $H_2$ evolution, involves charge-transfer across the double-layer, the electrode equivalent circuit must contain additionally a potential-dependent reaction resistance $R_f$, equal to $(RT/i_0F)$, referred to as the charge-transfer resistance, as pointed out earlier (see Eqn. 17). This equivalent circuit, along with other examples and their respective calculated impedances represented in terms of capacitative ($Z''$) vs ohmic ($Z'$) impedance components in complex-plane plots, are given in Fig. 3.1.

Electrode processes involving the adsorption of kinetically-involved adatom intermediates, can, under certain conditions, give rise to two or more arcs in the $Z''$ vs $Z'$ plots, depending on values of the characteristic rate constants involved. An appropriate example is given in Fig. 3.1b where the pseudocapacitance can give rise to the second semi-circle in the complex-plane plot under certain conditions.

Diffusional effects, sometimes involved in Faradaic processes, can also be represented in equivalent circuits in terms of the Warburg impedance element (Fig. 3.1c). In cases where diffusion polarization effects arise, a straight line of 45° slope will be observed in the lower frequency region of the complex-plane plots, which behaviour is electrically simulated by the Warburg impedance component giving a frequency-independent phase-angle of 45°.

Some other processes, usually anodic, can generate a surface film, often leading to passivation. This behaviour can lead to negative resistance and negative capacitance which corresponds to a pseudoinductance giving rise to a loop in the complex-plane plot at low
Plots of capacitance ($Z''$) vs ohmic ($Z'$) impedance components in the complex plane for various types of electrochemical process: (a) a regular reaction with a reaction resistance $R$ at an electrode with double-layer capacitance $C_{dl}$[145]; (b) a two-stage reaction involving, e.g., discharge and another surface reaction[146, 147]; (c) a process involving a reaction resistance $R$ with diffusion Warburg impedance; (d) a process coupled with surface reactions giving instability corresponding to a pseudoinductance[148,149].
frequencies\textsuperscript{146,150,151}. To ease the analysis of impedance spectroscopy results, Macdonald and Potter\textsuperscript{121} have recently developed a very general and flexible complex, nonlinear least-squares fitting program which can be applied to simulate the behaviour of a wide variety of equivalent circuits.

This "intuitive" method of analysis is, however, not always the best approach, since the elements of the experimentally derived equivalent circuit may be trivially identified with parameters of the electrical behaviour of the individual constituent steps of the reaction mechanism, viz. charge transfer resistances, pseudocapacitances associated with adsorption arising from charge transfer, and diffusional impedances. Following the seminal paper by Armstrong\textsuperscript{146,151}, Harrington, Conway and Bai\textsuperscript{115-116} have extended the development of a less arbitrary and more rigorous approach which involves a comparison of the experimentally recorded impedances with those derived kinetically from a theoretical model for a particular reaction mechanism. At controlled d.c. potential, this analysis method would subsequently provide calculated values of the adsorption parameters and assignment of values to rate constants of the constituent steps of the electrode process under study. In the "kinetic" approach to analysis of impedance behaviour, arbitrary equivalent circuit representation are avoided.

These authors applied their treatment particularly to a reaction mechanism involving a single adsorbed intermediate, as in the electrolytic $\text{H}_2$ evolution reaction.

In Chapter one, we mentioned that the h.e.r. is a multi-step process involving first, the discharge of a proton:

$$M(e) + \text{H}_2\text{O} \xrightleftharpoons[k_{f,1}]{k_{b,1}} \text{MH}_{\text{ads}} + \text{OH}^-$$

followed by either an electrochemical

$$\text{H}_2\text{O} + \text{MH}_{\text{ads}} + M(e) \xrightarrow[k_{f,2}]{k_{b}} \text{H}_2 + \text{OH}^- + 2M$$

(23)

(24)
or a chemical desorption step

\[ \text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} \xrightarrow{k_{\text{f,3}}} \text{H}_2 + 2\text{M} \quad (22) \]

Using \( v_1, v_2 \) and \( v_3 \) to denote the net rates (in mol cm\(^{-2}\) s\(^{-1}\)) of steps 23, 24 and 22 in the directions written,

\[
\begin{align*}
\frac{v_1}{v_2} &= k_{f,1}(1-\theta) \exp(\beta FE/RT) - k_{b,1}\theta \exp[-(1-\beta)FE/RT] \\
\frac{v_2}{v_3} &= k_{f,2} \theta \exp(\beta FE/RT) \\
\frac{v_3}{v_3} &= k_{f,3} \theta^2
\end{align*}
\]

then the rates of production of electrons, \( r_0 \), or of adsorbed intermediates, \( r_1 \), can be written as follows:

\[
\frac{i}{F} = r_0 = v_1 + v_2 \quad (57)
\]

and

\[
\left(\frac{q_1}{F}\right) \frac{d\theta}{dt} = r_1 = v_1 - v_2 - 2v_3 \quad (58)
\]

where \( \theta \) is again the fractional surface coverage of the adsorbed intermediate and \( q_1 \) is the charge required to attain monolayer coverage. It is assumed that mass transport is not rate-limiting, making \( r_0 \) and \( r_1 \) explicitly dependent on only \( \theta \) and the electrode potential, hereafter denoted* by \( E \). When a small sinusoidal modulation of potential is applied, both \( i \) and \( \theta \) will also vary sinusoidally, but with different amplitude and phase, as shown in the equations derived similarly to those in Armstrong's treatment\(^{146,151}\):

\[
\begin{align*}
E - E_{ss} &= \Delta E = |\Delta E| e^{i\phi} \\
\theta - \theta_{ss} &= \Delta \theta = |\Delta \theta| e^{i\phi}
\end{align*}
\]

*Here \( E \) is taken as an electrode potential experimentally measured against some reference electrode; it is to be distinguished from the hypothetical single metal-solution interface, \( \Delta \phi \), referred to in Chapter 1.
\[ i - i_{ss} = \Delta i = |\Delta i| e^{j\omega t} \]  

(61)

For small perturbations from the steady-state, the rates may be expanded in Taylor series form, neglecting second and higher order terms:

\[ \frac{i}{F} = r_o = r_{o,ss} + (\partial r_o / \partial E) \theta (E - E_{ss}) + (\partial r_o / \partial \theta) \theta (\theta - \theta_{ss}) \]  

(62)

and

\[ \frac{(q_1/F)d\theta}{dt} = r_1 = r_{1,ss} + (\partial r_1 / \partial E) \theta (E - E_{ss}) + (\partial r_1 / \partial \theta) \theta (\theta - \theta_{ss}) \]  

(63)

For clarity, it is useful to define three parameters A, B and C as follows

\[ A = F(\partial r_o / \partial E) \theta, \]  

(64a)

\[ B = F^2/q_1 (\partial r_1 / \partial \theta) (\partial r_1 / \partial E) \theta \]  

(64b)

and

\[ C = - F/q_1 (\partial r_1 / \partial \theta) \]  

(64c)

From Eqn. (60)

\[ \frac{d\theta}{dt} = \frac{d\Delta \theta}{dt} = j\omega |\Delta \theta| e^{j\omega t} \]  

(65)

Under steady-state conditions, \( r_{1,ss} = 0 \) by definition. Introducing Eqns. (59), (60) and (65) into Eqn. (63), and dividing by \( \Delta E \), one obtains an equation of the form

\[ \frac{\Delta \theta}{\Delta E} = \frac{(\partial r_1 / \partial E) \theta / [j\omega_0 / F + (\partial r_1 / \partial \theta) \theta]}{[j\omega_0 / F + (\partial r_1 / \partial \theta) \theta]} \]  

(66)

The Faradaic admittance, \( Y_f = \Delta i / \Delta E \), may finally be obtained by using Eqns. 59-62 and 64:

\[ Y_f = A + B/(j\omega + C) \]  

(67a)

\[ = \frac{1}{R_{\infty}} + \frac{1}{R_0 (1 + j\omega t)} \]  

(67b)

\[ = \left[ R_{\infty} + 1 / \left( \frac{1}{R_p} + j\omega C_p \right) \right]^{-1} \]  

(67c)

\[ = \frac{1}{R_{\infty}} + 1 / (R_0 + j\omega L_s) \]  

(67d)

\[ = \frac{1}{R_f} + 1 / (R_s + 1 / j\omega C_s) \]  

(67e)

\[ = [R_f + (1/R_L + 1/j\omega L_p)]^{-1} \]  

(67f)

where \( R_{\infty} = 1/A; \tau = 1/C; R_0 = C/B; R_f = C/(CA + B); R_p = -B/A(CA + B); C_p = -A^2/B; \)
\[ L_s = \frac{l}{B}; \quad C_s = \frac{-B}{C^2}; \quad R_s = -R_0 = \frac{-C}{B}; \quad R_L = \frac{-R_p}{B/A(CA + B)}; \quad R_L = \frac{-R_L}{B/(CA + B)^2}. \]

It is clear from Eqns. 64 - 67 that the parameters A, B, and C have a simpler meaning than the equivalent circuit elements, the behaviour of which must usually be represented by complex functions of the kinetic parameters. It is also obvious from the above equations that there could be more than one equivalent circuit in terms of which the impedance behaviour of a particular reaction mechanism could be simulated, e.g. here four equivalent circuits can be adequately used as depicted in Fig. 3.2, but the equations describing the frequency dispersion of their impedance will simply be different forms of the same equation. Consequently, equivalent circuits selected solely on intuitive grounds will not necessarily have any physical meaning, and no correct data interpretation can be made from the simulation of their impedance response, except in the simplest case of a parallel CR circuit or the Armstrong circuit (see below).

In this thesis no simulations made by the kinetic treatment itself are presented but analysis of the impedance spectra by means of Armstrong’s equivalent circuit for one adsorbed intermediate, which is found to be a correct equivalent circuit by the kinetic treatment, will be given.

It is also important to mention that this kinetic treatment, as for any equivalent circuits, cannot be satisfactorily applied to systems in which impedance spectra are affected by surface effects, such as roughness or porosity, unless they are acccounted for in the model used to mimic the impedance behaviour of the electrochemical system under study.
Fig. 3.2 Four equivalent circuits demonstrated to be correct from a kinetic point of view to mimic the impedance behaviour of a reaction mechanism involving one adsorbed intermediate[115].
Therefore, it is sometimes necessary to introduce a constant phase angle element (CPE) in the model used to simulate the true electrode impedance behaviour, e.g.*

\[ Z = A_1 \omega^{-\alpha} + A_2 j \omega^{-\alpha} \]  \hspace{1cm} (68)

Examples of equivalent circuits with the CPE will be considered in a later Chapter.

* This is only one of the possible examples of CPE which are used to mimic the impedance behaviour of electrochemical systems exhibiting the so-called anomalous "frequency dispersion", i.e. an apparent frequency-dependence of the capacitance at the double-layer.
CHAPTER 4

RESULTS

This chapter will be concerned with the analysis of the experimental results derived from measurements on the h.e.r. at several electrode materials investigated in 0.5 M aq. KOH. The results obtained are presented as graphs based on data collected experimentally, which, in some cases, has been processed by a mini-computer.

Several complementary electrochemical methods, as described in Chapter 3, were applied to the various cathode materials studied for the purpose of obtaining the necessary information required for a full kinetic study of the h.e.r. in relation to adsorption of the H intermediate. For example, the value(s) of the Tafel slope(s) and the shapes of the $\eta$ vs $\log i$ plots provide an indication as to which step is rate-determining in the multi-step process.

As indicated in Chapter 1, evaluation of the electrochemical adsorption behaviour of the kinetically-involved intermediates is of major importance, because the extent of the coverage by these chemisorbed adatoms is determined by the reaction mechanism, i.e. if $\theta \ll 1$, a discharge step is rate-determining, while a larger value of $\theta$, up to unity, corresponds to a multistep process with a desorption step being rate-controlling.

In the present kinetic study at various cathode substrates, in addition to the potential relaxation method, impedance spectroscopy has also been applied, but problems of interpretation of the results arise, due to effects which will be discussed in the next chapter. The results obtained by this latter technique were expected to provide complementary information on the rate constants controlling the kinetics of the h.e.r. in alkaline solutions, as was discussed in chapter 3.

For clarity, the experimental results obtained at the several electrode materials
investigated in 0.5 M KOH are presented here in the following sequence: pure Ni, Ni-Mo bulk alloys, Ni-W bulk alloy, electroplated Ni-W and Ni-V. The steady-state polarization and potential decay measurements will be discussed first for the above systems, with treatment of the impedance measurements being given in the next chapter.

4.1 Ni

Before any discussion of the results is presented, it should be indicated that electrode pretreatment is very important in order to obtain reproducible results. In this research project, all-Ni based bulk phase alloys, as well as nickel metal, were subjected to the same pretreatment. The electrodes were first polished, then thoroughly cleaned in an ultrasonic bath using doubly distilled water for 10 minutes. Then, the electrodes were immersed in a KOH solution previously bubbled with H$_2$ while being cathodically pre-polarized. Then the electrodes were polarized so that a current density of 0.1 mA/cm$^2$ was passed, during a time period of 18 hours, before any measurements were made.

4.1.1 Log (current-density) vs potential relations

We first refer to the Tafel relation for the pure Ni metal electrode in 0.5 M aq. KOH in order to characterize the polarization behaviour and to evaluate $C_{\Phi}$, the pseudocapacitance of the adsorbed intermediate H, as $f(\eta)$. Fig. 4.1 depicts the $\eta$ vs log i plot (curve a) experimentally observed at polished Ni at 298 K. As found previously$^{52}$, the $\eta$ vs log i plot exhibits a single Tafel slope, of 120 mV/decade.

4.1.2 Potential relaxation behaviour

It was explained in chapter 3 how the study of the course of potential relaxation in time$^{122,123,127,128,141}$, after interruption of a polarizing current, can give useful information on
Ni in 0.5 M KOH

Slope = 120 mV
decade$^{-1}$

Log (i)/A cm$^{-2}$ : Log (-dn/dt)/V s$^{-1}$

Fig. 4.1 $\eta$ vs log $i$ curve (a) experimentally observed at polished Ni at 298 K, along with curve $\eta$ vs log (-dn/dt). The slope of the Tafel line was estimated as 120 mV decade$^{-1}$, while the various dn/d log(-dn/dt) slopes are 1 120, 2 56 and 3 88 mV decade$^{-1}$. This plot also schematically shows how the C vs $\eta$ profiles are evaluated, following eqn. 45b.
Fig. 4.2 Potential relaxation curves at Ni, digitally recorded immediately after the interruption of a polarizing current and plotted as $\eta$ vs log t. The $d\eta/d\log t$ slopes
both the capacitance behaviour of the electrode interface\textsuperscript{122,123,141}, and the kinetic and mechanistic behaviour of the electrode reaction\textsuperscript{123,127,128}. For electrode processes involving chemisorbed, electroactive intermediates, e.g. H in the H\textsubscript{2} evolution reaction, the capacitance behaviour of the electrode interface exhibits a significant potential-dependence that is attributed to an adsorption pseudocapacitance\textsuperscript{73}. As in the present case, when $\theta$ is not negligible in comparison with 1, the potential relaxation slopes, expressed as $d\eta/d\log t$, differ from the Tafel slopes, $d\eta/d\log i$, over the same potential range in a way\textsuperscript{127,128} characteristic of the reaction mechanism and the potential-dependence of $\theta$.

