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EFFECTS OF CYCLIC CURRENT MODULATION ON CATHODE MATERIALS FOR THE HYDROGEN EVOLUTION REACTION

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

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ABSTRACT

Commercial industrial water electrolyser systems often operate discontinuously. The efficiency of the hydrogen evolution reaction (HER) requires cathode materials to have a high intrinsic electrocatalytic activity. Under intermittent operation, it is desirable that both the activity and the structure of the material remain stable.

In this study, intermittent industrial water electrolysis conditions were simulated in the laboratory with a cyclic current modulation test. A conventional material, commercially pure nickel sheet, and a novel material, amorphous Ni_{50}Co_{25}P_{15}B_{10} melt-spun ribbon were evaluated in 8 M KOH electrolyte at 70°C. The electrochemical activity of the material was determined with Tafel (overpotential vs. current density) plots and surface structure was assessed with scanning electron microscopy, energy dispersive x-ray analysis and x-ray photoelectron spectroscopy.

Nickel initially deactivated at constant current due to hydrogen absorption and remained deactivated during cyclic modulation. In a lower-purity electrolyte, nickel partially recovered activity during cycling due to surface growth from electrodeposition of iron impurities.

Ni_{50}Co_{25}P_{15}B_{10} deactivated in a similar manner to nickel but partially recovered activity with cyclic modulation. This is attributed to Ni enrichment at the surface via in-situ electrochemical dealloying; elements with lower HER activities were depleted. The amorphous alloy was embrittled under HER conditions.

For as-polished and cyclically modulated nickel and as-polished Ni_{50}Co_{25}P_{15}B_{10}, the rate-determining step for the HER at low overpotentials is H adsorption and at high overpotentials is H absorption. For cyclically modulated Ni_{50}Co_{25}P_{15}B_{10}, the rate determining step of HER at low overpotentials is H absorption.

With cathodic polarization and cyclic modulation, the surfaces were micro-roughened. After cathodic polarization, surface films on Ni metal and Ni_{50}Co_{25}P_{15}B_{10} were thickened and had a hydroxide character and Ni_{50}Co_{25}P_{15}B_{10} had an increased ratio of Ni:Co.
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-DA
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5. DISCUSSION

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Figure 5.37  EDX spectra of amorphous Ni₅₀Co₂₅P₁₅B₁₀: (a) as-polished and after cyclic current modulation in pre-electrolysed 8 M KOH: (b) wide area, (c) spot analysis of larger, lighter particles.

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Figure 5.39  Comparison of O 1s peaks: amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon after cathodic polarization in pre-electrolysed electrolyte versus NiO and Ni(OH)₂ standards [94].

Figure 5.40  Deconvolution of the Ni 2p₃/₂ spectrum of amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon cathodically polarized in pre-electrolysed electrolyte into divalent (Ni²⁺) and shake-up satellites (sat.) sub-peaks.

Figure 5.41  Deconvolution of the Co 2p₃/₂ spectrum of amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon cathodically polarized in pre-electrolysed electrolyte into divalent (Co²⁺) and shake-up satellites (sat.) sub-peaks.
LIST OF SYMBOLS AND ABBREVIATIONS

- $a_x$ = activity of species $x$
- (aq) = aqueous solution
- $A$ = area [m$^2$]
- AMA = amorphous metal alloy
- $b$ = Tafel constant, Tafel slope [mV/dec]
- $b_x$ = cathodic Tafel constant [mV/dec]
- $b_{high}$ = high-range Tafel slope [mV/dec]
- c.p. = commercial pure
- $C_x$ = molar concentration of species $x$
- CUS = coordinately unsaturated sites
- $D_B$ = breakthrough time diffusivity [cm$^2$/s]
- $D_{hi}$ = half-rise time diffusivity [cm$^2$/s]
- $e^-$ = electron
- $E$ = potential [V]
- $E^*$ = field strength [V/m]
- $E^*$ = standard potential of an electrochemical reaction [V]
- $E_b$ = electron binding energy [eV]
- $E_c$ = cathode potential [V]
- $E_i$ = potential at current density, $i$ [V]
- $E_k$ = kinetic energy of the emitted photoelectron [eV]
- $E_{rev,c}$ = reversible cathode potential [V]
- $E_Q$ = IR, ohmic losses [V]
- EDX = energy dispersive x-ray spectroscopy
- $F$ = Faraday's constant [96 487 C]
- FCC = face-centred cubic
- $\Delta G^*$ = Gibbs standard free energy change [J]
- $h\nu$ = energy of the incident photon
- $\Delta H$ = heat of adsorption [J]
- HE = hydrogen embrittlement
- HER = hydrogen evolution reaction
- $i_c$ = cathodic current density [A/m$^2$]
- $i_o$ = exchange current density [A/m$^2$]
- $i_n$ = current density at overpotential, $\eta$ [A/m$^2$]
- $i_n,high$ = high-range exchange current density [A/m$^2$]
- $I$ = current [A]
- $I_C$ = cathodic current [A]
- $I_O$ = exchange current [A]
- $K_{H_2O}$ = dissociation constant of water
- $l$ = length of field [m]
- $m_x$ = molality of ion $x$ [mol/kg]
- $mV_{Hg/HgO}$ = potential versus mercury/mercury oxide reference electrode
- $mV_{SHE}$ = potential versus standard hydrogen electrode (SHE)
- $M$ = metal species
- M = molarity [mol/L]
- $n$ = number of electrons transferred
- $N$ = number of cycles
- o.c. = open circuit
- $\phi$ = Osmotic Coefficient
- OER = oxygen evolution reaction
- p.e. = pre-electrolysed
ppm = parts per million
rds = rate determining step
R = universal gas constant [8.314 J/K·mol]
RHE = reference hydrogen electrode
RHP = reversible hydrogen potential
sat. = satellite
SEM = scanning electron microscopy
s.c. = short circuit
SHE = standard hydrogen electrode
t = time [s, min]
T = temperature [K]
tON = time at on current density [s, min]
tOFF = time at off current density [s, min]
tut = untreated
V-H = Volmer-Heyrovsky
V-T = Volmer-Tafel
XPS = X-ray photoelectron spectroscopy
Zv = valence

\( \alpha \) = transfer coefficient
\( \alpha_c \) = cathodic transfer coefficient
\( \beta \) = symmetry factor (0.5 for electron transfer step)
\( \phi \) = surface coverage of reactant
\( \phi_{wfc} \) = work function of spectrometer
\( \gamma \) = number of electron steps before the rds
\( \gamma^* \) = mean molal activity
\( \eta \) = overpotential [V]
\( \eta_a \) = anodic overpotential [V]
\( \eta_c \) = cathodic overpotential [V]
\( \eta_{range} \) = range of overpotential [V]
\( \eta_{H_2} \) = HER overpotential [V]
\( r \) = 1 if rds is electron transfer step or 0 if rds is a chemical reaction
\( \lambda_e \) = limiting equivalent conductivity [m²/Ωeq]
\( \nu \) = stoichiometric number of times rds occurs
\( \sigma \) = specific conductivity [1/Ωm]
\( \sigma_x \) = specific conductivities of species x
\( \Delta \Psi \) = solution resistivity
1 INTRODUCTION

1.1 HYDROGEN PRODUCTION BY ELECTROLYSIS OF WATER

Hydrogen (and oxygen) can be produced from water:

\[ H_2O (l) \Rightarrow H_2 (g) + \frac{1}{2}O_2 (g) \]  (1.1)

Electrochemical decomposition of water is called electrolysis, whereby water is converted to its elements when a direct current is passed through it:

\[ H_2O (l) + \text{electricity} \Rightarrow H_2 (g) + \frac{1}{2}O_2 (g) \]  (1.1')

There have been many reviews of theoretical and practical production of hydrogen by electrolysis [1-11]. Water electrolysis is a technology for obtaining hydrogen from non-fossil energy. Hydrogen and oxygen produced by electrolysis can easily and efficiently be recombined in a fuel cell (via the reverse of reaction (1.1)) to produce electricity with only water as a by product. As well, the gas is high-purity, there is flexibility of production and the process can be automated [3]. Because hydrogen can be utilized as an energy storage medium, production of hydrogen by water electrolysis during off-peak (lower cost) hours would provide energy storage and load leveling during off-peak demand periods for electric utilities, offsetting the generally high costs of electricity. Stored hydrogen, with relatively light weight and fast re-fuelling/re-charging, is of great interest as an energy storage medium for use in fuel-cell electric vehicles.

Although present development of hydrogen fuelled vehicles is immature, hydrogen is used industrially for many processes including synthesis of ammonia,
hydrogen chloride, hydrogen peroxide, methanol, etc.; hydrogenation of edible oils; protective atmospheres for welding; non-ferrous metal reduction; and semi-conductor processing.

The electrochemical reactor used for hydrogen production via Eqn. (1.1') is called an electrolysis cell (Figure 1.1). The main components of the electrolysis cell are: (i) a power source (ii) two electrodes, an anode and cathode, (iii) a semi-permeable electrode separator, and (iv) a conductive electrolyte. The power source must provide sufficient voltage to drive the decomposition.

Hydrogen gas is evolved at the cathode surface while oxygen is evolved at the anode surface. The electrodes must be electronic conductors, efficiently catalyze their respective reactions and be corrosion resistant when electrochemically polarized in the electrolyte. A separator is necessary to prevent the gases from mixing. Either an acidic or alkaline electrolyte can be used to provide the ionic conduction necessary for water electrolysis. Alkaline electrolyzers are favoured for construction due to reduced corrosion considerations. However, for optimum ionic conductivity it is necessary that alkaline electrolyte be highly concentrated.

Commercial alkaline water electrolyzers often are configured using monopolar cells. In the monopolar construction, each electrode has only one polarity and acts as either an anode or a cathode and each cell is connected in an electrical series. The monopolar design is favoured because of its relatively simple and sturdy tank construction, low cost, easy maintenance and low electrode corrosion under discontinuous operating conditions.
The disadvantage of monopolar design is that relatively long current paths in the electrode bus bar leads cause relatively high voltage losses and non-uniform current density distribution. However, recent cell designs are overcoming this limitation.

Figure 1.1 Schematic of alkaline electrolysis of water.
1.2 OPERATIONAL AND MATERIAL CONSIDERATIONS OF COMMERCIAL ELECTROLYSERS

Electrolysers can be operated either continuously (for tens and hundreds of hours) or intermittently (with interruptions of hours to tens of hours). Consequently, electrodes must be stable whether the cell is powered on or off. Electrode performance stability under discontinuous operation is dependent on the electrode material and the voltage experienced during operation.

The reasons for discontinuous operation are numerous but can be divided into controlled and uncontrolled interruption. Conditions where interruptions are expected include:

⇒ operating at off-peak periods when grid power cost is low; day-time or midday shut-downs can be expected when demand on the grid is highest (Figure 1.2.)
⇒ operating off a solar cell; there is no power input at night (Figure 1.3.)
⇒ installation of new cells

Conditions where interruptions are uncontrolled include:

⇒ operating off intermittent power generation, such as wind-generation (Figure 1.4.)
⇒ fluctuations in power generation, such as cloudy conditions for solar generation (Figure 1.3.)
⇒ grid-power blackouts and brownouts
⇒ electrolyser system repairs and maintenance

Consequently, there has been considerable interest in the performance of electrolysers under variable power input [12-15].
Figure 1.2 Intermittent water electrolysis current input: operation during low-demand periods of electric utility grid.

Figure 1.3 Intermittent water electrolysis power input: example of solar cell current profile (after [15]).

Figure 1.4 Intermittent water electrolysis power input: example of random current profile of a simulated windmill, where $E = f(I)$ (after [13]).
Commercially, it is desirable to reduce the power required (i.e. the cell voltage) or conversely to increase the product yield (i.e. the current density); about 80% of the cost of electrolytic hydrogen is the cost of electricity.

To reduce the cell voltage it is necessary to utilize and develop materials that efficiently catalyze the hydrogen and oxygen evolution reactions. Because of the strongly caustic conditions of alkaline water electrolysis, electrode corrosion is a concern. At open-circuit conditions, the corrosion of cathodes is greater than while current is flowing. The electrode must have long-term structural stability. Furthermore, it must have electrocatalytic stability under both on and off conditions.

Platinum and the platinum-group metals are excellent, and stable, electrocatalysts but because of their high costs, the most common electrode material has been iron which has low cost and is a good electrocatalyst. Nickel is more expensive than iron, but because it is a better electrocatalyst and is more corrosion resistant through the operating regime of alkaline electrolyzers, it is now commonly used for electrode materials. More advanced commercial hydrogen cathode materials are usually based on nickel.

Materials can be catalytically activated (i.e., efficiency is increased) by several processes. Sulphur activation, whereby nickel sulphides are formed, have low long-term stability forming coarse nickel coatings. Porous nickel (Raney nickel), produced from nickel-aluminum or nickel-zinc alloys by leaching out the aluminum/zinc in caustic electrolyte, has better stability. In both of these processes, the main effect is to produce a greater actual electrode area in the same space as a solid electrode. Improved hydrogen cathodes can also be produced by combining materials that have a synergistic effect.
Nickel-molybdenum alloys, in particular, are such materials. Degradation of these materials may be a concern because of their multiple phase nature.

Amorphous metal alloys are presently under consideration as electrode materials. They are produced by rapid cooling and exhibit a non-crystalline atomic structure. Amorphous materials have homogeneous microstructures and are free from crystalline defects such as grain boundaries. Because they also lack secondary phases and surface defects and (compared to conventional crystalline alloys) can be produced in unique compositions, they can be very corrosion resistant. For these reasons, they are of interest as stable electrode materials for electrocatalysis and particularly for intermittent electrolysis of water in a caustic environment.

1.3 OBJECTIVES

In consideration of the preceding introduction, the objectives of this project are:

(i) to simulate intermittent industrial water electrolysis conditions by developing a cyclic current modulation test procedure,
(ii) to determine the effects of intermittent operation on the cathodic hydrogen overpotential,
(iii) to determine changes of cathodic electrocatalytic parameters with intermittent operation,
(iv) to characterize the effects of intermittent operation on cathode surface chemistry and structure,
(v) to correlate the effects of intermittent operation on the reaction mechanism of the hydrogen evolution reaction, and
(vi) to suggest the suitability of electrode materials for use in industrial conditions under intermittent power supply.
2. BACKGROUND AND LITERATURE REVIEW

This section will discuss the principles of producing hydrogen from water by electrocatalysis and then review Ni-based hydrogen evolution cathode systems that have been reported in literature.

2.1 WATER ELECTROLYSIS

Water electrolysis is the electrochemical process by which H₂ and O₂ are produced from water present as an aqueous electrolyte to conduct the charge. The following section will discuss water electrolysis in alkaline environments.

2.1.1 ALKALINE WATER ELECTROLYSIS REACTIONS

A schematic of an alkaline water electrolysis cell is given in Fig. 2.1. The ionic species in an alkaline electrolyte are OH⁻ and K⁺ (or Na⁺) and the two electrode reactions (and resultant cell reaction) are:

\[
\begin{align*}
\text{Cathode:} & \quad 2\text{H}_2\text{O} + 2e^- \Rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{Anode:} & \quad 2\text{OH}^- \Rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \\
\text{Cell:} & \quad \text{H}_2\text{O} \Rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2
\end{align*}
\]

Reduction occurs at the cathode where H₂O is decomposed to form hydrogen gas (H₂) and hydroxyl (OH⁻) ions (reaction 2.1). At the anode OH⁻ ions are oxidized to form H₂O and O₂ (reaction 2.2). The overall reaction (1.1) is dissociation of water to hydrogen and
oxygen gas. The reduction and oxidation half-reactions are called, respectively, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

Figure 2.1 Schematic of alkaline electrolysis of water.
2.2 CATHODE REACTIONS AND HYDROGEN EVOLUTION

The hydrogen evolution reaction is the reaction of interest in this study:

\[
\text{HER: } 2\text{H}_2\text{O} + 2e^- \Rightarrow \text{H}_2 + 2\text{OH}^- \quad (2.1)
\]

Theoretically [16-19], the HER on nickel has been reported to consist of a:

(i) primary discharge step (Volmer reaction):

\[
\text{M} + \text{H}_2\text{O} + e^- \Rightarrow \text{MH}_{\text{ads}} + \text{OH}^- \quad (2.4)
\]

followed by either a:

(iiia) recombination reaction (Tafel reaction):

\[
\text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} \Rightarrow 2\text{M} + \text{H}_2 \quad (2.5)
\]

or:

(iiib) adatom desorption reaction (Heyrovsky reaction):

\[
\text{MH}_{\text{ads}} + \text{H}_2\text{O} + e^- \Rightarrow \text{M} + \text{H}_2 + \text{OH}^- \quad (2.6)
\]

The thermodynamic and kinetic considerations of the HER will be discussed in the following sections.
2.2.1 THERMODYNAMIC CONSIDERATIONS

The standard potential of an electrochemical reaction, $E^\circ$, is related to the Gibbs standard free energy change, $\Delta G^\circ$:

$$E^\circ = -\Delta G^\circ / nF$$  \hspace{1cm} (2.7)

where, $n =$ number of electrons transferred  
$F =$ Faraday’s constant [96 487 C]

and for the alkaline cathode reaction (2.1) the standard electrode potential, $E^\circ_c$, is:

$$E^\circ_c = -0.826 \text{ V vs. SHE}$$  \hspace{1cm} (2.8)

The equilibrium, or reversible electrode potential, $E_{\text{rev}}$, is related to the standard potential by the Nernst equation:

$$E_{\text{rev},c} = E^\circ_c - (RT/nF) \ln \left( \frac{a_{H_2} (a_{OH^-})^2}{(a_{H_2O})^2} \right)$$  \hspace{1cm} (2.9)

where, $E_{\text{rev},c} =$ reversible cathode potential [V]  
$R =$ universal gas constant [8.314 J/K*mol]  
$T =$ temperature [K]  
$a_x =$ activity of species x

The reversible hydrogen potential in 8M KOH (aq) at 70°C is -972 mV_SHE (Appendix B-2).

Under typical electrolysis conditions where hydrogen is produced at an appreciable rate at the cathode, the potential of the cathode, $E_C$, is comprised of several components:

$$E_C = E_{\text{rev},c} + \eta_c + E_\Omega$$  \hspace{1cm} (2.10)

where,  
$E_{\text{rev},c} =$ reversible cathode potential [V]  
$\eta_c =$ cathodic overpotential [V]  
$E_\Omega =$ IR, ohmic losses [V]

Overpotential is defined as the additional applied potential necessary to drive the reaction at a given rate. The $E_\Omega$ terms are the resistive losses in the electrolyte, at contacts of the wire leads and across surface films of the electrodes (i.e. surface oxides).
2.2.2 KINETIC CONSIDERATIONS

When the reaction is kinetically controlled (excluding mass transport and ohmic losses), the parameters of the potential-current relationship provide a means of evaluating electrocatalytic activity.

When \( E = E_{\text{rev}} \), there is zero net current. That is, the opposing anodic and cathodic currents, \( I_a \) and \( I_c \) respectively, are equal in magnitude and this absolute magnitude is the exchange current, \( I_o \):

\[
I_o = I_a = |I_c|
\]  

This expression can also be written in terms of the exchange current density based on the apparent geometric electrode surface area, \( A_{\text{apparent}} \):

\[
i_o = i_a = |i_c|
\]

where, \( i_x = I_x/A_{\text{apparent}} \)

When there is an applied potential, \( E = E_{\text{rev}} + \eta \), the current and the overpotential can be related to the exchange current by the Butler-Volmer equation:

\[
i = i_o \left[ \exp(-\alpha nF\eta/RT) - \exp((1-\alpha)nF\eta/RT) \right]
\]

where, \( \alpha = \) transfer coefficient

At high overpotentials, i.e. at a large cathodic overpotential where \( i_c \gg i_a \), this equation reduces to:

\[
i_c = i_o \exp(-\alpha nF\eta/RT)
\]

or,

\[
\log i_c = \log i_o - 2.303(\alpha nF\eta/RT)
\]
This logarithmic current-potential relationship is called the Tafel equation:

\[ \eta_c = b_c \log(i_c/i_o) \]  

(2.15)

where \( b_c \) is the Tafel constant:

\[ b_c = 2.303RT/\alpha_c F \]  

(2.16)

and \( \alpha_c \) is the transfer coefficient:

\[ \alpha_c = \gamma/v + r\beta \]  

(2.17)

where,

\[ \begin{align*}
\gamma &= \text{number of electron steps before the } rds \\
v &= \text{stoichiometric number of times } rds \text{ occurs} \\
r &= 1 \text{ if } rds \text{ is electron transfer step or} \\
0 &= \text{ if } rds \text{ is a chemical reaction} \\
\beta &= \text{symmetry factor (0.5 for electron transfer step)}
\end{align*} \]

The transfer coefficient relation (2.17) defines how the Tafel constant is related to the rate determining step \( (rds) \).

Practically, \( \log i_c \) (reaction rate) can be plotted vs. \( \eta_c \) (driving force) and the linearity observed is that described by the Tafel equation (Fig. 2.2). From this linear portion the extrapolated intercept at \( \eta_c = 0 \) is \( i_o \), the exchange current density and the slope, \( b_c \), is the Tafel slope.

2.2.3 TAFEL ANALYSIS TECHNIQUE

The exchange current density and the Tafel slope are both dependent on the electrode material. Examination of a hypothetical Tafel plot (Fig. 2.2) shows that more active materials will have high \( i_o \) (curve (i)) and/or low \( b \) (curve (ii)) values; for a given
Figure 2.2  Schematic of hypothetical cathodic Tafel plot.

Figure 2.3  Possible $\eta$–log $i$ phenomena for a non-corroding electrode system, $Z^+ + e^- \leftrightarrow Z$ (line ...): (a) activation polarization, (b) activation polarization and concentration polarization with limiting current, (c) resistance polarization and (d) second electrochemical (corrosion) process, $M^+ + e^- \leftrightarrow M$ (line ... ...)(after [20]).
driving force ($\eta_c$), curves (i) or (ii) will produce higher reaction rate ($i_c'$ and $i_c''$, respectively).

There is some uncertainty in the interpretation of $\eta$-log $i$ data when non-linearity (deviation from Tafel behaviour) is encountered. Stern and Geary's theoretical analysis of the shape of polarization plots summarized the kinetic phenomenon which can cause non-linearity [20]. For a non-corroding electrode (i.e. HER on Pt), deviations from activation polarization at high overpotentials can result from concentration polarization and/or resistance polarization. When the electrode is also corroding, complicating factors arise owing to the co-existing corrosion reaction. A shift of the open-circuit potential to the corrosion equilibrium potential and the corrosion reaction can cause the plot to bend at higher overpotentials. These phenomena are illustrated in Figure 2.3. With an additional electrode system the overall system would have further complexity.

2.2.4 HYDROGEN EVOLUTION REACTION

The HER in alkaline media, as described in Section 2.2, theoretically consists of two pathways: the Volmer (2.4) - Tafel (2.5) (V-T), or (b) the Volmer (2.4) - Heyrovsky (2.6) (V-H). Table 2-I lists the two pathways and the theoretical Tafel slopes associated with each step, corrected to 70°C. If the steps are consecutive, the rate determining step of the HER can be distinguished by the difference in Tafel slopes for reactions (i), (iia) and (iib).

Electrocatalytic activity is an intrinsic material dependent property. Different elemental materials have different activities. Similarly, different alloy systems and
Table 2-I  Hydrogen evolution reaction intermediary pathways: (a) Volmer-Tafel (V-T) or (b) Volmer-Heyrovsky (V-H).

| REACTANT | PATH | (a) V-T | b
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(i)</td>
<td>$\text{H}<em>2\text{O} + e^- \rightarrow \text{H}</em>{\text{ads}} + \text{OH}^-$</td>
<td>138 mV/dec</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>$\text{H}<em>{\text{ads}} + \text{H}</em>{\text{ads}} \rightarrow \text{H}_2$</td>
<td>35 mV/dec</td>
</tr>
<tr>
<td>PRODUCT</td>
<td></td>
<td>$%\text{H}_2 + \text{OH}^-$</td>
<td></td>
</tr>
</tbody>
</table>

Since electrocatalysis occurs at the material interface and the surface of a material usually differs from the bulk, the activity of the surface species is important. The surface species chemistry is a product of both the bulk (electrode) and the environment (electrolyte), so the composition of all three are interconnected. Electrode modulation which is the subject of this study, could affect both the exchange current density and the Tafel slope through modification of the surface properties. The interface between the electrode and the electrolyte may have different properties than the bulk phases. The morphology, microstructure and chemistry of the electrode, could be affected through the processes of:

- oxide formation and reduction,
- second phase dissolution and/or deposition, and
- adsorption and/or absorption

by changing the:

- real area,
- surface defects,
- chemical composition,
- oxidation state, and
- lattice spacing

of the surface.
If oxidation occurs:

- there could either be film growth or dissolution,
- the surface area could increase if the growth is rough or porous or if dissolution causes roughening,
- the surface area could decrease by electropolishing,
- the number of surface defects could increase or decrease,
- the substrate composition of an alloy could change by second phase dissolution to a more or less active composition,
- the surface film composition could change and could also have a different stoichiometry of alloying elements compared to the substrate,
- the oxidation state of film could change to more or less inherently active species, and
- there could be introduction of new ionic species into the electrolyte which could have a homogeneous catalytic effect.

If reduction occurs:

- there could be removal of oxidation products which were either more or less active than the substrate,
- there could be electrodeposition of ionic species from the electrolyte, which could yield a more active or less active surface than underlying substrate,
- the oxidation state of the surface film could change to more active or less active species,
- the surface area could increase by electrodeposits, and
- the surface area could be decreased by removal of the oxide film.
If adsorption/absorption occurs:

- absorption of electrolyte species into surface could cause film growth,
- absorption of electrolyte species could change the lattice spacing to more favourable or less favourable spacings,
- adsorption of electrolyte species onto the surface could aid or hinder electrocatalytic processes.

An increase in the real surface area can improve the apparent activity by increasing the apparent exchange current density. The intermediate reaction steps of adsorption tend to occur at surface atomic structure defects such as steps, kinks, ledges and dislocations, as well as at microstructural defects and edges. As mentioned, activity is an inherent property of chemical composition. Similarly, different atomic states (oxides, hydroxides, hydrides) have different activities for a given element. Absorption and adsorption are dependent on the lattice spacing.

These factors of electrocatalysis will be discussed in detail in the following sections.
2.3 ELECTROCATALYSIS

Electrocatalysis is catalysis where the rate of reaction is controlled by application of electric potential; the reaction occurs at an electrode (electrocatalyst), involving interaction between the electrode surface, the electrochemical reactants and the intermediates [21]. Electrocatalytic studies involve determining the dependence of the mechanism and rate of reaction on the physicochemical properties of the electrode material. Because the reaction rate is primarily controlled by an electrical potential, improved electrode activity is achieved through increasing the rate of electron transfer by the decrease of the activation energy of the rate determining step or through a more favourable sequence of reaction steps [22].

2.3.1 CHEMISORPTION

Electrocatalysis involves a chemisorption process; the adsorbate interacts with the adsorbant forming a chemical bond by rearrangement of electrons. The change in electrocatalytic activity among metals depends on chemisorption (measured by the heat of adsorption); plotting heat of hydrogen adsorption versus exchange current gives rise to a "volcano" curve relation (Figure 2.4(a)). This relationship acts as a guide to predict catalytic activity of a material.

As can be seen from the volcano curve, medium adsorption energy heats give rise to the highest electrocatalytic activities. If adsorption is weak, only a small portion of the electrode surface will be covered by the reactant and desorption will occur before the
Figure 2.4  Theoretical ‘volcano’ curve relationship between heat of adsorption of HER intermediate and activity.

Figure 2.5  Exchange current densities for electrolytic hydrogen evolution vs. bonding adsorption strength (enthalpy) of intermediate metal-hydrogen (M-H) bond formed during the electrode reaction itself (After [24]).
adsorbant can undergo an electrochemical or chemical transformation. With higher heats of adsorption there is a corresponding increase in surface coverage of the reactant ($\phi$) and activity, up until the adsorbant approaches full coverage ($\phi \rightarrow 1$). At yet higher heats of adsorption, activity will decrease because the reactant species is highly immobile and large activation energies are required for an electrochemical or chemical transformation or for removal of reaction products to provide open reaction sites. Hence, the maximum in the volcano curve results when surface coverage of the adsorbed intermediate approaches $\phi = 1$. This is illustrated in Figure 2.4 (a) and (b).

As will be seen in the following sections, adsorption is also related to electrode composition and surface microstructure.