At polished Ni electrodes, more than one region of the decay kinetics is observed in the $\eta$ vs $\log t$ plot. The initial flat part of the curve in Fig 4.2 corresponds to the region of the potential decay curves where $t \ll \tau$, the constant resulting from the integration of eqn. 40b (see p. 69). For $t > \tau$, the various $\eta(t)$ curves, measured from different initial current densities, all merge into one curve, which has two inflexion points and the slopes of this curve have different values from those of the Tafel relation, indicating an adsorption pseudocapacitance arising from chemisorbed H at the electrode interface that is dependent on potential.

The experimental data acquired during the course of the potential relaxation with time can also be processed by a minicomputer so that quantities, such as $d\eta/dt$, can be conveniently calculated. The plot of $\eta$ vs $\log (-d\eta/dt)$, as derived in eqn. 42, reveals two regions of the kinetics of decay, whereas the Tafel plot exhibits only a single slope, as is apparent in Fig. 4.1.

The significant difference in behaviour of these two plots will be reflected in the $C$ vs $\eta$ profile (Fig. 4.3), since $C$ can be expressed as the ratio, $i(\eta)/(-d\eta/dt)$, as derived in eqn. 45a. The dependence of $C$ on $\eta$ can also be represented graphically as in Fig. 4.1, since

$$\log (C_\phi + C_{dl}) = \log (C(\eta)) = \log i(\eta) - \log (-d\eta/dt)$$

(45b)
In agreement with what was previously measured in this laboratory, the plot of $C$ vs $\eta$ exhibits a maximum, as in fact is expected theoretically. Integration of the $C_0$ vs $\eta$ profile gives the electrochemical adsorption behaviour of the kinetically involved H in terms of the variation of coverage of the H adatoms with $\eta$, which reveals that at Ni a limiting coverage of approximately 0.1 is reached at high overpotentials, as depicted in Fig. 4.4. The purpose of including these results here is not to repeat what was previously done in this laboratory, but to compare the results obtained by this method with those derived by a new treatment of the potential relaxation curves, to be discussed below, and to make comparisons with the behaviour at other electrode materials.

4.1.3 **Initial potential decay rate, $(dn/dt)_{t=0}$, following current interruption**

Early attempts to evaluate the "differential capacity" associated with the h.e.r. at nickel electrodes had been made by measuring the initial rate of decay of $\eta$, $[(dn/dt)_{t=0}]$ with an analogue oscilloscope. In earlier work, the capacitance values obtained by this method were already found to be quantitatively different to those obtained by means of the rate of decay, $dn/dt$, read from the decay curve at any $\eta$. The capacitance was found to be not only a function of $\eta$ but also a function of the $\eta$ value prior to interruption of the current. However, at the time of that earlier work, $[(dn/dt)_{t=0}]$ could not be digitally evaluated owing to the unavailability of suitable instruments. Here, we introduce for the first time, a new method of analysis of the kinetics of the decay of $\eta$, immediately following the opening of the circuit. This new treatment, as was described in section 3.3, is based on fitting the digitally recorded $\eta(t)$ curves with an appropriate empirical function, which can later be accurately differentiated and evaluated at $t=0$. As pointed out earlier, a difference between the $C$ values obtained by this treatment and the one referred to in the previous section is observed. This difference, which may possibly be accounted for by hydride formation, is
Fig. 4.3 Capacitance C vs overpotential, η, derived by the two different treatments of the potential relaxation curves after the interruption of a polarizing current, and by a.c. impedance spectroscopy during cathodic evolution of H₂ at Ni.
Fig. 4.4 Coverage of θ(H) vs overpotential, η during cathodic evolution of H₂ at a polished Ni electrode in 0.5 M KOH. These plots have been derived by integration of the Cφ vs η profile from the previous figure.
however not as important as what was observed for the Ni-Mo alloys, to be described later. Since the $C_{\text{vs}}$ vs $\eta$ profiles evaluated by the two methods are different, so is the derived electrochemical adsorption behaviour, as depicted in Fig. 4.4.

Another transient method, i.e. a.c. impedance spectroscopy, has also been applied at the Ni electrode. Only one relaxation time constant was experimentally observed in the potential range under study, i.e. -50 to -500 mV, which means that a unique semicircular arc, lying on the ohmic resistance axis, is always observed in the "complex-plane plots", (the same applies to the Ni-Mo bulk phase alloys). Unfortunately, angular depression of the $z'$diameter of the measured semi-circle below the $z'$ axis is observed, which introduces a complication in the interpretation of the impedance response of Ni under conditions of H$_2$ evolution, as will be discussed in more detail in chapter 5.

Nevertheless, the impedance spectra, measured at various applied "d.c." potentials during the h.e.r. clearly reveal a single relaxation time constant at nickel, which indirectly means that the sum of both $C_{\text{dl}}$ and $C_{\phi}$ are simultaneously measured by the initial potential decay rate method, as experimentally observed. If two or more relaxation times would have been detected by a.c. impedance spectroscopy, then only the $C_{\text{dl}}$ would be evaluated by the method using $(d\eta/dt)_{t=0}$, since it is expected to be discharged first.

4.2 Ni-Mo bulk alloys

The atomic compositions of the Ni-Mo alloys studied were chosen in a region of the phase diagram where these binary alloys are known to form an homogeneous solid solution, as depicted in Fig. 1.7.
4.2.1 \textbf{Log (current-density) vs potential relations}

The Tafel relations for the various homogeneous Ni-Mo bulk alloys are illustrated in Fig. 4.5. In agreement with what was found previously\textsuperscript{154}, two regions are observed in the log (current-density) vs overpotential plots. At low overpotentials, a somewhat high slope region is observed, followed by a lower slope region at higher overpotentials. The various slopes, as well as the extrapolated exchange currents densities for the Ni-Mo bulk alloys are listed in Table 4.1, together with the chemical compositions of the binary Ni-Mo alloys.

Table 4.1 records the Tafel slopes at low and high overpotentials, as well as the corresponding extrapolated exchange current densities, for the various Ni-based bulk phase alloys.

It is interesting that the greater is the atomic percent of Mo in the binary alloy, the higher is the slope of the $\eta$ vs log $i$ plot at low overpotentials. Mo is known to adsorb H more strongly than nickel, as depicted in Fig. 1.5, and this could be the origin of the observed slope change with increase of Mo concentration in the low overpotential range, as will be conclusively discussed in more detail in a later section.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Composition of the alloy in atomic percent & $b_{\text{low}}/(\text{mV decade}^{-1})$ & $i_0, \text{ low}/(\mu\text{A cm}^{-2})$ & $b_{\text{high}}/(\text{mV decade}^{-1})$ & $i_0, \text{ high}/(\mu\text{A cm}^{-2})$ \\
\hline
Ni-Mo (99:1) & 145 & 6.9 & 121 & 2.5 \\
Ni-Mo (93.8:6.2) & 152 & 10 & 124 & 3.3 \\
Ni-Mo (88:12) & 168 & 13.6 & 118 & 1.7 \\
Ni-W (90:10) & 120 & 2.3 & 102 & 0.81 \\
\hline
\end{tabular}
\caption{Steady-state polarization performance parameters, $i_0$ and $b$, for bulk phase Ni-Mo and Ni-W alloys during the h.e.r. in 0.5 M KOH}
\end{table}
Fig. 4.5  Plots of Tafel relations measured at various homogeneous Ni-Mo bulk alloys illustrating how the $\frac{d\eta}{d\log i}$ slopes in the low $\eta$ regions depend on the chemical composition of the binary alloys.
4.2.2 Potential relaxation behaviour

The digitally acquired, potential relaxation data are shown as f(log (t)) in Fig 4.6 and as f(log (-\(d\eta/dt\))) in Fig. 4.7. Since the experimental data are similar at the three alloys, only the data for the alloy containing 6.2 atomic percent of Mo are presented here for these latter plots. Similarly to what was observed at Ni, the kinetics of the potential decay involve more than one region at these Ni-Mo alloys. The initial flat part of the curve in the \(\eta\) vs log t plot corresponds to the region where \(t \ll \tau\), and is always expected to be observed no matter what is the chemical composition of the electrode material. As the overpotential is decaying, the various \(\eta(t)\) curves measured from different initial current densities all merge into a single curve which has a slope value, 78 mV decade\(^{-1}\), differing from the Tafel one, which is the normal situation at electrode materials where the pseudocapacitance by o.p.d. H is significant.

At these three alloys, large capacitance values are found by this treatment of the potential relaxation curves, as recorded in Fig. 4.8.

4.2.3 Initial potential decay rate, \((d\eta/dt)_{t=0}\) following current interruption

The "differential capacities" evaluated by this treatment at "\(t = 0\)" are significantly different in magnitude from the values obtained using rates of decay, \(d\eta/dt\), read from the decay curve at any \(\eta\). The evaluated capacitance profiles, as a function of overpotential, obtained from the initial potential decay rate, \((d\eta/dt)_{t=0}\), following the interruption of a polarizing current, are shown in Fig. 4.9. The latter plots reveals that the more molybdenum there is in the binary alloy, the larger is the pseudocapacitance due to the chemisorbed H intermediate. The coverage vs potential relations for the kinetically involved H adatoms can be obtained by integration of the respective C vs \(\eta\) profiles. The extent of coverage by o.p.d.
A polished bulk Ni-Mo (93.8:6.2) alloy in 0.5 M KOH

Fig. 4.6 The potential relaxation curves, plotted as $\eta$ vs log(t), as digitally acquired immediately after interruption of currents for the cathodic $H_2$ evolution at bulk Ni-Mo (93.8:6.2) alloy.
A polished bulk Ni-Mo (93.8:6.2) alloy in 0.5 M KOH

Fig. 4.7 Illustrating the three following relations at a polished bulk Ni-Mo (93.8:6.2) alloy: (a) steady-state polarization behaviour plotted as $\eta$ vs $\log i$ along with (b) $\eta$ vs $\log (-d\eta/dt)$, where $d\eta/dt$ is read from the decay curve at any $\eta$, and (c) the $\eta$ vs $\log (-d\eta/dt)_{t=0}$ line derived from the method of fitting the decay curves to an empirical polynomial in $t$. 
Derived from the decay curve at any \( \eta \).

Ni-Mo bulk phase alloy in 0.5 M KOH

Fig. 4.8 Capacitance vs \( \eta \) profile for the Ni-Mo (93.8:6.2) bulk phase alloy (similar results were obtained for all three alloys) evaluated by means of rate of decay, \( d\eta/dt \), read from the whole decay curve at any \( \eta \).
Derived from the initial rate of decay of $\eta \left(\frac{d\eta}{dt}\right)_{t=0}$.

A plot of the evaluated capacitance profiles with overpotential at the three bulk phase Ni-Mo alloys, obtained by the analysis of the initial potential decay rates, $(d\eta/dt)_{t=0}$, following the interruption of polarizing currents, and by a.c. impedance spectroscopy.
Fig. 4.10 Coverage of $\theta$(H) vs overpotential $\eta$ for the h.e.r. at three Ni-Mo binary alloys having different elemental compositions.
H is again found to be dependent on the Mo concentration in the binary alloy as shown in Fig. 4.10.

4.2.4 Hydride at Ni-Mo bulk alloys

The question arises why is there such a large difference between the capacitance values evaluated by the two treatments of the potential relaxation curves at bulk phase Ni-Mo alloys? The results obtained by the two methods were first analysed and compared and the conclusion was reached that the major difference originates from the $dn/dt$ values.

Fig 4.7 shows that, as the potential is decreasing, the difference between the $(dn/dt)$ values derived by the two methods (for a given potential) is increasing. This may be rationalized as follows: as the potential is decreased, adsorbed atomic H species, stable at more negative potentials, become oxidized. Such species could very well originate from H that had been diffusing in the crystal lattice, as an hydride, during the electrolytic evolution of $H_2$ at more negative potentials. This receives further support from the fact that all three Ni-Mo bulk alloys, as well as the Ni-W bulk phase alloy (results to be shown later), give similar C vs $\eta$ profiles evaluated by means of the method based on the rate of decay, $dn/dt$, read from the whole decay curve at any $\eta$ and that the $dn/dt$ difference starts to increase from high overpotentials towards lower values, i.e. from approximately 300 mV, where the electrode metal is well cathodically protected. The slopes of the $\eta$ vs log $(-dn/dt)$ relations seem to depend on the applied $\eta$ prior to opening of the circuit, and this is especially pronounced at overpotential values below 0.3 V, as depicted in Fig. 4.11. Also Fig. 4.12 reveals that the C values derived from the rate of the decay, $dn/dt$, read from the decay curve at any $\eta$, depend for the Ni-Mo materials on the initial applied overpotential or the corresponding current-density. This latter phenomenon has also been observed in this laboratory$^{130}$ at electrodeposited Pt and Pt-Pd, for which the large C values observed can
Fig. 4.11 Effect of the applied overpotential, prior to current interruption, on the slopes of the $\eta$ vs log ($-\Delta\eta/dt$) relations at a bulk phase Ni-Mo (93.8:6.2) alloy.
Fig. 4.12 Plots of $C_0 + C_{dl}$ vs $\eta$ derived from the rate of decay, $d\eta/dt$, read from the whole decay curve of any $\eta$, for various $\eta$ values prior to opening of the circuit at a Ni-Mo (93.8:6.2) bulk phase alloy.
only be accounted for by formation of an hydride\textsuperscript{155}.

The possibility that these differences arise from a surface oxidation process must also be recognized since it is conceivable that corrosion of the electrode studied can take place during the decline of potential towards the reversible potential for the h.e.r., and could therefore give rise to observed $C_\phi$ values that are anomalously large by releasing electrons which would reduce the rate of decay of potential, $dn/dt$.

A corrosion experiment was therefore made at a Ni-Mo (88:12) alloy, three samples of which were analysed by concentration depth profiling in an Auger spectrometer\textsuperscript{*}:

(i) Sample 1 was polished only.

(ii) Sample 2 was polished and then immersed for 24 hrs in a 0.5 M KOH solution at 298 K.

(iii) Sample 3 was polished and then immersed for 24 hrs in a 0.5 M KOH solution at 298 K, in which it was cathodically polarized at -100 mV, RHE.

The concentration depth profiles, for each sample, revealed a depressed concentration of Mo at the very surface relative to that of nickel, as well as the presence of a significant oxide film at the outer layers. For all the sputter profiles, a 4 kV Ar\textsuperscript{+} ion current of 10 \mu\text{A} cm\textsuperscript{-2} at an incidence angle of 37° was used. The occurrence of a suppressed Mo signal for all three samples may be due to one of the following three conceivable effects. Firstly, the Mo Auger electrons, being lower in energy than those of Ni, are more suppressed by the unavoidable oxide "contamination" layer at the very surface. Secondly, there might be some preferential oxidation of Ni which would result in some segregation of it to the surface.

\textsuperscript{*}The measurements were performed at ALCAN International Ltd, Kingston, by Dr. Ross Underhill.
Thirdly, Ni may sputter preferentially to Mo, which means that as sputtering starts Ni will be depleted until a steady state is achieved. If this is the case, the steady state would be established in ca. 2 minutes.

Fig. 4.13 depicts an elemental survey of the sample 1 surface in d N(E)/dE form.

Fig. 4.14 depicts the raw data of a sputter profile done on sample 1 (peak to peak intensity of the dN(E)/dE vs sputter time). From this graph, it can be concluded that there is a significant oxide film at the outer layers of the bulk alloy.