2.3.2 ELECTROCATALYSIS FOR THE HER

The electrocatalytic activity of metals for the HER can be correlated to the heat of adsorption of the reaction intermediate (M-H) on the electrode surface [23]. An experimental volcano curve is shown in Figure 2.5 [24]. Although the volcano curve correlation is well known, the relationship between the magnitude of the heat of adsorption and the properties of a metal is less well understood. The two key properties of the electrode affecting chemisorption (measured by heat of adsorption) and catalytic activity are the electronic and geometric-surface structures.
2.3.2.1 **Electronic Factors**

A number of theories of electrocatalysis have been suggested based on electronic factors. The relationship is better understood for pure metals than for alloys. Generally, the electrocatalytic activity of a metal is a function of its group in the (Mendeleev’s) Periodic Table of the Elements. In particular, the d-band characteristics of transition metals are important for chemisorption. In transition metal catalysts, unpaired d-band electrons couple with unpaired s-band or p-band electrons from the adsorbate; for the HER, hydrogen is strongly adsorbed via electron pair formation. Group VIII elements, possessing a high percentage of paired electrons in the d-band and medium heats of adsorption, consistently exhibit the highest electrocatalytic activities, particularly Pt-group metals (Pt, Rh, Ir, Pd) and transition metals (Ni, Co, Fe, Mo).

Theory for the HER on alloys is less developed than that for pure metals. Enhanced electrocatalytic activity in composite materials derives from synergistic (i.e. more than simple linear combination) effects between the elemental components. Predictions based on combinations from opposing branches of volcano curve metals ($\Delta H_{M-H}$) only occasionally yield more active HER materials, notably Ni-Mo or Co-Mo combinations [25]. The electrocatalytic properties of such alloys are due to the resulting electronic structure being optimal for bonding conditions of $H_2O$ and H-H on the metal surface. These alloys imitate the electronic structure of Pt and Pt-metals. Revised theory [26], based on metallic bonding, suggests that combinations of elements from opposite ends of the transition periods in the Periodic Table will yield stable systems with enhanced electrocatalytic activity. The nearly empty d-bands of metals from the left-end of the transition series share electrons with the partly filled d-bands of metals from the right-end.
Consequently, group VIII metals and their alloys, particularly Ni, are employed commercially as HER electrodes because of their combination of high activity and low cost compared to Pt-group metals. Although they have good stability at high HER overpotentials, the stability under intermittent operating conditions is of interest because group VIII metals undergo hydroxide and oxide transformations at potentials near the reversible hydrogen potential. With modulation, the stoichiometries of the bulk alloy at the surface and the surface film could be altered and hence have a different intrinsic activity compared to the unmodulated material.

2.3.2.2 Geometric Structure

Surface geometric factors which affect chemisorption include interatomic spacing in crystals, the presence of coordinately unsaturated sites (CUS) and other crystal defects. The minimum activation energy of chemisorption of a reactant occurs at an optimum interatomic spacing. With smaller spacing, the chemisorption will be weak due to repulsion between the adsorbates while at greater spacing, the intermediate species will dissociate rather than be adsorbed. For such reasons, specific crystal planes may be more catalytically active than others [27].

CUS on the crystal surface, such as kinks, ledges and steps, have lower numbers of nearest neighbours than surface atoms within a crystal plane. These sites are at a high interaction energy state and possess high adsorption activity and favourable conditions for chemisorption [27]. Similarly, crystal defects (i.e. dislocations) within the surface can also have reduced activation energy for chemisorption.
Under intermittent HER conditions it is possible that surface growth and removal, through reduction/oxidation or dissolution/deposition, can change the CUS and hence the chemisorption conditions.

2.3.2.3 Applied Potential

For the Volmer-Heyrovsky HER mechanism (Eqn. (2.4) and (2.6)), Laisa and Rami [28] reported that the two steps are experimentally indistinguishable. Since different surface coverages are possible, a Tafel slope for one mechanism at a given $\phi$ is equal to the other Tafel slope at $(1 - \phi)$ for another. With increasing overpotential, assuming the first (Volmer) step as the rds leads to a decrease in $\phi$ but assuming the second (Heyrovsky) step as the rds causes an increase in $\phi$. A graph of surface coverage as a function of the potential for these two cases is shown in Figure 2.6. As chemisorption, and electrode activity, is dependent on surface coverage of adsorbed H, the nature of the coverage at the high overpotentials that can be encountered during the HER is very important.

![Figure 2.6](image-url)  
**Figure 2.6** Surface coverage, $\phi$, as a function of overpotential with Heyrovsky (line A) and Volmer (line B) mechanisms as rds (After [28]).
2.3.3 SURFACE ANALYSIS OF CATALYSTS

X-ray photoelectron spectroscopy (XPS) is a sensitive tool for characterizing the chemical and physical state of surfaces. XPS analysis provides information on the elements present, their relative amounts and their valence state; XPS is particularly suited to the study of catalysts because the surface sensitivity is on the order of 10 - 20 Å (i.e. several atomic layers).

2.3.3.1 X-Ray Photoelectron Spectroscopy Technique

The XPS technique involves irradiating a solid with x-rays. These photons interact with atoms in the surface and, if absorbed by an atom, eject an electron as a photoelectron [29]. Since the kinetic energy of the ejected photoelectrons is small, only photoelectrons near the surface can leave without energy loss and be detected, resulting in the high surface sensitivity of the XPS technique. An electron in a given element in a specific atomic shell is bound by a particular energy. The binding energy, $E_b$, is related to the energy of the incident photon and the emitted photoelectron by:

$$E_b = h\nu - E_k - \phi$$  \hspace{1cm} (2.20)

where, \[ \begin{align*}
E_b & = \text{energy of the incident photon} \\
h\nu & = \text{kinetic energy of the emitted photoelectron [eV]} \\
\phi & = \text{work function of spectrometer}
\end{align*} \]

The binding energy will shift slightly depending on the local chemical environment of the atom.
Although materials evaluation is the impetus of the study of electrocatalysis, the task of materials selection involves the consideration of additional factors. These factors include: (i) good electrocatalytic properties, (ii) large real surface area, (iii) long term electrocatalytic stability, (iv) good mechanical and structural stability, (v) low cost, and (vi) high availability [22,30].

While the exchange current ($I_0$) and the Tafel slope ($b$) are intrinsic properties of the electrode/electrolyte interface, the exchange current density is extensive; $I_0$ depends on the true surface area. Determination of the real electrocatalytic surface area is difficult [31]. Approximations can be made based on optical appearance (estimation of the order of magnitude of real area to geometric area): polished surfaces, 2-3, satiny, 5-10, matte/dark, 50-200 [32]. The implications are that, after an activation procedure, a change in Tafel slope value is due to mechanistic changes but a shift in Tafel slope (i.e. a change in exchange current) is due to either mechanistic changes or a change in the real surface area or both. Industrially, it is common practice to produce electrodes with extremely rough or porous surfaces to artificially increase activity by maximizing surface area.

Electrocatalytic active cathodes must be insensitive to mechanisms of deactivation with time, such as reduction or oxidation of active surface species, deposition of impurities, and absorption of atomic hydrogen into the lattice of the electrode. The cathode must be resistant to deterioration from corrosion or mechanical and thermal shocks which may be encountered throughout the operating conditions.

As seen in previous sections, the group of platinum metals has excellent electrocatalytic performance for the HER. However, the transition metals (Ni, Fe, Co)
also exhibit very good electrocatalytic HER performance at much lower cost than the Pt-group metals and, as a result, cathodes based on these transition metals and alloys are the most commercially relevant for alkaline water electrolysis.

The following sections are a review of literature pertaining to nickel and Ni-based materials for HER under alkaline (KOH or NaOH) electrolysis conditions.

2.4.1 CRYSTALLINE NICKEL METAL CATHODES

Tables 2-IIa and 2-IIb summarize reported electrochemical data of crystalline Ni HER cathodes in various electrolytes. Some cathodes exhibit two linear Tafel regions and two Tafel slopes are given. Two columns for Tafel data are tabulated, one is for fresh (initial condition) electrodes and the other for cathodes after continuous or intermittent HER polarization. For the latter case this includes polarization under the following conditions: continuous steady-state, steady-state with current interruption and potential cycling.

2.4.1.1 Initial Nickel Metal Tafel Data

Examination of the initial Tafel data on fresh Ni metal cathodes (Table 2-IIa) shows reported Tafel slopes vary from 80 mV/dec to 239 mV/dec, although most values fall into ca. \( b = 100-120 \ \text{mV/dec} \) and ca. \( b = 145-170 \ \text{mV/dec} \) windows; some reports indicate two Tafel slopes, for low and high overpotential ranges.
TABLE 2-IIa

Summary of Tafel data on crystalline Ni-metal HER electrodes in KOH and NaOH electrolytes.

<table>
<thead>
<tr>
<th>Nickel Metal Cathodes</th>
<th>Electrolyte+</th>
<th>Temp (°C)</th>
<th>Initial $b_c$ (mV/dec)</th>
<th>Initial $i_o$ (mA/cm²)</th>
<th>Final $b'_c$ (mV/dec)</th>
<th>Final $i'_o$ (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>148, 96</td>
<td>0.006</td>
<td>-</td>
<td>-</td>
<td>[33]</td>
</tr>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>120, 239</td>
<td>0.032, 0.63</td>
<td>-</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>139, 205</td>
<td>0.013</td>
<td>-</td>
<td>-</td>
<td>[35]</td>
</tr>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>158</td>
<td>0.015</td>
<td>-</td>
<td>-</td>
<td>[36]</td>
</tr>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>146</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>[37]</td>
</tr>
<tr>
<td>Ni</td>
<td>1M NaOH</td>
<td>25</td>
<td>110</td>
<td>0.0014</td>
<td>-</td>
<td>-</td>
<td>[38]</td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>1M NaOH</td>
<td>25</td>
<td>115</td>
<td>0.0018</td>
<td>-</td>
<td>-</td>
<td>[28]</td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>50</td>
<td>80, 167</td>
<td>0.14, 4.44</td>
<td>-</td>
<td>-</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni 200@100mA/cm²</td>
<td>30% KOH</td>
<td>37</td>
<td>100</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>[40]</td>
</tr>
<tr>
<td>Potential-Cycled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>70</td>
<td>99</td>
<td>0.055</td>
<td>-</td>
<td>-</td>
<td>[41]</td>
</tr>
<tr>
<td>Potential-Cycled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>50</td>
<td>111</td>
<td>0.045</td>
<td>-</td>
<td>-</td>
<td>[42]</td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>90</td>
<td>103</td>
<td>0.070</td>
<td>-</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>70</td>
<td>102</td>
<td>0.046</td>
<td>-</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>89</td>
<td>0.072</td>
<td>[45]</td>
</tr>
<tr>
<td>Ni@100mA/cm²</td>
<td>30% KOH</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>95</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Potential-Cycled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co@100mA/cm²</td>
<td>30% KOH</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>95</td>
<td>0.0325</td>
<td></td>
</tr>
<tr>
<td>Potential-Cycled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (99.9%)</td>
<td>30% KOH</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>95</td>
<td>0.0325</td>
<td></td>
</tr>
<tr>
<td>@2000mA/cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potential-Cycled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+pre-electrolysed
The discrepancies between the reported values may be due to interpretation of the Tafel regions and/or time effects. The overpotential ranges in which the Tafel linearity has been observed varies greatly between authors. In Figure 2.7 some reported overpotential ranges have been illustrated with the Tafel slopes values found in that range. It can be seen that the Tafel values tend to increase when measured at higher overpotential ranges. A common range in Figure 2.7 falls between $\eta_{H_2} = 200 - 325$ mV where $b$ has been reported from 104 mV/dec to 167 mV/dec. Since $i_0$ is often extrapolated from $b$, it is not unexpected that it has a similarly wide range of values.

Figure 2.7  Hydrogen overpotential ranges over which experimental Tafel slopes have been reported.
As will be seen in the following sections, HER Tafel slope values are also dependent on the time of cathodic polarization; the initial condition of some Ni electrodes in Table 2-IIa includes cathodic oxide-reduction pretreatments of 30 min. to 3 hr. at moderate cathodic overpotentials (i.e. $\eta_{H_2} \approx 300-400$ mV) [28,33,34,37,39] while for others the initial condition does not include such a pre-treatment [40,41].

The theoretical HER Tafel slopes increase with temperature (i.e. for Heyrovsky: $b_{25^\circ C} = 120$ mV/dec and $b_{70^\circ C} = 138$ mV/dec). This has been observed (with $i_o$ constant) [37] but others report nearly constant $b$ values (with $i_o$ increasing) [39,42].

2.4.1.2 **Nickel Metal Cathodes after Steady-State $i$-$t$ Operation**

Table 2-IIb presents a summary of studies of overpotential as a function of the time of continuous polarization involving nickel metal HER cathodes in alkaline electrolytes and lists the steady-state current densities (or overpotential) and duration of polarization. In general, there is a decrease in HER activity with increasing time of cathodic polarization. This will be discussed in the following sections.
### TABLE 2-IIb
Summary of studies of time variation effects on crystalline Ni-metal HER electrode materials.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temp (°C)</th>
<th>(i_\text{as} ) (mA/cm(^2))</th>
<th>Duration</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni plate</td>
<td>30% KOH</td>
<td>25</td>
<td>200-250</td>
<td>100 min.</td>
<td>[46]</td>
</tr>
<tr>
<td>Ni (99.9)</td>
<td>30% KOH</td>
<td>50</td>
<td>1.4 V</td>
<td>30 min.</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni sheet: as-received annealed</td>
<td>30% KOH (pe)(^t)</td>
<td>30</td>
<td>300</td>
<td>300 min. 175 min.</td>
<td>[47]</td>
</tr>
<tr>
<td>Ni 200</td>
<td>30% KOH (pe) (&lt;0.03 ppm Fe)</td>
<td>37</td>
<td>100 200 500</td>
<td>6 hr</td>
<td>[40]</td>
</tr>
<tr>
<td>Ni 200</td>
<td>30% KOH w/0.03 ppm Fe</td>
<td>37</td>
<td>250</td>
<td>27.7 hr</td>
<td>[48]</td>
</tr>
<tr>
<td>Ni (99.99)</td>
<td>30% KOH (0.5 ppm Fe)</td>
<td>70</td>
<td>100 200</td>
<td>55.6 27.7</td>
<td>[41]</td>
</tr>
<tr>
<td>Ni (99.99)</td>
<td>30% KOH (0.5 ppm Fe)</td>
<td>70</td>
<td>100</td>
<td>66.7 hr</td>
<td>[43]</td>
</tr>
<tr>
<td>Ni (99.99)</td>
<td>30% KOH +14 ppm Fe</td>
<td>70</td>
<td>100</td>
<td>66.7 hr</td>
<td>[44]</td>
</tr>
<tr>
<td>Ni (99.99)</td>
<td>30% KOH (pe) +14 ppm Fe</td>
<td>70</td>
<td>2000</td>
<td>16 hr</td>
<td>[45]</td>
</tr>
</tbody>
</table>

\(^t\)pre-electrolysed

#### 2.4.1.2a Changes in Tafel Parameters After Continuous Polarization

With time, continuously polarized nickel metal cathodes in KOH electrolyte exhibit an increase in the Tafel parameters (\(b_c\), \(i_0\) in Table 2-Ia) [39-41,43-45]. From an initial value of ca. \(b = 100 \text{ mV/dec}\), Tafel slopes start to increase within \(10^3-10^4\) s (0.27-2.77 hr) of polarization and eventually reach values of ca. \(b = 200-300 \text{ mV/dec}\).
2.4.1.2b *Time-Dependent Deactivation of Nickel Metal HER Cathodes With Continuous Polarization: Absorption of Hydrogen*

Galvanostatically polarized nickel metal cathodes in KOH electrolyte exhibit a decrease in operating efficiency with time characterized by a rise in the cathodic overpotential (Table 2-IIb) [40,41,43-45]. Cathode overpotentials initially (first $10^2$-$10^3$ s) exhibit a linear relationship with log time (70-100 mV/(decade time)). At a current density of 100 mA/cm² or greater, there eventually occurs a "jump" in the rate of change of potential; the "jump" occurs between $10^3$ and $10^4$ s and for times greater than $10^4$ s the potential plateaus (Figure 2.8) [40,41]. In relation to the change in Tafel slopes mentioned in the previous section and Table 2-IIa, before the jump $b \approx 100$ mV/(decade current) and $b \approx 200-300$ mV/dec after the jump.

It has been determined, via permeation measurements, that the initial increase of overpotential with time is due to hydrogen absorption [48]. The overpotential "jump" then occurs simultaneously with a marked decrease in the absorption rate of hydrogen (measured by permeation current) (Figure 2.9). It was proposed that the formation of a nickel hydride acts as a barrier to continued hydrogen diffusion because hydrogen bonding causes the d-band of nickel to be filled. It has been suggested that the observed phenomena of continuing H₂ gas evolution on Ni after interruption of current can be attributed to decomposition of a three-dimensional hydride formed at high cathodic overpotentials [49]. After cathodic polarization for several hours, hydride formation has been detected by ex-situ X-ray diffraction [47].
Figure 2.8 Nickel cathode potential behaviour with time under galvanostatic control as a function of six current densities (mA/cm²) in 30 % KOH at 37°C (After [40]).

Figure 2.9 Permeation current with time and cathode voltage with time for 50 mA charging current for 12.5 μm nickel foil in 30 % KOH at 37°C (After [48]).
2.4.1.2c  Effects of Fe Impurity on Deactivation of Nickel HER Cathodes During Continuous Polarization

Under electrolysis conditions, small amounts of dissolved metallic impurities in the electrolyte can electroplate onto the cathode and affect the rate and magnitude of deactivation. Ni metal HER cathodes are, in particular, influenced by the presence of iron in the electrolyte. Iron is commonly introduced via impurities in the source KOH and from steel cell components in industrial electrolyzers. Deposition is dependent on the degree of polarization, concentration of dissolved Fe, and duration of polarization.

Electrodeposition occurs at moderate to high cathodic polarizations, starting at ca. 100 mA/cm² galvanostatically [40] or ca. 400 mV_{SHE} potentiostatically [42]. Tables 2-IIa and 2-IIb includes reported concentrations of Fe in the electrolytes. These range from 0.03 ppm (purification by pre-electrolysis) to 0.5-3.0 ppm (inherent Fe impurity in the KOH sources) to 14 ppm (intentionally added to replicate industrial concentrations).

For c.p. Ni cathodically polarized for $10^5$ s, overpotentials were ca. 300 mV less in electrolyte containing 3 ppm Fe than in pre-electrolysed electrolyte containing 0.03 ppm Fe (Figure 2.10) [50]. The lessened deactivation under the former condition was ascribed to an increase in the active surface area by deposition of a rough layer of iron on the smooth nickel. In comparison, for a case of 0.5 ppm Fe, the deactivation was found to be intermediate [41,43]. The overpotential-time curve showed two distinct regions of deactivation; after the previously mentioned (§2.4.1.2(a), Fig. 2.8) plateau in potential at
Figure 2.10 Nickel cathode potential behaviour with time under galvanostatic control at 250 mA/cm$^2$ in 30% KOH at 37°C; 0.03 ppm dissolved Fe (circle, triangle) and 3.0 ppm dissolved Fe (square, diamond) (After [50]).

Figure 2.11 Nickel cathode potential behaviour vs. time under galvanostatic control in 30% KOH at 70°C: (a) 100 mA/cm$^2$, (b) 200 mA/cm$^2$ (After [26]).
ca. $10^4$ s a second deactivation occurs which is associated with the onset of Fe deposition and is characterized by a slope of ca. 100 mV/(decade time) (Figure 2.11). A subsequent study found that 14 ppm Fe in the electrolyte activates Ni metal [44]; iron deposition starts to appear after $10^3$ s and corresponds to the commencement of activation. A similar trend of concentration of Fe impurity is observed on platinum metal cathodes; compared to pre-electrolysed electrolyte, 0.5 ppm Fe deactivates Pt while 14 ppm Fe activates Pt [51].

2.4.1.2d Recovery after Depolarization from Continuous Polarization due to Anodic Reactions

After several hours of continuous cathodic polarization (allowing deactivation of Ni to occur), interruption of the HER by open circuit, short-circuit, or depolarization to the RHP causes anodic reactions which, upon re-polarization to the HER, reverse the time-dependent deactivation to a great degree [40,41,47]. Cyclic voltammograms show the presence of two anodic peaks: the first at $\eta_a = 100-200$ mV corresponding to oxidation of absorbed hydrogen, and the second at $\eta_a = 400-500$ mV corresponding to either Ni(OH)$_2$ formation (Figure 2.12) [40] or oxidation of deposited iron (Figure 2.13) [41]. The magnitudes of the peaks increased with increasing time of continuous cathodic polarization. The recovery from deactivation was observed to primarily occur with depolarization from HER to the potential regime of the first anodic peak.
Figure 2.12  Anodic portions of single-cycle voltammograms for nickel before and after deactivation in 30 % KOH at 37°C; the peaks are attributed to oxidation of adsorbed hydrogen (A1) and to formation of Ni(OH)$_2$ (A2) (After [40]).

Figure 2.13  Influence of the duration of the cathodic polarization on the anodic portion of the single-cycle voltammograms in 30 % KOH at 70°C for (a) 60s, (b) 0.36 x 10$^2$s, (c) 33.7 x 10$^4$s. The peaks are attributed to oxidation of adsorbed hydrogen (A1) and to oxidation of deposited Fe (A2) (After [41]).
2.4.1.3 Potential-Cycled Nickel Metal Cathode

There are a number of reports of treating Ni electrodes by repeated cycling between the HER and OER potential regimes with triangular [28,34-36] or square [52,53] waveforms. This potential-cycling treatment yields better HER activity for as-polished nickel metal with lower $b$ and higher $i_0$ (Table 2-IIa). Although there are surface roughening effects, the higher activity has been primarily attributed to the formation of a $\beta$-Ni(OH)$_2$ film.

2.4.2 Crystalline Nickel-Based Cathode Materials

Tables 2-IIIa, 2-IIIb and 2-IV summarize, respectively, reported Tafel parameters, reports of continuous polarization and reports of discontinuous polarization of crystalline Ni-based HER cathodes in various electrolytes. The alloying elements of these materials are generally Group VIII transition metals (TM) (Fe, Co), refractory metals (Mo, Cr) or reactive elements (Al, Zn). The production methods include electroplating, powder-pressing and Raney-Ni (R-Ni).

2.4.2.1 Tafel Parameters of Crystalline Ni-Based Materials

Although Table 2-IIIa lists a number of very low reported Tafel values (i.e. $b < 100$ mV/dec) reported, many of these are measured at very low overpotentials (i.e. $\eta_{H_2} < 100$ mV). At higher overpotentials, the Tafel slopes are similar to those seen
TABLE 2-IIIa  Summary of Tafel data on crystalline Ni-based HER electrodes in KOH and NaOH electrolytes.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte†</th>
<th>Temp (°C)</th>
<th>Initial</th>
<th>After</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$b_c$ (mV/dec)</td>
<td>$i_o$ (mA/cm$^2$)</td>
<td>$b_c'$ (mV/dec)</td>
</tr>
<tr>
<td><strong>Nickel-Based Cathodes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$_2$Co</td>
<td>1M KOH</td>
<td>30</td>
<td>155, 103</td>
<td>0.003</td>
<td>-</td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28% KOH (pe)$^\dagger$</td>
<td>60</td>
<td>145, 115</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-30Co</td>
<td></td>
<td></td>
<td>150, 140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td>105, 140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo</td>
<td>6M KOH</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>112, 175</td>
</tr>
<tr>
<td>Ni-Zn</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>50, 175</td>
</tr>
<tr>
<td>Ni-Co</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>35, 245</td>
</tr>
<tr>
<td>Ni-W</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>25, 225</td>
</tr>
<tr>
<td>Ni-Fe</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>25, 150</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>150, 170</td>
</tr>
<tr>
<td>Ni smooth</td>
<td>6M KOH</td>
<td>25</td>
<td>150</td>
<td>0.020</td>
<td>-</td>
</tr>
<tr>
<td>surf. skeleton catal.</td>
<td></td>
<td></td>
<td>90</td>
<td>0.055</td>
<td>-</td>
</tr>
<tr>
<td>ssc w/Cd</td>
<td></td>
<td></td>
<td>50</td>
<td>0.400</td>
<td>-</td>
</tr>
<tr>
<td>Ni (Electrodep. on mild steel)</td>
<td>28% KOH (pe)</td>
<td>25</td>
<td>184</td>
<td>0.129</td>
<td>-</td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-Fe</td>
<td>6M KOH</td>
<td>80</td>
<td>115, 165</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Mo-Cu</td>
<td></td>
<td></td>
<td>28, 180</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Mo-Zn</td>
<td></td>
<td></td>
<td>24, 116</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Mo-W</td>
<td></td>
<td></td>
<td>28, 150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Mo-Co</td>
<td></td>
<td></td>
<td>26, 140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Mo-Cr</td>
<td></td>
<td></td>
<td>32, 165</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Al (LPP)</td>
<td>25% KOH 1M NaOH</td>
<td>70</td>
<td>84</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>59</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Sandblasted Ni</td>
<td>25% KOH</td>
<td>23</td>
<td>110</td>
<td>0.006</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>110</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>Raney-Ni-Al</td>
<td></td>
<td>23</td>
<td>-130</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>-130</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td>28% KOH (pe)</td>
<td>25</td>
<td>50, 140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>31Ni-79Fe</td>
<td></td>
<td>70</td>
<td>91, 115</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>57Ni-43Zn</td>
<td></td>
<td>70</td>
<td>62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>51Ni-14Co-34Zn</td>
<td></td>
<td>70</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td>28% KOH</td>
<td>60</td>
<td>69, 105</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35Ni-65Fe</td>
<td></td>
<td>80</td>
<td>72, 108</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
for elemental Ni-metal (b = 100 ~ 250 mV/dec). However, the exchange current densities are several orders of magnitude higher than those for elemental Ni-metal. This is because of the greater real surface areas produced on these materials; the materials having the highest $i_0$ have extremely rough surface morphology. Laisa et al. prepared HER electrodes by powder pressing Ni with reactive metals which leach out to produce extremely porous electrodes [65-68]. They determined that roughness factors (R) were $10^2$ to $10^3$ times greater than polished Ni but that the real current densities ($i_0/R$) were unchanged [65,68].
2.4.2.2 Continuously Polarized Nickel-Based Cathodes

There have been many reports of continuous polarization of nickel-based or nickel-containing alloys in the laboratory [53-55,58,61-63,69] (Table 2-IIIb) and in pilot commercial unipolar electrolysers [9,11,12,14,70]. In comparison to studies on nickel metal, the duration of tests are 1-2 orders of magnitude longer. In general, under continuous galvanostatic polarization most materials listed in the table are more active than plain metal (i.e. Ni, mild steel or Ni-plated mild steel) cathodes by several hundred mV and many have stable overpotentials even after $10^2$ to $10^3$ hours. However, when deactivation occurs, it is ca. 25-60 mV after these time periods (Figure 2.14). Among alloying additions, Mo and Zn produce the most active, stable cathodes although the mechanisms are different; Mo has a synergistic effect while Zn leaches out of Ni [55]. Other favourable Ni additions include Co and Fe.

![Figure 2.14](image)

Figure 2.14 Potential vs. time behaviour of electrodeposited cathodes under 300 mA/cm² galvanostatic control in 6 M KOH at 70°C (After [55]).
### TABLE 2-IIIb
Summary of studies of time variation effects on crystalline Ni-base HER electrode materials.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temp (°C)</th>
<th>$i_{ss}$ (mA/cm$^2$)</th>
<th>Duration</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28% KOH (pe)</td>
<td>60</td>
<td>135</td>
<td>24 hr</td>
<td>54</td>
</tr>
<tr>
<td>Ni-30Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Fe</td>
<td>5N KOH (-30%)</td>
<td>70</td>
<td>1000</td>
<td>- 2500 hr</td>
<td>69</td>
</tr>
<tr>
<td><strong>Ni mesh: as-received activated</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Electrodep. on mild steel:</strong></td>
<td>28% KOH</td>
<td>60</td>
<td></td>
<td>1200 hr</td>
<td>62</td>
</tr>
<tr>
<td>Ni(35%)-Fe</td>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo</td>
<td></td>
<td>28% KOH (pe)</td>
<td>70</td>
<td>125 hr 200</td>
<td>61</td>
</tr>
<tr>
<td>Ni-Mo-Fe</td>
<td>6N KOH</td>
<td>80</td>
<td>300</td>
<td>1500 hr 950 300 250 200 100</td>
<td>55</td>
</tr>
<tr>
<td>Ni-Mo-Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Therm. dep: Ni/Mo</td>
<td>10M KOH</td>
<td>100</td>
<td>1000</td>
<td>250 hr 50 hr</td>
<td>63</td>
</tr>
<tr>
<td>Raney-Ni: (Al)</td>
<td></td>
<td></td>
<td>400</td>
<td>~50 hr 1300 hr</td>
<td></td>
</tr>
<tr>
<td>Raney-Ni: (Al+Mo+Ti)</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney-Ni: NiO$_x$</td>
<td>2.5M KOH</td>
<td>25</td>
<td>200 mV (potentio-static)</td>
<td>80 hr</td>
<td>53</td>
</tr>
<tr>
<td>Raney-Ni: NiO$_x$+Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney-Ni: NiO$_x$+Fe+Co$_3$O$_4$(doped)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4.2.3 Discontinuously Polarized Nickel-Based Cathodes

Many of these materials have been subjected to discontinuous operation (Table 2-IV). Tests include: (i) sporadic or repeated interruptions at periods of several hours to several days, and (ii) rapid, repeated cycles.