Figs. 4.15 to 4.17 show the sputter profiles for samples 1 to 3, plotted as the Ni and Mo atomic percent vs sputter time. It can be noticed from these sputter profiles that the atomic percent Mo is somewhat more depressed in the case of sample 2, indicating possible leaching out of Mo when no negative potential is applied. It is also important to keep in mind that during the potential decay experiments, the sample is still cathodically protected until the decaying potential approaches the mixed potential for corrosion near the reversible potential for H2 evolution. This latter point, along with what was said earlier about the dependence of C on the initial η, an effect that was also observed at Pd (a metal that is well known to form hydrides) practically rules out the possibility that corrosion could be the sole reason for the large capacitances measured at the Ni-Mo alloys by the method in which the rate of decay, dη/dt, is read from the decay curve at any η. Therefore, it is felt by the author of this thesis that only the oxidation of an hydride, electrolytically produced at the Ni-Mo alloys during the h.e.r., is left as an explanation for the anomalously large capacitance values experimentally measured. After all, it is not unreasonable to suppose that adsorbed H adatoms produced at the surface, tend to diffuse through the grain boundaries of the polycrystalline material or into the crystal lattice of the bulk alloy itself, given that large concentration gradients of H adatoms must exist from the surface to the bulk. It is also important to indicate here, that besides works done in our group on hydride formation,
Fig. 4.13 Elemental survey of the Ni-Mo (88:12) polished surface in dN(E)/dE form (the data were actually recorded in the distribution of energy form, N(E), which was then numerically differentiated).
Fig. 4.14 Plot of the raw data of a sputter profile done on the Ni-Mo (88:12) polished surface
(peak to peak intensity of the dN(E)/dE vs sputter time).
Fig. 4.15 The sputter profile of the Ni-Mo (88:12) bulk phase alloy, which was polished only, plotted as the Ni and Mo atomic percent vs sputter time.
Figure 4.16: The sprout profile of the Ni-Mo (88:12) bulk phase alloy, which was polished and then immersed for 24 hrs in a 0.5 M KOH solution, plotted as the Ni and Mo atomic percent vs sprout time.
The Ni and Mo atomic percent vs. sputter time.

Then cathodically polarized at -100 mV for 24 hrs in an 0.5 M KOH solution, plotted as

Fig. 4.17. The sputter profile of the Ni-Mo (88:12) bulk phase alloy, which was polished and

Sputter Time/min.

Composition, Atomic %
others have also proposed the existence of hydrides at Ni-Mo alloys.

4.3 **Ni-W (90:10) bulk alloy**

Once again, in order to achieve reproducible and meaningful results, the elemental composition of the bulk phase alloy was chosen in a region where the binary alloy forms an homogeneous solid solution, as depicted in the phase diagram for this alloy (Fig. 1.7).

4.3.1 **Log (current-density) vs potential relation**

The log(current)-potential relation (Fig 4.18) for the h.e.r. at bulk phase Ni-W (90:10) alloy, in 0.5 M KOH at 298K, exhibits two distinct regions characterized as follows: at low overpotentials, a slope of 120 mV decade$^{-1}$ is observed, followed by a region of somewhat lower slope (100 mV decade$^{-1}$) at higher overpotentials. The exchange current densities corresponding to the extrapolation of the low and high overpotential regions of the Tafel relation are respectively 2.3 and 0.81 $\mu$A cm$^{-2}$. Although the kinetic parameters for Ni-W differ from those for Ni-Mo electrodes, the sequence of the high and low slope regions in the Tafel plots is the same, possibly because the same reaction mechanism applies for both electrode substrates. This similarity in the polarization behaviour of these materials is indeed not very surprising since both W and Mo belong to the same group in the Periodic Table of the elements.

4.3.2 **Potential relaxation behaviour**

The potential-relaxation transients for the h.e.r. at the bulk phase Ni-W (90:10) alloy, are plotted as $\eta$ vs log (t) and $\eta$ vs log (-d$\eta$/dt) in Figs. 4.19 and 4.20, respectively.
Ni-W (90:10) bulk phase alloy in 0.5 M KOH.

Slope = 120 mV

Slope = 100 mV

Fig. 4.18 Plot of log (current-density) vs overpotential for the h.e.r. at bulk phase Ni-W (90:10) alloy, in 0.5 M KOH at 298 K.
Fig. 4.19 Plot of the decay of potential with time, $\eta$ vs log $t$, following interruption of current at several different cathodic current densities for the bulk phase Ni-W (90:10) cathode.

Ni-W (90:10) bulk phase alloy in 0.5 M KOH.
Ni-W (90:10) bulk phase alloy in 0.5 M KOH

Slope = 64 mV

Slope = 106 mV

Fig. 4.20 Plot of log (-d\eta/dt) vs \eta for the bulk phase Ni-W (90:10) cathode, where d\eta/dt is read from the whole decay curve at any \eta.
The plot of \( \eta \) vs \( \log(t) \) reveals two distinct regions. At low \( \eta \) values, a slope of -64 mV is measured, which is very different from the Tafel slope of 120 mV for the same potential region, implying that large capacitances will arise when evaluated by this method.

Similarly, the plot of \( \eta \) vs \( \log(-d\eta/dt) \) reveals two regions of the decay of kinetics: (i) at high \( \eta \) values, a slope of approximately 106 mV is evaluated, similar to the value of the slope of the Tafel relation, and (ii) at low \( \eta \) values, the \( \eta \) vs \( \log(-d\eta/dt) \) slope is 64 mV decade\(^{-1}\), which is significantly different from the \( b \) value of the corresponding \( \eta \) vs \( \log(i) \) plot, over the potential region where \( C \) varies appreciably with \( \eta \), as shown in Fig. 4.21.

The \( C \) vs \( \eta \) profile, derived from the decay rate, \( d\eta/dt \), read from the transient curve at any \( \eta \), reveals that the capacitance of the electrode interface is constant at high \( \eta \) values, where only \( C_{dl} \) is significant, while \( C \) reaches a maximum at large values, approximately 4 mF cm\(^{-2}\), at lower overpotentials.

**4.3.3 Initial potential decay rate, \((d\eta/dt)_{t=0}\), following current interruption**

Here, for a better understanding of the results obtained by this potential relaxation treatment, a brief description of the a.c. impedance behaviour of Ni-W has first to be made, although the results obtained by this technique will be fully discussed in a later part of this thesis (Chapter 5). It was indicated earlier (p. 91) that Ni and Ni-Mo alloys have impedance responses characterized by a single relaxation time, corresponding to only one semi-circular arc being observed in their respective complex-plane plots. For electrode materials exhibiting this kind of impedance behaviour, the initial potential decay rate, \((d\eta/dt)_{t=0}\), will contain information pertaining to both the double-layer capacitance, \( C_{dl} \), and the pseudocapacitance, \( C_\phi \), of the adsorbed intermediate. However, for electrochemical behaviour where more than one relaxation time is distinguished by a.c. impedance spectroscopy, e.g. at Ni-W, during the h.e.r., \( C_{dl} \) is very likely to be the only quantity
Ni-W (90:10) bulk phase alloy in 0.5 M KOH.

Fig. 4.21 Plot of the total interfacial capacitance vs $\eta$ at a polished bulk phase Ni-W (90:10) alloy, evaluated by means of the decay rate, $d\eta/dt$, read from the whole decay curve at any $\eta$. 
measurable by the treatment using the initial potential decay rate. Hence, although appreciable coverage by o.p.d. H may be present at the Ni-W alloy, only the $C_{dl}$ is measured when C is derived from the treatment based on the initial potential decay rate measurements. The experimental results obtained by this latter treatment are plotted in Fig. 4.22 and, although they are unproductive for the evaluation of o.p.d. H behaviour, these results are still of substantial significance for the electrode kinetic study of the h.e.r., as will be discussed in a subsequent section, 4.4.3.

4.3.4 Corrosion test at Ni-W bulk phase alloy

The question arises why are such large C values obtained by the first decay treatment? The anomalously large C values cannot unambiguously be attributed to hydride oxidation during the decay of potential, unless corrosion of the electrode at its surface can be ruled out. This is why the following corrosion test, similar to the one done at the Ni-Mo (88:12) alloy (see p. 103), was conducted at the Ni-W bulk phase alloy under study.

Three samples, pretreated as follows, were analysed by concentration depth profiling:

(i) Sample 1 was polished only.

(ii) Sample 2 was polished and then immersed for 24 hrs in a 0.5 M KOH solution.

(iii) Sample 3 was polished and then immersed for 24 hrs in a 0.5 M KOH solution, in which it was cathodically polarized at -100 mV.

Similarly to what was observed at the Ni-Mo alloy, the concentration depth profiles for each sample, revealed a depressed concentration of W at the very surface relative to that for nickel, as well as the presence of a significant oxide film at the outer layers. The fact that all three samples show an "apparent" depletion of W at the surface cannot be attributed to corrosion since at no point was sample 1 immersed in a corrosive medium, but the effect...
Fig. 4.22 Plots of the $C_{dl}$ vs $\eta$, for both bulk phase and electroplated Ni-W, obtained from the initial potential decay rate, $(d\eta/dt)_{t=0}$, following interruption of the polarizing current.
could be due to one of the unwanted processes discussed in subsection 4.2.4. However, a comparison between sample 2 and 3 with sample 1 (taken as the standard) reveals no major differences, except for a slight depletion of W, in the case of immersed samples that were not cathodically protected.

Fig. 4.23 depicts the elemental survey of the sample 1 surface in dN(E)/dE form.

Fig 4.24 depicts the raw data of a sputter done on sample 1 (peak to peak intensity of the dN(E)/dE vs sputter time). From this graph it can be concluded that there is a significant oxide film at the outer layers of the bulk alloy, as at the Ni-Mo one.

Figs. 4.25 to 4.27 show the sputter profiles on samples 1 to 3, plotted as the Ni and W atomic percent vs sputter time. It is noticed from these profiles that the atomic percent of W is somewhat more depressed at sample 2, indicating possible leaching out of W when no negative potential was applied. Since, in the potential relaxation experiments, the electrode material is cathodically protected until the decaying potential approaches the mixed corrosion potential near the reversible potential for H₂ evolution, and because the C values are already anomalously large at potentials as negative as -150 mV, it is felt again that corrosion of the surface of the Ni-W surface cannot account, in the present case, for the large capacitances evaluated by the potential decay treatment in which dη/dt is read over the whole η(t) curve at any η.

4.4 Electrodeposited Ni-W alloy

The procedure used to electroplate this Ni-W alloy was described in chapter 2. The elemental composition of the Ni-W (92:8) electrocoated film was determined by x-ray emission analysis in a S.E.M.
Fig. 4.23 Elemental survey of the Ni-W (90:10) polished surface in dN(E)/dE form (the data were actually recorded in distribution of energy form, N(E), which was then numerically differentiated).
Fig. 4.24 Plot of the raw data of a sputter profile done on the polished Ni-W (90:10) bulk phase alloy (peak to peak intensity of the dN(E)/dE vs sputter time.)
Fig. 4.25 The sputter profile of the Ni-W (90:10) bulk phase alloy, which was polished only, plotted at the Ni and W atomic percent vs sputter time.
The sputter profile of the Ni-W (90:10) bulk phase alloy, which was polished and then
immersed for 24 hrs in a 0.5 M KOH solution, plotted as the Ni and W atomic percent.

Figure 4.26
Ni and W atomic percent vs. sputter time.

Cathodically polarized at -100 mV for 24 hrs in a 0.5 M KOH solution, plotted as the sputter profile of the Ni-W (90:10) bulk phase alloy, which was polished and then...
4.4.1 Log (current-density) vs potential relations

The electrochemically active surface area was evaluated by comparing the $C_{dl}$ of the sample with that of the polished Ni-W bulk phase alloy. The surface roughness, i.e. the real to apparent surface ratio, was thus evaluated as 60. The area and IR drop-corrected steady-state polarization behaviour of the electroplated Ni-W, depicted in Fig. 4.28, appears to be significantly different from the plot of log(current density) vs potential at the Ni-W bulk phase alloy. This electroplated alloy is characterized by a Tafel line having a slope of 75 mV·decade$^{-1}$, with an extrapolated exchange current-density of 0.65 μA cm$^{-2}$. At current-densities greater than 10$^{-2}$ A cm$^{-2}$ or overpotentials larger than 300 mV, diffusion limitation appears to become significant giving rise to a positive deviation of the Tafel line.

4.4.2 Potential relaxation behaviour

In the $\eta$ vs log $t$ plot depicted in Fig. 4.29, the various $\eta(t)$ curves measured from different initial current densities all merge into one curve which has a slope of $-52$ mV decade$^{-1}$ at low overpotentials, appreciably different from the Tafel slope over the same potential region, so that a significant potential dependence of $C$ should be observed. The plot of $\eta$ vs log (-d$\eta$/dt), as derived in eqn. 42, reveals two regions of the kinetics of decay (see Fig 4.30): (i) at high $\eta$ values, a decay slope of 78 mV decade$^{-1}$ is observed and this value is approximately the same as the Tafel slope (no dependence of $C$ on $\eta$ is observed in this potential region); (ii) at low $\eta$ values, a decay slope of 50 mV decade$^{-1}$, different from the Tafel one, indicates that $C$ will certainly depend on $\eta$. Not surprisingly the plot of $C$ vs $\eta$, depicted in Fig. 4.31, reveals that at low overpotential, $C$ varies appreciably with $\eta$, reaching a maximum of about 7 mF cm$^{-2}$, while at higher overpotentials, $C$ remains constant at a lower value, probably corresponding to the double-layer capacitance.
Electrodeposited film of Ni-W in 0.5 M KOH.

Fig. 4.28 Tafel polarization line for the h.e.r. at an electrodeposited film of Ni-W (92:8).
Fig. 4.29 Plot of η vs log t for several η(t) curves collected at different cathodic current densities for the Ni-W (92:8) electroplated composite.
Fig. 4.30 Plot of $\eta$ vs $\log(-d\eta/dt)$ for the Ni-W (92:8) electroplated composite in 0.5 M KOH, where $d\eta/dt$ is read from the whole decay curve at any $\eta$. 

Slope = 78 mV
Slope = 50 mV
Electrodeposited film of Ni-W in 0.5 M KOH.

Fig. 4.31 Plot of C vs $\eta$ evaluated during electrolytic H$_2$ evolution at the electrodeposited Ni-W (92:8) alloy, using the rate of decay, $d\eta/dt$, read from the whole decay curve at any $\eta$. 
4.4.3 Initial potential decay rate, \((d\eta/dt)_{t=0}\), following current interruption

At electrodeposited Ni-W, as was observed at the bulk phase alloy, the potential decay rate, \((d\eta/dt)_{t=0}\), immediately following the opening of the circuit, contains only information pertaining to the double-layer capacity. As explained earlier, this arises at electrode materials for which more than one relaxation time can be detected by means of a.c. impedance spectroscopy. The results obtained by this potential decay treatment (see Fig. 4.22), although somewhat less informative regarding o.p.d. H behaviour, still have their significance in electrochemical studies, as mentioned already in 4.3.3, e.g. for real area evaluation from the double-layer capacitance.

4.5 Electrodeposited Ni-V alloy

The Ni-V alloy was electrodeposited onto an Fe wire according to the plating procedure described in chapter 2. The elemental composition of the Ni-V (94.5:5.5) electrocoated film was determined by x-ray emission analysis in a S.E.M.

4.5.1 Log (current-density) vs potential relations

Assuming that the \(C_{dl}\) value for this electro-coated material, is similar to that for pure nickel (since no bulk reference of similar chemical composition was available for comparison of the \(C_{dl}\) values), the real to apparent electrochemically active surface ratio was arbitrarily estimated as 95, based on comparison with the \(C_{dl}\) value for Ni. In Fig. 4.32, which shows the area-, and solution-resistance corrected plot of the log (current-density) vs potential relation for the Ni-V electroplated composite material, only a single slope relation arises. The Tafel slope is 110 mV decade\(^{-1}\) and the extrapolated exchange current density is approximately 5.3 µA cm\(^{-2}\). This same plot also indicates that diffusion, possibly of H, starts
Electrodeposited Ni-V alloy in 0.5 M KOH.

Slope $= 110 \text{ mV}$

Fig. 4.32 Plot of log (current-density) vs overpotential for an electrodeposited Ni-V (94.5:5.5) alloy measured during the cathodic evolution of $\text{H}_2$. 
to influence the steady-state polarization behaviour of this alloy at about -380 mV, on the hydrogen reference electrode scale or some increased component of recombination control.

4.5.2 Potential relaxation behaviour

The digitally acquired potential relaxation data are shown as $f(\log(t))$ in Fig. 4.33 and as $f(\log(-d\eta/dt))$ in Fig. 4.34.

The initial flat part of the curve in Fig. 4.33 where $t \ll \tau$, is followed by a linear region having a slope of $-71 \text{ mV decade}^{-1}$, where the various $\eta(t)$ curves, measured from different initial current densities, all merge into a single curve as in other cases discussed in previous paragraphs. Since the $d\eta/d\log t$ slope differs from the Tafel slope, $d\eta/d\log i$, over the same potential range, a potential-dependence of the capacitance behaviour of the electrode interface can be anticipated over the same potential region.

The plot of $\eta$ vs $\log(-d\eta/dt)$ further supports the latter expectation, since the single region of the kinetics of decay is characterized by a decay slope, $70 \text{ mV decade}^{-1}$, that differs from the $d\eta/d\log i$ slope, as shown in Fig. 4.34. For this, a surprising fact arises, i.e. a continuous dependence of $C$ on $\eta$ arises over the whole potential range, as depicted in Figs. 4.35 and 4.36. It should also be mentioned here that the slope of $\log C$ vs $\eta$ line depends on the initial current density passing prior to the opening of the circuit. This latter observation indicates once more the possible involvement of hydride oxidation during the potential relaxation process.

4.5.3 Initial potential decay rate, $(d\eta/dt)_{t=0}$ following current interruption

As was found with the Ni-W alloys, the behaviour of electrodeposited Ni-V is characterized by two distinguishable relaxation times, implying again that the only quantity measurable from the initial potential decay rate, $(d\eta/dt)_{t=0}$, is the double-layer capacity, as
Electrodeposited Ni-V alloy in 0.5 M KOH.

Fig. 4.33 Plots of $\eta$ vs log t for several $\eta(t)$ curves collected at different cathodic current densities for the Ni-V (94.5:5.5) electroplated composite.
Electrodeposited Ni-V alloy in 0.5 M KOH.

Slope = 70 mV

Log (-dη/dt)/V s⁻¹

Overpotential/V

Fig. 4.34 Plot of η vs log (-dη/dt) for the electroplated Ni-V (94.5:5.5) composite in 0.5 M KOH, where dη/dt is read from the whole decay curve at any η.
Fig. 4.35  Plot of the $C \text{ vs } \eta$ evaluated at the electrodeposited Ni-V (94.5:5.5) alloy by the potential decay method, using the rate of decay, $d\eta/dt$, read from the whole potential relaxation curve at any $\eta$. 
Electrodeposited Ni-V alloy in 0.5 M KOH

Fig. 4.36  Plot of the log C vs \( \eta \), evaluated at an Ni-V (94.5:5.5) electroplated composite (note the linear relationship).
illustrated in Fig. 4.37. The results obtained by this method for this case therefore have the same limitation as that discussed for the other cases earlier.

4.6 Problems in a.c. impedance measurements and interpretation

The reader of this manuscript must wonder why the results obtained by a.c. impedance spectroscopy have been kept separate from the ones obtained by the other electrochemical methods. The answer is because, during the course of the present research project, a non 90° phase shift of the current response to a sinusoidally modulated voltage was measured, meaning in other words that the a.c. impedance spectra plotted as semi-circles in the complex-plane plots were "depressed" below the z' axis. Hence a full discussion on this anomaly, and what we believe gives rise to it, needs to be made first, before the reader can clearly understand the approach taken in the present work to analyse the a.c. impedance results.
Electrodeposited Ni-V alloy in 0.5 M KOH

Fig. 4.37 Plot of the C_{dl} vs η. (The C values have been obtained by the initial potential decay rate, (dη/dt)_{t=0}, following the interruption of a polarizing current and normalized so that the apparent C_{dl} value would correspond to the one measured at a polished Nickel sample.)
5.1 Rotation of the $Z'$ or $Z''$ semi-circle plots in the complex-plane

During the course of this research in the h.e.r. at various metals, it was experimentally observed in many instances (e.g. for Ni and Ni-Mo alloys), that the plots of impedance behaviour in the complex-plane are (in the usual way) semi-circles, but with their centres lying beneath the real ($Z'$) axis, as shown in Fig. 5.1. Such a rotation has been observed not only for the h.e.r., but also for the case of oxygen evolution kinetics at noble metals\textsuperscript{157} and nickel, and for the Kolbe reaction of acetate at platinum\textsuperscript{158}. Similar rotations have been observed with the impedance behaviour of dielectric materials\textsuperscript{159,160} and they have been attributed, in those cases, to a distribution of relaxation times in the system, although the physical meaning of this effect has not yet been completely clarified. These impedance spectra plots in the complex plane may be looked upon as semi-circles rotated in the clockwise sense around the origin by a certain angle, $\phi$.

In this section, a detailed discussion will be presented concerning the significance of the rotation of the semi-circle plots since it is felt that no proper interpretation of the impedance measurements can be achieved unless this rotation phenomenon is better understood.

The factors influencing charge-transfer across an interface between two dissimilar substances, e.g. a metal electrode and an aqueous or a solid electrolyte, still remain incompletely understood today. However, it is well known that the electric current, at an applied potential, encounters Ohmic resistance ($R$) in both phases and a capacitance ($C$) across the interface. Unfortunately, such an interface rarely has the a.c. response of a simple
Fig. 5.1a Experimental impedance diagrams measured at Ni at various current-densities. The data plotted in the complex-plane are semi-circles but with their centres lying below the real axis on a common line.
Fig. 5.1b Experimental impedance diagrams measured at the bulk phase Ni-Mo (93.8:6.2) alloy at various current-densities. The data plotted in the complex plane are semi-circles with their centres lying under the real axis on a common line.
"RC" circuit. Because of this, it is frequently found necessary to include a so-called constant phase angle (CPA) element (e.g. as per eqn.68) in the electrical circuit required to model correctly the electrical behaviour of the electrode interface as a function of frequency. In our opinion, the constant phase angle (CPA) effect must substantially influence the frequency dispersion of the interfacial admittance, even for the case of quite small rotation angles (\(\phi = 2\text{-}4^\circ\)). Especially, at such small angles, the effect is likely to be ignored, which could lead to significant errors in the determination of faradaic rate parameters and thus to quantitative misinterpretation of results.

The CPA effect is generally believed to originate from a non-uniform distribution in the current-density along the electrode surface as a result of surface inhomogeneity. This can be inferred from the analogy with the behaviour of porous electrodes (and other electrodes with intentional inhomogeneity), which has been extensively discussed by de Levie\textsuperscript{161-163}. In his work, de Levie derived the impedance due to V-shaped grooves in a flat surface, under the assumption that the grooves are straight and infinite in length. His approach reveals that such surface roughness can account for the apparent frequency dependence of the double-layer capacitance and this has been experimentally confirmed\textsuperscript{161}.

The involvement of a CPE in the case of solid electrodes, and its absence in the case of electrodes like mercury, has provided another strong incentive for several researchers to rationalize the frequency dispersion of impedance at electrode interfaces in terms of surface roughness\textsuperscript{161-171} and, more particularly, in terms of fractal structures\textsuperscript{165-171}, i.e. electrode surfaces having a self-similar structure with dissimilar sites at which an electrode process can take place (Fig 5.2 depicts a schematic representation of a fractal surface). Much theoretical work\textsuperscript{165-169} has been done recently on this latter approach, but little has been, or can be done experimentally\textsuperscript{166-167} to support conclusively that frequency dispersion is in fact caused by surface microroughness at otherwise "polished" solid electrodes. Thus, despite these recent
Fig. 5.2 Schematic representation of a fractal surface.
works, the frequency dispersion, which up to now has been an obstacle in the quantitative interpretation of results from application of fast transient techniques (e.g. potentiostatic and galvanostatic step functions and impedance measurements) to solid electrodes, has remained not well understood.

Because of this situation, an attempt has been made in the present research project to clarify this obscure phenomenon. The results obtained and described below, reveal that surface roughness is certainly not the only cause of frequency dependence of the electrode impedance, although a probable cause in some cases, since we have experimentally observed,

Table 5.1 The radii\textsuperscript{172,174} of various anions (cf. refs. 172, 174) and the depression angles, $\varphi$.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Radii of the anion (Pm)</th>
<th>Depression angle $\varphi$ ($\pm 0.5^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>123</td>
<td>10$^\circ$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>167</td>
<td>7.5$^\circ$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>182</td>
<td>6.8$^\circ$</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>236</td>
<td>4.2$^\circ$</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>230 + H*</td>
<td>4.0$^\circ$</td>
</tr>
<tr>
<td>IO$_4^-$</td>
<td>249</td>
<td>3.5$^\circ$</td>
</tr>
<tr>
<td>CF$_3$SO$_3^-$</td>
<td>280** ± 15</td>
<td>2.7$^\circ$</td>
</tr>
</tbody>
</table>

*The radius of the HSO$_4^-$ anion could not be found, so the size of SO$_4^-$ was put into the table with H to indicate that the size of the H atom is not accounted for.

**The radius of this molecule ion was approximated by means of a molecular model. The results of this rough approximation are included here, not in order to prove a linear relationship between the radii of the anions and the depression angle, but to demonstrate that the extent of the depression definitely decreases with increase in anion size.
Fig. 5.3 Complex-plane plots of the measured impedance at Au, in 0.5 M KOH, for various cathodic current densities corresponding to cathodic H\textsubscript{2} evolution.
Fig. 5.4  Complex-plane plots of the measured impedance at Au, in 0.5 M HCl, for various cathodic current densities corresponding to cathodic H$_2$ evolution.
Fig. 5.5 Complex-plane plots of the measured impedance at Au, in 0.5 M HBr, for various cathodic current densities corresponding to cathodic H$_2$ evolution.
Fig. 5.6 Complex-plane plots of the measured impedance at Au, in 0.1 M H$_2$SO$_4$, for various cathodic current densities corresponding to cathodic H$_2$ evolution.
Fig. 5.7 Complex plane plots of the measured impedance at Au, in 0.1 M HClO₄, for various cathodic current densities corresponding to cathodic H₂ evolution.
Fig. 5.8 Complex plane plots of the measured impedance at Au, in 0.1 M HIO₄, for various cathodic current densities corresponding to cathodic H₂ evolution.
Fig. 5.9 Complex plane plots of the measured impedance at Au, in 0.1 M CF₃SO₃H, for various cathodic current densities corresponding to cathodic H₂ evolution.
Fig. 5.10 Plot of the anion radii vs the depression angle (for data taken from Table 5.1) for diameters of complex-plane plots.
for the behaviour of the h.e.r. on gold, that the extent of rotation of the $Z'$ or $Z''$ semi-circle in the complex-plane is inversely related to the size of the anions that are specifically adsorbed at the electrode metal.

The various results for the impedance behaviour of the h.e.r. at Au, plotted in the complex-plane, reveal, for various electrolytes, well-defined semi-circles having their centres lying below the $Z'$ axis, and their diameters at an angle to that axis, as depicted in Figs. 5.3 to 5.9. Fig 5.10 reveals an apparent relationship between the depression of the semi-circle, taken as the angle $\phi$ between the line joining all centres and the $Z'$ axis, and the size of the anions believed to be specifically adsorbed at the electrode surface. The order of the size of the anions with increasing depression effect is also the same at nickel, although the respective depression angles for the same anions are numerically different.

In view of these results, an attempt was made to measure the impedance at Hg in the presence of $I^-$ and $Br^-$, ions which are well known to be specifically adsorbed at Hg (see Fig 5.11). Unfortunately no depression was observed at Hg under conditions of cathodic $H_2$ evolution, as expected. However, this is to be anticipated since, when the applied potential is in a range in which $H_2$ is evolved at appreciable rates, a large negative potential must be applied, e.g. $\eta = -0.85$ V so that a strongly negatively charged metal surface is generated that is no longer electrostatically favourable for specific adsorption of anions. So the question arises why should there be no surface excess of anions at potentials more (appreciably) negative to the potential of zero charge (p.z.c.) at Hg, yet detectable extents of specific adsorption of anions arise at other metals that are solid, giving rise seemingly to the anion-dependent $\phi$ values. An explanation for this discrepancy can be an obvious difference in surface microroughness at the two kinds of metals. Fig. 5.12 schematically illustrates this: at a perfectly smooth surface, e.g. the interface of liquid mercury with the electrolyte, anions
Fig. 5.11 Complex-plane plot for the h.e.r. in (a) HI and (b) HBr solutions at Hg.
Fig. 5.12 A schematic representation illustrating the effect of the anion size on its possible interactions with a metal surface.
will have only a single contact point with the metallic substrate, at which stabilizing interactions promote specific adsorption.

It is also well recognized that no matter how well a solid electrode is polished, surface defects will always remain, and this, even at the best prepared single crystals. Hence small anions could probably position themselves at small surface defects in order to increase the number of contact points (coordination sites) between themselves and the metal, therefore making specific adsorption by anions possible in potential regions rather more negative than the p.z.c.. However, as the size of the anions increases, the number of contact points, for a particular surface microroughness would tend to decrease. Limitingly, infinitely large anions would only touch the metal at a single contact point, so that an impedance behaviour similar to that measured at Hg should arise, as suggested by the plot of the anion size vs the depression angle in Fig. 5.10.

In order to verify that the effect, associated with the CPA, referred to in the description of the preceding experiments is related to the microroughness, not macroroughness, of the electrode surface, a.c. impedance spectroscopy measurements were made on the h.e.r. in 0.5M KOH at two gold wires, one of them being purposely roughened with a 240 grit silicon carbide sandpaper.

Although the S.E.M. pictures (see Fig. 5.13) of these two wires showed pronounced differences in their surface smoothness, similar depression angles were observed in their complex-plane plots.

In view of these experimental results, it is suggested that the existence of the CPE effect is just an intrinsic property of the electrical double-layer at solid metals. Specifically adsorbed anions being subject to extremely high electric field strengths and small fluctuations of energy due to the superimposed a.c. voltage, could, as a result, suffer atomic movements in the interfacial structure, arising from application of the alternating potential.
Fig. 5.13  S.E.M. picture at a magnification scale of 10 μm per cm of two gold wires, one of them (b) being purposely scratched with a 240 grit silicon carbide paper.
This would be accompanied by a dissipation of energy during a cycle of a.c. perturbation as a consequence of mechanical coupling to neighbouring atoms. Due to time restrictions, no more work could be pursued by the present author on this topic. However, it would be useful and of great interest if extended research could be done on this particular topic.

5.2 The constant phase-angle element (CPE)

Since the constant phase angle, which influences the frequency dispersion of the interfacial admittance, is in no way directly related to the kinetics of the h.e.r., it is found necessary to include a constant phase angle element (CPE) in the electrical circuit used to model correctly the electrical behaviour of the electrode interface under study, and the electrode process involved.