The activity of many of these cathodes is sensitive to depolarization. Raney Ni-(Zn) and Ni-(Al) electrode HER overpotentials are stable under continuous polarization and when the current is interrupted without short-circuiting [63,71]. They deactivate with modulated polarization (on for 10 hr/off for 14 hr), attributed to the residual Zn/Al metal contents falling below sufficient amounts (via dissolution) to maintain undisturbed grain boundary structures. Raney-Ni-(Zn) and electrodeposited Ni-Mo were found to deactivate irreversibly after short-circuited interruptions (Figure 2.15) [63].

Figure 2.15 Ni/Mo cathode potential time-dependence (1000 mA/cm² in 10 M KOH at 100°C) with interruptions (s.c. indicates short-circuiting, n.s.c. without) (After [63]).
**TABLE 2-IV**  
Interrupted, intermittent and/or cyclic operation of crystalline Ni-based HER electrode materials.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temp (°C)</th>
<th>Polarizing (ON) Current Density (mA/cm²)</th>
<th>Operation¹</th>
<th>Total Duration</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Raney-Ni  
*Therm dep on Ni:*  
NiO₂  
CoO₄  
NiO₄+Fe  
CoO₄(doped) | 2.5M KOH | 25 | approx. 200 | pot. sq. wave (1 min. 'ON'/1 min. 'OFF') | 80 hr | [53] |
| Electrodep.  
on steel:  
Ni-Mo-Fe  
Ni-Mo-Cu  
Ni-Mo-Zn  
Ni-Mo-W  
Ni-Mo-Co  
Ni-Mo-Cr  
Ni-plated | 6M KOH | (30-80) | 300 | (i) ON + 5 hr HIGH every 5 days  
(ii) 5-10 day interruptions | (i) 1500 hr.  
(ii) 10-60 days | [58] |
| Raney-Ni(Zn)  
Ni sheet  
*Electrodep. on Ni:*  
Ni/Mo  
Ni/Mo/V  
Ni/Mo/Cd  
*Therm. act. Ni/Mo/Cd*  
*Therm. dep:*  
Ni  
Ni/Mo  
*Ni mesh:*  
*as-received coated*  
Ni plate, screen | 8M KOH | 100 | 400 | 10 hr ON/14 hr OFF | 15700 hr | [71] |
| Ni/O₂+Fe  
CoO₄(doped) | 10M KOH | 100 | 1000 | o.c.¹ decay | - | [63] |
| Ni/Mo  
Ni/Mo/V  
Ni/Mo/Cd  
16hr o.c.  
250 hr. | 400 | 1000 | 16-136 hr o.c.  
15 hr s.c.  
10-100 hr s.c.  
1100 hr | - | 550 hrs | |
| Raney-Ni:  
(Zn)  
(AI)  
(AI)w/Mo  
(AI)w/Ti | 400 | 400 | 400 | 10-100 hr s.c.  
2x1 hr s.c.  
" | 1100 hr  
~50 hr  
" | - | |
| Ni mesh:  
*as-received coated*  
Ni plate, screen | 5N (~30%) KOH | 70 | 1000 | 24-48 hr o.c. | - | [69] |
| 30% KOH | 25 | 200-250 | per 1-3 days:  
(i) 15 min. s.c.  
(ii) 15 min. o.c. | - | - | [46] |

¹ o.c. = open circuit, s.c. = short circuit
The Ni-Mo electrode deactivation was ascribed to the successive destruction of the already cracked surface coatings and an increase in the contact resistance. However, Ni-Mo and Ni-Mo-(TM) electrodes were found to have good stability after open-circuit interruptions [55,58,63]. Trasatti et al. [53] also found Raney-Ni, Ni-oxide and Co-oxide electrodes to deactivate under intermittent polarization [on for 1 min./off for 1 min.].

2.4.3 AMORPHOUS CATHODE MATERIALS

Amorphous metal alloys (AMA) possess unique attributes compared to conventional crystalline alloys, including corrosion and catalytic properties. Metallic glasses are often produced by rapidly quenching (cooling rate > \(10^6 \text{ K/s}\)) liquid metal solutions. The resulting metastable solid has an atomic structure similar to a liquid, lacking long-range structural order, but having a homogeneous microstructure and short range chemical ordering. Unique alloy compositions can be achieved because the rapid cooling produces supersaturated solid solutions. Because of the need for such fast cooling rates, amorphous alloys are produced as wires, ribbons, powders and coatings.

2.4.3.1 Activity of Ni/Co/Fe-Based Amorphous Cathodes

Most electrochemical studies have focused on the corrosion resistance of these materials but currently there is active study of the HER on amorphous alloys in alkaline electrolytes. Table 2-V summarizes HER Tafel parameters of late-transition-metal (Ni, Co, Fe) -based (and related composition) AMA cathodes in KOH and NaOH electrolytes.
TABLE 2-V Summary of HER Tafel data on amorphous late transition-metal-based electrode materials in KOH and NaOH electrolytes.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temp ('C)</th>
<th>Initial</th>
<th>After</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( b_c )</td>
<td>( i_o )</td>
<td>( b_c' )</td>
</tr>
<tr>
<td>ribbon:</td>
<td>1M KOH</td>
<td>30</td>
<td>90</td>
<td>0.003</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>127</td>
<td>0.000003</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Co(<em>{50})Ni(</em>{25})S(<em>{15})B(</em>{10})</td>
<td>30</td>
<td>174</td>
<td>0.027</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>120</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ni(<em>{39})Fe(</em>{39})Mo(<em>{2})Si(</em>{12})B(_{8})</td>
<td>30</td>
<td>123</td>
<td>0.010</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>173</td>
<td>0.013</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ni(<em>{58})Co(</em>{10})Si(<em>{12})B(</em>{12})</td>
<td>30</td>
<td>140</td>
<td>0.001</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>155</td>
<td>0.020</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ni(<em>{40})Fe(</em>{50})B(_{20})</td>
<td>30</td>
<td>174</td>
<td>0.134</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>230</td>
<td>0.053</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe(<em>{60})Co(</em>{10})Si(<em>{10})B(</em>{10})</td>
<td>30</td>
<td>128</td>
<td>0.069</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>132</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>melt-spun ribbon</td>
<td>30% KOH</td>
<td>70</td>
<td>138</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe(<em>{60})Co(</em>{10})Si(<em>{10})B(</em>{10}) (cathodized [-340 mV])</td>
<td>-</td>
<td>-</td>
<td>71</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>anodized (+0.2 mA/cm(^2))</td>
<td>-</td>
<td>-</td>
<td>77</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>anodized (+0.5 mA/cm(^2))</td>
<td>-</td>
<td>-</td>
<td>77</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>anodized (+1 mA/cm(^2))</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>anodized (+5 mA/cm(^2))</td>
<td>-</td>
<td>-</td>
<td>99</td>
<td>1.6</td>
</tr>
<tr>
<td>Ni(<em>{51})Co(</em>{23})Cr(<em>{10})Mo(</em>{7})Fe(<em>{8})B(</em>{4})</td>
<td>1M NaOH</td>
<td>120</td>
<td>0.0025</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>oxidized (pot. cycled)</td>
<td>-</td>
<td>-</td>
<td>120</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{50})Co(</em>{25})P(<em>{15})B(</em>{10})</td>
<td>1M KOH</td>
<td>30</td>
<td>144, 101</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>acid etched</td>
<td>-</td>
<td>-</td>
<td>166, 111</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{50})Co(</em>{25})Si(<em>{15})B(</em>{10})</td>
<td>178, 110</td>
<td>0.002</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>acid etched</td>
<td>-</td>
<td>-</td>
<td>145, 91</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Co(<em>{50})Ni(</em>{25})Si(<em>{15})B(</em>{10})</td>
<td>174, 124</td>
<td>0.0016</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>acid etched</td>
<td>-</td>
<td>-</td>
<td>172, 110</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>melt-spun ribbon:</td>
<td>1M KOH</td>
<td>30</td>
<td>147</td>
<td>0.010</td>
<td>-</td>
</tr>
<tr>
<td>Ni(<em>{72})Co(</em>{28})Mo(<em>{2})B(</em>{20}) potential cycled</td>
<td>-</td>
<td>-</td>
<td>109, 170</td>
<td>0.0050, 0.004</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{72})Co(</em>{28})Mo(<em>{2})B(</em>{20}) potential cycled</td>
<td>110, 132</td>
<td>0.0006, 0.002</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{72})Co(</em>{28})Mo(<em>{2})B(</em>{20}) potential cycled</td>
<td>114</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>pressed powder</td>
<td>1M NaOH</td>
<td>70</td>
<td>104</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td>Ni(<em>{66})B(</em>{33}) potential cycled</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{58})Mn(</em>{10}) (30%) KOH</td>
<td>70</td>
<td>63</td>
<td>29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni(<em>{58})Mo(</em>{15})</td>
<td>63</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>{16})Co(</em>{72})P(_{10}) on mild steel:</td>
<td>1M KOH</td>
<td>70</td>
<td>140</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>on (Al_2O_3):</td>
<td>6M KOH</td>
<td>70</td>
<td>110</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>
Ni-Co and Ni-Mo amorphous metal alloys have good short-term stability. Lian and Birss [76] compared the HER behaviour of as-received and oxidized (via potential cycling) Ni$_{51}$Co$_{23}$Cr$_{10}$Mo$_{7}$Fe$_{5.3}$B$_{3.5}$ ribbons. At low overpotentials, the oxidized surface had a lower HER rate which was ascribed to a barrier effect of the oxide film. However, at high overpotentials ($\eta_{\text{H}_2} > 400$ mV), it had a higher current density characterized by a flattening (decreasing 'b') of the polarization curve, attributed to oxide reduction and formation of a more active surface. Later, Lian et al. [77] found that as-prepared ribbons of Ni-Co-B-(P, Si) based amorphous alloys were less electrocatalytically active for the HER than crystalline Ni and Co metals and alloys. However, acid etching of these amorphous alloys produced better electrocatalytic activity than the crystalline analogues, which could not be solely attributed to an increase in surface area. Suzuki investigated the HER behaviour of amorphous Ni-(Co-Mo)-B melt-spun ribbons [34]. After voltammetric potential cycling the amorphous ribbons had higher exchange current densities than in the as-polished condition. On an apparent area basis, the amorphous alloys were less active than crystalline nickel. However, after potential cycling, crystalline Ni was attacked while the amorphous alloys displayed good stability of the electrode surface.

In general, the most important transition metal alloying element for HER activity is Fe followed by Ni and Co. Kreysa and Håkansson studied a dozen amorphous metal compositions for HER and OER suitability [37]. Two Fe AMA alloys (Fe$_{60}$Co$_{20}$Si$_{10}$B$_{10}$ and Fe$_{40}$Ni$_{40}$B$_{20}$) had greater HER activity than Ni metal, however, cyclic voltammetry of the Fe-based AMA's indicate low corrosion stability near the reversible hydrogen potential (i.e. under open- or short-circuit conditions). Huot et al. activated a Fe$_{60}$Co$_{20}$Si$_{10}$B$_{10}$ melt-

---

1 Amorphous alloy compositions are expressed with the atomic fraction as a subscript of the alloying element; i.e. Ni$_{50}$Co$_{22}$P$_{18}$B$_{10}$ = Ni(50%)-Co(25%)-P(15 %)-B(10%).
spun ribbon for HER by an anodic oxidation process [72]. Surface studies revealed that the oxidized electrode is covered by a thick and porous film of Fe\textsubscript{3}O\textsubscript{4} which reduces and replates onto the cathode as fine Fe particles which grow and coalesce into a highly porous coating.

Cathodes produced from powder have very high exchange current densities. Huot et al. produced nanocrystalline Ni-Mo powders by high energy ball milling [74]. No deactivation was observed after 14 hours of steady-state polarization. No surface area effect was found; the authors indicated that electrocatalytic activity was due to decreased crystallinity and increased lattice spacing, which occurred with increased milling time. Los and Laisa reported on the activity of cathodes prepared from amorphous 'Ni\textsubscript{2}B' powder [73]. The electrodes had good electrocatalytic activity which was ascribed to a high real surface area.

2.4.3.2 Continuously Polarized Amorphous Alloy Cathodes

Literature on the continuous steady-state catalytic stability of amorphous late-transition-metal-based electrodes is very limited. However, there has been some discussion of amorphous alloys composed of Ni and early transition group metals, in particular, the Ni-Zr system in hot, concentrated KOH electrolytes[78-83].

It has been found that it is necessary to pre-treat Ni-Zr AMA’s with an acid etch to attain an active surface for HER; dissolution of Zr and Zr-oxide leaves a porous Ni-rich surface [79-83]. When cathodically polarized with a potentiostatic hold, they deactivate with time as characterized by a decrease in the cathodic current density in the first hour [79,82,83]. As for nickel metal, this deactivation is ascribed to absorption of
hydrogen. Rapidly-quenched Ni-Zr materials are known to readily dissolve great quantities of H and form hydrides [84,85]. H absorption due to cathodic polarization causes structural changes and embrittlement in Ni-Zr metallic glasses.

Zr-Co-Ni amorphous ribbons exhibit similar time-dependent deactivation as Ni-Zr materials[80,81]. It is of interest that the pre-etch selectively dissolves Zr, leaving a low porosity Ni-Co rich surface [81].

Huot et al. reported that Ni-Nb, Ni-Al-B and Ni-Mo-Si-B amorphous cathodes for the HER had low activities which were not affected by pre-treatment and that, while they had a low susceptibility to embrittlement, very large time-dependent deactivations occurred during steady-state cathodic polarization [78].
2.4.4 SURFACE ANALYSES OF NICKEL MATERIALS

Nickel metal and its surface products have been well characterized by XPS. The distinction between pure states of Ni metal, NiO and Ni(OH)$_2$ is well documented [86-94]; these are the species that might be expected to be found in the E-pH regime of modulated HER cathodes. For alkaline reducing conditions, reports of XPS are few for crystalline Ni and none for Ni-AMA.

2.4.4.1 XPS Analysis of Pure Nickel and Simple Nickel-Cobalt Compounds

Reported XPS analyses of the peak positions of Ni 2p$_{3/2}$ and O 1s spectra in standard samples of Ni, NiO and Ni(OH)$_2$ are given in Table 2-VI; peak positions are given as binding energies. The compounds can be distinguished by a shift in binding energy of the core-level peaks of Ni and O and by the presence and position of additional spectral lines (multiplet splitting and/or shake up satellites). The positions of the Ni 2p$_{3/2}$ shake-up satellite and the Ni 2p$_{1/2}$ peak are given in reference to the Ni 2p$_{3/2}$ value.

For pure Ni, the 2p$_{3/2}$ line shows a variation of 0.5 eV among the reported values. Although not explicitly mentioned in the literature, several published spectra [86,87,92] show a low intensity satellite (ca. 6.4 eV) above the principal line. The NiO and Ni(OH)$_2$ spectra have more distinct satellites.

The Ni 2p spectrum of NiO, compared to pure Ni, has a doublet structure for the 2p$_{3/2}$ and O 1s spectra. The binding energy separation of the doublet peaks is not well
TABLE 2-VI Ni 2p and O 1s XPS peak binding energies. Peak full width half maximum (FWHM) values, where reported, are given in parentheses.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni 2p(_{3/2}) (eV)</th>
<th>Δ-sat (eV)</th>
<th>Δ-2p(_{3/2}) (eV)</th>
<th>O 1s (eV)</th>
<th>[Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>852.5</td>
<td>-6.4</td>
<td>-</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>Ni</td>
<td>852.8</td>
<td>-6.5</td>
<td>-</td>
<td>-</td>
<td>[87]</td>
</tr>
<tr>
<td>Ni</td>
<td>852.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td>Ni</td>
<td>852.3</td>
<td>-4.4</td>
<td>17.2</td>
<td>-</td>
<td>[90]</td>
</tr>
<tr>
<td>Ni</td>
<td>852.7</td>
<td>-6.3</td>
<td>17.3</td>
<td>-</td>
<td>[91]</td>
</tr>
<tr>
<td>Ni</td>
<td>852.8</td>
<td>-</td>
<td>17.5</td>
<td>532.2</td>
<td>[92]</td>
</tr>
<tr>
<td>NiO</td>
<td>854.0, 855.8</td>
<td>6.5, 7.2</td>
<td>-</td>
<td>529.6, 531.1</td>
<td>[86]</td>
</tr>
<tr>
<td>NiO</td>
<td>854.6, 856.0</td>
<td>7.0</td>
<td>-</td>
<td>529.6, 531.4</td>
<td>[87]</td>
</tr>
<tr>
<td>NiO</td>
<td>854.5</td>
<td>-</td>
<td>-</td>
<td>529.9, 531.9</td>
<td>[88]</td>
</tr>
<tr>
<td>NiO</td>
<td>854.1</td>
<td>-</td>
<td>-</td>
<td>529.5</td>
<td>[90]</td>
</tr>
<tr>
<td>NiO</td>
<td>855.0</td>
<td>6.8</td>
<td>18.1</td>
<td>-</td>
<td>[91]</td>
</tr>
<tr>
<td>NiO</td>
<td>853.8, 855.7</td>
<td>-6.8</td>
<td>-</td>
<td>529.1</td>
<td>[92]</td>
</tr>
<tr>
<td>Ni(OH)(_2)</td>
<td>854.9, 856.8 (2.27)</td>
<td>6.2</td>
<td>17.9</td>
<td>529.1</td>
<td>[94]</td>
</tr>
<tr>
<td>NiCo(_2)O(_4)</td>
<td>855.6 (3.6)</td>
<td>-</td>
<td>17.4</td>
<td>529.3, 530.7</td>
<td>[95]</td>
</tr>
</tbody>
</table>

TABLE 2-VII Ni 3s and Ni 3p XPS binding energies. Peak full width half maximum (FWHM) values, where reported, are given in parentheses.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni 3s (eV)</th>
<th>Δ-sat (eV)</th>
<th>Ni 3p (eV)</th>
<th>Δ-sat (eV)</th>
<th>[Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>110.7</td>
<td>-</td>
<td>66.3</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>Ni</td>
<td>110.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[94]</td>
</tr>
<tr>
<td>NiO</td>
<td>111.8</td>
<td>2.3, 6.0</td>
<td>67.3</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>NiO</td>
<td>111.9 (6.0)</td>
<td>6.0</td>
<td>67.8 (3.7)</td>
<td>4.8</td>
<td>[94]</td>
</tr>
<tr>
<td>Ni(OH)(_2)</td>
<td>112.7</td>
<td>5.5</td>
<td>68.0</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>Ni(OH)(_2)</td>
<td>112.7 (5.2)</td>
<td>5.2</td>
<td>67.5 (3.3)</td>
<td>4.5</td>
<td>[94]</td>
</tr>
<tr>
<td>NiCo(_2)O(_4)</td>
<td>111.8</td>
<td>-</td>
<td>67.5 (4.0)</td>
<td>-</td>
<td>[95]</td>
</tr>
</tbody>
</table>
TABLE 2-VIII  Co XPS binding energies. Peak full width half maximum (FWHM) values, where reported, are given in parentheses.

<table>
<thead>
<tr>
<th>Material</th>
<th>Co 2p$_{3/2}$ (eV)</th>
<th>$\Delta$-sat (eV)</th>
<th>$\Delta$-2p$_{3/2}$ (eV)</th>
<th>Co 3p (eV)</th>
<th>Co 3s (eV)</th>
<th>O 1s (eV)</th>
<th>[Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>778.0 (1.7)</td>
<td>-</td>
<td>-</td>
<td>59.3</td>
<td>101.0</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>778.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>778.3</td>
<td>-</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>777.9</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>777.9</td>
<td>-</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[93]</td>
</tr>
<tr>
<td>CoO</td>
<td>780.0, 782.1</td>
<td>5.6, 6.4</td>
<td>-</td>
<td>60.2</td>
<td>102.0</td>
<td>529.6</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>(2.7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>780.6</td>
<td>6.1</td>
<td>15.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>780.4</td>
<td>-</td>
<td>15.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[92]</td>
</tr>
<tr>
<td>Co(OH)$_2$</td>
<td>781.0 (3.2)</td>
<td>-5.0</td>
<td>-</td>
<td>61.1</td>
<td>102.6</td>
<td>531.2</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>780.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[92]</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>779.9</td>
<td>-</td>
<td>15.0</td>
<td>60.8</td>
<td>102.6</td>
<td>529.3, 530.7</td>
<td>[95]</td>
</tr>
</tbody>
</table>

indicated; several authors state only a single value for the lower energy peak, despite showing a split spectrum. However, it appears that the Ni 2p$_{3/2}$ doublet peaks are separated by ca. 1.8 eV. The position of the broad satellite structure of NiO is not uniformly characterized in the literature, likely because of the narrow separation of the sub peaks that make up the satellite. For both the Ni 2p and O 1s spectra of Ni(OH)$_2$, the chemical shift of the principal peaks is greater than for NiO; the Ni 2p$_{3/2}$ satellite separation is less for Ni(OH)$_2$ than for NiO.

Further differentiation of Ni oxide and hydroxide species can be found in the Ni 3s and 3p spectra [86,94] (Table 2-VII). For NiO, Ni 3s has a prominent satellite structure while Ni 3p is comparatively weak and diffuse. The Ni 3s and 3p lines for Ni(OH)$_2$ have stronger satellite bands compared with NiO.

Table 2-VIII gives Co 2p, 3p, 3s and O 1s binding energies reported for cobalt and some cobalt compounds.
2.4.4.2 XPS Analyses of Ni Materials in Alkaline Reducing Environments

Bradke and Schnurnberger examined Ni polarized in 25% KOH [89]. The XPS measurements of the chemical shifts of Ni 2p\textsubscript{3/2} and 3s peaks for air-oxidized and anodized Ni compared well to previously published values of NiO and Ni(OH)\textsubscript{2}, respectively, but the peak positions for cathodically polarized Ni were extremely high (BE\textsubscript{Ni2p\textsubscript{3/2}} = 857.3 eV, BE\textsubscript{Ni3s} = 114.2 eV). However, no suggestions were given as to what these species might be.

McIntyre et al. exposed Ni\textsubscript{66}-Cu\textsubscript{33} (Monel-400) alloy to pH 10 LiOH solution at high temperature and H\textsubscript{2} overpressure (285°C, 100 KPa) and found no significant change from the Ni 2p\textsubscript{3/2} line of pure nickel [29]. A small O 1s peak, at 531.7 eV, was attributed to minor concentrations of surface oxygen species.
3. EXPERIMENTAL

3.1 MATERIALS

3.1.1 ELECTRODE MATERIALS

Two cathode materials have been evaluated: commercially pure (c.p.) nickel and a Ni-based (Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$) amorphous metal alloy (AMA) developed at the University of Toronto.

The nominal chemical composition of the c.p. nickel (Ni 200) is given in Table 3-I. Ni 200 was evaluated as 0.5 mm thick rolled sheet which were sanded with 600 grit SiC paper and then polished to a 6 μm and then a 1μm finish (Struers® diamond paste in Buehler® Metad® extender fluid (water-based)) and then degreased with, in order, reagent grade acetone, reagent grade methanol and deionized (DI) water (18 MΩ). The AMA composition is given in Table 3-II. AMA electrodes prepared from melt-spun ribbons (~1cm wide x 40μm thick) were given a 1 μm diamond polish and then degreased. Ni materials were provided by ECL while AMA ribbons were prepared by Zbig Wronski at CANMET in Ottawa, Canada.

<table>
<thead>
<tr>
<th>TABLE 3-I</th>
<th>Nominal chemical composition of commercially pure Nickel 200.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Ni</td>
</tr>
<tr>
<td>wt. % (max.)</td>
<td>99.5(*)</td>
</tr>
</tbody>
</table>

*Includes cobalt
TABLE 3-II  Nominal and actual chemical compositions of Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ amorphous metal alloy [94].

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>P</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition (at. %)</td>
<td>50</td>
<td>25</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Average actual composition</td>
<td>49</td>
<td>26</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2  ELECTROCHEMICAL

3.2.1  ELECTRODE PREPARATION

Electrodes were prepared from the cathode materials by joining a length (ca. 15 cm) of insulated copper wire (AWG 14G) lead, using Pb-Sn solder, to a coupon (ca. 1 cm x 1.5 cm) of cathode material. In the case of the AMA (which is coiled from the melt-spinning process), ribbon coupons were first tack-soldered to a secondary coupon of nickel sheet, to produce a flat surface, which was in turn joined to the wire lead. After soldering, the joint was degreased in acetone, methanol and DI water and then air-dried. A specific square or rectangular surface area was masked out of the polished surfaces and the remainder of the material, the exposed end of the wire lead and the joint were insulated with a non-conductive epoxy paint (Amercoat® 90HS). The polished areas to be coated with epoxy were first sanded with 320 grit SiC paper and then degreased to assure adherence. The epoxy was painted on these areas; three coats were applied to ensure insulative integrity. Cathode (apparent) areas were 0.20 ± 0.03 cm$^2$ for the Ni sheet and AMA ribbon. Apparent area measurements were performed using LECO IA-3001 V1.20 PC-based image
analysis software via an Olympus SZ-11 stereo microscope and a LECO/Sony XC-77 video camera CCD module.

3.2.2 ELECTROLYTE

The electrolyte was an 8 M KOH solution prepared by dissolving Analar grade KOH pellets in deionized water. The pH was calculated to be 14.3 at 70°C (Appendix A). Later test electrolytes were purified by electrolysis, using inert platinum mesh electrodes to electroplate out metallic impurities present in the KOH pellets; impurities in the Analar grade source are listed in Table 3-III. Pre-electrolysis was performed under galvanostatic control at a current which produced a cathodic potential of over ca. -2000 mV. Figure 3.1 shows EDX analysis (§3.3.1) of the surface of a platinum electrode after pre-electrolysis. After a 24 hr period, the electroplated impurities were stripped from the electrodes by immersion in concentrated nitric acid after which pre-electrolysis was repeated. After the electrolyte was added to the test cell, but prior to cathode insertion, the electrolyte was purged with argon gas for 1 hour to remove dissolved oxygen. For some tests, the electrolyte was also pre-electrolysed in-situ in the test cell for ca. 12 hours using platinum or nickel mesh working electrodes, to ensure that there was no contamination after transfer from the pre-electrolysis beaker to volumetric flask to test cell.
TABLE 3-III  Maximum limits of impurities in Analar grade KOH pellets (minimum assay 85%).

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Max. Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃</td>
<td>1.0%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0005</td>
</tr>
<tr>
<td>N</td>
<td>0.0005</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.0005</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.005</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.0005</td>
</tr>
<tr>
<td>Al</td>
<td>0.001</td>
</tr>
<tr>
<td>Ca</td>
<td>0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0002</td>
</tr>
<tr>
<td>Other heavy metals</td>
<td>0.0005</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0005</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0005</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0005</td>
</tr>
<tr>
<td>Na</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 3.1  EDX analysis of impurities electroplated onto platinum cathode during pre-electrolysis of 8 M KOH electrolyte.
3.2.3 **CELL AND APPARATUS**

The electrochemical test apparatus is illustrated in Figure 3.2 showing the test cell and the data acquisition system. A three-electrode Teflon cell was used consisting of a working electrode (the HER cathode), a Pt counter electrode and an external Hg/HgO reference electrode connected via a salt bridge, against which all potentials were measured. The reference electrode potential is less than 1 mV versus the Standard Hydrogen Electrode (Appendix B). A schematic of the cell is shown in Figure 3.3. The cell had an inlet and an outlet for purging argon gas; the outlet was connected to a condenser to minimize water evaporation from the electrolyte. The cell temperature was maintained by immersion in a water bath controlled by a Cole-Parmer Polystat 1253-00 heater-circulator with a temperature control of ±0.1°C.

Between electrochemical tests, the Teflon cell was cleaned using the regimen in Table 3-IV.

**TABLE 3-IV**  Cleaning procedure for Teflon electrochemical cell.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rinse under running water (10 min.)</td>
</tr>
<tr>
<td>2</td>
<td>Ultrasonic cleaning in concentrated nitric acid (10 min.)</td>
</tr>
<tr>
<td>3</td>
<td>Rinse under running water (10 min.)</td>
</tr>
<tr>
<td>4</td>
<td>Ultrasonic cleaning in dilute purified KOH (aq) (10 min.)</td>
</tr>
<tr>
<td>5</td>
<td>Rinse under running water (10 min.)</td>
</tr>
<tr>
<td>6</td>
<td>Rinse with stream of deionized water</td>
</tr>
<tr>
<td>7</td>
<td>Ultrasonic cleaning in deionized water (10 min.)</td>
</tr>
<tr>
<td>8</td>
<td>Rinse with stream of deionized water</td>
</tr>
<tr>
<td>9</td>
<td>Dry with compressed air</td>
</tr>
</tbody>
</table>
Figure 3.2  Schematic of electrochemical test apparatus.