This has in fact been done for the case of gold, as illustrated in Fig 5.14, using a CPE, as described by eqn. 68, in the equivalent circuit shown in Fig 5.15a. The capacitance values picked in this simulation were such that they coincided with the values experimentally obtained from the initial potential decay rate, \((dq/dt)_{t=0}\), following current interruption.

One major disadvantage of introducing an arbitrary CPE in the model which otherwise correctly represents the a.c. impedance behaviour of the electrode under study (e.g. the kinetic treatment or an equivalent circuit) is that it becomes impossible to determine the true C behaviour or rate constants characterizing the electrochemical system under study, since an infinite set of values of these parameters can be found for an infinite set of constants involved in the CPE of eqn. 68. For example, the simulation of the impedance response at gold during electrolytic \(H_2\) evolution could have also been achieved with C values other than the one used in the simulation of the behaviour shown in Fig. 5.14, if different values of the parameters in the CPE had been picked.
Fig. 5.14 Impedance response, measured at a Au electrode during the h.e.r. in 0.5 M KOH plotted in the complex-plane, and fitted with the equation that is used to calculate the impedance of the equivalent circuit in Fig. 5.15a.
Two equivalent circuits that are found to produce calculated impedances that represent well the impedance behaviour observed for a Faradaic process characterized by a resistance $R_F$, across the electrode interface having a double-layer capacitance, $C_{dl}$, and for which "frequency dispersion" is observed.
Since more than one (CPE, C) pair in the equivalent circuit depicted in Fig. 5.15a were found to produce a calculated impedance response that correctly represents that of the gold electrode during the h.e.r., a simpler circuit was required, e.g. Fig. 5.15b.

The impedance of the equivalent circuit in Fig. 5.15b can be written as follows

$$Z = \frac{1}{(1/R) + (j\omega)^{1-\alpha}}$$

(69)

where R represents the charge-transfer resistance and C the capacitance of the electrode interface. The parameter $\alpha$ represents a phase angle which is independent of frequency and is analytically related to the depression angle, $\varphi$, as follows:

$$\varphi = \alpha 180/2$$

(70)

Since the parameter $\alpha$ is constant for all applied overpotentials, as shown in eqn. 70, only a unique pair of ($\alpha$, C) values should reproduce the calculated impedance values matching the ones experimentally recorded. This was indeed found for the h.e.r. at Au in 0.5 M KOH. Hence, it may be concluded that the latter circuit is the simplest equivalent circuit that can adequately mimic the impedance response at the Au interface.

In electrochemical systems where a pseudocapacitance due to adsorbed H intermediates is significant, a more complicated situation arises because it is not clear yet how this differential capacity, $C_\varphi$, is affected by the factors that give rise to the depression in

---

*The imaginary and real contributions to the total impedance of the equivalent circuit shown in Fig. 5.15 b and Fig. 5.16 b, can only be separated with great difficulty because of the $\alpha$ term (see eqn. 69). Nevertheless, separation of $Z$ into $\tilde{Z} = z' + jz''$ can still be accomplished in such complicated cases, if one uses trigonometric functions to represent the complex vector. Using this approach, Cole and Cole [159] have derived $z'$ and $z''$ for the equivalent circuit depicted in Fig. 5.15 b.
the semi-circular $Z'-Z''$ plot. It should also be indicated that the arbitrary introduction of a CPE, such as that represented by eqn. 68, in an equivalent circuit such as the one in Fig. 5.16a, is not necessarily very useful, because such a CPE can be too flexible and, similar to the situation that arises with the circuit of Fig. 5.15a, a multitude of combinations of (CPE, $C_{dl}$, and $C_\phi$) can represent the impedance of the electrochemical system as a function of frequency. On the other hand, a simpler CPE element, such as the one in Fig. 5.16b, could be used to simulate the measured a.c. response, although arbitrarily selected $\alpha$ values, might have to be used as demonstrated later in section 5.5.

5.3 Armstrong's equivalent circuit for one adsorbed intermediate

Although "frequency dispersion" causes the a.c. impedance spectra, plotted in the complex-plane, to appear as depressed semi-circles, we would be tempted to think that it should not distort the impedance response of an electrode interface, in the case where $C_\phi$ is important, to an extent where the two normally semi-circular arcs frequently observed in the complex-plane plot, are no longer resolvable through the whole potential range under study.

Simulations with the Armstrong equivalent circuit (i.e. the equivalent circuit in Fig. 5.17, demonstrated earlier to be a correct equivalent circuit from a kinetic point of view by Conway and Harrington\textsuperscript{115}, to represent the impedance response of an electrode process with one adsorbed intermediate) will be used here to illustrate, a priori, some of the expected shapes of the impedance spectral responses that could arise during the h.e.r. at good electrocatalysts, as shown in Fig. 5.18.

5.4 A.C. Impedance spectroscopy at Ni and Ni-Mo bulk alloys

At metals such as Ni and bulk Ni-Mo alloys, where it is believed that considerable H adsorption takes place, conflicting a.c. impedance spectra are always measured. Contrary to
\[ Z_p(\omega) = A_1 \omega^{-\alpha_1} - j A_2 \omega^{-\alpha_2} \]

\[ Z_{\text{total}} = \left[ \frac{1}{R_\infty + \frac{1}{R_p + (j\omega C_p)^{1 - \alpha_2}}} \right] \]
Fig. 5.17 Armstrong’s equivalent circuit (see ref. [141]).

\[ \tau_1 = C_{dl} \cdot (R_p + R_\infty) \]

\[ \tau_2 = C_p \cdot R_p \]
Fig. 5.18 Simulation of the impedance behaviour arising with the Armstrong equivalent circuit, plotted in the complex-plane in a 3-dimensional plot for various combinations of $R$ and $C$ values that can arise in the potential range under study during the h.e.r., where H chemisorption is appreciable.
what was expected, these metals exhibit a single apparent relaxation time in their impedance spectra over the potential range studied, i.e. -50 to -500 mV on the r.h.e. potential scale, as shown in Fig. 5.1. This puzzling behaviour made the simulation of the impedance with the Armstrong equivalent circuit unsuccessful at these metals, since even if coinciding relaxation times can arise at low overpotentials, \( \tau_1 = \tau_2 \), and a unique time constant can be observed at high overpotentials \( \tau_1 = R_C C_D \), due to the double-layer capacitance alone, a transition region necessarily has to arise at some intermediate potential values where \( \tau_1 \neq \tau_2 \) has to apply, as depicted in Fig. 5.18.

The surprising fact that only a single relaxation time is detectable by a.c. impedance spectroscopy at these metals, and that this behaviour is observed over the whole potential range studied, makes it necessary to consider that the impedance behaviour at Ni and Ni-Mo bulk phase alloys can be modelled by the empirical equivalent circuit of Fig. 5.19, although it does not have a corresponding kinetic significance.

Since capacitors in parallel behave as if they were condensed additively to one, it is not incorrect to mimic the impedance behaviour of these metals with impedances calculated from eqn. 69, similarly to what was done for Au in 0.5 M KOH. Once again, good fits of the experimental impedances could be achieved but what is more important here is that the derived C values corresponded to the ones determined from the potential relaxation treatment, using the initial potential decay rate, \( (d\eta/dt)_{t=0} \), following the interruption of a polarizing current, as illustrated in Figs. 4.3 and 4.9. The agreement between \( C_{ac} \), derived from the a.c. data which is "corrected" for the unwanted effect giving rise to the non-90° phase shift arising from the finite phase angle \( \alpha \), and \( C_{decay} \), derived at \( [d\eta/dt]_{t=0} \), is of special significance here, because it demonstrates that the C vs \( \eta \) profiles evaluated by our fitting method are in no way affected by the frequency dispersion, which always distorts the measured a.c. impedance spectra at solid electrodes through the CPA \( \phi \)-effect.
Fig. 5.19 An arbitrary equivalent circuit which can model very well the impedance behaviour at Ni and Ni-Mo bulk phase alloys, in 0.5M KOH during the h.e.r.
5.5 **A.C. Impedance spectroscopy at bulk Ni-W and electroplated Ni-V electrodes**

The a.c. impedance spectra for the h.e.r. at bulk Ni-W and electroplated Ni-V, exhibit two semi-circles corresponding to two relaxation times at lower overpotentials. The pseudocapacitance, due to chemisorbed H adatoms, is thus noticeable in the complex-plane plots for the Ni-W bulk phase alloys up to 300 mV. At higher overpotentials, the potential-dependent coverage by o.p.d. H seems to no longer increase, which is reflected in the impedance spectra through their representation by a single semi-circular arc, arising from the double-layer capacitance alone.

As to the a.c. impedance spectra recorded at electrodeposited Ni-V (Fig. 5.21), they clearly reveal a potential dependence of the coverage by o.p.d. H which is spread out over a rather wider potential range.

The impedance behaviour of the h.e.r., at bulk Ni-W and at electroplated Ni-V electrodes was fitted by means of the equivalent circuit shown in Fig. 5.16 b. The $\alpha$ values were chosen empirically in order to obtain good fits with reasonable R and C values as shown in Tables 5.2 and 5.3.
Fig. 5.20  A.C. impedance spectra for the h.e.r. at the Ni-W (90:10) bulk phase alloy for the three indicated applied overpotential values.
Fig. 5.21 A.C. impedance spectra for the h.e.r. at the electroplated Ni-V composite for the three indicated applied overpotential values.
Table 5.2  A.C. impedance fitting parameters for the h.e.r. at the bulk phase Ni-W alloy in 0.5 M KOH.

<table>
<thead>
<tr>
<th>overpotential/mV</th>
<th>$\alpha_1 = 0.078$</th>
<th>$\alpha_2 = 0.140$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\infty}/\Omega \cdot \text{cm}^{-2}$</td>
<td>$C_{dl}/\mu \text{F} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>385</td>
<td>1.5</td>
<td>84</td>
</tr>
<tr>
<td>345</td>
<td>6</td>
<td>84</td>
</tr>
<tr>
<td>300</td>
<td>28</td>
<td>84</td>
</tr>
<tr>
<td>250</td>
<td>150</td>
<td>84</td>
</tr>
<tr>
<td>200</td>
<td>195</td>
<td>84</td>
</tr>
<tr>
<td>150</td>
<td>1300</td>
<td>84</td>
</tr>
<tr>
<td>100</td>
<td>4343</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 5.3  A.C. impedance fitting parameters for the h.e.r. at the electrodeposited Ni-V alloy in 0.5 M KOH.

<table>
<thead>
<tr>
<th>overpotential/mV</th>
<th>$\alpha_1 = 0.14$</th>
<th>$\alpha_2 = 0.15$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\infty}/\Omega \cdot \text{cm}^{-2}$</td>
<td>$C_{dl}/\mu \text{F} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>320</td>
<td>16.5</td>
<td>60</td>
</tr>
<tr>
<td>260</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>140</td>
<td>176</td>
<td>60</td>
</tr>
<tr>
<td>100</td>
<td>1100</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>2089</td>
<td>60</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIVE DISCUSSION

Interpretation of the experimental data base, obtained for the h.e.r. at the various metallic substrates by means of complementary theoretical modeling, should lead to useful kinetic information about the h.e.r. This is why the theoretical models will be first presented in this final chapter, followed by individual conclusions drawn for the behaviour of each of the cathode metals studied.

6.1 Current density-overvoltage relationships

6.1.1 The Tafel slope of a rate-determining step in the h.e.r.

The hydrogen evolution reaction, often viewed as a prototype for multistep electrode processes, involves always two consecutive steps. Such a mechanistic scheme is always characterized by a "slow" step that controls the overall rate of the reaction, i.e. the step with the smaller rate constant and higher $\Delta G^\ne$ value. In order to find the rate-determining step which is characterized by a certain charge transfer coefficient in a multistep process, use can be made of the following empirical approach. The potential dependent current-density of a multistep reaction can, at sufficiently high $\eta$, be written in the following simplified form

$$i = i_0 \exp(\alpha F \eta / RT)$$

which is a general expression of the Tafel equation, with a Tafel slope of

$$b = d\eta / d \log i = 2.3 \, RT / \alpha F$$

where

$$\alpha = \beta (n - \vec{n} \cdot \vec{n}) + \vec{n}$$

Here $n$ is the total number of electrons transferred and $\vec{n}$ and $\vec{n}$ are the numbers of electrons
transferred before and after the rate-determining step, respectively, all for one act of the overall reaction.

The stoichiometric number, \( v \), can be defined as the number of times a given step must take place for the overall reaction to occur once.

From the above equations, the possible values of the transfer coefficient can be evaluated for various reaction mechanisms, as listed in Table 6.1

**Table 6.1** Predicted transfer coefficients for various hydrogen-evolution reaction mechanisms.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Transfer coefficient ( \alpha ), assuming ( \beta = 0.5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge-rate determining followed by chemical desorption</td>
<td>0.5</td>
</tr>
<tr>
<td>Discharge followed by rate-determining chemical desorption</td>
<td>2.0</td>
</tr>
<tr>
<td>Coupled discharge-chemical desorption</td>
<td>0.5</td>
</tr>
<tr>
<td>Discharge-rate determining followed by electrochemical desorption</td>
<td>0.5</td>
</tr>
<tr>
<td>Discharge followed by rate-determining electrochemical desorption</td>
<td>1.5</td>
</tr>
<tr>
<td>Coupled discharge-electrochemical desorption</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Note on Table 6.1: \( \beta \) is the barrier symmetry factor for charge-transfer steps.

**6.1.2 Rate-controlling steps and a two-slope Tafel relation**

In section 1.9, a well established treatment for consecutive and alternative processes, which helps to rationalize the mechanism of the multistep process when more than one Tafel slope is observed in the \( \eta \) vs log(current-density) plot, was discussed. According to this latter
approach, it is always the step with the smallest rate constant that is rate-determining in consecutive reactions, giving a low followed by an higher Tafel slope at larger overpotentials. For alternative processes in a given multi-step mechanism, an opposite sequence of the Tafel slope magnitudes will be observed, as graphically represented in Fig. 1.8. This latter relation arises because it is the path which proceeds with the greatest velocity (current-density) that characterizes the kinetics in alternative rate-determining pathways.

Here we shall demonstrate that this latter assumption is not necessarily true when the coverage by H varies appreciably with \( \eta \), and we will emphasize the significance of the quantitative experimental evaluation of the coverage, \( \theta_H \), by o.p.d. H for proper elucidation of reaction mechanisms.

In section 1.8 we previously discussed the relationship between the Tafel slope, \( b \), and the isotherm for adsorption of an intermediate. More precisely, an explicit relation between the H adsorption behaviour and the reciprocal of the Tafel slope can be given as follows:

\[
\frac{1}{b} = \frac{d \log i}{d \eta} + \frac{d \log f(\theta_H)}{d \eta} + \frac{2.303 F}{RT} \tag{25}
\]

Using this latter equation for the case where discharge is rate-controlling with \( d \log (1 - \theta)/d \eta \) as the adsorption isotherm factor, an interesting sequence of slopes is obtained which would normally be only attributed to a mechanism with alternative rate-controlling desorption steps. An example, illustrated in Fig. 6.1, has been derived for the condition where \( d \log (1 - \theta)/d \eta \) is believed to change linearly with potential in the lower potential range, which is not an unreasonable assumption. In this example, the maximum value of \( \theta \) for the discharge step limitingly to be rate-controlling is 0.5, corresponding to \( k_1 \leq k_2 \) (eqns. 23, 24, p. 10 and see eqn. 83, p. 177). Then it is found for this limiting case,
and for \( \theta \) varying over ca. 200 mV from almost 0 to almost 0.5, that the adsorption isotherm factor in eqn. (25) is:

\[
\frac{d \log (1 - \theta)}{d \eta} = \frac{\log(1 - 0.5) - \log(1 - 0)}{0.2(V) - 0.0(V)} = -1.5
\]

Using this latter approach, with \( d \log (1 - \theta)/d\eta = -1.5 \), it is possible to account for Tafel slopes having values higher than 120 mV decade\(^{-1}\), e.g. the observed 143 mV decade\(^{-1}\), for electrochemical reactions having Tafel lines of similar sequences of dual slopes.