Figure 3.3  Schematic of electrochemical cell.
3.2.4 SOFTWARE AND INSTRUMENT CONTROL

Waveforms were generated using a Hokuto Denko HB 105 function generator and a HA 501G potentiostat/galvanostat. Instruments were automatically controlled and data was recorded with a Hewlett Packard 319C computer data acquisition/control system. Existing software for cyclic voltammetry was significantly modified for generating the cyclic current modulations; the software modifications are appended (Appendix C). Data was also recorded with a Kipp & Zonen BD-112 x-y-t chart recorder. Data was transferred from HP-LIF format to PC-DOS using PC-based LIF2DOS software (Freeware release V.2.0 Green Grass Software <umist.idh@mst.ac.uk>).

3.2.5 CYCLIC MODULATIONS AND TAFEL SLOPE WAVEFORMS

Accelerated modulations simulated industrial conditions with a trapezoidal waveform. The steady 'on' and 'off' conditions were galvanostatic holds at 250 mA/cm$^2$ and 0 mA/cm$^2$, respectively. Ramps to the 'on' and 'off' condition were fast, ca. 1 (mA/cm$^2$)/s. Time of the 'on' holds ($t_{ON}$) were 5 to 720 mins. while the 'off' hold times ($t_{OFF}$) were 5 or 60 mins. Number of cycles (N) ranged from 2, for essentially single interruptions, to over 180, for accelerated cycling. A schematic of the trapezoidal waveform is given in Figure 3.4. The test notation used throughout is $t_{ON}/t_{OFF}/N$. Table 3-V summarizes the applied waveforms. The duration of the current modulation tests were ca. 24 hours, except for several tests which were up to 48 hours. Prior to some accelerated modulation tests on Ni, Tafel measurement (2 potentiodynamic scans, as described below) of the as-prepared
electrodes was performed. To produce a more uniform initial condition, the electrodes that were tested in the pre-electrolysed electrolyte were conditioned prior to the start of modulations with a 24 hr galvanostatic hold at 'on' current density, until the potential reached a steady state. Tafel measurements of as-polished materials in pre-electrolysed electrolyte were performed separately from modulation.

Cathodic Tafel data was acquired by performing quasi-steady-state potentiodynamic polarizations at a slow scan rate of 2 mV/min. Scans were between ca. 0 to 500 to 0 mV overpotential. Scans were performed twice and Tafel slope data was taken from the second sweep between 500 and 0 mV. Tafel measurements were made of the as-polished materials either before modulations were performed (the case for c.p. Ni) or separately (for AMA). Tafel measurements were made after modulation for both crystalline and amorphous materials, except for samples that were analysed by XPS technique (§3.3.2). The electrochemical test schedule is given in Table 3-VI.

---

**Figure 3.4** Schematic of current density waveform for cyclic modulation.
TABLE 3-V Summarization of current modulations.

<table>
<thead>
<tr>
<th>$t_{ON}$ (min.)</th>
<th>$t_{OFF}$ (min.)</th>
<th>N</th>
<th>Waveform ($t_{ON}$/$t_{OFF}$/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>720</td>
<td>5</td>
<td>2,3</td>
<td>720/5/xx</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>20</td>
<td>60/5/20</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>100-175</td>
<td>5/5/xxx</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>12, 20</td>
<td>60/60/xx</td>
</tr>
</tbody>
</table>

TABLE 3-VI Schedule of electrochemical test sequences.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrochemical Test Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.p. Ni</td>
<td>• Tafel + Modulation + Tafel</td>
</tr>
<tr>
<td></td>
<td>• Cathodic Hold + Modulation + Tafel</td>
</tr>
<tr>
<td></td>
<td>• Tafel</td>
</tr>
<tr>
<td></td>
<td>• Tafel + Modulation $\Rightarrow$ Surface Analysis</td>
</tr>
<tr>
<td>AMA</td>
<td>• Cathodic Hold + Modulation + Tafel</td>
</tr>
<tr>
<td></td>
<td>• Tafel</td>
</tr>
<tr>
<td></td>
<td>• Cathodic Hold + Modulation $\Rightarrow$ Surface Analysis</td>
</tr>
</tbody>
</table>

3.3 **SURFACE ANALYSIS**

Three surface analysis techniques were used to evaluate the cathode surfaces: scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and x-ray photoelectron spectroscopy (XPS).

3.3.1 **SCANNING ELECTRON MICROSCOPY/ ENERGY DISPERSIVE X-RAY ANALYSIS**

SEM was used to evaluate surface morphology. Specimens were first sputter-coated with gold to reduce charging effects. An Hitachi S-2500 microscope was used with an accelerating voltage of 20 keV and and emission beam current of 100 $\mu$A. SEM
photographs were taken on Kodak Verichrome pan film (VP 120) or digitally acquired with PCI DOS/Windows software. Low magnification (< 1000x) images were acquired using the lower detector and a working distance of 15mm while high magnification images used the upper detector at a working distance of 2-5mm. An accompanying LINK EDX system was employed to study bulk (i.e. several thousand atomic layers depth) changes in chemistry. EDX was used with a Si X-ray detector and a working distance of 30-35mm.

3.3.2 X-RAY PHOTOELECTRON SPECTROSCOPY

XPS is a sensitive technique that was used to indicate the elements present at the electrode surface (1-2 atomic layers depth) and their bonding states. XPS acquisition was performed by Dr. Rana Sodhi using a Leybold MAX 200 system with unmonochromatized Mg-Kα radiation at 15 kV and 20 mA emission current. The binding energy scale was calibrated to Ag 3d5/2 and Cu 2p3/2 with binding energies of 368.3 and 932.7 eV, respectively. The high resolution pass energy was 48 eV and all spectra were adjusted to the C 1S peak at 284.6 eV. Peak deconvolution was performed using ESCATools/MATLAB software on a DOS/Windows PC.
4. RESULTS

4.1 ELECTROCHEMICAL

This section presents the electrochemical results (cyclic current modulations, Tafel plots) for the cathode materials.

4.1.1 CYCLIC MODULATIONS

This section presents the results of cyclic current modulation on the cathode materials. The notation used to denote the modulation cycles is as given in Table 3-V.

4.1.1.1 Commercially Pure Nickel In Untreated KOH Electrolyte

This section presents the results of modulation of c.p. nickel in untreated 8 M KOH electrolyte, after an initial Tafel scan. The 'on' and 'off' potential responses during modulations 720/5/2, 60/5/20, 5/5/100+, 60/60/12 are shown in Figures 4.1 to 4.4, respectively (n.b.: for the 720/5/2 modulation, the up and down ramps between the 'on' and 'off' potentials are shown but for clarity the ramps are omitted from the other figures).

For the modulations, the potential upon initial application (i.e. within the first 60 seconds during the first cycle) of the 'on' current, is ca. -1550 mV\textsubscript{Hg/HgO}. The potential rises at a rapid but decreasing rate during the first 60 – 120 minutes of modulation. A potential maximum is reached at ca. -1950 mV\textsubscript{Hg/HgO} and with further modulation the 'on' potential then decreases 100 – 150 mV during a 24 hour period. After a depolarization
(i.e. to 'off' current), the potential upon resumption of the 'on' current is several mV more cathodic than at the end of the previous 'on' cycle, but decays again.
Figure 4.1  C.p. Ni in untreated 8 M KOH electrolyte: potential response to cyclic modulation 720/5/2 (average of three tests).

Figure 4.2  C.p. Ni in untreated 8 M KOH electrolyte: potential response to cyclic modulation 60/5/20 (average of four tests).
Figure 4.3  C.p. Ni in untreated 8 M KOH electrolyte: potential response to cyclic modulation 5/5/100+ (average of six tests).

Figure 4.4  C.p. Ni in untreated 8 M KOH electrolyte: potential response to cyclic modulation 60/60/12 (average of two tests).
4.1.1.2 Commercially Pure Nickel in Pre-Electrolysed KOH Electrolyte

This section presents the results of c.p. nickel modulated in pre-electrolysed 8 M KOH electrolyte after an initial 24 hour cathodic hold at 250 mA/cm\(^2\). The 'on' and 'off' potential responses during modulations 720/5/3, 60/5/20, 5/5/100+, 60/60/20 are shown in Figures 4.5 to 4.8, respectively. Except for the 5/5/100+ figure, the ramps between the 'on' and 'off' potentials are omitted from the figures for clarity.

During the initial 24 hour hold, the potential increases during the first 6 - 12 hours from initially ca. -1450 mV\(_{\text{Hg/HgO}}\) before eventually stabilizing at ca. -1930 mV\(_{\text{Hg/HgO}}\). With modulation, the 'on' potentials do not differ greatly from this value.
Figure 4.5  C.p. Ni in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 720/5/3 (average of three tests).

Figure 4.6  C.p. Ni in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 60/5/20 (average of three tests).
Figure 4.7  C.p. Ni in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 5/5/100+ (one test).

Figure 4.8  C.p. Ni in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 60/60/20 (average of two tests).
4.1.1.3 Amorphous Ni_{50}Co_{25}P_{15}B_{10} in Pre-Electrolysed KOH

This section presents the results of cyclic current modulation on amorphous metal alloy cathodes in pre-electrolysed 8 M KOH electrolyte after an initial 24 hour cathodic hold at 250 mA/cm². Modulations 720/5/2, 60/5/20, 5/5/100+, 60/60/20 are shown in Figures 4.9 to 4.12, respectively. Except for the 60/60/20 figure, the ramps between the 'on' and 'off' potentials are omitted from the figures for clarity.

During the initial 24 hour hold, the potential increases during the first 6 – 12 hours from initially ca. -1500 mV_{Hg/HgO} before eventually stabilizing at ca. -1960 mV_{Hg/HgO}.

With modulation, the potential decreased for the 720/5/2, 60/5/20, 60/60/20 cycles but not for the 5/5/100+ cycle. The potential tended to decrease rapidly. In general, there are two steady-state potentials seen at the 'on' current density, one near the initial steady-state potential of ca. -1950 mV_{Hg/HgO}, and the other near ca. -1800 mV_{Hg/HgO}. 
Figure 4.9 Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 720/5/2 (average of six tests).

Figure 4.10 Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 60/5/20 (average of five tests).
Figure 4.11 Amorphous Ni₅₀Co₂₅P₁₅B₁₀ in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic modulation 5/5/100+ (average of four tests).

Figure 4.12 Amorphous Ni₅₀Co₂₅P₁₅B₁₀ in pre-electrolysed 8 M KOH electrolyte: potential response to cyclic current modulation 60/60/20 (one test).
4.1.2 TAFEL PLOTS

The following sections will present the Tafel (overpotential, $\eta$ vs. current density, i) plots measured prior to and after the cyclic current modulations of §4.1.1.

4.1.2.1 Before Cyclic Modulation

The following sub-sections present the cathodic Tafel plots of as-polished c.p. Ni in (a) as-prepared (untreated) 8 M KOH, (b) in pre-electrolysed 8 M KOH, and (c) as-polished AMA in pre-electrolysed 8 M KOH. Table 4-I gives the kinetic parameters (slope (b) and intercept ($i_o$)) derived from the $\eta$-log i plots. Two sets of $b$ and $i_o$ are tabulated, for the low and high regions, along with the overpotential range ($\eta_{range}$) of the regions. Additionally, the open-circuit potential ($E_{o,c}$) measured prior to Tafel measurement is given.

4.1.2.1a Commercially-Pure Nickel in Untreated KOH Electrolyte

Figure 4.13 shows the Tafel plot of c.p. Ni in untreated 8 M KOH. This electrolyte also contains the impurities listed in Table 3-III. This plot is of the average value at each point from fifteen tests. It can be seen that the corrosion potential is cathodic ca. 60 mV to the $H_2$ evolution equilibrium potential (i.e. $\eta_{H_2} = 0$). The plot is linear between $\eta_{H_2} \sim 100 - 380$ mV and at higher overpotentials it starts to steepen and the scatter increases.
4.1.2.1b  Commercially Pure Nickel in Pre-Electrolysed KOH Electrolyte

Figure 4.14 shows the Tafel plot of c.p. Ni in 8 M KOH pre-electrolysed to remove dissolved impurities such as iron. This plot is of the average value at each point from four tests. The plot is quite linear over its range although at high overpotentials the scatter increases and it starts to curve upwards slightly.

4.1.2.1c  Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in Pre-Electrolysed KOH Electrolyte

Figure 4.15 shows the Tafel plot of AMA in 8 M KOH pre-electrolysed to remove dissolved impurities such as iron. This plot is of the average value at each point from four tests. The corrosion potential is cathodic ca. 80 mV to the H$_2$ evolution equilibrium potential. The plot deviates slightly from linearity, steepening with increasing overpotential.

<table>
<thead>
<tr>
<th>Environment</th>
<th>$E_{oc}$</th>
<th>$b_c$</th>
<th>$i_o$</th>
<th>$b_{high}$</th>
<th>$i_{o,high}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated electrolyte</td>
<td>-948</td>
<td>144</td>
<td>0.029</td>
<td>289</td>
<td>0.53</td>
</tr>
<tr>
<td>pre-electrolysed</td>
<td>-839</td>
<td>154</td>
<td>0.035</td>
<td>206</td>
<td>0.12</td>
</tr>
<tr>
<td>electrolyte</td>
<td>-966</td>
<td>177</td>
<td>0.033</td>
<td>236</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Figure 4.13  HER Tafel plot of as-polished c.p. Ni sheet in untreated 8 M KOH electrolyte (average of five tests).

Figure 4.14  HER Tafel plot of as-polished c.p. Ni sheet in pre-electrolysed 8 M KOH electrolyte (average of five tests).
Figure 4.15 HER Tafel plot of as-polished amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in pre-electrolysed 8 M KOH electrolyte (average of five tests).
4.1.2.2  After Cyclic Modulation

The following sections presents plots of the cathodic Tafel plots of current modulated c.p. Ni in (a) as-prepared (untreated) 8 M KOH, (b) in pre-electrolysed 8 M KOH, and (c) current modulated AMA Ni_{50}Co_{25}P_{15}B_{10} in pre-electrolysed 8 M KOH. Two sets of b and i_o are tabulated, for the low and high regions (b, i_o and b_{high}, i_{o,high}), along with the overpotential range (\eta_{range}) of the regions. Additionally, the open-circuit potential (E_{o.c.}) measured prior to Tafel measurement is given.
4.1.2.2a *Commercially Pure Nickel in Untreated KOH Electrolyte*

This section presents the results of Tafel measurements made after modulation of c.p. nickel in untreated 8 M KOH electrolyte. Tafel measurements after modulations 720/5/2, 60/5/20, 5/5/100+, 60/60/12 are shown in Figures 4.16 to 4.19, respectively. With modulation there is, generally, a flattening of the curve, particularly in the high overpotential region. The corrosion potential is cathodic at $\eta_{H_2} \approx 100$ mV. Table 4-II gives the kinetic parameters derived from the $\eta$-log $i$ plots and the open-circuit potential ($E_{o,c.}$) observed prior to Tafel measurement.

**TABLE 4-II** Tafel parameters of c.p. Ni after cyclic current modulation in untreated 8 M KOH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$E_{o,c.}$ (mV$_{Hg/HgO}$)</th>
<th>$b_{low}$ (mV/dec)</th>
<th>$i_0$ (mA/cm$^2$)</th>
<th>$b_{high}$ (mV/dec)</th>
<th>$i_{0,high}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>720/5/2</td>
<td>-1014</td>
<td>151</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/5/20</td>
<td>-1015</td>
<td>170</td>
<td>0.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/5/100+</td>
<td>-991</td>
<td>161</td>
<td>0.023</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/60/12</td>
<td>-1020</td>
<td>138</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.16  HER Tafel plot of c.p. Ni sheet after cyclic current modulation 720/5/2 in untreated 8 M KOH electrolyte (average of three tests).

Figure 4.17  HER Tafel plot of c.p. Ni sheet after cyclic current modulation 60/5/20 in untreated 8 M KOH electrolyte (average of four tests).
Figure 4.18 HER Tafel plot of c.p. Ni sheet after cyclic current modulation 5/5/100+ in untreated 8 M KOH electrolyte (average of five tests).

Figure 4.19 HER Tafel plot of c.p. Ni sheet after cyclic current modulation 60/60/12 in untreated 8 M KOH electrolyte (average of two tests).
4.1.2.2b  Commercially Pure Nickel in Pre-Electrolysed KOH Electrolyte

This section presents the results of Tafel measurements made after modulation of c.p. nickel in pre-electrolysed 8 M KOH electrolyte. Tafel measurements after modulations 720/5/3, 60/5/20, 60/60/20 are shown in Figures 4.20 to 4.22, respectively. With modulation there is a bowing of the curve in the low to moderate overpotential range and a steepening at high overpotentials. The corrosion potential is seen at $\eta_{H_2} \approx 50$ mV. Table 4-III gives the kinetic parameters derived from the $\eta$-log $i$ plots and the open-circuit potential ($E_{o.c.}$) observed prior to Tafel measurement.

### TABLE 4-III  Tafel parameters of c.p. Ni after cyclic current modulation in pre-electrolysed 8 M KOH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$E_{o.c.}$ (mV$_{Hg/HgO}$)</th>
<th>$b_{low}$ (mV/dec)</th>
<th>$i_0$ (mA/cm$^2$)</th>
<th>$b_{high}$ (mV/dec)</th>
<th>$i_{0,high}$ (mA/cm$^2$)</th>
<th>$E_{o.c., high}$ (mV$_{Hg/HgO}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>720/5/3</td>
<td>-915</td>
<td>133</td>
<td>0.025</td>
<td>270</td>
<td>0.31</td>
<td>-850</td>
</tr>
<tr>
<td>60/5/20</td>
<td>-904</td>
<td>147</td>
<td>0.030</td>
<td>296</td>
<td>0.31</td>
<td>-820</td>
</tr>
<tr>
<td>60/60/20</td>
<td>-977</td>
<td>166</td>
<td>0.074</td>
<td>313</td>
<td>0.46</td>
<td>-800</td>
</tr>
</tbody>
</table>
Figure 4.20  HER Tafel plot of c.p. Ni sheet after cyclic current modulation 720/5/3 in pre-electrolysed 8 M KOH electrolyte (average of three tests).

Figure 4.21  HER Tafel plot of c.p. Ni sheet after cyclic current modulation 60/5/20 in pre-electrolysed 8 M KOH electrolyte (average of three tests).
Figure 4.22  HER Tafel plot of c.p. Ni sheet after cyclic current modulation 60/60/20 in pre-electrolysed 8 M KOH electrolyte (average of two tests).
4.1.2.2c  *Amorphous Ni<sub>50</sub>Co<sub>25</sub>P<sub>15</sub>B<sub>10</sub> in Pre-Electrolysed KOH Electrolyte*

This section presents the results of Tafel measurements made after modulation of AMA in pre-electrolysed 8 M KOH electrolyte. Tafel measurements after modulations 720/5/2, 60/5/20, 5/5/100+, 60/60/12 are shown in Figures 4.23 to 4.26, respectively. With modulation there is a shift of the curve to the left (to lower current densities) and there is an arching or a steepening of the curve at low to moderate overpotentials. The corrosion potential is η<sub>H2</sub> ≈ 120 mV. Table 4-IV gives the kinetic parameters derived from the η-log i plots and the open-circuit potential (E<sub>o.c.</sub>) observed prior to Tafel measurement.

**TABLE 4-IV**  Tafel parameters of AMA after cyclic current modulation in pre-electrolysed 8 M KOH electrolyte.

<table>
<thead>
<tr>
<th>Condition</th>
<th>E&lt;sub&gt;o.c.&lt;/sub&gt; (mV&lt;sub&gt;Hg/HgO&lt;/sub&gt;)</th>
<th>b&lt;sub&gt;low&lt;/sub&gt; (mV/dec)</th>
<th>i&lt;sub&gt;0&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>b&lt;sub&gt;high&lt;/sub&gt; (mV/dec)</th>
<th>i&lt;sub&gt;0,high&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
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<td>720/5/2</td>
<td>-1014</td>
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<td>0.0083</td>
<td>182</td>
<td>0.0036</td>
</tr>
<tr>
<td>60/5/20</td>
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<td>281</td>
<td>0.015</td>
<td>185</td>
<td>0.0029</td>
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<tr>
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<td>-1051</td>
<td>287</td>
<td>0.019</td>
<td>213</td>
<td>0.0059</td>
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<tr>
<td>60/60/20</td>
<td>-1080</td>
<td>169</td>
<td>0.013</td>
<td>257</td>
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</tr>
</tbody>
</table>
Figure 4.23  HER Tafel plot of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cyclic current modulation 720/5/2 in pre-electrolysed 8 M KOH electrolyte (average of three tests).

Figure 4.24  HER Tafel plot of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cyclic current modulation 60/5/20 in pre-electrolysed 8 M KOH electrolyte (average of four tests).
Figure 4.25 HER Tafel plot of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cyclic current modulation 5/5/100+ in pre-electrolysed 8 M KOH electrolyte (average of four tests).

Figure 4.26 HER Tafel plot of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cyclic current modulation 60/60/20 in pre-electrolysed 8 M KOH electrolyte (one test).
4.2 SURFACE ANALYSIS

This section presents the surface analysis results from scanning electron microscopy, energy dispersive x-ray analysis and x-ray photoelectron spectroscopy on the cathode materials.

4.2.1 SCANNING ELECTRON MICROSCOPY/ENERGY DISPERSIVE X-RAY ANALYSIS

The following sections present scanning electron microscopy and energy dispersive x-ray analysis results prior to and after cyclic modulation.

4.2.1.1 Before Cyclic Modulation

The following sections present SEM and EDX of as-polished c.p. Ni sheet and amorphous metal alloy ribbon.
4.2.1.1a Commercially Pure Nickel

This section presents SEM and EDX analysis of c.p. Ni sheet polished to a 1 μm finish. The scanning electron micrograph in Figure 4.27(a) shows the nearly featureless surface of c.p. nickel, ground and polished to a 1 μm finish. The planar surface shows only polishing scratches. The EDX spectrum of this clean surface (Figure 4.27(b)) shows only Ni; the presence of the other expected impurities in the material (Table 3-I) are below the detection limits (Atomic Number < 14 (Si)) of the x-ray analyzer.

![Figure 4.27](image.png)

Figure 4.27 (a) SEM image and (b) EDX spectrum of as-polished c.p. Ni sheet.
4.2.1.1b Amorphous $\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}$ Ribbon

This section presents SEM analysis of AMA polished to a $1 \, \mu\text{m}$ finish. Figure 4.28(a) shows the SEM micrograph of polished AMA and Figure 4.28(b) gives the EDX spectrum of the surface. The scanning electron micrograph shows the surface of AMA ribbon is smooth showing only polishing scratches. The EDX spectrum of this alloy, $\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}$ shows Ni, Co and P; B is below the detection limit of the x-ray analyser.

![Figure 4.28](image)

**Figure 4.28** As-polished $\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}$ ribbon: (a) SEM image and (b) EDX spectrum.
4.2.1.2 After Cyclic Modulation

The following sections present SEM, EDX and XPS of modulated c.p. Ni sheet and amorphous metal alloy ribbon.

4.2.1.2a Commercially Pure Nickel in Untreated KOH Electrolyte

This section presents SEM and EDX analysis of c.p. Ni sheet modulated in untreated 8 M KOH. One representative specimen surface is shown in Figure 4.29. The SEM in Figure 4.29(a) shows the roughened surface of c.p. nickel, with nodular and crystallite growth. The EDX spectrum of this surface shows Ni and the presence of iron (gold is an artifact from the microscopy technique (§3.3.1)).

Figure 4.29 Ni sheet after cyclic current modulation in untreated electrolyte: (a) SEM micrograph and (b) EDX spectrum.
4.2.1.2b Commercially Pure Nickel in Pre-Electrolysed KOH Electrolyte

This sections presents SEM and EDX analysis of c.p. Ni sheet modulated in pre-electrolysed 8 M KOH. The scanning electron micrograph in Figures 4.30(a)-(d) shows roughened surfaces of c.p. nickel, with nodular growth. These areas had similar EDX spectra. A representative spectrum is given in Figure 4.31 showing Ni and the presence of metallic impurities such as iron and zinc (gold is an artifact from the microscopy technique (§3.3.1)).
Figure 4.30 SEM images of c.p. Ni after cyclic current modulation in pre-electrolysed 8 M KOH: (a) 720/5/3, (b) 60/5/20, (c) 5/5/100+, (d) 60/60/20.

Figure 4.31 EDX spectrum of c.p. Ni after cyclic current modulation in pre-electrolysed 8 M KOH
4.2.1.2c **Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in Pre-Electrolysed KOH Electrolyte**

This section presents SEM and EDX analysis of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ modulated in pre-electrolysed 8 M KOH. The scanning electron micrograph in Figures 4.32(a)-(d) shows the roughened surfaces of the amorphous alloys, with nodular growth. These areas had similar EDX spectra. A representative spectrum is given in Figure 4.33 showing Ni and the presence of potassium from the electrolyte and iron impurity.
Figure 4.32 SEM images of amorphous Ni_{50}Co_{25}P_{15}B_{10} after cyclic current modulation in pre-electrolysed 8 M KOH: (a) 720/5/2, (c) 60/5/20, (d) 5/5/100+, (e) 60/60/20.
4.2.2 X-RAY PHOTOELECTRON SPECTROSCOPY

The following sections present x-ray photoelectron spectroscopy results prior to and after cyclic modulation. The photoelectron peak for the 2p shell, which is the most useful for identification of Ni species [92], is presented in each section. Ni 2p has two spin components, 2p\textsubscript{3/2} and 2p\textsubscript{1/2}, which are labeled in each figure.

4.2.2.1 Before Cyclic Modulation

The following sections present XPS of as-polished c.p. Ni sheet and amorphous Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} alloy ribbon.

4.2.2.1a Commercially Pure Nickel

This section presents the results of XPS on as-polished c.p. Ni sheet. Figure 4.34 shows the Ni 2p spectrum; the spin components, 2p\textsubscript{3/2} and 2p\textsubscript{1/2}, are labeled in the figure. For each, there are peaks that are attributed to metallic nickel (Ni\textsuperscript{0}), divalent nickel (Ni\textsuperscript{2+}) and the shake-up satellites (sat.) of each. The largest Ni 2p\textsubscript{3/2} peak is positioned at 852.7 eV and is attributed to metallic nickel, and the corresponding metallic Ni 2p\textsubscript{1/2} peak is separated from it by 17.7 eV. The shorter Ni peak shows a shift to a higher binding energy, ca. 855-856 eV, and is attributed to divalent nickel.
Figure 4.34 XPS of as-polished c.p. Ni sheet: Ni 2p spectrum showing the 2p$_{3/2}$ and 2p$_{1/2}$ regions and the metallic (Ni$^0$), divalent (Ni$^{2+}$) and satellite (sat.) peaks.
4.2.2.1b *Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ Ribbon*

This section presents the results of XPS of as-polished Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon. Figures 4.35 and 4.36 show the Ni and Co 2p peaks, respectively. For each, there are components that are attributed to metallic (Ni$^0$, Co$^0$), divalent (Ni$^{2+}$, Co$^{2+}$) species and their respective shake-up satellites (sat.).

The Ni 2p spectrum is similar to crystalline Ni. The largest Ni 2p$_{3/2}$ peak is positioned at 852.7 eV and is attributed to metallic nickel, and the corresponding metallic Ni 2p$_{1/2}$ peak is separated from it by 17.2 eV. The shoulder on the metallic Ni peak (at ca. 855-856 eV) is attributed to the binding energy shift of divalent Ni. The Co 2p spectrum has similar features to Ni 2p, namely the split between 2p$_{3/2}$ and 2p$_{1/2}$ and the presence of metallic (Co$^0$), divalent (Co$^{2+}$) and shake-up satellite (sat.) peaks. The largest Co 2p$_{3/2}$ peak is positioned at 777.9 eV and the corresponding metallic Co 2p$_{1/2}$ 15.2 eV higher is attributed to metallic Co. The second 2p$_{3/2}$ peak, located at ca. 781 eV is attributed to divalent Co.
Figure 4.35  XPS of as-polished amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon: Ni 2p spectrum showing the 2p₃/2 and 2p₁/2 regions and the metallic (Ni⁰), divalent (Ni²⁺) and satellite (sat.) peaks.

Figure 4.36  XPS of as-polished amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon: Co 2p spectrum showing the 2p₃/2 and 2p₁/2 regions and the metallic (Co⁰), divalent (Co²⁺) and satellite (sat.) peaks.
4.2.2.2  After Cyclic Modulation

The following sections give Tafel plots and XPS spectra of the cathode materials after modulation.

4.2.2.2a  Commercially Pure Nickel in Untreated KOH Electrolyte

This section gives the results of commercially pure nickel after cyclic modulation. Figure 4.37 shows the Ni 2p spectrum. Only one set of peaks was detected; the $2p_{3/2}$ peak present at ca. 855 eV is attributed to divalent Ni.

Figure 4.37  XPS of c.p. Ni sheet after cathodic polarization in untreated electrolyte: Ni 2p spectrum showing the $2p_{3/2}$ and $2p_{1/2}$ regions and the divalent ($Ni^{2+}$) and satellite (sat.) peaks.
4.2.2.2b Commercially Pure Nickel in Pre-Electrolysed KOH Electrolyte

This section gives the results of commercially pure nickel after cyclic modulation. Figure 4.38 shows the Ni 2p spectrum. Two sets of peaks were detected. Smaller peaks were attributed to metallic nickel (Ni$^0$) (Ni 2p$_{3/2}$ = 852.6 eV, Δ-2p$_{1/2}$ = 17.1 eV), while the taller peaks (Ni 2p$_{3/2}$ at ca. 856 eV) were attributed to divalent Ni.

![Figure 4.38 XPS of c.p. Ni sheet after cathodic polarization in pre-electrolysed electrolyte: Ni 2p spectrum showing the 2p$_{3/2}$ and 2p$_{1/2}$ regions and the metallic (Ni$^0$), divalent (Ni$^{2+}$) and satellite (sat.) peaks.](image)

Figure 4.38 XPS of c.p. Ni sheet after cathodic polarization in pre-electrolysed electrolyte: Ni 2p spectrum showing the 2p$_{3/2}$ and 2p$_{1/2}$ regions and the metallic (Ni$^0$), divalent (Ni$^{2+}$) and satellite (sat.) peaks.
4.2.2.2c  Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in Pre-Electrolysed KOH Electrolyte

This section presents XPS spectra of AMA after cathodic polarization in pre-electrolysed 8 M KOH electrolyte. The Ni 2p spectrum is given in Figure 4.39, the Co 2p spectrum is given in Figure 4.40. One set of peaks was detected for both Ni and Co species (i.e., Ni 2p$_{3/2}$ at ca. 855 eV, Co 2p$_{3/2}$ at ca. 781 eV) and was attributed to divalent species.

Figure 4.39 XPS of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ after cathodic polarization in pre-electrolysed electrolyte: Ni 2p spectrum showing the 2p$_{3/2}$ and 2p$_{1/2}$ regions and the divalent (Ni$^{2+}$) and satellite (sat.) peaks.
Figure 4.40 XPS of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ after cathodic polarization in pre-electrolysed electrolyte: Co 2p spectrum showing the 2p$_{3/2}$ and 2p$_{1/2}$ regions and the divalent (Co$^{2+}$) and satellite (sat.) peaks.
5. DISCUSSION

5.1 INITIAL CONDITIONS

5.1.1 SURFACE ANALYSIS

This section will discuss the surface morphology and chemistry of the as-polished electrode materials, commercially pure Ni sheet and amorphous Ni$_{30}$Co$_{25}$P$_{15}$B$_{10}$ ribbon, which were finely polished (as described in §3.1.1) prior to electrochemical characterization and/or treatments to produce uniform surfaces with minimal roughness and minimal residual oxide film (Appendix D-1).

5.1.1.1 Scanning Electron Microscopy/ X-Ray Analysis

The following sections discuss SEM and EDX examination of the as-polished cathode materials.

5.1.1.1a Commercially Pure Nickel Sheet

From macroscopic observation, the as-received Ni sheet was nominally flat but appeared satiny, indicating that the surface was moderately oxidized and/or roughened. After polishing, the surface had a bright mirror finish. The scanning electron micrograph
Figure 5.1  SEM micrographs and EDX spectra of as-polished c.p. Ni sheet ((a), (b)) and of as-polished amorphous Ni_{50}Co_{25}P_{15}B_{10} ribbon ((c), (d)).
in Figure 5.1(a) of the as-polished c.p. Ni surface shows that the polishing treatment produced an electrode surface which has a low roughness; only at the high magnifications of the micrograph are sub-micron scratches from the polishing media apparent. The EDX spectrum of the surface (Figure 5.1(b)) shows only Ni; the presence of the other expected impurities which might be expected in the material (Table 3-I) are below the detection sensitivity limits (< 0.1%) of the x-ray analyzer.

5.1.1.1b Amorphous Ni₅₀Co₂₅P₁₅B₁₀ Ribbon

The as-received amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon was dull on the side that had contacted the melt-spinning wheel, but bright on the non-contacted side. The bright side was polished to a mirror finish. The scanning electron micrograph of the as-polished AMA surface in Figure 5.1(c) shows that, as for the c.p. Ni sheet, the polishing treatment produces an electrode which has minimal roughness. The EDX spectrum of this alloy in Figure 5.1(d) shows Ni, Co and P; B is below the elemental detection limit (Z < 14(Si)) of the x-ray analyser.
5.1.1.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy allows analysis of only the top several atomic layers of a surface, providing information on not only the relative amounts of the elements present but also the binding state of elemental species present at the surface. EDX, by comparison, provides 'bulk' compositional information of which elements are present.

The following sections discuss XPS examination of the as-polished cathode materials.

5.1.1.2a Commercially Pure Nickel Sheet

This section presents XPS results on as-polished c.p. Ni sheet. Nickel is a passivating metal, thus it is expected that under ambient conditions there will be a thin air-formed oxide layer on the surface. Nickel that is bound with oxygen has a higher binding energy than metallic nickel.

The most useful photoelectron peak for identification of Ni species is for the 2p shell [75]. Figure 4.34 shows the Ni 2p peak from as-polished Ni sheet.

The largest Ni 2p$_{3/2}$ peak at 852.5 eV and the corresponding Ni 2p$_{1/2}$ peak at +17.1 eV were attributed to metallic nickel (analysis of various nickel metal samples (Appendix D) showed the Ni 2p$_{3/2}$ peak position to be 852.7±0.2 eV) and are in good agreement with the values previously reported in literature (Table 2-VI).
The shorter Ni peak at ca. 855-856 eV was attributed to divalent nickel. Since so much metallic (i.e., sub-surface) nickel was detected, the film (i.e. divalent nickel) must be very thin. However, the large contribution from the metallic species hinder determination of the exact divalent species. This will be discussed in the following paragraphs.

Comparison to Standards for Divalent Nickel

In an attempt to identify the divalent species, spectra from the as-polished Ni were compared to XPS standards of NiO and Ni(OH)$_2$ produced by Lian [94], a previous researcher at the author's laboratory; spectra for Ni 2p, 3p and 3s and for O 1s were compared.

In Figure 5.2, the spectrum of Figure 4.34 is overlaid with those of Lian's divalent standards, since NiO and Ni(OH)$_2$ can be best distinguished from the Ni 2p peak shape and positions [86,94]. The low intensity of the non-metallic species made it difficult to verify that the surface consists of either compound, based only on the Ni 2p peaks.

Comparison of the 3p and 3s peaks of as-polished Ni sheet to NiO and Ni(OH)$_2$ standards did not provide useful information because the standards do not show significant differentiation between each other (Figure 5.3).

NiO and Ni(OH)$_2$ have distinct O 1s peaks; the oxide has a doublet shape, while the hydroxide is shifted to a higher binding energy. In Figure 5.4 the O 1s spectrum from the polished c.p. Ni sheet is compared to the oxide and hydroxide standards and it shows a strong shift to a higher binding energy. In general, the O 1s peak for metals may
Figure 5.2  Comparison of Ni 2p peaks: as-polished c.p. Ni sheet versus NiO and Ni(OH)$_2$ standards (after [94]).

Figure 5.3  Comparison of Ni 3s and 3p peaks: as-polished c.p. Ni sheet versus NiO and Ni(OH)$_2$ standards (after [94]).
Figure 5.4 Comparison of O 1s peaks: as-polished c.p. Ni sheet versus NiO and Ni(OH)$_2$ standards (after [94]).

show sub-peak contributions from oxides (i.e. O$^1$) at ca. 529-530 eV, from hydroxides (i.e., OH$^-$) at ca. 531-532 eV and/or from water (H$_2$O) at ca. 533 eV [92]. It appears that the surface of polished Ni sheet is hydrated; water could be adsorbed from the air after polishing. Hydrated nickel oxide is related to nickel hydroxide:

$$\text{NiO} \cdot \text{H}_2\text{O} \rightleftharpoons \text{Ni(OH)}_2$$

(5.1)

However, McIntyre and Cook found a O 1s peak shaped similarly to that of Figure 5.4 for lightly oxidised Ni metal [86]. Thus, the surface film of polished c.p. Ni sheet has both oxide and hydroxide characteristics and it was not possible to distinguish one from the other.
Surface Film Composition and Thickness

The surface composition was determined by deconvoluting the Ni 2p spectrum of polished c.p. Ni into metallic and divalent sub-peak components. Figure 5.5 shows the Ni 2p$_{3/2}$ peak with sub-peaks for metallic, divalent and shake-up satellite components (deconvolution of either Ni 2p or just Ni 2p$_{3/2}$ yielded nearly identical compositional results, thus, for clarity, only the latter is presented). Although the film appeared to have both oxide and hydroxide characteristics, for simplicity the deconvolution was based only on the fit parameters for NiO [94] (Appendix D-3). As expected, there is imperfect agreement using only the oxide fit parameters; using both the oxide and hydroxide fit parameters might produce a better fit. However, a reasonable estimate of the composition can be made based on the sub-peak intensities (area) of Figure 5.5 (Appendix D-3); it was found that the ratio of Ni$^{2+}$ to Ni$^{0}$ was ca. 2:3 (39% divalent Ni and 61% metallic Ni).

The surface film thickness was estimated to be 0.00025 μm (Appendix D-3) based on the following relationship [96]:

\[
\frac{I_{sub}}{I_{film}} = \frac{(\exp[-d/\lambda])}{1-\exp[-d/\lambda]} \quad (5.2)
\]

where, \(I_{sub}, I_{film}\) = measured intensities of substrate, film
\(\lambda\) = photoelectron inelastic mean free path
\(d\) = film thickness

Thus, the starting surface film is 3-4 atomic layers thick (the atomic radii of Ni and Ni$^{2+}$ are ca. 0.00013 μm and 0.00007 μm, respectively [97]).
Figure 5.5  Deconvolution of the Ni 2p₃/₂ spectrum of as-polished c.p. Ni sheet, showing metallic (Ni°) and divalent (Ni²⁺) sub-peaks and their respective shake-up satellites (sat.).
5.1.1.2b Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ Ribbon

XPS results on as-polished amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon are discussed in this section. Like nickel, cobalt is a passivating metal, thus under ambient conditions there should be a thin air-formed oxide layer on the surface. Also as for nickel, the most useful photoelectron peak for identification of Co species is for the 2p shell [92]. Figures 4.35 and 4.36 show the Ni and Co 2p peaks, respectively, from as-polished AMA ribbon.

The largest Ni 2p$_{3/2}$ peak at 852.7 eV and the corresponding Ni 2p$_{1/2}$ peak at +17.1 eV are in good agreement both with the values found for metallic Ni for polished c.p. Ni sheet and those reported in the literature (Table 2-VI). The main Co 2p$_{3/2}$ peak at 778.0 eV and the corresponding 2p$_{1/2}$ peak located +15.1 eV higher are in agreement with literature values (Table 2-VI) and are attributed to metallic cobalt.

The Ni 2p$_{3/2}$ high binding energy shoulder, ca. 855-856 eV, was attributed to a divalent nickel and the second Co 2p$_{3/2}$ peak, located at ca. 781 eV was assigned to divalent Co species, based on the literature values in Table 2-VI. The weaker divalent peaks are consistent with a thin surface film.

Comparison to Commercially Pure Nickel

Figure 5.6 shows the Ni 2p peaks of polished AMA (Figure 4.34) together with those for as-polished c.p. Ni (Figure 4.35). Both show strong metallic Ni (i.e. sub-surface) signals indicating that the surface film is thin, although, since the film of the amorphous ribbon has a high Co content, the c.p. Ni shows a stronger divalent signal.
Figure 5.6  Comparison of Ni 2p peaks: as-polished Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ versus as-polished c.p. Ni sheet.

Figure 5.7  Comparison of O 1s peaks: as-polished Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ versus as-polished c.p. Ni sheet.
In Figure 5.7, the O 1s spectrum from the polished Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon is compared to the polished c.p. Ni sheet. The AMA spectrum is shifted to a higher binding energy at ca. 533 eV, which is associated with the oxygen in water. Thus it would appear that the surface of polished AMA foil has a hydrated nature, more so than the polished Ni sheet. Amorphous alloys are known to be readily hydrated [98] so it is likely that the surface contains bound water and that the surface film may have a hydrated oxide and/or hydroxide nature, i.e.:

\[
(Ni,Co)O\cdot H_2O \leftrightarrow (Ni,Co)(OH)_2
\]

*Surface Film Composition and Thickness*

An approximate surface composition was determined by deconvoluting the Ni and Co 2p spectra of polished Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$.

For simplicity, the 2p deconvolutions (Figure 5.8, 5.9) were based, as in §5.1.1.2a, only on oxide fit parameters [86,94]. The Ni and Co 2p$_{3/2}$ peaks are shown with sub-peaks for metallic (M$^0$), divalent (M$^{2+}$) and shake-up satellite (sat.) components.

The composition was then determined from the sub-peak areas. The ratio of all Ni to all Co detected was 3:2 (61% Ni, 39% Co), marginally lower than the bulk composition of the alloy (Table 3-II). The distribution of Ni and Co is summarized in Table 5-I(a). It can be seen that the Co distribution is greater among the divalent species. If the divalent species represents the surface film, then it appears there is cobalt enrichment in the oxide/hydroxide layer from the underlying substrate. Analysis of
Figure 5.8  Deconvolution of the Ni 2p3/2 spectrum of as-polished Ni50Co25P15B10, showing metallic (Ni0) and divalent (Ni2+) sub-peaks and their respective shake-up satellites (sat.).

Figure 5.9  Deconvolution of the Co 2p3/2 spectrum of as-polished Ni50Co25P15B10, showing metallic (Co0) and divalent (Co2+) sub-peaks and their respective shake-up satellites (sat.).
thermally oxidized crystalline Co-Ni alloys has indicated CoO forms preferentially to NiO due to a high diffusivity of Co$^{2+}$ [91]. Since Co is less stable than Ni in KOH electrolytes, the AMA, compared to nickel metal, could be expected to have quite different electrocatalytic and/or corrosion properties in KOH electrolytes.

Table 5-Ia  The distribution of Ni and Co in as-polished amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon: in bulk (Table 3-II), at surface, metallic species at surface, divalent species at surface.

<table>
<thead>
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<th>Surface, Divalent</th>
<th>Total</th>
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</thead>
<tbody>
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<td>Ni</td>
<td>65%</td>
<td>61%</td>
<td>76%</td>
<td>39%</td>
</tr>
<tr>
<td>Co</td>
<td>35%</td>
<td>39%</td>
<td>34%</td>
<td>61%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

The M$^0$/M$^{2+}$, Ni$^0$/Ni$^{2+}$, Co$^0$/Co$^{2+}$ compositions are given in Table 5-I(b). The ratio of divalent (Ni$^{2+}$ + Co$^{2+}$) to metallic (Ni$^0$ + Co$^0$) species detected was ca. 2:3 (42% M$^0$ and 58% M$^{2+}$), about the same as for polished c.p. Ni. The surface film thickness was then estimated to be 0.00016 $\mu$m (Eqn. (5.2)), indicating that the surface film is only 1-2 monolayers thick.

Table 5-Ib  The distribution of metallic and divalent species in as-polished amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon as detected by XPS: Ni and Co at surface, nickel at surface, cobalt at surface.

<table>
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<th>Species</th>
<th>Ni Distribution</th>
<th>Co Distribution</th>
<th>Total Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic</td>
<td>58%</td>
<td>77%</td>
<td>35%</td>
</tr>
<tr>
<td>Divalent</td>
<td>42%</td>
<td>23%</td>
<td>65%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
5.1.2 ELECTROCHEMICAL

The following sections discuss the electrochemical parameters of as-polished commercially pure nickel and amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ alloy in 8 M KOH electrolytes, prior to cyclic modulation.

5.1.2.1 Commercially Pure Nickel

This section discusses the Tafel plots of c.p. Ni cathodes in untreated and pre-electrolysed 8 M KOH electrolyte.

5.1.2.1a Nickel in Untreated KOH Electrolyte

The $\eta$–log $i$ plot of c.p. Ni in untreated 8 M KOH electrolyte at 70°C is shown in Figure 4.13. Prior to the Tafel measurement, the nickel was cathodically polarized for 3 hrs at -1300 mV$_{H_2/H_2O}$ ($\eta_{H_2} = 330$ mV). The slope of the lower, linear portion of this plot is $b = 144$ mV/dec (Table 4-I) which is in good agreement with the theoretical value of 138 mV/dec for the Volmer/discharge reaction (§2.2.4, Equation (2.4)). Since Tafel slope values vary with the duration of polarization (§2.4.1.2), the experimental value is considered among the range of literature values (for similar cathodic polarization times) as given in Table 2-IIa and Figure 2.6. Suzuki [34], using an identical experimental protocol, except with untreated 1 M KOH at 30°C, found that for nickel $b = 139$ mV/dec.
for a similar overpotential range. For a hot, concentrated environment (70°C, 30% KOH),
across a moderate to low overpotential range, Huot et al. found a value of \( b = 103 \) mV/dec (after polarization at -1500 mV \( \text{Hg/HgO} \) for 1 hr) \([42,43]\), while Kibria et al. reported
a value of \( b = 166 \) mV/dec \([39]\).

The exchange current density of \( i_0 = 0.029 \) mA/cm\(^2\) (Table 4-I) extrapolated from
the Tafel slope is of the same order of magnitude as those seen in the literature. The
uncertainty in Tafel slope fit and in real electrode surface area results in considerable
variation of \( i_0 \) values.

Above \( \eta_{H_2} \equiv 380 \) mV, the \( \eta \)-log \( i \) plot bends upwards and the scatter increases. A
line fitted through the points above \( \eta_{H_2} \equiv 380 \) mV yields a slope of \( b_{\text{high}} = 289 \) mV/dec.
Suzuki reported a slope of \( b_{\text{high}} = 239 \) mV/dec at high overpotentials in 1 M KOH at 30°C
\([34]\).

5.1.2.1b Ni in Pre-Electrolysed KOH Electrolyte

The \( \eta \)-log \( i \) plot of c.p. Ni in pre-electrolysed 8 M KOH electrolyte at 70°C is
shown in Figure 4.14. The slope of the lower portion of this plot, as given in Table 4-I, is
\( b = 152 \) mV/dec, similar to the value in untreated electrolyte. This value is also within
the range of values seen in the literature (Table 2-Ia and Figure 2.6). Stemp's results on
c.p. Ni with an identical environment and method, but using a faster sweep rate of
6 mV/min, produced a slope of \( b = 204 \) mV/dec over the range \( \eta_{H_2} \equiv 30 - 500 \) mV \([99]\).
The higher slope is attributed to the faster potential sweep rate than the present study
(which more closely approximates steady state potentiostatic measurements [34]). Rommal and Moran [40] reported that in pre-electrolysed 30% KOH electrolyte ([Fe] < 0.03 ppm), the Tafel slope after a 0.27 hour cathodic polarization at $i_c = 100 \text{ mA/cm}^2$ was $b = 125 \text{ mV/dec}$, while after 2.77 hours it was $b = 300 \text{ mV/dec}$. However, these researchers used extremely fast (galvanostatic) sweep rates of $30 \text{ (mA/cm}^2)/\text{sec}$ (equivalent to ca. 25 mV/sec) and tested through a moderate-to-high polarization range ($10^0 - 10^2 \text{ mA/cm}^2$), making direct comparisons difficult.

The values for $b_{\text{high}}$ and $i_{o,\text{high}}$ were 193 mV/dec and 0.09 mA/cm$^2$, respectively.

5.1.2.1c Comparison of c.p. Ni in Untreated and in Pre-Electrolysed KOH

The η-log $i$ plots of c.p. Ni in both treated and untreated electrolyte are shown together in Figure 5.10. It is difficult to attain reproducible Tafel results on nickel in alkaline solutions, as has been noted previously [28,34]. This was the case even where the data is the average of 15 experiments, as for Ni in untreated electrolyte, particularly at higher overpotentials.

The Tafel curves over most of the overpotential range are in very close agreement and the Tafel slopes indicate that the Volmer step/primary discharge is rate determining (Eqn. (2.6)). Another useful method to compare activity is to note values at specific points on the η-log $i$ curve; either with $\eta = f(i)$ or $i = f(\eta)$. Table 5-II gives current density ($i_\eta$) measured at $\{500, 325, 225\} \text{ mV}_H_2O$ and the Potential ($E_{250}$) at 250 mA/cm$^2$ projected from the $b_{\text{high}}$ and $i_{o,\text{high}}$ values by combining Equations (2.12) and (2.17):
\[ E_{250} = E^\circ_{H_2/H_2O} + (b_{\text{high}} \log(250/i_{o,\text{high}})) + E_\Omega \]  

(5.4)

It can be seen that the \( i_\eta \) values are nearly identical for both electrolyte conditions and that, although the \( E_{250} \) for Ni in pre-electrolysed electrolyte is lowest, it is not significant.

The slopes measured in the high overpotential range of the plots cannot be strictly called a Tafel slope because of: (i) the uncertainty of the contributions of reactions other than hydrogen evolution (§2.3), and (ii) the increased scatter encountered (also noted by Suzuki [34]). Most commercial electrolyzers operate at high current densities, therefore behaviour in this range is of great interest. The 'Tafel-like' value (\( b_{\text{high}} \)) and its intercept (\( i_{o,\text{high}} \)) are a useful comparative measures of activity between different electrode conditions and materials.

In both electrolytes, above \( \eta_{H_2} \approx 350 \) mV, the \( \eta \)-log \( i \) plot starts to bend upwards and the scatter increases. The presence of the curvature indicates that a different rate-determining step is occurring in this range due to the absorption of hydrogen.

These are likely time- and overpotential-dependent effects, caused by the absorption of atomic hydrogen and/or the onset of deposition of Fe impurities. Time-dependent increases of Tafel slope (and decreased catalytic activity) have been reported by Huot and Brossard [41,43-45] and by Rommal and Moran [40] (as reviewed in §2.4). The deactivation process is also dependent on the magnitude of polarization; a time-dependent 'jump' in the deactivation has previously been observed for overpotentials greater than 400 mV after times of \( 10^3 \) to \( 10^4 \) seconds (0.27 - 2.7 hr).
Figure 5.10  HER Tafel ($\eta$-log $i$) plots of freshly prepared c.p. Ni in untreated and pre-electrolysed electrolyte and amorphous Ni$_{x}$Co$_{y}$P$_{z}$B$_{w}$ in pre-electrolysed electrolyte

TABLE 5-II  Comparison of $\eta$-log $i$ parameters of freshly prepared electrodes measured directly from the plots or calculated from the extrapolated $b_{\text{high}}$ and $i_{0,\text{high}}$ values.

<table>
<thead>
<tr>
<th>System</th>
<th>$i_{\eta=225}$ (mA/cm$^2$)</th>
<th>$i_{\eta=325}$ (mA/cm$^2$)</th>
<th>$i_{\eta=500}$ (mA/cm$^2$)</th>
<th>$E_{b&gt;250}$ (mV$_{Hg/HgO}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.p. Ni untreated electrolyte</td>
<td>1.0</td>
<td>5.0</td>
<td>29</td>
<td>-1739</td>
</tr>
<tr>
<td>c.p. Ni pre-electrolysed electrolyte</td>
<td>0.93</td>
<td>3.9</td>
<td>33</td>
<td>-1633</td>
</tr>
<tr>
<td>AMA pre-electrolysed electrolyte</td>
<td>0.60</td>
<td>2.2</td>
<td>14</td>
<td>-1762</td>
</tr>
</tbody>
</table>
In the present study, an initial cathodic cleaning was applied at $\eta_{H_2} = 330$ mV for 3 hours followed by a one hour open-circuit potential measurement. It is expected that the time-potential contribution of this procedure was minor, being at only moderate overpotential. However, deactivation has previously been observed [40] at overpotentials greater than 400 mV, after times of $10^3$ to $10^4$ seconds (0.27 - 2.7 hr). During the Tafel scans, the overpotential was scanned above $\eta_{H_2} = 400$ mV for a duration of 200 min ($10^4$ sec) and this time-overpotential history could have led to the onset of deactivation, hence the scatter.

For metals capable of absorbing H, such as nickel, there is a possible parallel and competitive reaction to (2.5) and (2.6) of interfacial transfer of adsorbed H to the absorbed H state, followed by H diffusion into the metal bulk:

$$M-\text{H}_{\text{ads}} \Rightarrow M-\text{H}_{\text{abs}} \Rightarrow M-(\text{H}_{\text{diff}})$$

This can limit the discharging/charging kinetics and act as the rate-determining step, increasing the Tafel slope [100], as discussed in the previous two sections.

For both electrolytes there are differences between the corrosion potentials ($E_{\text{corr}}$) observed during the $\eta$-$\log i$ measurement (Figure 5.10) and open-circuit potentials ($E_{o.c.}$) measured after 3 hours of cathodic cleaning (Table 4-I).

Immersion of Ni in either electrolyte produced an instantaneous open-circuit potential of ca. $-750$ mV$_{\text{Hg/HgO}}$, anodic to the reversible hydrogen potential (RHP) of $-972$ mV$_{\text{Hg/HgO}}$. 

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The corrosion potential of Ni in untreated 8 M KOH is cathodic to the reversible hydrogen potential but the open-circuit potential was close to the RHP. This is due to time effects while at steady-state; the open-circuit potential decreased during the hour before the measurement was taken.

The Tafel plot of Ni in pre-electrolysed 8 M KOH crosses below the reversible hydrogen potential; thus since the corrosion potential was not observed, it must be anodic to the RHP. The steady-state open-circuit potential measurements made before the Tafel scan were slightly anodic to the hydrogen equilibrium potential and the values are close to the Ni/Ni(OH)\(_2\) equilibrium potentials (Appendix B-2).

The difference in low-overpotential behaviour of Ni in the untreated solutions may be attributed to a parallel redox reaction involving the iron impurity. Huot proposed that, at low overpotentials, electrodeposition of ferric ions is a two step process; reversible reduction of Fe\(^{3+}\) to Fe\(^{2+}\) near the reversible hydrogen potential is followed by reduction of Fe\(^{2+}\) to Fe\(^+\) near \(\eta_H = 200\) mV [42]. This is supported by the Pourbaix diagrams for nickel and iron (Appendix B-3). Thus it is expected that nickel metal will be stable at all potentials of hydrogen evolution, while iron undergoes corrosion reactions at low HER overpotentials. The reaction could be represented as:

\[
\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe(OH)}_2 + 2\ e^- \quad (5.6)
\]

or,

\[
\text{Fe} + 2\text{OH}^- \leftrightarrow \text{HFeO}_2^- + 2\ e^- \quad (5.7)
\]
5.1.2.1d *Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ Ribbon*

The $\eta$-log $i$ plot of as-polished AMA ribbon in pre-electrolysed 8M KOH electrolyte at 70°C is shown in Figure 4.15. The plot is slightly less active than c.p. Ni in the same electrolyte, as evidenced by lower cathodic current densities and steeper slope for a given overpotential (Figure 5.10, Table 5-II). The exchange current density is similar, but the plots diverge with increasing overpotential. The low-range Tafel slope, $b = 177$ mV/dec (Table 4-III) is higher than many reported values for Ni-Co-based amorphous alloys (Table 2-IV), although most of these studies are at weaker solution concentration and/or temperature.

The effect of electrolyte temperature increase is unclear since some alloy systems exhibit a decrease in Tafel slope [36]. However, the general trend is an increase in Tafel slope with increasing temperature, as is expected from Equation (2.16). Kreysa and Haakanson reported a small increase in the Tafel slope of Ni$_{58}$Co$_{20}$Si$_{10}$B$_{12}$ in 1 M KOH when the solution temperature is raised from 30°C to 70°C [37].

The higher Tafel slope of the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ alloy compared to c.p. Ni is possibly due to absorption of hydrogen via Eqn. (5.4). At higher overpotentials (Figure 5.1, above $\eta_{H_2} \approx 350$ mV) the slope increases moderately ($b_{\text{high}} = 236$ mV/dec), possibly from further H absorption. Stemp, for the same alloy, environment and method, but using a fast sweep rate of 6 mV/min, reported a slope of $b = 213$ mV/dec over the range $\eta_{H_2} \approx 30$ to 500 mV [98], which is intermediate to the $b$ and $b_{\text{high}}$ values discussed above.
The values given in Table 5-II show that the $i_\eta$ values are slightly lower for AMA than for c.p. Ni. Similarly, the calculation of $E_{250}$ from the $\eta$-log $i$ parameters gives a slightly higher voltage.

Unlike nickel metal, the corrosion potential of this amorphous alloy at low overpotentials (Figure 5.1) is cathodic ($\eta_{H_2} \approx 60$ mV) to the reversible hydrogen potential, which may be attributed to oxidation of cobalt. The steady-state open-circuit potential measured prior to this ($E_{o.c.} = -966$ mV$_{Hg/HgO}$) was nearer to the RHP. The difference between $E_{corr}$ and $E_{o.c.}$ on the AMA is likely due to time effects from slow desorption of hydrogen absorbed at higher overpotentials.
5.2 CYCLIC MODULATIONS

The following sections discuss the effects induced in the cathode materials by polarization and modulated/intermittent operation in the HER regime.

5.2.1 NICKEL IN UNTREATED ELECTROLYTE

This section discusses c.p. nickel metal modulated in untreated 8 M KOH electrolyte.