In the contrary case, where the electrochemical desorption step would be rate-controlling over the whole potential region under study, with \( d \log(\theta)/d\eta \) as the adsorption isotherm factor, an opposite sequence of slopes to the one above should arise because \( d \log(\theta)/d\eta \) will always be a positive term due to the fact that the limiting o.p.d. H coverage becomes \( \geq 0.5 \) when the rate constant for the initial discharge step is greater or equal to that for the desorption step (see eqn. 84 later).

The shape of the \( \eta \) vs \( \log i \) relation for the h.e.r. at a metal where a chemical recombination step is rate-determining is characterized by the two following limiting cases:

i) for low \( \theta_H \) with \( \theta_H = f(\eta) \), \( -d\eta/d \log i = 2.3 \text{ RT}/2F = b \); and

ii) for \( \theta_H \rightarrow 1 \), where \( -d\eta/d \log i \rightarrow \infty \) corresponding to a limiting current, which is activation-, not diffusion-controlled. In this case, \( -d\eta/d \log i \rightarrow \infty \).

### 6.2. \( \text{H} \) coverage and \( C_{\phi} \) behaviour

The following simulations have been previously presented by Conway and Bai\(^{108}\). However, it is important to reiterate such simulations at this point so that a better understanding of the new experimental data presented can be gained.
Fig. 6.1  Schematic representation illustrating how the adsorption isotherm factor can influence the $\eta$ vs log i relation when the discharge step is rate-controlling.
We have seen earlier that the decay of potential after interruption of a polarizing current, can give, indirectly, information on H coverage through the pseudocapacitance \( C_\phi = q_1 \, \frac{d\theta_H}{d\eta} \), i.e. \( \theta_H \) or the change of \( \theta_H \) with \( \eta \) can be evaluated by integrating the experimentally determined relation between \( C_\phi \) and \( \eta \). The Langmuir and Frumkin isotherms relating \( \theta_H \) to \( \eta \) have also been discussed previously in section 1.10.

The steady-state H coverages evaluated at Ni and Ni-Mo alloys were evaluated to be substantially less than a monolayer. This, as well as the observed Tafel slopes, indicates that recombination of chemisorbed H cannot be the rate-determining step in the electrolytic H\(_2\) evolution at the Ni metal and the Ni-Mo alloy surfaces.

In a reaction scheme involving first a discharge step
\[
M + H_2O + e \xrightarrow{k_1} MH_{ads} + OH^- \quad (74)
\]
followed by the electrochemical desorption of H
\[
MH_{ads} + H_2O + e \xrightarrow{k_2} M + H_2 + OH^- \quad (75)
\]
we can show, as follows, that limiting steady-state H coverages are significantly smaller than unity, unless the rate constant for the discharge process is much larger than that for the desorption step, in which case, \( \theta_H \) should be close to unity. The relevant rate equations for processes (74) and (75) are:

\[
v_1 = k_1 \, (1 - \theta_H) \exp\{\beta \eta F/RT\} \equiv \ell (1 - \theta_H) \text{ say}; \quad (76)
\]

\[
v_{-1} = k_{-1} \, \theta_H c_{OH^-} \exp\{-(1 - \beta) \eta F/RT\} \equiv m \theta_H \text{ say} \quad (77)
\]

\[
v_2 = k_2 \theta_H \exp\{\gamma \eta F/RT\} \equiv n \theta_H \text{ say} \quad (78)
\]

where \( \beta \) and \( \gamma \) are charge-transfer symmetry factors and \( \ell, m \) and \( n \) are defined obviously by comparisons within the relations (76), (77) and (78). The steady-state condition for H coverage is then
\[
d\theta_H/dt = 0 = v_1 - v_{-1} - v_2 \quad (79)
\]
i.e.

\[ \alpha(1 - \theta_H) - m\theta_H - n\theta_H = 0 \]  

(80)

or

\[ \theta_H = \frac{\alpha(\ell + m + n)}{\ell} \]  

(81)

noting that \( \ell, m \) and \( n \) are exponential functions of \( \eta \) as in (76), (77) and (78). Corresponding to equation (81), the pseudocapacitance \( q_j \frac{d\theta_H}{d\eta} \) is

\[ C_\varphi = \frac{Fq_j}{RT} \frac{\alpha m}{(\ell + m + n)^2} \]  

(82)

taking \( \beta = \gamma = 0.5 \) (here effects of significant H interactions are ignored).

Inserting the potential-dependent factor, we obtain

\[ \theta_H = \frac{1}{(1 + K_{f1}c_{OH}^{-}\exp[-\eta F/RT] + k_2/k_1)} \]  

(83)

At appreciable cathodic overpotentials, it is seen that \( \theta_H \) reaches limiting values for the mechanism 74, 75 given by

\[ \theta_{H,\text{lim}} = \frac{1}{(1 + k_2/k_1)} \]  

(84)

Eqn. 84 indicates a clear dependence of the limiting coverage on the \( k_2/k_1 \) ratio.

When \( k_2/k_1 > 1 \), the limiting coverage by o.p.d. H is necessarily smaller than 0.5, as observed experimentally. The calculated plots of \( \theta_H \) vs overpotential for three \( k_2/k_1 \) values, using eqn. 81, and the corresponding \( C_\varphi \) vs overpotential plots using eqn. 82, taking \( C_{OH}^{-} = 1 \), \( q_1 = 257 \mu C \text{ cm}^{-2} \) (for H and Ni) and \( T = 298 \text{ K} \), are shown in Fig. 6.2. The calculated limiting coverages \( \theta_{H,\text{lim}} \), for the above reaction mechanism, for various \( k_2/k_1 \) ratios have been plotted in Fig. 6.3.

In a more general case, where lateral H interactions (Frumkin isotherm) are taken into account, the steady-state condition allows the following relation to be written:

\[ \frac{1 - \theta_H}{\theta_H} \exp[-\eta \theta_H] = k_2/k_1 + K_{f1}^{-1} \exp[-\eta F/RT] \]  

(85)

\( \theta_H \) then has limiting values at appreciable cathodic overpotentials dependent on \( g \) as well as
Fig. 6.2 Calculated plots of a) $\theta(H)$ vs overpotential for three $k_2/k_1$ values, using eqn. 81;
b) $C_\phi$ vs overpotential using eqn. 82, taking $C_{OH^-} = 1$, $q_1 = 257 \mu C \ cm^{-2}$, $T = 298 K$,
$k_1 = 1$, $k_{-1} = 30$ with ① $k_2 = 0.1$; ② $k_2 = 1$; ③ $k_2 = 10$ (arbitrary units for $k$'s)
Fig. 6.3 Calculated plots of limiting coverage $\theta_{H,\text{lim}}$ for the reaction mechanism 74, 75 vs $k_2/k_1$, using eqn. 84.
Fig. 6.4  Calculated plots of $\theta(H)$ vs $\eta$, using eqns. 85 and 86 respectively, with $k_2/k_1 = 10^{-3}$ and $K_1 = 0.1$ for three $g$ values: $g = 0, 2$ and $5$ (here it is assumed that step 74 is in quasi-equilibrium).
on the rate constant ratio $k_2/k_1$. Correspondingly, the H pseudocapacitance also depends on these two parameters, and can only be explicitly evaluated numerically, but is given by

$$C_\phi = \frac{Fq_1}{RT} \cdot \frac{K_1^{-1}\exp(-F\eta/RT)}{\exp(-g\theta_H)((g\theta_H + 1)/\theta_H^2 + g)}$$

As may be expected, for $g > 0$, a much wider spread of values of the ratio $k_2/k_1$ is required** to cause $\theta_{H,lim}$ to vary from 1 to small values than in the case for Langmuir adsorption ($g = 0$) as illustrated in Fig. 6.4.

This latter figure demonstrates not only the relation between $C_\phi$ and $\eta$ (calculated from eqn. 86), and that between $\theta_H$ and $\eta$ (calculated form eqn. 85), but also the effect of the lateral H interaction parameter, $g$, on these profiles for cases where $g$ may be significant.

6.3 Initial Potential Decay Rates in Relation to Decay Rates at Other Times

The experimental results obtained at several of the cathode materials investigated show that $\eta/dt$ values and associated capacitances, derived for $t = 0$, i.e. immediately after current interruption, are not always identical with values of $\eta/dt$ at corresponding potentials, read from a whole $\eta(t)$ curve covering the same potential range within which ($\eta/dt)_{t=0}$ data were separately determined. It is this difference which gives rise to the difference of $C_\phi$ vs $\eta$ profiles determined by two methods for the h.e.r. at some of the alloys investigated (e.g. see Fig. 4.7 in chapter 4).

In this section, it will be shown that if the same processes are taking place throughout a whole potential relaxation curve ($t > 0$) as at the beginning of the transient ($t = 0$), then $\eta/dt$ at any given potential $\eta^*$ in the whole transient will be identical with ($\eta/dt)_{t=0}$ values measured separately at the same $\eta^*$ values taken as the initial potentials at the moments of current interruption*.

**In the case where $g$ may be significantly $> 0$, it follows from eqn. (85) that the ratio $k_2/k_1$ required for a given value of $\theta_{H,lim}$ to be attained is smaller.

*The derivation here was worked out in collaboration with Dr. J. Woitowicz in our laboratory.
We write the "RC" time-constant for the process as $\tau$ and refer to two potential relaxation curves, ① and ②, in Fig. 6.5. One starts from an initial potential $\eta_{1,1}$ and the other from a lower initial potential $\eta_{1,2}$.

For curve ① the equation for the $\eta(t)$ transient is

$$\eta_1(t) = \eta_{1,1} e^{-t/\tau}$$  \hspace{1cm} (87)

or

$$(\frac{d\eta}{dt})_1 = \frac{-\eta_{1,1}}{\tau} e^{-t/\tau}$$  \hspace{1cm} (88)

Similarly

$$\eta_2(t) = \eta_{1,2} e^{-t/\tau}$$  \hspace{1cm} (89)

At time $t^*$ in transient ①, for which $\eta(t)$ has fallen to $\eta_{1,2}$, the initial potential for transient ②,

$$(\frac{d\eta}{dt})_{1,t^*} = \frac{-\eta_{1,1}}{\tau} e^{-t^*/\tau}$$  \hspace{1cm} (90)

But at $t = t^*$, $\eta_1(t^*) = \eta_{1,2}$ for which $t = 0$ on t-varient ②;

i.e.

$$(\frac{d\eta}{dt})_{2,t=0} = \frac{-\eta_{1,2}}{\tau} e^{-t^*/\tau} = \frac{-\eta_{1,2}}{\tau}$$  \hspace{1cm} (91)

Then in eqn (92)

$$\frac{(\frac{d\eta}{dt})_{1,t^*}}{(\frac{d\eta}{dt})_{2,t=0}} = \frac{-\eta_{1,1}}{\tau} e^{-t^*/\tau} = \frac{\eta_{1,1} e^{-t^*/\tau}}{-\eta_{1,2}/\tau}$$  \hspace{1cm} (92a)

$$= \frac{\eta_{1,1} e^{-t^*/\tau}}{\eta_{1,2}}$$  \hspace{1cm} (92b)

Also, on transient ①

$$\eta_{1,2} = \eta_{1,1} e^{-t^*/\tau}$$  \hspace{1cm} (93)
Fig. 6.5 A schematic representation illustrating how the potential decay rates, $d\eta/dt$, should always be the same at a given $\eta$ value in the absence of complicating H sorption effects.
Hence

\[ \frac{(d\eta/dt)_{1,t^*}}{(d\eta/dt)_{2,t=0}} = 1 \]  

(94)

so that the slope of curve 1 at \( \eta = \eta_{i,2} \) (i.e. after time \( t = t^* \)) is identical with the initial slope of curve 2, i.e. for \( t = 0 \). Hence capacitances derived from \( d\eta/dt \) at any assigned potential on a transient curve should be identical with the capacitance derived from the initial decay rate in a transient initiated separately from that assigned potential.

Therefore, when systematic differences arise between these two kinds of results, as is observed for some cases of the h.e.r. (see Fig 4.7), their origin must be sought in some special time-dependent behaviour of the electrode process and/or the properties of the electrode interface, not taken into account by the basic potential-relaxation equation (40).

6.4 \textbf{H diffusion: order of magnitude calculation}

At metals where H coverage is indicated as appreciable (e.g. Ni-Mo alloys), it is not unreasonable to suppose that some H adatoms diffuse inside the crystal lattice, forming interstitial hydride near its surface species that could influence the rate of decay of potential after the interruption of a polarizing current.

In chapter 4, it was suggested that the differences referred to above in section 6.3 arise at some metals on account of time-dependent sorption of H; they do not arise in the behaviour of the h.e.r. at Hg or Au where H sorption is known not to occur.

In this section, an order of magnitude calculation is presented to support the view that hydride formation could influence the potential relaxation curves in the time scales that the transients have been recorded.

Say H diffuses into a metal M to a depth of \( \text{ca. } 10^{-7} \text{cm} \) and its diffusion constant \( D \) is \( \text{ca. } 10^{-10} \text{ cm}^2 \text{ s}^{-1} \). Then according to the Stokes-Einstein diffusion displacement
law:

\[(\Delta X)^2 = 2 \Delta t \text{ or } \Delta X = \sqrt{2 \Delta t}\]

For \(\Delta X = 10^{-7} \text{ cm}\)

\[10^{-7} \text{ cm} = \sqrt{2 \times 10^{-10} \times t};\]

due to the times.

This is a plausible time for part of the potential decay curve and 10 Å of H in M would usually correspond to about 5 equivalent layers of H. Formation of such surface-region hydride species could therefore well account for the large C values evaluated by means of the rate of decay of potential, \(d\eta/dt\), at any \(\eta\) at metals such as the Ni-Mo alloys.

6.5 **Time dependence of H diffusion**

H diffusion into the crystal lattice is also further supported from the differences that arise between the decay curves recorded at Ni-W (90:10) bulk phase alloy after various polarization times. If the decay curves are plotted as \(\eta \text{ vs } \log t\), as shown in Fig 6.6, it can be clearly observed that the longer the polarization time prior to the recording of the decay curve, the lower is the value of the term \(-d\eta/d \log t\), i.e. the slower is the decay rate. This can be rationalized as follows. As the polarization time increases prior to the recording of the \(\eta \text{ vs } \log t\) curves, larger amounts of H, diffused into the crystal lattice, are available to diffuse back out and to be consequently oxidized at the surface when the polarizing current is interrupted, therefore slowing down the decay rate after the interruption of a polarizing current. As a result of this reduced rate of decay, \(d\eta/dt\), large capacitance \(\text{vs } \eta\) profiles will be evaluated from the method which involves the potential decay rate, \(d\eta/dt\), read at any \(\eta\) value of the potential relaxation curve, after the interruption of the current. This can also be better understood with the help of eqn. 45a:
Fig. 6.6  $\eta$ vs log $t$ curves recorded after various polarization times at 300 mV at a Ni-W (90:10) bulk phase alloy.
\[ C(\eta) = \frac{i(\eta)}{(-d\eta/dt)} \quad (45a) \]

where it will be noticed that the smaller is \( d\eta/dt \), the larger should \( C(\eta) \) become.