5.2.1.1 Cyclic Modulations

For c.p. nickel in untreated 8 M KOH, the electrode specimens were modulated after the initial Tafel measurement. The cyclic modulations (Figures 4.1 – 4.4) are shown overlaid together for the first 24 hours of modulations in Figure 5.11.

The 720/5/2 cycle (Fig. 4.1, Fig. 5.11) can be considered first, being nearest to a steady-state reference. Upon initial application of current, the potential jumps to ca. -1500 mV_{Hg/HgO}, within the first minute, and continues to rise during the first 60-120 (ca. 10^2) minutes before reaching a maximum potential of ca. -1940 mV_{Hg/HgO}. In comparison, the calculated E_{250} (Table 5-III) is -1824 mV_{Hg/HgO}. 
Figure 5.11  'ON' and 'OFF' potential response of c.p. nickel to cyclic current modulations in untreated electrolyte.
After the initial deactivation, the activity starts to recover as the overpotential decreases at a rate of ca. 0.2 mV/min. After 720 minutes (12 hours) of cathodic polarization, the potential has decreased to -1830 mV\textsubscript{Hg/HgO}. After switching to the 'off' current for 5 minutes, upon resumption of the 'on' current, the potential rapidly rises again before decaying at a similar rate to reach a value of ca. -1790 mV\textsubscript{Hg/HgO} after 24 hours. It appears that the depolarization slightly delays the reactivation process.

Examination of the other modulation cycles (Figure 5.11) indicates that the depolarization currents neither aid the recovery of the activity nor cause any further deactivation beyond the initial deactivation, other than delaying the recovery. Figure 5.12 normalizes the potentials against time spent at the 'on' current density. The recovery after the initial deactivation is dependent only on the time of polarization at the 'on' condition. The small loss of deactivation after a current interruption has only a very small effect on the values of Figure 5.12.

It is suggested that the initial deactivation is due to hydrogen absorption into the nickel and that the subsequent reactivation is due to the reduction, and subsequent deposition, of Fe\textsuperscript{2+} ions from the electrolyte causing an increase in the real area of the cathode. In addition, it has also been reported that H diffusion can be reduced by 'decorating' grain boundaries and surface defects, which have a higher H diffusivity, with metallic deposits from the electrolyte [101].

Modulation between the 'on' and 'off' currents has a minimal effect owing to the nominally 'off' ca. 0.0 A/cm\textsuperscript{2} producing a small cathodic overpotential (Appendix E). This test condition was implemented to simulate an industrial modulation whereby the cells are 'turned off' by turning down a controlling rectifier. The 'off' overpotentials at
Figure 5.12 'ON' potential response of c.p. nickel to cyclic current modulations in untreated electrolyte: (i) measured during the modulation (lines with solid markers), and (ii) extrapolated from the post-modulation \( \eta \)-log \( i \) plots (lines with open markers).

This 'off' current density are ca. -1170 mV\(_{\text{Hg/HgO}}\) so the 'off' potentials can be considered as low 'on' potentials (i.e. \( \eta_{\text{H}_2} \approx 200 \) mV). The small loss of activation by modulation to the 'off' current may be due to oxidation of the Fe deposits. Because the 'off' potentials still have significant overpotentials to the HER, it is unlikely that there is discharge of absorbed hydrogen.
5.2.1.2 Tafel Plots

Figure 5.13 shows the \( \eta \)-log \( i \) plots of c.p. Ni made after cyclic modulation in untreated 8 M KOH (Figures 4.16 – 4.19) as well as the plot from the as-polished condition (Figure 4.13).

The similar slopes for all conditions \( (b = 138 \text{ to } 170 \text{ mV/dec} \text{ (Table 4-II)}) \) in the mid-range \( (i.e., \text{ for } \eta_{H_2} = 120 \text{ to } 380 \text{ mV}) \) indicate that the rate-determining step is the Volmer reaction \( (b_{\text{Volmer}} = 138 \text{ mV/dec}) \). At higher overpotentials, the inflection in Tafel slope for the initial condition may be due to the absorption of \( H \) (§2.4.1.2b) and the formation of a hydride that inhibits the Volmer reaction. Meanwhile, the flattening of the upper part of the curve with modulation can be attributed to increased roughness and surface area due to the Fe deposition (§2.4.1.2c). Compared to the initial condition, after modulation the corrosion potentials are ca. 40 mV more cathodic (Figure 5.13) while the open-circuit potentials are ca. 60 mV more cathodic (Table 4-II). This is likely due to increased deposition of Fe and/or oxidation of deposited Fe.

With modulation, the slope of the low range of the curve does not change but there is a flattening of the curve in the high overpotential range which is reflected in the decrease of \( b_{\text{high}} \) values in Table 4-II. This can be related primarily to the amount of time spent at the 'on' current density (Figure 5.12).

From the high \( \eta \) range parameters, the expected potential at \(-250 \text{ mA/cm}^2\) (Table 5-III) was extrapolated (Eqn. (5.4)) and was plotted in Figure 5.12. The value calculated from the pre-modulation is plotted at \( t = 0 \) (star symbol). The activity of the
TABLE 5-III  Comparison of observed and extrapolated electrochemical values from c.p. Ni before and after cyclic current modulation in untreated 8 M KOH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>( i_{n=225} ) (mA/cm(^2))</th>
<th>( i_{n=325} ) (mA/cm(^2))</th>
<th>( i_{n=500} ) (mA/cm(^2))</th>
<th>( E_{\eta=250} ) (mV(H_2/HgO))</th>
<th>( E_{\eta=250} ) † (mV(Hg/HgO))</th>
</tr>
</thead>
<tbody>
<tr>
<td>720/5/2</td>
<td>1.1</td>
<td>4.7</td>
<td>50</td>
<td>-1587</td>
<td>-1700 ± 68</td>
</tr>
<tr>
<td>60/5/20</td>
<td>0.69</td>
<td>2.5</td>
<td>19</td>
<td>-1687</td>
<td>-1729 ± 62</td>
</tr>
<tr>
<td>5/5/100+</td>
<td>0.58</td>
<td>2.3</td>
<td>21</td>
<td>-1674</td>
<td>-1764 ± 59</td>
</tr>
<tr>
<td>60/60/12</td>
<td>0.89</td>
<td>4.7</td>
<td>27</td>
<td>-1731</td>
<td>-1749 ± 31</td>
</tr>
</tbody>
</table>

†IR-corrected

Figure 5.13  HER Tafel (\(\eta\)-log \(i\)) plots of c.p. Ni cathodes in untreated electrolyte: before and after cyclic current modulation.
post-modulation Tafels are plotted as open symbols on the E-t\textsubscript{ON} plot in Figure 5.12 at the same times as their respective modulation's final 'on' current. The calculated E\textsubscript{250} values follow the same time-'on' dependence although the calculated values are slightly low. This is likely due to the difficulty in determining the \( b\text{\textsubscript{high}} \) and \( i\text{\textsubscript{0,high}} \) values and/or to a change in activity during the Tafel sweeps.

For c.p. Ni, in untreated electrolyte, the cyclic modulations applied had a minimal effect on the potential response. The cathodes initially tended to deactivate rapidly, then partially reactivated at a slower rate, regardless of the 'on' and 'off' cycle.
5.2.1.3 Scanning Electron Microscopy/ X-Ray Analysis

This section discusses the SEM examination and EDX analysis of the c.p. Ni cathodes after modulation in untreated electrolyte. The morphology showed some sample variation which was attributed to: (i) possible oxidation/corrosion during test shut-down, subsequent water-rinsing, air-drying and specimen transfer, and (ii) difficulty in resolving fine features during microscopy due to high magnifications and sample surface film charging. It is not thought that the variation was due to cycling, as the electrochemical response was similar for all samples.

Figures 5.14(a) and (b) compare a representative SEM image and EDX spectrum (Figure 4.29) of modulated Ni sheet surface with the as-polished surface (Figure 4.27). There is extensive film growth on the previously smooth surface, while the EDX spectrum shows an new peak for iron (n.b. there is an additional peak for gold, an artifact of the gold-coating mentioned in §3.3.1). The film topography consists of small (ca. 0.1 μm), dark nodules dispersed with larger (1.0 – 3.0 μm) grey-white crystallites. Spot EDX indicated that the iron was associated with the latter features. To the unaided eye, this (previously shiny) surface was matte and grey-black or brown-black in colour. In relation to the deactivation and reactivation (§5.2.1.1), it has been reported that the diffusion of hydrogen is greater through bright surfaces than matte ones [100,102].

By applying adhesive electroplating tape to this modulated film, the upper layer of this film was removed. Because the electroplating tape left minimal residue, the tape-lifted surface could be re-examined. Figure 5.15 shows an SEM image of the boundary
between the modulated surface film and the tape-lifted surface. At higher magnification (Figure 5.16) it can be seen that the large crystallites were removed, while the small nodules remained; the EDX confirmed that Fe was also removed. Thus, a significant portion of the film morphology was caused by growth of iron-containing crystallites with only moderate mechanical adhesion.

**Figure 5.14** SEM micrographs and EDX spectra of c.p. polished Ni: (a) as-polished, and (b) after cyclic current modulation in untreated electrolyte.
**Figure 5.15** SEM image of c.p. Ni after cyclic current modulation in untreated electrolyte showing the interface between the as-modulated (top) and tape-cleaned (bottom) areas.

**Figure 5.16** SEM micrograph and EDX spectrum of c.p. polished Ni after cyclic current modulation in untreated electrolyte after tape-cleaning.
5.2.1.4 X-Ray Photoelectron Spectroscopy

This section discusses XPS analysis of c.p. Ni after cyclic current modulation in untreated 8 M KOH electrolyte. Based on the cathodic polarization necessary for hydrogen evolution, reduction of any air-formed surface oxides or films would be expected. However, as was seen from SEM of this condition, there was extensive film growth and impurity deposition. The oxidation product that might be expected to form in the E-pH regime (Appendix B-2) of testing would be Ni(OH)₂.

The Ni 2p peaks are shown in Figure 4.37. The only 2p₃/₂ peak is at ca. 855 eV, indicating that only divalent Ni is detected at the surface. Thus, the metallic nickel substrate is obscured because the divalent film and/or the attendant iron-rich crystallite deposits (see previous section) are at least as thick as the XPS sampling depth of ca. 0.003 μm. This is not unexpected from the morphology of Figure 5.14.

Comparison to Standards for Divalent Nickel

To identify the divalent species, Ni 2p, 3p, 3s and O 1s spectra from the modulated c.p. Ni were compared to Lian's XPS standards of NiO and Ni(OH)₂ [94].

The Ni 2p spectrum is overlaid with those the standards in Figure 5.17. The shape and position of the 2p peaks match the NiO standard, although the shake-up satellite is much broader. The 3s and 3p peaks (Figure 5.18) are both broader and do not correspond well with either divalent standard. The O 1s peak (Figure 5.19) appears to be intermediate to the two standards, having a mixed O²⁻ and OH⁻ nature. However, the
**Figure 5.17** Comparison of Ni 2p peaks: c.p. Ni sheet after cathodic polarization in untreated electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).

**Figure 5.18** Comparison of Ni 3s, 3p peaks: c.p. Ni sheet after cathodic polarization in untreated electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).
Figure 5.19  Comparison of O 1s peaks: c.p. Ni sheet after cathodic polarization in untreated electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).
O 1s spectra must take into account other oxygen containing species such as residue from the aqueous KOH and any oxidation of the iron-containing crystallites. Nonetheless, a mixed oxide/hydroxide Ni content in the film is possible given: (i) the initial oxide/hydroxide nature of the pre-immersion surface, (ii) possible hydroxide formation during immersion in KOH electrolyte, and (iii) air exposure on the order of hours during ex-situ transfer time to the XPS vacuum. Thus it appears that the Ni in the film has a mixed oxide - hydroxide character.

The XPS analysis did not take into consideration the presence of iron, but it is expected that it would be in the form of iron hydroxide, as discussed in §5.1.2.1. Metallic iron is deposited during cathodic polarization and then is likely oxidized during depolarization. A spectroscopic study on iron cathodes found that, after prolonged cathodic polarization, there were residual amounts of unreduced Fe(OH)₂ [103]. Corrigan et al. prepared precipitated Ni(OH)₂ cathodes incorporated with 10% Fe and found that the Fe/Ni(OH)₂ had a cathodic voltammetric peak at \( \eta_{H_2} = 135 \) mV [104]. This corresponds well to the corrosion potential observed in Figure 5.13. They suggested that the Fe ions in solution react with the hydroxide ions to form metal hydroxides, as in the reaction given in Equation (5.6).
5.2.2 *NICKEL IN PRE-ELECTROLYSED ELECTROLYTE*

This section reviews c.p. nickel metal in pre-electrolysed 8 M KOH. As discussed in previous sections, the difficulty of reproducible Tafel measurements on fresh Ni metal at high cathodic overpotentials indicates a time-dependent instability. For measurements in this section, an initial Tafel measurement did not precede the cyclic modulations. Instead, the as-polished Ni cathodes were galvanostatically polarized and allowed to reach a steady-state potential prior to commencing the cyclic modulations.

5.2.2.1 *Initial Deactivation*

The initial galvanostatic hold was at the 'on' current density ($i_c = 250$ mA/cm$^2$). During a 24 hour period, the potential increased at a decreasing rate before approaching a steady-state value (Figure 5.20(a)). With application of the current, the instantaneous (first minute) potential was ca. -1430 mV$_{Hg/HgO}$ and it then increased rapidly during the first 6-12 hours before eventually reaching a steady-state value of ca. -1930 mV$_{Hg/HgO}$ (-1845 mV$_{Hg/HgO}$ (IR-corrected)) after 12 to 24 hours. After the initial increase, the potential remained constant even when polarized for up to 72 hours in duration.

In comparison, the IR-corrected $E_{250}$ determined from the $b_{high}$ and $i_{o,high}$ parameters (Eqn. 5.4) of as-polished Ni is -1739 mV$_{Hg/HgO}$ (Table 5-III). From
Figure 5.20  Time dependent deactivation of c.p. Ni in pre-electrolysed electrolyte during initial 24 hour hold at 250 mA/cm²: (a) linear time scale (average of six tests), (b) log time scale (also showing an individual specimen).
Figure 5.20(a) this value indicates that the entire Tafel scan procedure induces time-overpotential deactivation equivalent to approximately 3 hours (180 min.) of steady-state galvanostatic deactivation. As found with earlier measurements, the variability in both the high-range of the \( \eta \)-log \( i \) plot and in the 3 hour range of the \( E \)-t plot is large.

When plotted on a log time scale (Figure 5.20(b)), the curve has an "S" characteristic with a rapid increase in potential between \( 10^{3.5} \) and \( 10^{4.5} \) seconds. The slope of this region is ca. 330 mV/(decade \( t \)). This phenomenon has been attributed by Rommal and Moran [40] to absorption of hydrogen and then formation of a hydride. They reported a 'jump' in slope of 450 mV/(decade \( t \)) (Figure 2.8); the difference of slope and the indistinct curve transitions in this study are attributed to time averaging on a potential basis. The 'jump' occurred between -1600 and -1700 mV\(_{\text{Hg/HgO}}\) and the time required for the potential to reach -1650 mV\(_{\text{Hg/HgO}}\) is \( 10^{3.5} \) seconds. It can be noted that the domain of stability of the hydride ion is calculated to be -1684 mV\(_{\text{Hg/HgO}}\) (Appendix B-2).

Electrolysis of Ni (i.e. cathodic polarization) readily induces hydrogen diffusion; electrolytic charging is equivalent to room-temperature \( \text{H}_2 \) gas-phase charging pressures of ca. 6000 atm [105]. Below a \( \text{H/Ni} \) ratio of 0.03 the hydride formed is \( \alpha \)-NiH, a simple solid solution, above 0.6 it is \( \beta \)-NiH and between these ratios there is a mixture of \( \alpha \)- and \( \beta \)-NiH.

Rommal and Moran attributed the slow initial increase of potential with log time to a surface increase of H (presumably as a mixture of \( \alpha \)- and \( \beta \)-hydride) and the 'jump'

\[ \text{\dagger} \text{To illustrate, a curve from an individual specimen is shown overlaid with the average curve; the time at which the potential started to jump varied by about an order of magnitude.} \]
to formation of $\beta$-NiH (as the H/Ni ratio reaches 0.6) which acts as a barrier to further hydrogen diffusion [48]. The formation of the hydride has two effects: a 5.5% expansion of the nickel FCC lattice [106] and a filling of the d-band of Ni. Soares et al. [47] suggested that the although the former should provide a more beneficial lattice spacing for the HER to occur, the latter inhibits H adsorption which, in turn, is the $rds$ for the HER. They confirmed the presence of hydride using x-ray diffraction and proposed that hydrogen absorption changes the d-character of the metal to a less electrocatalytically favourable s-p character for the NiH [47]. Thus, it appears that with strong cathodic polarization, hydrogen absorption and the resulting hydride formation in nickel slows hydrogen gas evolution, as characterized by time-dependent overpotential increases and increased Tafel slopes.

5.2.2.2 Intermittent Operation

The cyclic modulations of c.p. nickel in pre-electrolysed 8 M KOH were not initiated until after the potential had reached a steady-state value. The individual cyclic modulations shown in Figures 4.5 – 4.8 and the average initial hold shown in Figure 5.20 are combined in Figure 5.21 (the ramps between 'on' and 'off' are omitted for clarity). From this figure, it can be seen that there is no significant effect of either further deactivation or re-activation with modulation; the 'on' potentials reached during modulation are very close to the final steady-state value reached during the initial hold.

First the 720/5/3 cycle is considered. The potential transients after each 5 minute
Figure 5.21  Cyclic current modulations of c.p. Ni in pre-electrolysed 8 M KOH electrolyte.
interruption (at 'off' current) are shown in Figure 5.22 with the transient from the initial 24 hour hold. After successive interruptions the transient decreases (1-3 hours) and stabilizes by the third cycle. This phenomenon has previously been observed in hydrogen permeation studies where the diffusivity of hydrogen through Ni was higher after two or more successive transients [107]. It can be seen that after the second interruption the starting potential is ca. $-1750 \text{ mV}_{\text{Hg/HgO}}$, and no 'jump' occurs (Figure 5.22(b)), which indicates that the H concentration is maintained near the transition to $\beta$-hydride. This is likely due to incomplete H discharge from the initially formed hydride during the short 'off' cycle and/or hydrogen trapping.

The 60/5/20 cycle interrupts the current earlier in the 'on' transient (1 hour) delaying the deactivation during the first few cycles. But, with successive interruptions the transient occurs faster. Similarly, for the 5/5/100+ modulation the 'on' potentials also reach the steady state potential faster than during the initial hold.

Dislocations and impurities in the crystal lattice of Ni favour the hydride transformation and also act as H 'traps' where some of the diffused H is irreversibly bound [106]. As well, among various forms of nickel metal, hydride formation and stability is greatest in bright, unannealed c.p. Ni plate, due to surface crystal orientation and microstructure anisotropy (grain and twin boundaries) [101,108].

For 60/60/20 modulation, the deactivation transient also increases in the first few cycles before stabilizing by the fifth cycle. During the 'off' cycles, the potential response during cycling changes from a slow decay to a fast decay and then jumps incrementally more cathodic (Figure 5.23). Since the 'on' potentials indicate that
Figure 5.22  Deactivation during 'on' cycle of c.p. Ni in pre-electrolysed electrolyte with successive current interruptions from 250 mA/cm² during 720/5/3 cyclic current modulation: (a) linear time scale, (b) log time scale.
Figure 5.23  Cathodic shift of 'off' potential with successive cycles during 60/60/20 cyclic modulation of c.p. Ni in pre-electrolysed electrolyte.

complete hydride decomposition had not occurred, it is suggested that the decay is due to partial H discharge (from $\beta$-NiH) and the shifts in 'off' potentials are due to decomposition/transformation of Ni species in the surface film via oxidation and/or dissolution (Appendix B-2).

Nickel hydride decomposition is a relatively slow process at open circuit, although it has been reported to be responsible for recovery of Ni activity. Conway et al. reported that H$_2$ slowly evolved from Ni-based cathodes after current interruption over a period of 20 minutes as open-circuit potential decayed from $\eta_{H_2} \approx 75$ mV to $\eta_{H_2} \approx 10$ mV [49]. They proposed a mixed corrosion type mechanism involving a (nearby)
reversible anodic hydride decomposition coupled with the cathodic hydrogen evolution reaction (§2.2):

\[
\begin{align*}
\text{Anode:} & \quad \text{Ni}_x\text{H} + \text{OH}^- & \Rightarrow & \quad x \text{Ni} + \frac{1}{2} \text{H}_2\text{O} + e^- \quad (5.8) \\
\text{Cathode:} & \quad \frac{1}{2} \text{H}_2\text{O} + e^- & \Rightarrow & \quad \frac{1}{2} \text{H}_2 + \text{OH}^- \quad (2.1)
\end{align*}
\]

Soares et al. reported that nickel that had previously deactivated (with a transient from \(-1500 \text{ mV}_{\text{Hg/HgO}}\) to \(-1950 \text{ mV}_{\text{Hg/HgO}}\)) recovered activity when left at open-circuit for 24 hours, [47]. Rommal and Moran reported that recovery is possible by an anodic scan; a single cycle CV after cathodic deactivation displayed a peak between ca. \(\eta_{\text{H}_2} = -20 \text{ mV}\) and \(\eta_{\text{H}_2} = -150 \text{ mV}\) which was attributed to the oxidation of hydrogen [40].

In the present study, the 5-60 minute 'off' times do not allow the cathodes to discharge appreciably. Within five minutes the potential decays from ca. \(-1000 \text{ mV}_{\text{Hg/HgO}}\) to ca. \(-950 \text{ mV}_{\text{Hg/HgO}}\). This is in proximity to the reversible hydrogen potential of \(-972 \text{ mV}_{\text{Hg/HgO}}\) which is consistent with the presumption that hydrogen is being evolved under (pseudo-)open-circuit conditions. For the 60 minute 'off's, during the first interruptions the potential decays to ca. \(-900 \text{ mV}_{\text{Hg/HgO}},\) near to the \(\text{Ni(OH)}_2\) equilibrium potential of \(-860 \text{ mV}_{\text{Hg/HgO}}\). With successive interruptions, the potential decays to ca. \(-960 \text{ mV}_{\text{Hg/HgO}},\) close to the reversible hydrogen potential. This may suggest stabilization of the \(\text{Ni(OH)}_2\) surface film during modulation, since \(\text{Ni(OH)}_2\) has good electrocatalytic activity for the HER, the process of H absorption dominates the deactivation process.

Thus, for the cyclic modulations, c.p. Ni HER cathodes deactivate the same magnitude as the initial polarization but with a faster rate, which was due to the initially formed hydride not decomposing.

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This section discusses Tafel measurements made on c.p. nickel sheet after cyclic current modulation in 8 M KOH electrolyte. Figure 5.24 shows the $\eta$-log $i$ plots made post-modulation (Figures 4.20 – 4.22) and the plot from the as-polished condition (Figure 4.14). After modulation there is a bowing of the curve in the low-moderate overpotential range ($\eta_{H_2} < 320$ mV) and a steepening at higher overpotentials. This is seen in the shifts of Tafel slopes in Table 4-III and in the changes of the $i_\eta$ values which are given in Table 5-IV.

There is good correlation between the $E_{250}$ values observed from galvanostatic testing and calculated from the Tafel parameters, as given in Table 5-IV. The calculated $E_{250}$ values (Eqn. 5.4) are all similar to each other and also to the 'on' potentials observed at the end of modulation. The high-range activity is lower compared to the initial condition, in accordance with the faster deactivation after successive modulation cycles.

At higher overpotentials, the change from $b$ to $b_{\text{high}}$ with modulation is due to hydride formation which is not favourable for the Volmer/adsorption reaction (2.4). For hydrogen absorbing metals, the mechanisms of the HER (§2.2) can be re-stated [83]:

(i) $H$ adsorption (Volmer):
$$M + H_2O + e^- \Rightarrow M-H_{\text{ads}} + OH^-$$

followed by:
(iiia) desorption (Heyrovsky):
$$M-H_{\text{ads}} + H_2O \Rightarrow H_2 + M + OH^-$$

(iiib) $H$ absorption and hydrogenation:
$$M-H_{\text{ads}} \Leftrightarrow M-H_{\text{abs}} \Rightarrow MH_x$$

(5.5')
Figure 5.24 HER Tafel ($\eta$-log $i$) plots of c.p. Ni cathodes in untreated electrolyte: before and after cyclic current modulation.

TABLE 5-IV Comparison of observed and extrapolated electrochemical values from c.p. Ni before and after cyclic current modulation in pre-electrolysed 8 M KOH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$i_{\eta=225}$ (mA/cm$^2$)</th>
<th>$i_{\eta=325}$ (mA/cm$^2$)</th>
<th>$i_{\eta=500}$ (mA/cm$^2$)</th>
<th>$E_{l=250}$ (mV$_{Hg/HgO}$)</th>
<th>$E_{l=250}^*$ (mV$_{Hg/HgO}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-polished</td>
<td></td>
<td></td>
<td></td>
<td>-1759</td>
<td>-1809 ± 16</td>
</tr>
<tr>
<td>720/5/3</td>
<td>1.3</td>
<td>4.4</td>
<td>21</td>
<td>-1759</td>
<td>-1809 ± 16</td>
</tr>
<tr>
<td>60/5/20</td>
<td>1.1</td>
<td>3.4</td>
<td>15</td>
<td>-1832</td>
<td>-1760 ± 86</td>
</tr>
<tr>
<td>60/60/20</td>
<td>1.8</td>
<td>4.7</td>
<td>17</td>
<td>-1827</td>
<td>-1845 ± 28</td>
</tr>
<tr>
<td>5/5/100+</td>
<td>1.2</td>
<td>4.7</td>
<td>17</td>
<td>-1827</td>
<td>-1845 ± 28</td>
</tr>
</tbody>
</table>

$^*$IR-corrected, $^*$not tested
After H adsorption, reaction (5.5') occurs simultaneously (in a coupled manner) with reaction (2.6) and competes with it, thus limiting the charging/discharging kinetics [109]. The increase in Tafel slope at high overpotentials indicates a change in \( r_{ds} \) to the former reaction.

The similar \( \eta_{H_2} < 320 \text{ mV} \) values for all conditions indicate that the rate-determining step is the Volmer reaction. Conway et al. reported that the coverage of \( H_{ads} \) attains limiting values at \( \eta_{H_2} = 150 \) to \( 250 \text{ mV} \) [110].

The cathodic corrosion potential and flattening of the curve at low overpotentials are likely due to the mixed corrosion type mechanism of HER and H discharge from the hydride, as mentioned in §5.1.2.1. The flattening of the curve near the corrosion potential suggests that the Heyrovsky/desorption reaction (2.6) may be the rate-determining step. The likely mechanisms of hydride decomposition are [83]:

(iii) hydride recombination:
\[
 MH_x \Rightarrow M + x/2 H_2 \tag{5.9}
\]

(iiib) hydride oxidation:
\[
 MH_x + OH^- \Rightarrow x/2 H_2O + M + e^- \tag{5.10}
\]

The post-modulation corrosion potentials observed in Figure 5.24 are ca. 60 mV cathodic to the HER. In comparison, the open-circuit potential (Table 4-III) of modulations with 5 min. 'offs' (720/5/3 and 60/5/20) were ca. 60 mV anodic to the RHP. This is a reflection of the 'off' potential decay through the RHP that was seen in Figure 5.23.
The difference between the corrosion potentials measured before and after cyclic modulation is likely due to hydrogen charging; the as-polished Ni had not had sufficient time to absorb appreciable amounts of H. Conway et al. concluded that for hydride discharge at open-circuit, it is probable that the coverage of adsorbed H (\(\phi_H\)) is high and the lattice site fraction of H (\(X_H\)) is low [49]; the high \(\phi_H\) would favour the desorption reaction (2.6).
5.2.2.4 SEM/EDX

This section discusses the SEM examination and EDX analysis of the c.p. Ni cathodes after modulation in pre-electrolysed electrolyte. After modulation, upon removal of the Ni cathodes, the specimen surfaces were observed to range from clear to light gold-brown and the reflectance ranged from shiny to shiny-satiny. When there was colouration to the surface, it would often start to fade with time and/or rinsing with deionized water.

Examination by SEM showed no surface features at magnifications lower than 1000x. Some relatively large particles (ca. 50 μm) across were confirmed by x-ray analysis to be artifacts from the KOH electrolyte. However, at higher magnifications (10 000x), a fine surface structure was revealed consisting of a coverage of very fine (0.01 – 0.1 μm) nodules with lighter, larger (ca. 0.1 – 1.0 μm) dispersed particles.

In Figure 5.25, SEM images of the modulated surfaces (Figure 4.30) are shown in contrast to the the as-polished surface (Figure 4.27). It can be seen that there is roughening and/or growth after modulation. There is some variation in the size of the surface features (about an order of magnitude of particle/nodule diameter) on the 720/5/3, 60/5/20 and 5/5/100+ surfaces. However, there was inter- and intra-sample variation, so it was not possible to correlate closely surface features to modulation cycle, except for the 60/60/20 modulation. Also, the still apparent polishing scratches give an indication of the relative thickness of the film.
Figure 5.25  SEM images of (a) as-polished c.p. Ni and after cyclic current modulation in pre-electrolysed 8 M KOH: (b) 720/5/3, (c) 60/5/20, (d) 5/5/100+, (e) 60/60/20.
The 60/60/20 surface has less deposit and more corrosion which appears to be related to the time spent near open circuit (Figure 5.23). This correlates with the changes in 'off' potential seen in Figure 5.23 that were presumed to be caused by oxidation or dissolution of surface films. It appears that the electrodes from the 60/60/20 modulation have been cleaned of residual hydroxides and/or oxides, producing a smoother surface.

The roughness of the other specimens is likely due to reduction/oxidation of the surface film. The roughening would be expected to increase the electrocatalytic activity due to increased real surface area and CUS’s. If it is assumed that the coverage of the surface nodules is uniform and that the nodules are roughly spherical, then for a given apparent surface area there is an increase in area proportional to the area increase of a sphere over a circle, i.e., the increase in real area of the surface is at least four times that of the as-polished surface. It is likely that the increase in real surface area is still greater than this. However, the exchange current densities (Table 4-III) do not decrease as would be expected. Furthermore, the 'on' potentials and Tafel parameters for the 60/60/20 condition are similar to the other modulations despite the variation in surface morphology. This supports hydride formation as an overriding factor controlling the cathode deactivation in c.p. nickel.

X-ray analysis of the cathode area (Figure 4.31) showed little change from the EDX spectra of the as-polished surface (Figure 4.27(b)), with the exception of the detection of small peaks for Fe and Mn. The micrographs (except 60/60/20) and spectra of c.p. Ni modulated in pre-electrolysed electrolyte were similar to those of the tape-lifted surface of Figure 5.16. Spot analysis of the larger, lighter coloured particles indicated transition elements, namely Fe, Mn, Cu and Zn. Two such representative
Figure 5.26  EDX spectra of (a) as-polished c.p. Ni and after cyclic current modulation in pre-electrolysed 8 M KOH: (b) wide area, (c) and (d) spot analysis of larger white particles.

spectra are shown in Figure 5.26 together with the spectra from Figures 4.31 and 4.27(b). Despite the steps taken to remove impurities from the electrolyte (§3.2.2), the conditions for reduction and deposition of contaminants were favourable during galvanostatic polarization, with high magnitudes and long times of polarization, and there were still trace amounts present. The origins of these impurities are the KOH source and/or the nickel metal (Tables 3-I and 3-III). Manganese is present in the c.p. Ni in the form of MnS inclusions [111] which could be dissolved and then replated by
local galvanic action. Small pores were observed that had concentrated distribution of the larger lighter particles in their vicinity. Huot and Brossard reported like depositions of Fe and Cu and/or Zn from concentrated KOH electrolyte onto pure nickel [43], platinum [112] and cobalt [113] cathodes.

These impurities, by causing further deactivation upon deposition, could account for the scatter seen during the initial time-dependent deactivation and at the steady-state 'on' potential. Iron and copper have a lower activity for the HER (Figure 2.5). It has been reported that impurity deposition on Pt causes further deactivation after the initial deactivation from H absorption [110]. Deposition from ionic species improves the activity of nickel only when there is sufficient concentration to cause large deposition coverage and growth on (and massive increases of the real) surface area (§2.4.1.2c, §5.2.1, [43,114]).
5.2.2.5 X-Ray Photoelectron Spectroscopy

This section discusses XPS analysis of c.p. Ni after cathodic polarization at 250 mA/cm² in pre-electrolysed 8 M KOH electrolyte. The oxidation product that might be expected to form in the E-pH regime (Appendix B) of testing would be Ni(OH)₂.

The Ni 2p peaks are shown in Figure 4.38. Two sets of peaks were detected. The smaller peaks attributed to metallic nickel (Ni 2p₃/₂ = 852.6 eV, Δ-2p₁/₂ = 17.1 eV) are in good agreement with the literature (Table 2-VI). The taller peaks are attributed to divalent Ni. Compared to nickel cathodically polarized in untreated KOH electrolyte, there is minimal impurity deposition and obstruction of the nickel substrate.

Comparison to Standards for Divalent Nickel

To identify the divalent species, Ni 2p and O 1s spectra from the modulated c.p. Ni were compared to XPS of NiO and Ni(OH)₂ standards [94]. Minimal distinctions could be garnered from the Ni 3s and 3p spectra, so they are not included.

The Ni 2p peaks are overlaid with the divalent standards in Figure 5.27. The shape and position of the divalent 2p peaks match the Ni(OH)₂ standard very well. The O 1s peak, shown in Figure 5.28 is also in very good agreement with the Ni(OH)₂ standard. The O 1s spectra also have a small oxide shoulder on the low binding energy side. The ex-situ specimen transfer time was on the order of minutes, so the possibility of oxidation during air exposure was minimized, but this could account for the oxide
**Figure 5.27** Comparison of Ni 2p peaks: c.p. Ni sheet after cathodic polarization in pre-electrolysed electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).

**Figure 5.28** Comparison of O 1s peaks: c.p. Ni sheet after cathodic polarization in pre-electrolysed electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).
shoulder. Thus the c.p. Ni cathodically polarized in untreated KOH electrolyte is interpreted to have a mainly Ni(OH)$_2$ character.

Surface Film Composition and Thickness

An approximate surface composition was determined by deconvoluting the Ni 2p spectrum of polished c.p. Ni into metallic and divalent sub-peak components based on fit parameters for Ni(OH)$_2$ [94]. The fit parameters were applied to within the detection limits of the analyzer (±0.2 eV, Appendix D-1). Figure 5.29 shows the Ni 2p$_{3/2}$ peak with sub-peaks for metallic, divalent and shake-up satellite components. Based on the sub-peak intensities (area) of Figure 5.29 it was found that the ratio of Ni$^{2+}$ to Ni$^0$ detected was ca. 7:3 (71% divalent Ni and 29% metallic Ni). The surface film thickness was estimated to be 0.00046 μm (Equation (5.2)), about twice that of the initial film (§5.1.1.2a).

Thus, with cathodic polarization in pre-electrolysed 8 M KOH, the surface film is not reduced but grows thicker than was initially present after polishing.
**Figure 5.29** Deconvolution of the Ni 2p$_{3/2}$ spectrum of c.p. Ni sheet cathodically polarized in pre-electrolysed electrolyte, showing metallic (Ni$^0$) and divalent (Ni$^{2+}$) sub-peaks and their respective shake-up satellites (sat.).
5.2.3 AMORPHOUS Ni_{50}Co_{25}P_{15}B_{10} RIBBON IN PRE-ELECTROLYSED ELECTROLYTE

This section discusses electrochemical testing of amorphous Ni_{50}Co_{25}P_{15}B_{10} ribbon in pre-electrolysed 8 M KOH. As with c.p. Ni in pre-electrolysed electrolyte, the cathodes were galvanostatically polarized and allowed to approach a steady-state potential prior to commencing the cyclic modulations.

5.2.3.1 Initial Deactivation

During the initial galvanostatic hold at 250 mA/cm², the amorphous alloy deactivated in a similar manner to c.p. nickel (Figure 5.30(a))(§5.2.2.1). The instantaneous potential was ca. -1490 mV_{Hg/HgO} and increased during the first 12 hours, eventually approaching a steady-state value of ca. -1950 mV_{Hg/HgO} (-1865 mV_{Hg/HgO} IR-corrected). The potential remained steady-state even with hold times up to 72 hours in duration.

The (IR-corrected) $E_{250}$ of as-polished AMA calculated from the $b_{\text{high}}$ and $i_{0,\text{high}}$ parameters (Eqn. 5.3) (Table 4-I) was -1762 mV_{Hg/HgO}. Thus, the entire Tafel scan is estimated to incur a time-overpotential deactivation equivalent to ca. 4 hours (240 min.) of constant galvanostatic polarization.
Figure 5.30 Time dependent deactivation of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in pre-electrolysed electrolyte during initial 24 hour hold at 250 mA/cm$^2$: (a) linear time scale (average of thirteen tests), (b) log time scale (with an individual specimen and with c.p. nickel).
When plotted on a log time scale (Figure 5.30(b)), the curve has an "S" shape similar to that of c.p. Ni and a rapid increase in potential occurs between $10^3$ and $10^5$ seconds. So, it is assumed that the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon absorbs hydrogen and, as H concentration increases, forms a hydride.

The 'jump' occurs between ca. -1650 and -1850 mV$_{Hg/HgO}$, the time until the average potential is -1750 mV$_{Hg/HgO}$ is $10^{3.9}$ seconds and the slope is ca. 450 mV/(dec t). For thin (9 - 12 μm) foils of crystalline nickel, it was reported that the time for the 'jump' increases with increasing thickness of the foil [48]. In the present study, despite the c.p. Ni sheet being 10 times thicker than the AMA foil, the difference in time until the 'jump' occurred was small (Figure 5.30(b)). Metallic glasses often have lower diffusivities than their crystalline counterparts (Table 5-V), although they are known to be very efficient H-absorbers.

Low breakthrough time diffusivities ($D_B$) are characteristic of a (surface) barrier to H entry, while low half-rise time diffusivities ($D_{hr}$) are indicative an overall hindrance for hydrogen permeation due to internal trapping. Diffusivities of Ni and Ni-based AMA's vary, but for metal (Ni, Co, Fe)-metalloid (P, B, Si) metallic glasses they are generally about one order of magnitude lower than crystalline Ni metal (Table 5-V). Amorphous Co$_{50}$Ni$_{25}$Si$_{15}$B$_{10}$ had hydrogen permeation currents two to three orders of magnitude higher than Ni because the H concentration of the AMA was ca. $10^4$ times higher [33]. Compared to Ni, permeation currents are slightly higher through Ni$_{92.7}$Si$_{4.5}$B$_{2.8}$ and one order of magnitude higher through Ni$_{81}$P$_{19}$ [114].

---

*As with c.p. Ni, the 'jump' is not distinct due to potential averaging on a time basis so a single specimen is overlaid with the average to illustrate the jump phenomenon.*
Table 5-V  Diffusivity of hydrogen in crystalline nickel and amorphous (Ni, Co, Fe)-based alloys.

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<tr>
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<td></td>
</tr>
<tr>
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<td>0.050</td>
<td>1.17</td>
<td>0.72</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Fe₈₁S₅B₁₄₄Si₁₄</td>
<td>0.035</td>
<td>0.44</td>
<td>0.29</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>melt spun ribbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₅₀Zr₄₀</td>
<td>-</td>
<td>-</td>
<td>2.2 - 4.5</td>
<td>-</td>
<td>[83]</td>
</tr>
<tr>
<td>sputtered film</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₅₀Zr₄₀</td>
<td>0.025</td>
<td>~2.5</td>
<td>10</td>
<td>-</td>
<td>[85]</td>
</tr>
</tbody>
</table>

According to Flis et al. [116], hydrogen embrittlement (HE) of Ni- and Fe-amorphous alloys increases as the D_B/D_% ratio (Table 5-V) increases (a correlation of HE to chemical composition could not be made); Fe₄₀Ni₄₀P₁₄B₆ had very high resistance to HE, but Ni₈₁P₁₉ only had a moderate resistance. Thus, alloys for which H entry was easy (i.e. low D_B, related to the surface conditions of the amorphous alloys) were susceptible to HE. Despite a high D_B/D_% ratio, Lian reported that there was no evidence of embrittlement of Co₅₀Ni₁₂₅Si₁₅B₁₀, possibly because of a relatively low D_B value [33].
As evidence of considerable H absorption and hydriding, it was observed that the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ electrodes were easily fractured under normal handling after prolonged HER polarization. In contrast, the as-fabricated ribbons could be folded back on themselves without breakage. Although no diffusion data was available for Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$, embrittlement of the ribbon is indicative of the relative ease of entry of hydrogen.

There are three possibilities for the absorption of hydrogen into the amorphous alloy: (i) it remains in solution so there is no hydride formed, (ii) the alloy is uniformly hydrided, (iii) the alloy is selectively hydrided.

The first case would cause structural relaxation, removing residual strain, and embrittlement would not be observed. For the second case, given that there should be a difference in the development of Ni-hydride and Co-hydride, it is unlikely that there is formation of a uniform AMA-hydride. So, it is suggested that the AMA is selectively hydrided. It is likely that this is a mixture consisting of Ni-H in the amorphous alloy. If there was a decomposition to two phases, crystallization would be expected; no crystallization was observed at the resolution limits of the microscopic techniques employed in this study (ca. 50 000X).

The process can be explained in terms of surface structure and chemistry. Barrier effects from the as-polished passive film appear minimal (§5.1.1.1b). Nickel would be preferentially hydrided; the solubility of H in Co is lower than in Ni [117] and the heat of formation of Ni-H is more negative than that of Co-H [118]. As discussed, H absorption and hydride formation hinder the HER. The metalloids are hydrogen recombination poisons and reduce the d-band character of Ni but Lian found that immersion of
Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ into 1 M KOH leached P out of the alloy and enriched the metallic sites [33].

Thus, with strong cathodic polarization, the amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbons lost electrocatalytic activity by hydrogen absorption and nickel hydride formation, as characterized by increased time-dependent overpotentials and embrittlement.

5.2.3.2 Intermittent Operation

The individual cyclic modulations on Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ (Figures 4.9 - 4.12) are shown together in Figure 5.31 (the ramps between 'on' and 'off' are omitted for clarity). The electrodes were conditioned with the previously discussed hold of 24 hours prior to the start of modulation to allow the potential to reach steady-state.

With modulation, the phenomenon was varied; when the 'on' time was relatively long (i.e., 720/5/2, 60/5/20, 60/60/20), some recovery of activity was seen. Two distinct steady-state potentials were noted at the 'on' current density: the initial steady-state potential of ca. -1950 mV$_{\text{Hg/HgO}}$, and a second steady-state potential near ca. -1775 mV$_{\text{Hg/HgO}}$. The occurrence of the second, reactivated state was not very predictable. With short 'on' and 'off' times (5/5/100+), the potential remained near to the higher steady-state. The first, higher, potential state is nearly the same as seen for c.p. Ni; the cause of deactivation is the formation of β-NiH at very cathodic polarizations, as discussed earlier. Therefore, the lower potential state is likely caused by an impedement to β-hydride stability.
Figure 5.31: Cyclic current modulations of amorphous NiPdCoFeB in pre-electrolyzed 8 M KOH electrolyte.
First, the 720/5/2 modulation is considered in comparison to the initial deactivation. After the first interruption to the 'off' current, the 'on' potential transient was quite varied in the rate and the magnitude of deactivation (Figure 4.9); the average potential transient was intermediate to the two above-mentioned states (Figure 5.32(a)). After the second interruption, the deactivation transient was faster and the 'on' potential only rose to the lower state. This is illustrated in Figure 5.32 where the 'on' potential transients of the 720/5/2 cycle are overlaid with the initial 24 hour transient. It can be seen that the potential at the end of the second cycle is ca. 160 mV lower (i.e. more active) than the initial steady-state potential. In Figure 5.32(b), it can be seen that the second cycle transient stabilizes close to the 'jump' transition potential, which corroborates the suggestion that β-Ni hydride formation is constrained. Compared to c.p. Ni (Figure 5.22(b)), the transient starts lower and stabilizes lower. Note that there is still residual deactivation compared to a freshly polished surface, indicating retention of absorbed hydrogen.

For the 60/5/20 cycle, the 'on' potential decreased during modulation (Figure 4.10). With successive modulation, the 'on' transient came faster and to lower potentials. At the sixth cycle, it can be seen that the rising transient suddenly decays, after which subsequent 'on' potentials ascend only to the low potential state, near -1800 mV\text{Hg/HgO}. For individual tests, the shift to the lower potential state generally occurred within the first ten cycles.

For the 60/60/20 modulation (Figure 4.12), the result is similar to 60/5/20 with a quick shift to the lower potential state after the first ten cycles. The 'on' transient also changes from rising to decaying within the first few cycles. During the first interruption,
Figure 5.32 Deactivation during 'on' cycle of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ in pre-electrolysed electrolyte with successive current interruptions from 250 mA/cm$^2$ during 720/5/2 cyclic current modulation: (a) linear time scale, (b) log time scale.
Figure 5.33  Cathodic shift of 'off' potential with successive cycles during 60/60/20 cyclic modulation of amorphous Ni$_{30}$Co$_{23}$P$_{15}$B$_{10}$ in pre-electrolysed electrolyte.

The 'off' potential decays to a steady $-960 \text{ mV}_{\text{Hg/HgO}}$, a similar value to open-circuit potential of the as-polished state (Table 4-I), but then it abruptly jumps to ca. $-985 \text{ mV}_{\text{Hg/HgO}}$ (Figure 5.33). The 'off' potential stabilizes there during the next two interruptions but then, with further modulation, the 'off' potentials decay to successively higher 'off' potentials, approaching ca. $-1040 \text{ mV}_{\text{Hg/HgO}}$ after 20 cycles.

For the 'off' potentials, the differences are electrode dependent since the electrolyte, and hence the impurity content, is the same as for c.p. Ni. During the first 'off' cycle the potential decays to near the equilibrium HER potential of $-972 \text{ mV}_{\text{Hg/HgO}}$, likely due to hydride decomposition (Figure 5.33). The sudden jump in potential during this 'off' period may be related to a change in the surface species (Appendix-B). In the
next two 'off's, the transient changes from decay to rise after about 30 min, possibly due to the onset of oxidation of the surface. The 'off' potential eventually stabilizes near -1040 mV\text{Hg/HgO}, near the equilibrium potential for ionic Ni$^{2+}$ and Co$^{2+}$ species, indicating surface oxidation.

Thus, there is likely a corrosion product forming on the surface of the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ alloy during the longer 'off' cycles. However, it does not seem to affect the recovery of activity during the 'on' cycles. It is likely that hydride decomposition governs the activity.

It is possible that the improved activity after current interruption is due to compositional changes to the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$. As previously discussed, both Co and the metalloids are less electrocatalytically favourable than Ni for the HER, and are less stable than Ni in KOH. Thus, it is likely that there is partial depletion of Co and/or the metalloids at the surface, resulting in greater activity. Lian reported that selective dissolution of Co from the surface of Ni$_{50}$Co$_{25}$Si$_{15}$B$_{10}$ optimized active sites and lattice spacings for the HER [33].

Thus, it appears that, after partial H discharge during current interruption, there is enrichment of Ni on and in the surface of modulated Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$. This leads to improved H adsorption and/or reduced H absorption/hydride formation and, therefore, decreased deactivation during subsequent HER polarization.
This section discusses Tafel measurements made on Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} ribbon after cyclic current modulation in 8 M KOH electrolyte. Figure 5.34 shows the \( \eta \)-log \( i \) plots made after cyclic modulation (Figures 4.23 - 4.24) together with the plot from the as-polished condition (Figure 4.15). There is a shift of the plots to the left, indicating a lower activity after modulation. This is also indicated by the \( i_\eta \) and \( E_{250} \) values given in Table 5-VI. The plot is steeper in the lower region (\( \eta_{H_2} \approx 140-400 \) mV), but at high overpotentials (\( \eta_{H_2} > 400 \) mV) the slopes of the modulated AMA are lower and indicate that the Volmer step of the HER is rate determining.

All Tafel plots for the modulated cathodes show less activity than the as-polished condition. This is in apparent contradiction to what was observed in the cyclic modulation experiments. Although the modulated Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} alloy did not allow \( \beta \)-NiH to reform, it was seen that there was still residual \( \alpha \)-hydride and/or absorbed hydrogen which caused the residual deactivation seen in Figure 5.33(b). Furthermore, during the post-modulation Tafel sweeps, there was hysteresis in the potential response between the first up-sweep and last down-sweep (shown in the Tafel plots) and there was poor reproducibility of the plots, as seen in Figures 4.23 - 4.24. The electrochemical hysteresis is likely due to hydrogen absorption/desorption hysteresis behaviour [119]. This phenomena was observed previously (Figure 5.35) in foils of crystalline Co and Ni metal [70].
Figure 5.34 HER Tafel (\(\eta\)-log \(i\)) plots of amorphous Ni\(_{50}\)Co\(_{25}\)P\(_{15}\)B\(_{10}\) cathodes in untreated electrolyte: before and after cyclic current modulation.

TABLE 5-VI Comparison of observed and extrapolated electrochemical values from amorphous Ni\(_{50}\)Co\(_{25}\)P\(_{15}\)B\(_{10}\) before and after cyclic current modulation in pre-electrolysed 8 M KOH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>(i_{\eta=225}) (mA/cm(^2))</th>
<th>(i_{\eta=325}) (mA/cm(^2))</th>
<th>(i_{\eta=500}) (mA/cm(^2))</th>
<th>(E_{i=250}) (mV(\text{Hg}_2\text{Hg}_2\text{O}))</th>
<th>(E_{i=250})(^+) (mV(\text{Hg}_2\text{Hg}_2\text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Polished</td>
<td>[\text{Not applicable}]</td>
<td>[\text{Not applicable}]</td>
<td>[\text{Not applicable}]</td>
<td>[\text{Not applicable}]</td>
<td>[\text{Not applicable}]</td>
</tr>
<tr>
<td>720/5/3</td>
<td>0.085</td>
<td>0.23</td>
<td>1.9</td>
<td>-1850</td>
<td>-1705 ± 62</td>
</tr>
<tr>
<td>60/5/20</td>
<td>0.098</td>
<td>0.20</td>
<td>1.3</td>
<td>-1893</td>
<td>-1737 ± 92</td>
</tr>
<tr>
<td>5/5/100+</td>
<td>0.12</td>
<td>0.24</td>
<td>1.3</td>
<td>-1954</td>
<td>-1835 ± 40</td>
</tr>
<tr>
<td>60/60/20</td>
<td>0.28</td>
<td>1.2</td>
<td>7.4</td>
<td>-1865</td>
<td>-1650</td>
</tr>
</tbody>
</table>

\(^{+}\)IR-corrected
Additionally, although there is decreased absorption and hydride formation at very high cathodic polarizations in structurally transformed AMA, the decomposition of the hydride that is formed may be hindered at lower cathodic overpotentials. There were likely considerable amounts of trapped H in the bulk which, given the low diffusivity of amorphous alloys, could be expected to discharge very slowly. Since the Tafel scans were estimated to be the equivalent of 4 hours of H charging (§5.2.3.1), the discharge time was estimated to be 16 hrs (20 hr of scan - 4 hr of charging). Using an approximate diffusivity of $0.5 \times 10^{-10}$ cm$^2$/s (Table 5-V), and the formula:

$$x_H = (Dt)^{1/2}$$  \hspace{1cm} (5.11)

where, $x =$ discharge distance from half-thickness,
$D =$ diffusivity,
$t =$ discharge time,

the discharge of H from the middle of the ribbon is estimated to be 15-20µm, indicating that hydrogen discharge may not be complete during the Tafel scans.

This would account for both: (i) the shift to lower current densities in the lower overpotential region of the $\eta$-log $i$ plot in Figure 5.36, and (ii) and the reversal of the $b$ and $b_{\text{high}}$ values (and rds) between the initial and post-modulated plots. The post-modulation $\eta$-log $i$ measurements correspond to the higher 'on' potential state discussed in the previous section (i.e. -1900 to -1950 mV$_{\text{Hg/HgO}}$) while the initial $\eta$-log $i$ measurement corresponds to the lower 'on' potential state (i.e. -1700 to -1800 mV$_{\text{Hg/HgO}}$).

It is noted that the corrosion potential on the post-modulation $\eta$-log $i$ plots is at $\eta_{H_2} \approx 120$ mV, or ca. $-1090$ mV$_{\text{Hg/HgO}}$, which is in good agreement with the 'off' potentials seen in Figure 5.33.
Thus, due to time-dependent hysteresis related to hydrogen charging and discharging, the Tafel-type measurements did not provide an accurate technique for measuring and predicting electrochemical activity of HER cathodes at very high overpotentials.
This section will discuss the SEM examination and EDX analysis of the amorphous Ni₅₀Co₂₅P₁₅B₁₀ cathodes after modulation in pre-electrolysed electrolyte. After modulation, upon removal of the AMA cathodes, the surface was similar to c.p. nickel (§5.1.2.4), exhibiting a clear or light golden-brown film that tended to fade with time. In Figure 5.36, SEM images of the modulated surfaces (Figure 4.32) are shown along with the as-polished AMA surface (Figure 4.28). The modulated AMA was similar to modulated c.p. nickel; new surface features only became apparent at higher magnifications (ca. 10 000x). Surface films were found to consist of a coverage of very fine nodules and particles in the ca. 0.1 – 1.0 μm range. However, there appears to be less deposit and less corrosion of the substrate than was the case with c.p. Ni because polishing scratches are still visible. This likely is due to the microstructurally homogeneous amorphous alloy forming a more uniform corrosion layer.

There was some variation of morphology between different specimens of the same modulation condition and also across the same specimen, thus it was difficult to correlate surface features with modulation. A comparison of the 720/5/2 and 60/60/20 cycles (having very different t_{off} and N) suggests that most growth occurs during the initial 24 hour hold, since the morphologies are similar (the large white particles seen in the upper region of Figure 5.36(e) were seen on most specimens and will be discussed below).

X-ray analysis of the cathode area (Figure 5.37(b)) showed little change from the EDX spectrum of the as-polished surface (Figure 5.37(a)). A representative EDX spot
analysis (Figure 5.37(c)) of the larger, lighter particles (Figure 5.36(e)) indicated that they contained Fe, Cu and Zn, similar to those seen on the surface of c.p. Ni (Figures 5.26(c,d)). Thus, these impurities originate from the KOH source, as the alloying elements are of high purity (i.e. 99.9 – 99.99%). It appears that the effect of impurity deposition on the AMA is small and hence the deactivation behaviour must be more related to hydrogen charging and hydride formation.
Figure 5.36  SEM images of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$: (a) as-polished and after cyclic current modulation in pre-electrolysed 8 M KOH: (b) 720/5/2, (c) 60/5/20, (d) 5/5/100+, (e) 60/60/20.
Figure 5.37 EDX spectra of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$: (a) as-polished and after cyclic current modulation in pre-electrolysed 8 M KOH: (b) wide area, (c) spot analysis of larger, lighter particles.
This section discusses XPS analysis of amorphous \( \text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10} \) after cathodic polarization at 250 mA/cm\(^2\) in pre-electrolysed 8 M KOH electrolyte. The Ni 2p and Co 2p peaks are shown in Figures 4.39 and 4.40, respectively. Peaks were not seen for metallic Ni nor Co species; only divalent species (i.e., Ni 2p\(_{3/2}\) at ca. 855 eV, Co 2p\(_{3/2}\) at ca. 781 eV) were detected. This is in contrast to the as-polished condition, which is strongly metallic, and thus indicates further surface film formation, as expected from the SEM.

*Comparison to Standards for Divalent Nickel*

To identify the divalent nickel species, Ni 2p and O 1s spectra from the modulated c.p. Ni were compared to standards for NiO and Ni(OH)\(_2\) [94]. The Ni 2p peaks are shown with those of the divalent standards in Figure 5.38. The shape, width and satellites of the divalent 2p peaks agreed with the Ni(OH)\(_2\) standard very well but the Ni 2p binding energy was ca. 1.0 eV low. The O 1s peak, shown in Figure 5.39 also showed a similar trend in binding energy shift (n.b. the ex-situ specimen transfer time was on the order of minutes, so the possibility of oxidation during air exposure was minimized). Although cobalt standards were not available to compare with the experimental Co 2p peaks, the O 1s peaks of the nickel standards would be the same as cobalt counterparts. Thus, the experimental O 1s peak is representative of both the Ni and Co surface species (as well as any residual KOH which was present on the low resolution XPS survey).
Figure 5.38 Comparison of Ni 2p peaks: amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cathodic polarization in pre-electrolysed electrolyte versus NiO and Ni(OH)$_2$ standards ([94]).

Figure 5.39 Comparison of O 1s peaks: amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon after cathodic polarization in pre-electrolysed electrolyte versus NiO and Ni(OH)$_2$ standards (after [94]).
There are two possible explanations for the shift to lower binding energy: (i) the surface also has some NiO character, as the peak positions are intermediate to the oxide and hydroxide standards, and/or (ii) Ni(OH)$_2$ is as an insulator and can induce charging, causing energy loss [120]. This phenomenon was noted previously [86] and possibly is due to poor grounding of the specimen in the spectrometer. Since the binding energy shift also occurred for the Ni 3s and 3p spectra (which were not shown as the standards show very little distinction between the oxide and hydroxide), it seems that the latter explanation is most likely. Thus, it appears that amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ alloy cathodically polarized in pre-electrolysed 8 M KOH forms a surface film which has a hydroxide nature.