### 6.6 Conclusions for the various cathode metals investigated

#### 6.6.1 Ni

1. The steady-state polarization measurements for the h.e.r. at Ni in 0.5 M KOH are represented by a single line having a slope of 120 mV decade\(^{-1} \). Such a Tafel slope could correspond simply to a reaction mechanism with a rate-determining discharge step at 298 K, for \( \beta = 0.5 \). The fact that a single-slope Tafel line is observed for the whole potential range under study suggests that the electrochemical adsorption factor (eqn. 25) does not significantly determine the \( d\eta/d \log i \) slope. Using the approach suggested in section 6.1.2, with a \( \theta_{H,\text{lim}} = 0.065 \) reached at -300 mV, the conclusion can be reached that the coverage vs potential dependence will not determine the value of \( b \) to more than 2 mV decade\(^{-1} \). This small calculated slope component could explain why no apparent kink is observed in the Tafel line at Ni metal. If a desorption rate-determining step was clearly to apply at Ni, contributions of the H adsorption isotherm factor to the Lefat slope (eqn. 25) would be important enough to give rise to a noticeable inflexion point in the Tafel line at higher overpotentials because, by definition, the o.p.d. H coverage has to increase to at least half a monolayer.

2. The small value of the limiting coverage, \( \theta_{H,\text{lim}} = 0.065 \), evaluated by the fitting method (as well as by a.c. impedance spectroscopy) provides further evidence that a discharge rate-determining step is involved here. If the reaction scheme of section 6.2 applies, the small value of the evaluated limiting coverage corresponds to a \( k_2/k_1 \) ratio of approximately 14.
3. The author of this thesis also believes that the differences in the potential-dependent pseudo-capacitance profiles evaluated by the two potential relaxation methods can be attributed to the oxidation of a small amount of hydride upon decay of potential, as was suggested earlier. A metal such as Ni cannot be expected to adsorb H only at the surface, with no H diffusing into the crystal lattice, because this would require an infinitely large concentration gradient of the sorbed H. Because the hydride H oxidation is a process that releases electrons, which will reduce the rate of the decay of potential, $\frac{dn}{dt}$, and since this latter quantity is inversely proportional to $C$, larger capacitances are evaluated by the method using the calculated $\frac{dn}{dt}$ at any $n$ along the decay curve, where time is allowed for diffusion of H from the supposed near-surface hydride, to the surface, to occur.

4. The a.c. impedance spectra were found to be always represented by a single relaxation time at Ni in 0.5 M KOH, no matter what was the applied overpotential in the potential range under study. This is contrary to what was anticipated from a theoretical point of view (see p. 165), for unknown reasons, which may or may not be related to what gives rise to the CPA.

6.6.2 Ni-Mo bulk phase alloys

1. The $\eta$ vs log i relations for the three bulk phase alloys investigated reveal a single Tafel slope of approximately 120 mV decade$^{-1}$ in the high overpotential region, but somewhat different slopes at lower overpotentials, depending on the concentration of Mo in the bulk phase alloy. Once again we suspect a rate-determining discharge step at these alloys, not only because of the experimental Tafel slope of approximately 120 mV decade$^{-1}$ observed at higher overpotentials, but also because of the shape of the Tafel relation.

2. Since the shape of the Tafel relation is also similar to the one in Fig. 6.1, this suggests that a discharge step must be rate-controlling at these alloys. However, using the
\[ C(\eta) = \frac{i(\eta)}{-d\eta/dt} \quad (45a) \]

where it will be noticed that the smaller is \( d\eta/dt \), the larger should \( C(\eta) \) become.

6.6 Conclusions for the various cathode metals investigated

6.6.1 Ni

1. The steady-state polarization measurements for the h.e.r. at Ni in 0.5 M KOH are represented by a single line having a slope of 120 mV decade\(^{-1}\). Such a Tafel slope could correspond simply to a reaction mechanism with a rate-determining discharge step at 298 K, for \( \beta = 0.5 \). The fact that a single-slope Tafel line is observed for the whole potential range under study suggests that the electrochemical adsorption factor (eqn. 25) does not significantly determine the \( d\eta/d \log i \) slope. Using the approach suggested in section 6.1.2, with a \( \theta_{H,\text{lim}} = 0.065 \) reached at -300 mV, the conclusion can be reached that the coverage vs potential dependence will not determine the value of \( b \) to more than 2 mV decade\(^{-1}\). This small calculated slope component could explain why no apparent kink is observed in the Tafel line at Ni metal. If a desorption rate-determining step was clearly to apply at Ni, contributions of the H adsorption isotherm factor to the Lefat slope (eqn. 25) would be important enough to give rise to a noticeable inflexion point in the Tafel line at higher overpotentials because, by definition, the o.p.d. H coverage has to increase to at least half a monolayer.

2. The small value of the limiting coverage, \( \theta_{H,\text{lim}} = 0.065 \), evaluated by the fitting method (as well as by a.c. impedance spectroscopy) provides further evidence that a discharge rate-determining step is involved here. If the reaction scheme of section 6.2 applies, the small value of the evaluated limiting coverage corresponds to a \( k_2/k_1 \) ratio of approximately 14.
It is also interesting to point out that the higher is the atomic concentration of Mo in the binary alloy, the smaller is the calculated barrier symmetry factor for the lower potential region. This would mean in terms of reaction coordinates, the more Mo there is in the alloy, the closer is the transition state to the MH intermediate produced during the proton discharge step. This reasoning would also imply that once high enough overpotentials are reached there is no more potential dependence of the coverage by chemisorbed H, and a common value of the barrier symmetry factor should apply, which is not inconceivable.

3. The limiting coverages evaluated by means of [(d\(\eta/dt\))\(t=0\)] for each of the three Ni-Mo alloys were found to be less than 0.5, implying a discharge rate-determining step, as discussed in section 6.2.

4. The large C values obtained by the rate of the decay of potential, d\(\eta/dt\), read from the whole decay curve at any \(\eta\) are believed, once more, to be too large because of the oxidation of hydride species (sorbed H). It seems that H can diffuse through the Ni-Mo crystal lattices much more easily than at pure Ni, and this is probably due to a less compact crystal lattice of these binary alloys.

6.6.3 Ni-W bulk phase alloy

1. The Tafel relation for the h.e.r. at this binary alloy in 0.5M KOH is characterized by two slopes, 120 and 100 mV decade\(^{-1}\) for the low and high overpotential regions, respectively. The slope sequence is again similar to the one in Fig. 6.1, and to what was observed at the Ni-Mo bulk phase alloys. This characteristic shape of the Tafel relation, along with the high values of the measured slopes, suggests again a rate-determining discharge step. However, analysis of the whole potential-decay curve for this case leads to \(C_\phi\) values that are too large to correspond to the pseudo-capacitance of only the chemisorbed H, so it has been presumed, as also found for H at Pt (and much more so for H at Pd), that the
capacitance associated with the adsorbed H is observed by a larger capacitance associated with absorbed H in an hydride shape near the metal surface (cf. the discussion on p. 184).

2. The $C$ vs $\eta$ profiles, evaluated by means of the rate of decay, $d\eta/dt$, read from the decay curve at any $\eta$, are too large. As suggested in the case of for the Ni-Mo bulk phase alloys, these anomalously large $C$ values are believed to arise because of hydride oxidation upon decay of potential. What should be pointed out here is that there should not be such a significant amount of hydride at Ni-W, if there were no appreciable coverage by the kinetically involved H on the electrode surface itself. This latter argument receives further support from the fact that the h.e.r. at Au in 0.5M KOH, the coverage by chemisorbed H is known to be small ($\theta_H < 1\%$), so that both of the potential decay treatments presented in this thesis gave similar $C$ vs $\eta$ profiles (if there would have been any difference between the two profiles, it would have been caused by either the oxidation of hydrides or of the electrode metal surface), and the measured capacitances correspond to a constant double-layer capacity.

3. Because there is more than one relaxation time revealed by a.c. impedance spectroscopy (Fig. 5.20, p. 168), only the double-layer capacitance will be obtained from the initial potential decay rate, $(d\eta/dt)_{t=0}$, following interruption of a polarizing current. This means that unambiguous information on the coverage by the o.p.d. H alone cannot be obtained by either of the two potential decay methods.

4. However, some semi-quantitative information can be obtained on the electrochemical adsorption behaviour of H by fitting the impedance response at bulk Ni-W with the equivalent circuit of 5.16b. The term "semi-quantitative" information is used here for two reasons: the first is that the $\alpha$ values used were arbitrarily selected to achieve a good fit with reasonable R and C parameters, as listed in Table 5.2; the second is that although $C_p$ has a significance different from that of $C_\phi$ (as discussed by Conway and Harrington$^{115}$), in
the case of the h.e.r., at low overpotentials, these two quantities can almost coincide under appropriate conditions. Assuming $C_\phi = C_p$, it can be concluded from the evaluated $C_p$ values that, for the h.e.r. at this electrode metal, $\theta_{H,\text{limiting}}$ is necessarily $< 0.5$. The latter conclusion implies that the kinetics of the h.e.r. at this binary alloy in 0.5M KOH are controlled by the discharge step, as argued for other cases above.

6.6.4. Electrodeposited Ni-W composite

1. The steady-state polarization measurements of the h.e.r. kinetics on an Ni-W electrodeposited film in 0.5 M KOH are characterized by a Tafel line having a slope of 75 mV decade$^{-1}$, with an extrapolated exchange current-density of 0.65 $\mu$A cm$^{-2}$. The area and IR drop-corrected steady-state polarization behaviour of the electroplated Ni-W, shown in Fig. 4.28, appears significantly different from the plot of log (current-density) vs potential at the Ni-W bulk phase alloy.

The electrodeposited Ni-W composite electrode material has a large real/apparent area ratio and thus a micro-porous structure. It is also amorphous as indicated by the absence of any distinct x-ray diffraction pattern. These observations indicate the probability of a quasi-3-dimensionally disordered porous structure at which chemisorption of H could well be substantially different from that at interfaces of well formed crystallites in the surface of a corresponding well defined bulk phase. The significant difference in the polarization behaviour at these two alloys of similar chemical compositions could be caused by stabilizing three-dimensional interactions of adsorbed H with the electroactive sites on the micro-porous material thereby reducing the Tafel slope value. These three-dimensional interactions at such electroactive sites could also account for the excellent polarization performance observed at the Ni-Mo electrocoated materials$^{107-108}$ that is not found at the bulk phase alloy of similar chemical composition. Because of these supposed three-dimensional interactions, which it is
believed give rise to the lower value of the single Tafel slope observed at the electrodeposited Ni-W alloy, it is difficult to draw any conclusions as to which step could be rate-determining based only on information from the steady-state polarization measurements.

2. Similarly to what was observed at the bulk phase Ni-W, not much information can be gained on the coverage by the o.p.d. H on the electrocoated film by the two potential decay treatments presented in this thesis. The C vs η profiles seem, once again, to be affected by the oxidation of hydride species upon decay of potential, if they are evaluated by means of the rate of decay, dη/dt, read from the decay curve at any η. If the capacitance values are derived using the initial potential decay rate, (dη/dt)_{t=0}, following the interruption of a polarizing current, only the C_{dl} is evaluated.

3. Based on the information obtained experimentally that has been presented here, it is difficult to draw any conclusion as to which step is rate-determining in the h.e.r. at this electrodeposited Ni-W film.

6.6.5 Electroplated Ni-V alloy

1. This electroplated alloy is characterized by a single Tafel line having a slope of 110 mV decade^{-1}.

2. The potential relaxation behaviour at this electrocoated material, evaluated by means of the rate of decay, dη/dt, read from the decay curve at any η, reveal a surprising dependence of C on η over the whole potential range investigated. This, in combination with the large C values evaluated, and the fact that the slope of log C vs η line depends on the initial current density passing prior to the opening of the circuit, suggests again that there are hydride species being oxidized during the decay of potential on open-circuit.

Since, in this case, more than one relaxation time is detectable by means of a.c. impedance spectroscopy, this means that only the double-layer capacitance is detectable at
the Ni-V electroplated composite, as at the Ni-W material, by the new decay treatment which uses the initial potential decay rate, \((\text{d}\eta/\text{d}t)_{t=0}\), immediately following opening of the circuit.

3. Therefore, the analysis of the impedance during the h.e.r. at this electrodeposited film is the only alternative left to derive information on the coverage by the kinetically involved H. Although the \(\alpha\) values used in the simulations of the behaviour of the equivalent circuit in Fig. 5.16b have been selected to provide a proper fit with reasonable R and C values, this semi-quantitative analysis still reveals to us, with little doubt, that the discharge step must be rate-determining at this electrode coating, (see the \(C_p\) values in Table 5.3) because the estimated \(C_p\) values, although significant, are too small to give rise to a \(C\) vs \(\eta\) profile that, once integrated, would correspond to electrochemical behaviour for which the \(\theta_{H,\lim} \geq 0.5\).

6.7 Overall Conclusions

1. Care must be taken in the interpretation of the evaluated \(C\) vs \(\eta\) profiles by means of the rate of decay, \(d\eta/dt\), determined digitally along the whole decay curve at any \(\eta\), because at some electrode metals, oxidation of hydride species can give rise to larger \(C\) values than those that would be obtained if \(C_{dl} + C_{\phi}\) were truly measured.

2. Under the condition that a single relaxation time is observed by a.c. impedance spectroscopy, the new decay treatment has been demonstrated to provide a quantitative evaluation of the electrode's interfacial capacitance behaviour by means of the initial rate of decay of potential \([(d\eta/dt)_{t=0}]\), determined immediately following the opening of the circuit, e.g. at Ni and Ni-Mo bulk phase alloys.

3. This latter approach, which involves fitting the potential relaxation curves to an arbitrary extrapolation function, is also advantageous because it allows us to evaluate the "true" \(\eta_{t=0}\) value, when the fitting function is evaluated at \(t = 0\). This subsequently means
that a better IR$_u$ correction, so crucial at high current-densities in steady-state polarization measurements, can be achieved as a result of more reliable $\eta_{i=0}$ values.

4. The agreement between the $C$ values, obtained by the new potential decay treatment that makes use of the fitting function, and the impedance analysis that takes into account the constant phase angle element, is of importance here because it implies that the values obtained by the above decay treatments are not influenced by the cause that gives rise to the disturbing CPA effect observed in the measured a.c. impedance spectra.

5. This latter aspect, along with our new findings from the a.c. impedance studies about the dependence of the depression angle with the anion size, are important clues which certainly help to understand the puzzling "frequency dispersion" that arises almost always at solid-metal solution interfaces. In Chapter 5, we tentatively proposed an explanation that could account for this "frequency dispersion" phenomenon, but more work has to be done on this topic before this phenomenon is better understood.

6. On page 16 of the Introduction, we discussed the Brewer-Engel theory, a treatment that has been much praised by Jaksic$^{34,35,39,48}$ as a meaningful model for prediction of the enhanced synergism in electrocatalysis when metals, such as Ni-W or Ni-Mo, are alloyed. Although the present author agrees with Jaksic on the fact that the electrocoated Ni-Mo or Ni-W are good electrocatalysts, he feels that the model which Jaksic praises so much is quite inadequate because very poor polarisation performance has been observed in the present work for the bulk phase "Brewer-Engel" alloys of similar chemical compositions to those of the electrocoated ones. (In particular high Tafel slopes have been measured). It is felt that the three-dimensional interactions referred to on p. 192, that can arise at the electroactive sites of electrodeposited composites, should receive more attention.
Contributions to Original Research

1. A method for the quantitative evaluation of the coverage by the kinetically involved H intermediate produced during electrolytic H\(_2\) evolution has been developed. The electrochemical adsorption behaviour of the "overpotential-deposited" H has been evaluated by indirectly determining the interfacial capacitance at an electrode interface for various \(\eta\) values in the potential range under study. This new technique makes use of the digital evaluation of the initial rate of decay of potential, \([(d\eta/dt)_{t=0}]\), following the interruption of a polarizing current; \((d\eta/dt)_{t=0}\) is obtained by numerically differentiating the \(\eta(t)\) function at \(t = 0\) that was used to fit the open-circuit potential relaxation curves.

2. A data acquisition and processing procedure, using a digital oscilloscope and a main-frame computer in order to fit a large number of open-circuit potential relaxation curves, was developed.

3. Fitting of the open-circuit potential relaxation curves with a non-linear function was also demonstrated to lead to an accurate evaluation of the true \(\eta_{t=0}\) value after the interruption of the polarizing current.

4. By means of this new potential relaxation treatment, along with both the potential decay method developed earlier in this laboratory and a.c. impedance spectroscopy, useful kinetic and adsorption information has been obtained. Steady-state polarization measurements and the above transient techniques were applied to study the h.e.r. in alkaline solution at Ni metal, at Ni-Mo and Ni-W bulk phase alloys, and at electroplated Ni-W and Ni-V composite electrodes.

5. By comparing the experimental results obtained at the various investigated cathode materials by means of the two types of decay treatments, hydrides were shown to be
occasionally generated during the h.e.r., e.g. at Ni-Mo and Ni-W bulk phase alloys, at Ni-W and Ni-V electrocoated films.

6. A.C. impedance measurements were also applied at Au, at which a relation between the constant phase angle and the size of the anions in solution was demonstrated for the first time. Similar results were found at Ni but, significantly, for Hg—an ideally smooth electrode, no such effects were observable.

7. Relations between the electrocatalytic activities of the bulk alloy electrodes and the electroplated composite materials, for the h.e.r., to their bulk and surface compositions were determined and critically discussed in terms of the Brewer-Engel theory of alloy properties and in relation to results of earlier works.


61) B.E. Conway and J.O'M. Bockris, Naturwissenschaften, 19 (1956) 446.


64) B.E. Conway, Modern Aspects of Electrochemistry 16 (1985) 103.


79) D.L. Chapman, Phil. Mag., 25 (1913) 475.

80) O. Stern, Z. Elektrochem., 30 (1924) 508.


A.1

APPENDIX

Much effort was put into developing suitable software for digital treatment of the experimental data in order to evaluate quantities such as the capacitance at the double-layer and adsorption pseudocapacitance. In order to ease the task for future users who would like to pursue similar works to those described in this thesis, it was felt necessary by the author of this manuscript to devote a section to description of the software used in his work.

A.1 Data transfer from an IBM mini-computer to the University of Ottawa

Main-frame computer

First, a Kermit software program is used in order to allow a micro computer, in this case the IBM-PC or a PC clone, to communicate with the mainframe service.

Once the Kermit software is installed on the hard disk of your IBM-PC, you need to type the following series of commands, so that your PC emulates a VT-100 terminal:

1. C:\cd Kermit [ENTER]
2. # call 3300 [ENTER]
   enter terminal type: VT100 [ENTER].

Then you Logon

1. Logon userid [ENTER]
2. enter password [ENTER]

In order to transfer files, you need to access the mainframe kermit. So you type:

1. Micro [ENTER]
2. Kermit [ENTER]

The screen shows: Kermit - CMS >

Then you type: Receive [Enter]

The screen shows:
kermit-CMS ready to receive
please escape to local Kermit now to SEND the file(s)

Then you type: [CONTROL] ], then C
The screen shows: Kermit-MS>

Then you type: send a:filename.filetype [ENTER]

After the data transfer is completed, the screen will show:

```
Kermit-MS: V2.30 8 Jan 1988
File name: NIW08250.NIW
KBytes transferred: 1
Percent transferred: 100%
Sending: Completed

Number of packets: 12
Packet length: 4
Number of retries: 0
Last error: None
Last warning: One
```

Then you type: connect
The screen shows:

Kermit-CMS ready to receive.
please escape to local Kermit now to SEND the file(s)

Then you just type: quit (it will be typed over what is already written on the screen.)

### A.2 Software for the nonlinear fitting of $\eta(t)$ curves

The fitting of the $\eta(t)$ curve has been by means of the S.A.S. (Statistical Analysis Software) programming language. Using a nonlinear regression subroutine, $\eta(t)$ curves can be fitted, using an equation similar to eqn. 49 as the nonlinear function. For the benefit of future users, two types of programs are described here. An interactive SAS program will be first presented which involves having a user waiting for the results while the program is running. Subsequently, non interactive programs will be discussed since they allow the user to run or edit other programs at the same time as program 1 is running, i.e. you will be using the virtual machine to run program 1. In order to make use of the VMBATCH machine, you
need, in addition to the SAS program, an execution file.

A.2.1 Running an SAS program in the interactive mode

To edit a program, type:

X filename SAS [ENTER]

To run a program, type:

SAS filename [ENTER]

Below is an example of a curve-fitting program designed for the user to work interactively.

FILE: DECIBM SAS * UNIV D'OF OTTAWA CMS

/* THIS PROGRAM HAS THE PURPOSE OF FITTING POTENTIAL RELAXATION CURVES WITH A NONLINEAR FUNCTION. THIS IS A PROGRAM THAT WORKS IN THE INTERACTIVE MODE*/;

/* THE TWO FOLLOWING LINES ARE JUST SPECIAL OPTIONS*/;

CMS FI SASDATA DISK DUMMY DUMMY A;
CMS FI WORK DISK AAA BBB F;

/* THE FOLLOWING SET OF LINES ALLOWS YOU TO READ THE FILE FILENAME FILETYPE WHICH COULD HAVE THE FOLLOWING TWO FORMATS:
   1) INPUT Y WHICH OCCUPIES THE COLUMNS 1 TO 10, INPUT X WHICH OCCUPIES THE COLUMNS 11 TO 20
   OR
   2) INPUT X WHICH IS ON THE FIRST LINE, THEN INPUT Y */;

DATA;
   CMS FILEDEF ONE DISK FILNAME FILETYPE A;
   INFILE ONE FIRSTOBS=1 OBS=500 ;
   * INPUT Y 1-10 X 11-20 ;
   INPUT X /Y;

/* THIS IS THE NON-LINEAR PROCEDURE USED(SEE SAS USER'S STATISTICS GUIDE FOR THE DETAILS ON THE VARIOUS POSSIBLE OPTIONS */;

PROC NLIN BEST=01
   CONVERGE=1E-5 METHOD=GAUSS MAXITER=050 ;
BOUNDS B5 > 0 ;
PARMS B0=.062
   B1=2.01
   B2=-.001
   B3=-.001
   B4=-.0801
   B5=.0001;
MODEL Y =B0+B1*X+B4*LOG(X+B5)+B2*X**2+B3*X**3 ;
DER.B0 =1;
DER.B1 = X;
DER.B2 = X**2;
DER.B3 = X**3;
DER.B4 = LOG(X+B5);
DER.B5 = B4/(X+B5);

OUTPUT OUT=SASDATA.FITPARA1 P=YHAT PARMS=B0 B1 B2 B3 B4 B5;

/* THE OUTPUT OF THE NLIN PROCEDURE IS SAVED IN A SAS PERMANENT
DATA SET (LINE ABOVE), AND THE EXPERIMENTAL AND CALCULATED CURVE
ARE PLOTTED BY THE FOLLOWING SUBROUTINE */;

/* FOR THOSE OF YOU WHO ARE USING A GKERMIT, USE THE PROGRAM AS IS.
FOR THOSE OF YOU WHO ARE USING A GRAPHIC IBM 3179 TERMINAL, DO NOT
USE THE NEXT THREE LINES AND REMOVE THE STAR IN FRONT OF THE FOURTH
LINE */;

GOPTIONS NOTEXT82
GPROTOCOL=GSAS7171 DEVICE=TEK4010
GPROLOG='180'C'X GEPILOG='18'X ;
* GOPTIONS DEVICE=IBM3179 NOTEXT82;
GOPTIONS CBACK=WHITE COLORS=(BLACK RED BLUE GREEN WHITE) ;
TITLE J=L H=1 F=NONE C=BLACK ' CURVE FITTING OF DECAY CURVES ;
H=3 F=SIMPLEX A=90 ' ,
SYMBOL1 W=1 ORED V-STAR ;
FOOTNOTE1 J=L H=1 F=NONE C=BLACK ' NO2420 DAT ' ;
FOOTNOTE2 J=L H=1 F=NONE C=BLACK ' HYDROGEN ' ;
SYMBOL2 W=1 C=BLUE I=JOIN V=DOT ;

PROC GPLOT DATA=SASDATA.FITPARA1;
PLOT Y*X=1
   YHAT*X=2/OVERLAY
   CFRA ME=NONE HMIN OR=O VMIN OR=O ;
RUN :
/* THE LAST SET OF LINES INVOLVES FIRST THE PRINTING OF YOUR PERMANENT
DATA SET FOLLOWED BY A ROUTINE WHICH WILL PUT VTO AND DVDT(T=0)
IN A FILE THAT CAN BE EDITED OR SEND BACK TO A PC VIA KERMIT
(I.E. THIS IS NOT A SAS PERMANENT DATASET, E.G. CUT FDATA) */;
PROC PRINT DATA=SASDATA.FITPARA1:
CMS FILEDEF FDATA DISK CUT FDATA A(DISP MOD;
DATA;
    SET SASDATA.FITPARA1 END=LAST;
    KEEP B0 B1 B2 B4 B5;
    FILE FDATA MOD;
    IF LAST THEN DO VTO=B0+B4*LOG(B5);
       DV=B1+(B4/B5);
       PUT (VTO DV) (E18.);
A.2.2 Running an SAS program non-interactively

In order to run an SAS program non-interactively, three programs are required:

1. The SAS program to be run.
2. An execution program which will run the SAS program.
3. A SAS program that will plot the output received from the virtual machine.

An example of each program is given below:

1. The SAS program to be run.

```sas
FILE: DECMUL SAS * UNIV D'/OF OTTAWA CMS

* THIS IS A MULTIPLE FITING PROGRAM; 
*/
CMS FI SASDATA DISK DUMMY DUMMY A;

DATA;
   CMS FILEDEF ONE DISK AU2 AU *;
   INFILE ONE FIRSTOBS=1 OBS=500;
   INPUT X / Y;
PROC NLIN BEST=01
   CONVERGE=1E-14 METHOD=GAUSS MAXITER=100 ;
P ARMS B0=.062
   B1=.201
B2=.001
B3=.001
B4=.0801
B5=.0001;
   MODEL Y =B0+B1*X+B4*LOG(X+B5)+B2*X**2+B3*X**3 ;
   BOUNDS 0<B5;
   DER.B0 =1;
   DER.B1 = X ;
   DER.B2=X**2 ;
   DER.B3=X**3; 
   DER.B4 =LOG(X+B5) ;
   DER.B5 =B4/(X+B5) ;
   OUTPUT OUT=SASDATA.FITPARA1 P=YHAT PARMS=B0 B1 B2 B3 B4 B5 ;
   CMS FILEDEF FDATA DISK DUMMY DUMMY A ;
   DATA;
   SET SASDATA.FITPARA1 END=LAST;
   KEEP B0 B1 B2 B3 B4 B5;
   FILE FDATA MOD;
   IF LAST THEN DO;
   VTO=B0+B4*LOG(B5);
   DV=B1+(B4/B5);
   PUT (VTO DV) (E18.);
```
END;
RUN;

222222222222222222222222222222222222222222222222222222222222222222222;
CMS FI SASDATA DISK DUMMY DUMMY A;
DATA;
  CMS FILEDEF ONE DISK AU2 AU *
  INFILE ONE FIRSTOBS=501 OBS=1000;
  INPUT X / Y;

PROC NLIN BEST=01
  CONVERGE=1E-14 METHOD=GAUSS MAXITER=100 ;
PARMS B0=.062
B1=-2.01
B2=-.001
B3=-.001
B4=-.0801
B5=.0001;
MODEL Y =B0+B1*X+B4*LOG(X+B5)+B2*X**2+B3*X**3 ;
BOUNDS 0<X5;
DER.B0 =1;
DER.B1 = X
DER.B2=X**2
DER.B3=X**3;
DER.B4 =LOG(X+B5); 
DER.B5 =B4/(X+B5); 
OUTPUT OUT=SASDATA.FITPARA2 P=YHAT PARMS=B0 B1 B2 B3 B4 B5 ;
CMS FILEDEF FDATA DISK EST FDATA A (DISP MOD;
DATA;
  SET SASDATA.FITPARA2 END=LAST;
  KEEP B0 B1 B2 B3 B4 B5;
  FILE FDATA MOD;
  IF LAST THEN DO;
    VTO=B0+64*LOG(B5);
    DV=B1+(B4/B5);
    PUT (VTO DV) (EL18.);
  END;

2. The execution program which will run the SAS program.

FILE: DECMUL EXEC * UNIV D'/OF OTTAWA CMS

/* */
'CP LINK 345638 191 192 RR';
'ACCESS 192 B';
'EXEC SAS DECMUL';
'EXEC SENDFILE EST FDATA TO 345638';
'EXEC SENDFILE DECMUL LISTING TO 345638';
'EXEC SENDFILE DECMUL SASLOG TO 345638';
'exec sendfile sasdata fitpara1 to 345638';
'exec sendfile sasdata fitpara2 to 345638';
A.7

3. An SAS program that will plot the output received from the virtual machine.

FILE: PLOTVT SAS * UNIV D'/OF OTTAWA CMS

CMS F1 WORK DISK AAAAAAA CCCCCCC F;
GOPTIONS NOTEXT82 BORDER
GPROTOCOL=GSAS7171 DEVICE=TEK4010
GPROLOG='180C'X GEPLOG='18'X
GOPTIONS CBACK=WHITE COLORS=(BLACK RED BLUE GREEN WHITE) ;
TITLE J=C H=1 F=NONE C=BLACK ' CURVE FITTING OF DECAY CURVES '
H=3 F=SIMPLEX A=90 ' ',
H=3 F=SIMPLEX A=-90 ' ',
SYMBOL 1 W=1 ORED V=STAR;
FOOTNOTE 1 J=C H=1 F=NONE C=BLACK ' NO3520 BAT ' ;
FOOTNOTE2 J=C H=1 F=NONE C=BLACK ' HYDROGEN ' ;
SYMBOL2 W=1 C=BLUE I=JOIN V='.' ;

PROC GPLOT DATA=SASDATA.FITPARA1;
PLOT Y*X=1
    YHAT*X=2/OVERLAY
CFRAME=NONE HMINOR=0 VMINOR=0 ;

RUN ;

When the time comes to run the SAS program, a user must submit his EXEC file to VMBATCH. An EXEC file, once setup, can be submitted to VMBATCH as a batch job via the SUBMIT command.

Type: Submit filename exec(options
    e.g. Submit filename exec(id test 1 class I sec 900

For more details about VMBATCH type: tutorial.

Then indicate the number corresponding to VMBATCH. In order to find out about the various batch classes, type: X BATCH classes Y.