*Comparison to Cathodically Polarized Nickel Metal*

In contrast to cathodically polarized crystalline Ni (§5.2.2.5), no metallic species were observed. However, based on the respective SEM morphologies, the film on the amorphous ribbon did not appear thicker. Since no metallic nickel species were detected, the divalent film must be at least as thick as the XPS sampling depth of ca. 0.003 μm. It is likely then that the amorphous alloy has a tenacious film with very uniform coverage and thickness, while the crystalline metal has an inconsistent film, due to deeper oxidation/corrosion damage, as evidenced by the rougher SEM morphology (Figure 5.25).
Surface Film Composition and Thickness

An approximate surface composition was determined by deconvoluting the Ni 2p and Co 2p spectra of cathodically polarized Ni₅₀Co₂₅P₁₅B₁₀ into sub-peak components based on fit parameters for Ni(OH)₂ [94] and previously reported data for Co(OH)₂ [86], respectively. Figures 5.40 and 5.41 show the Ni and Co 2p₃/₂ peaks with sub-peaks for divalent (M²⁺) and shake-up satellite (sat.) components.

The overall ratio of Ni to Co detected was ca. 5:2: (72% Ni, 28% Co). Compared to the as-polished condition there is now Co depletion/Ni enrichment near the surface (Table 5-VII), as proposed in §5.2.3.2. This indicates that cobalt has been preferentially oxidized from the surface. As mentioned in §5.2.3.2, segregation of alloy elements has been observed in amorphous alloys after H absorption/desorption; elemental Ni is more stable in the corrosion regime of the cathodic polarization than elemental Co (Appendix B-2). Additionally, from the low-resolution XPS survey, peaks for boron and phosphorous were not readily discernable, likely due to leaching/dissolution, as discussed previously. The surface of the amorphous alloy after cathodic polarization is enriched with Ni, which is more electrocatalytically active than the other alloy components.

Thus, after cathodic polarization, the amorphous Ni₅₀Co₂₅P₁₅B₁₀ ribbon surface appears to consist of a uniform film that is Ni enriched due to segregation and leaching of other alloy components. This contributes to the improved electrocatalytic activity of the material during subsequent modulation.
TABLE 5-VII The distribution of Ni and Co in amorphous Ni_{50}Co_{25}P_{15}B_{10} ribbon: bulk ([94]), as-polished surface, cathodically polarized surface.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Composition</th>
<th>As-Polished Surface Composition</th>
<th>Cathodic. Pol. Surface Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>67%</td>
<td>61%</td>
<td>72%</td>
</tr>
<tr>
<td>Co</td>
<td>33%</td>
<td>39%</td>
<td>28%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure 5.40 Deconvolution of the Ni 2p_{3/2} spectrum of amorphous Ni_{50}Co_{25}P_{15}B_{10} ribbon cathodically polarized in pre-electrolysed electrolyte into divalent (Ni^{2+}) and shake-up satellites (sat.) sub-peaks.
Figure 5.41  Deconvolution of the Co $2p_{3/2}$ spectrum of amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ ribbon cathodically polarized in pre-electrolysed electrolyte into divalent (Co$^{2+}$) and shake-up satellites (sat.) sub-peaks.
6. CONCLUSIONS

(I) Intermittent operation of industrial water electrolyzers was successfully simulated using a combination of 'on' and 'off' cyclic modulation. Software was modified to accomplish the above.

(II) During cyclic modulation operation, the 'on' HER cathode potential:
- of c.p. Ni in untreated KOH electrolyte increases ca. 550 mV during the first 1 to 2 hours of modulation and then during the next ca 24 hours slowly decreases ca. 150 mV,
- of c.p. Ni in pre-electrolysed KOH increases 500 mV with the application of current and maintains that potential for the duration of the cyclic modulation,
- of amorphous Ni₅₀Co₂₅P₁₅B₁₀ increases 500 mV with the application of current but rapidly recovers 175 mV for most cyclic modulations.

(III) For freshly polished cathodes, all combinations of cathode material and electrolyte produced Tafel slopes of ca. 140-170 mV/dec at low overpotentials and Tafel slopes of ca. 200-290 mV/dec at higher overpotential. After modulation:
- c.p. Ni in untreated KOH had similar Tafel slopes,
- c.p. Ni in pre-electrolysed KOH had similar low-range Tafel slopes but higher high-range Tafel slopes of ca. 200-300 mV/dec, while
- amorphous Ni₅₀Co₂₅P₁₅B₁₀ had lower high range Tafel slopes but higher low range Tafel slopes of ca. 200-280 mV/dec.

(IV) After cathodic polarization, the previously clean electrode surfaces exhibited chemical and morphological changes:
- c.p. Ni in untreated KOH had relatively large iron-rich crystallites of ca. 1-3μm electrodeposited from the electrolyte, which caused macroscopic roughening, while the Ni at the surface had both oxide and hydroxide characteristics,
- c.p. Ni and amorphous Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} in pre-electrolysed KOH both had microscopic nodules of ca. 0.1 – 1.0 µm and had sparser deposition of iron, copper and zinc impurities from the electrolyte, while both surface films had primarily hydroxide characteristics,
- amorphous Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} had surface Ni enrichment due to Co and metalloid depletion from oxidation and dissolution.

(V) After cathodic polarization and cyclic modulation, the \textit{red} reaction mechanism at high HER overpotentials changed from hydrogen adsorption to hydrogen absorption.

(VI) For utilization under intermittent industrial conditions, c.p. Ni sheet has good structural stability but readily deactivates in purified caustic electrolyte. However, in untreated electrolyte, it shows reactivation which is not affected by modulation, while the substrate shows only moderate damage from electrodeposits. Amorphous Ni\textsubscript{50}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} shows low corrosion in purified caustic, but deactivates readily and shows embrittlement. Under cyclic/intermittent current conditions it can have moderate, but relatively sudden, reactivation gains. In a commercial/industrial environment the amorphous ribbons, in the present form, may require delicate handling.
7. REFERENCES

33 K. Lian, Master's Thesis, University of Toronto (1990)


96  J.D. Andrade, in Surface and Interfacial Aspects of Biomedical Polymers, Vol. 1, ed. J.D.


98  T. Matsumoto, K. Hashimoto and M. Naka, in Rapidly Quenched Metals III. vol. 2, ed. B. Cantor


106  J. Pielaszek, in Hydrogen Degradation of Ferrous Alloys, eds. R.A. Oriani and J.P. Hirth, Noyes


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APPENDIX A. ELECTROLYTE CALCULATIONS

A-1 Calculation of IR Drop

IR drop (ohmic polarization) is due to resistive losses in the electrolyte, at contacts of the wire leads and across surface films of the electrodes.

The IR drop due to the solution resistivity, $\Delta \Psi$, is related to the specific conductivity, $\sigma$, by the following expression:

\[
E = \frac{I}{\sigma A} = \frac{\Delta \Psi}{l} \quad \text{(A.1a)}
\]

\[
\Delta \Psi = I(\frac{1}{\sigma A}) \quad \text{(A.1b)}
\]

where, $E = \text{field strength [V/m]}$
$I = \text{current [A]}$
$\sigma = \text{specific conductivity [1/\Omega m]}$
$A = \text{area [m}^2\text{]}$
$l = \text{length of field [m]}$

Specific conductivity is also defined as:

\[
\sigma = \sigma_e + \sigma_{H_2O} \quad \text{(A.2)}
\]

\[
\sigma_e = Z_e C_e \lambda_e \quad \text{(A.3)}
\]

where, $\sigma_e$, $\sigma_{H_2O} = \text{specific conductivities of electrolyte, water, respectively}$
$Z_e = \text{valence}$
$C_e = \text{molar concentration}$
$\lambda_e = \text{limiting equivalent conductivity}$

For 8M KOH solution:

$\sigma_{H_2O} (25^\circ C) = 7.127 \times 10^{-6}$ [1/\Omega m]
$\lambda_{KOH} (70^\circ C) = 183 \times 10^{-4}$ [m$^2$/\Omega eq]
$C_{KOH} = 8000$ [moles/m$^3$]

For a field length (salt bridge tip to sample) of $l = 5$mm and ignoring $\sigma_{H_2O}$ because it is very small ($\sigma_e >> \sigma_{H_2O}$, so, $(\sigma_e + \sigma_{H_2O}) \equiv \sigma_e$):

\[
\Delta \Psi = I^*l/\sigma = I^*l/(Z_e C_e \lambda_e) \quad \text{(A.4)}
\]

\[\therefore \Delta \Psi(I) = \frac{I(5 \times 10^{-3} \text{ [m]})}{(1 \text{[eq/mol]})(8000 \text{[mol/m}^3\text{]})(183 \times 10^{-4} \text{[m}^2/\text{\Omega eq]}))}
\]
This relation is plotted in Figure A.1 for 0.25, 1, 2.5, 10, 25, 100 and 250 mA/cm²:

![Plot of IR drop versus current density for 8M KOH solution at 70°C](image)

**Figure A.1** Plot of IR drop versus current density for 8M KOH solution at 70°C
A-2  *pH Calculation*

pH of an electrolyte is a function of (i) the concentration (activity) of H⁺ (or OH⁻) species and (ii) the dissociation of water.

*(i) Activity*

For KOH:  
\[ a_{OH^-} = f(a_{KOH}) \]

\[ KOH \rightarrow K^+ + OH^- \]

Since K⁺ and OH⁻ have the same ion size parameter,

\[ a_{KOH} = a_{K^+}a_{OH^-} = (a_{OH^-})^2 \]  \hspace{1cm} (A.5)

Also, K⁺ and OH⁻ have the same molal concentration,

\[ a_{KOH} = \gamma^2_{e}m_{K^+}m_{OH^-} = \gamma^2_{e}(m_{OH^-})^2 \]  \hspace{1cm} (A.6)

*where,*  
\[ a_{OH^-} = \text{molal ionic activity of hydroxide ion} \]
\[ a_{K^+} = \text{molal ionic activity of potassium ion} \]
\[ a_{KOH} = \text{activity of KOH} \]
\[ m_{OH^-} = \text{molality of hydroxide ion assuming complete dissociation of KOH} \]
\[ \gamma^e = \text{mean molal activity} \]

So, combining (A.5) and (A.6):

\[ (a_{OH^-})^2 = \gamma^e (m_{OH^-})^2 \]  \hspace{1cm} (A.7)
\[ a_{OH^-} = \gamma^e m_{OH^-} \]  \hspace{1cm} (A.7')

For 8 M KOH,

8 M KOH = 34 wt% KOH = 9.18 m KOH

The mean molal ionic activity, \( \gamma^e \), for 8 KOH is [1]:

At 70°C, \( \gamma^e \approx 3.37 \)
\[ a_{OH^-} = (3.37)(9.18 \text{ [kg/mol]}) = 30.94 \]

At 25°C, \( \gamma^e \approx 5.7 \)
\[ a_{OH^-} = (5.7)(9.18 \text{ [kg/mol]}) = 52.3 \]

---

(ii) **Dissociation Constant of Water**

The dissociation constant of water at 25°C (303K) [2]:

- At 25°C (298K), \( K_{H_2O} = 10^{-14} \Rightarrow -\log K_{H_2O} = 14.0 \)
- At 70°C (343K), \( K_{H_2O} = 1.513 \times 10^{-13} \Rightarrow -\log K_{H_2O} = 12.8 \)

The dissociation of water,

\[
H_2O \rightarrow H^+ + OH^- \tag{A.8}
\]

\[
K_{H_2O} = a_{H_2O} = a_{H^+}a_{OH^-} \tag{A.9}
\]

So,

\[
a_{H^+} = \frac{K_{H_2O}}{a_{OH^-}} \tag{A.9'}
\]

Then pH is defined as:

\[
\text{pH} = -\log a_{H^+} = -\log \left(\frac{K_{H_2O}}{a_{OH^-}}\right) \tag{A.10}
\]

So the pH of 8M KOH is calculated to be:

- At 25°C, \( \text{pH} = \log(52.3) + 14 = 15.7 \)
- At 70°C, \( \text{pH} = \log(30.9) + 12.8 = 14.3 \)

**Activity of Water:**

Osmotic Coefficient (\( \Theta \)) of KOH at 25°C [3]

\[
\Theta = 2.095
\]

\[
\Theta = -1000 \ln[a_w]/(\nu MM_w) \tag{A.11}
\]

\[
2.095 = -1000 \ln[a_w]/((2)(9.000)(18.015))
\]

\[
a_w = 0.507
\]

---


APPENDIX B. ELECTRODE POTENTIALS

B-1 Hg/HgO Reference Electrode Potential

\[
\text{HgO(s) + H}_2\text{O} + 2e^- \Leftrightarrow \text{Hg(l) + 2OH}^-, \quad 25^\circ\text{C} \quad (B.1)
\]

\[
E_{\text{Hg/HgO}} = E_{\text{Hg/HgO}}^* - (RT/F) \ln[a_{\text{OH}}/V_{aw}] \quad (B.2)
\]

\[
E_{\text{Hg/HgO}} = +0.0976 - (8.314)(298)/(96487) \ln[32.59/(0.507)^{0.5}]
\]

\[
E_{\text{Hg/HgO}} = -0.00058 \text{ V}_{\text{SHE}}, \text{ at } 25^\circ\text{C}
\]

B-2 Electrode Redox Potentials and Pourbaix Diagrams


In this section, equilibrium potentials of oxidation/reduction reactions are calculated for possible chemical species encountered during the HER in aqueous 8M KOH electrolyte at 70°C. The calculations are based on thermodynamic data in Pourbaix's E-pH diagrams for the pertinent elements and E-pH regime.

Data:

\[
T = 70^\circ\text{C} = 343 \text{ K}
\]

\[
8 \text{ M KOH (aq, 343 K) } \equiv \text{pH } = 14.3
\]

\[
R = 8.314 \text{ [J/mol-K]}
\]

\[
F = 96487 \text{ [C/mol]}
\]

\[
E_{\text{Hg/HgO}} = 0.00058 \text{ V}_{\text{SHE}} = 0.6 \text{ mV}_{\text{SHE}}
\]

\textbf{Hydrogen Evolution Reaction Equilibrium Potential}
(See Figure B.1, line (6)-(a))

\[ \text{H}_2 / \text{H}_2\text{O} \ (\equiv 2\text{H}^+ + 2\text{e}^- \Leftrightarrow \text{H}_2) \]  \hspace{1cm} \text{(B.3)}

\[ \begin{align*}
E_{\text{H}_2/\text{H}_2\text{O}} &= 0.000 - 2.303(\text{RT}/\text{F})\text{pH} \\
&= 0.000 - 0.973 \\
&= -0.973 \ V_{\text{SHE}} \\
&= -972 \ mV_{\text{Hg/HgO}}
\end{align*} \hspace{1cm} \text{(B.4)}

\textbf{Domain of Hydroxide/Hydride Equilibrium}
(See Figure B.1, line (3'))

\[ \text{H}^+ / \text{OH}^- \]

\[ \begin{align*}
E_{\text{H}^+/\text{OH}^-} &= -0.711 - 2.303(\text{RT}/\text{F})\text{pH} \\
&= -0.711 - 0.973 \\
&= -1.684 \ V_{\text{SHE}} \\
&= -1683 \ mV_{\text{Hg/HgO}}
\end{align*} \hspace{1cm} \text{(B.5)}

\textbf{Nickel Redox Potentials in Alkaline Solutions}

\text{Ni}/\text{Ni}^{3+}
(See Figure B.2, lines (2), (10))

(i) \[ \text{NiO} + 2\text{H}^+ + 2\text{e}^- \Leftrightarrow \text{Ni} + \text{H}_2\text{O} \]  \hspace{1cm} \text{(B.6)}

\[ \begin{align*}
E_{\text{Ni/NiO}} &= 0.116 - 0.973 \\
&= -0.857 \ V_{\text{SHE}} \\
&= -856 \ mV_{\text{Hg/HgO}}
\end{align*} \hspace{1cm} \text{(B.7)}

(ii) \[ \text{Ni(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \Leftrightarrow \text{Ni} + 2\text{H}_2\text{O} \]  \hspace{1cm} \text{(B.8)}

\[ \begin{align*}
E_{\text{Ni/Ni(OH)}_2} &= 0.116 - 0.973 \\
&= -0.863 \ V_{\text{SHE}} \\
&= -862 \ mV_{\text{Hg/HgO}}
\end{align*} \hspace{1cm} \text{(B.9)}

(iii) \[ \text{HNiO}_2^- + 3\text{H}^+ + 2\text{e}^- \Leftrightarrow \text{Ni} + 2\text{H}_2\text{O} \]  \hspace{1cm} \text{(B.8)}

\[ \begin{align*}
E_{\text{Ni/HNiO}_2^-} &= 0.648 - 2.303(3\text{RT}/2\text{F})\text{pH} + 2.303(\text{RT}/2\text{F})\log(a_{\text{HNiO}_2^-}) \\
&= 0.648 - 1.460 - 0.204 \\
&= -1.016 \ V_{\text{SHE}} \\
&= -1015 \ mV_{\text{Hg/HgO}}
\end{align*} \hspace{1cm} \text{(B.9)}

B-6
**Iron Redox Potentials in Alkaline Solutions**

\[ \text{Fe/Fe}^{2+} \]

(i) \[ \text{Fe(OH)}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{Fe} + 2\text{H}_2\text{O} \]  
See Figure B.3, line (12)  

\[ E_{\text{Fe}/\text{Fe(OH)}_2} = -0.047 - 0.973 \]
\[ = -1.020 \text{ V}_{\text{SHE}} \]
\[ = -1019 \text{ mV}_{\text{Hg/HgO}} \]

(ii) \[ \text{HFeO}_2^- + 3\text{H}^+ + 2e^- \leftrightarrow \text{Fe} + 2\text{H}_2\text{O} \]  

\[ E_{\text{Fe}/\text{HFeO}_2^-} = 0.493 - 2.303(3\text{RT}/2\text{F})\text{pH} + 2.303(\text{RT}/2\text{F})\log(a_{\text{Fe}/\text{HFeO}_2^-}) \]
\[ = 0.493 - 1.460 - 0.204 \]
\[ = -1.116 \text{ V}_{\text{SHE}} \]
\[ = -1115 \text{ mV}_{\text{Hg/HgO}} \]

**Cobalt Redox Potentials in Alkaline Solutions**

\[ \text{Co/Co}^{2+} \]

(See Figure B.4, lines (4), (12))

(i) \[ \text{Co(OH)}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{Co} + 2\text{H}_2\text{O} \]  

\[ E_{\text{Co}/\text{Co(OH)}_2} = 0.095 - 0.973 \]
\[ = -0.878 \text{ V}_{\text{SHE}} \]
\[ = -877 \text{ mV}_{\text{Hg/HgO}} \]

(ii) \[ \text{HCoO}_2^- + 3\text{H}^+ + 2e^- \leftrightarrow \text{Co} + 2\text{H}_2\text{O} \]  

\[ E_{\text{Co}/\text{HCoO}_2^-} = 0.659 - 2.303(3\text{RT}/2\text{F})\text{pH} + 2.303(\text{RT}/2\text{F})\log(a_{\text{Co}/\text{HCoO}_2^-}) \]
\[ = 0.659 - 1.460 - 0.204 \]
\[ = -1.005 \text{ V}_{\text{SHE}} \]
\[ = -1004 \text{ mV}_{\text{Hg/HgO}} \]
Figure B.1 Potential-pH equilibrium diagram for the system hydrogen-water, at 25°C; shaded area shows approximate E-pH regime of this study (after [4]).

Figure B.2 Potential-pH equilibrium diagram for the system nickel-water, at 25°C; shaded area shows approximate E-pH regime of this study (after [4]).
Figure B.3  Potential-pH equilibrium diagram for the system iron-water, at 25°C; shaded area shows approximate E-pH regime of this study (after [4]).

Figure B.4  Potential-pH equilibrium diagram for the system cobalt-water, at 25°C; shaded area shows approximate E-pH regime of this study (after [4]).
Recent studies have revised the E-pH (Pourbaix) diagrams for nickel and iron.

Silverman [5,6] suggested that some compounds in Pourbaix’s atlas do not exist or exist in a different form. Revised E-pH diagrams were presented using data from recent thermodynamic, spectroscopic and electrochemical characterization studies. The diagrams for nickel and iron are given in Figures B.5 and B.6. The following points were made:

For nickel,
- $\alpha$–Ni(OH)$_2$ converts to $\beta$ on standing in alkaline solutions; $\beta$–Ni(OH)$_2$ is consistent with NiO (hyd.)
- Ni$^{2+}$ can be hydrolyzed to: NiOH$^+$, dissolved Ni(OH)$_2$ and Ni(OH)$_3^-$ (instead of HNiO$_4^{2-}$)

For iron,
- Fe(OH)$_3^-$ as the dissolved ferrous ion species in strongly basic solution (instead of HFeO$_2$)
- increasing activity of dissolved species: expands the region of stability of Fe(OH)$_2$ and decreases the region of stability of Fe(OH)$_3^-$

---

Figure B.5  Revised nickel-water E-pH diagram at 25°C. All metals containing ionic species are at $10^{-6}$ activity (after [5]).
Figure B.6  Revised iron-water E-pH diagram at 25°C.: (a) ionic species at $10^{-6}$ activity (b) ionic species at $10^{-4}$ activity (after [6]).
Another study recalculated the original Pourbaix diagram in terms of KOH concentration, instead of pH, and for several temperatures, instead of 25°C [7]. A diagram for nickel and iron is shown in Figure B.7.

Figure B.7 Potential–concentration diagram for the redox couples H₂/H₂O, Ni/Ni(OH)₂, Fe/Fe(OH)₂, FeO²⁻/Fe in KOH at four different temperatures (After [8]).

---


APPENDIX C. SOFTWARE

• Current-Control Modulation Program

The Current-Modulation program (CURMOD2) used to generate the waveforms and collect the data was based on a Cyclic-Voltammetry (CV) program. The many modifications include:

<table>
<thead>
<tr>
<th>Modifications/additions</th>
<th>Cyclic Voltammetry</th>
<th>Current Modulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>triangular waveform</td>
<td>trapezoidal waveform</td>
</tr>
<tr>
<td></td>
<td>potential control</td>
<td>current control</td>
</tr>
<tr>
<td></td>
<td>n/a</td>
<td>automatic selection of galvanostat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>current-range during ‘on’, ‘off’ and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>‘ramp’ portions of waveforms</td>
</tr>
</tbody>
</table>

The core extract of the Current Modulation program is given below. Exclamation marks precede comment text. The programming language is HP-BASIC 5.1.

30 !*********************************************************************
40 ! CYCLIC MODULATION (II): CURRENT CONTROL
50 ! GRID POWER SIMULATION
60 ! TRAPEZOIDAL WAVEFORM
70 ! Modified by David Anthony, Feb 10, 1996
80 ! PSEUDO-Ecorr OFF-CURRENT
90 ! Modified by David Anthony, June 10-July 3, 1997
100! Specialized for IR compensation by HI-203
110!*********************************************************************
120!

5030 !'----------
5040 !' Cyclic Current Modulation
5050 !'----------

5131 !' Reference value for auto-ranging current range
5140 !' Oncd=Onpot
5150 5160 Onpot$=VAL$(Onpot)
5170 5170 Offpot$=VAL$(Offpot)
5180 5180 PRINT "Onpot$",Offpot$",Onpot$,Offpot$
5190 !' 5200 !' Round off inputted current densities to 3 places
5210 !' for input into F.G.
5220 5220 Oni=DROUND(Oni,3)
5230 5230 Offi=DROUND(Offi,3)
5240 5240 PRINT "Oni,Offi",Oni,Offi
5241 !' 5250 !' Scale the ON-c.d. to determine the order of magnitude of c.d.
5260 !' in preparation to (a) convert to potentials for input to F.G.
5270 !' and (b) determine a On-c.d. current-range of G-STAT
5300 PRINT "llog,lrint;llog,lrint"
5310 ! Convert the c.d. ramp-rates to pot. ramp-rates
5320 ! for input into F.G.
5330 IF Rmpup$[LEN(Rmpup$);1]="M" THEN
5340 Rmpup=VAL(Rmpup$[1;LEN(Rmpup$)-1])
5350 Rmpup=Rmpup*10^(-lrint+2)
5360 Rmpup$=VAL$(Rmpup)
5370 Rmpup$[LEN(Rmpup$)+1]="M"
5380 ELSE
5390 Expu$=Rmpup$[LEN(Rmpup$);1]
5400 Expu=VAL(Expu$)
5410 Expu=Expu+(-lrint+2)
5420 Expu$=VAL$(Expu)
5430 Rmpup$=Rmpup$[1;LEN(Rmpup$)-1]&Expu$
5440 END IF
5450 IF Rmpdn$[LEN(Rmpdn$);1]="M" THEN
5460 Rmpdn=VAL(Rmpdn$[1;LEN(Rmpdn$)-1])
5470 Rmpdn=Rmpdn*10^(-lrint+2)
5480 Rmpdn$=VAL$(Rmpdn)
5490 Rmpdn$[LEN(Rmpdn$)+1]="M"
5500 ELSE
5510 Expd$=Rmpdn$[LEN(Rmpdn$);1]
5520 Expd=VAL(Expd$)
5530 Expd=Expd+(-lrint+2)
5540 Expd$=VAL$(Expd)
5550 Rmpdn$=Rmpdn$[1;LEN(Rmpdn$)-1]&Expd$
5560 END IF
5570 PRINT "Rmpup$,Rmpdn$"
5580 Fp=(VAL(Fp$)^10^(-lrint+2))
5590 ! The initial potential must equal the final potential
5600 IF Ipq$="y" THEN
5610 Ip=Oni
5620 Potone=Offi
5630 Rmpone$=Rmpdn$
5640 Hldone$=Ofhld$
5650 Pottwo=Oni
5660 Rmptwo$=Rmpup$
5670 Hldtwo$=Onhld$
5680 ELSE
5690 Ip=Offi
5700 Potone=Oni
5710 Rmpone$=Rmpup$
5720 Hldone$=Ofhld$
5730 Pottwo=Offi
5740 Rmptwo$=Rmpdn$
5750 Hldtwo$=Ofhld$
5760 END IF
5770 PRINT "ip$":ip
5780 PRINT "Potone,Rmpone$,Hldone$";Potone,Rmpone$,Hldone$
5790 PRINT "Pottwo,Rmptwo$,Hldtwo$";Pottwo,Rmptwo$,Hldtwo$
5791 ! Adjust the inputted c.d.'s to scale properly on the F.G.
5800 Potone=(Potone*10^(-lrint+2))
5810 Pottwo=ROUND(Pottwo,0)
5820 IP=ROUND(IP,0)
5830 Pottwo=Pottwo*10^(-lrint+2)
5840 IP=ROUND(IP,0)
5850 ip=(Ip*10^(-lrint+2))
5860 ip=ROUND(ip,0)
5870 PRINT "Potone,Pottwo,ip$";Potone,Pottwo,lp
5871 '
5880 ' Select current-range for On-c.d.
5890 lrange=int+5
5890 lrange$=VAL$(lrange)
5900 Newrng=lrange
5910 !Onpot$=VAL$(SGN(Onpot)*INT(lp-Onpot))
5910 Newrng$=VAL$(Newrng)
5920 !Onpot$=VAL$(SGN(Onpot)*INT(lp-Onpot))
5930 Potone$=VAL$(Potone)
5940 !Ofpot$=VAL$(SGN(Onpot)*INT(lpOfpot))
5950 Pottwo$=VAL$(Pottwo)
5960 Ip$=VAL$(lp)
5970 PRINT "lp$,lhold$";lp$,lhold$
5970 PRINT "Potone$,Rmpone$,Hldone$";Potone$,Rmpone$,Hldone$
5980 B=SPOLL(702)
5990 B=SPOLL(702)
6000 OUTPUT 701;"F0P"&lp$&"S0H1'&lhold$
6010 OUTPUT 701;"1P"&Potone$&"S"&Rmpone$&"H"&Hldone$
6020 WAIT 2
6030 OUTPUT 701;"EL1" ! Select Current Range
6040 WAIT 4
6050 OUTPUT 701;"E11" ! External Input 1 ON
6060 WAIT 2
6070 Pol: GOSUB Samp
6080 !' Initiate current control by HB105
6090 !' Check C.D. - if it is very low c.t. ON-C.D then set
6100 IF Cur=.000004 THEN Pol
6110 IF Newrng=1 THEN
6120 ELSE
6130 IF Abs(Cur)>Abs(.85*Oncd*10^(-9)) THEN Selrng=lrange
6140 ELSE
6150 IF Abs(Cur)<Abs(.01*Oncd*10^(-3)) THEN Selrng=1
6160 END IF
6170 IF Newrng<>Selrng THEN
6180 Newrng=Selrng
6190 Newrng$=VAL$(Newrng)
6200 OUTPUT 701;"DCI"&Newrng$
6210 END IF
6220 IF Taime=Stime+Da$ THEN GOTO Pol
6230 Stime=Taime
6240 IF Vold WVocyc AND Vcyc>=V THEN
6250 CyC=Cyc+1
6260 PEN (INT(Cyc/50) MOD 2)*8+4
6270 Ocyc=200-Cyc+1
6280 PRINT TABXY(1,1);Ocyc;
6290 END IF
6300 OUTPUT @F;Cur*10^6;V !' Record Current Density and Potential
APPENDIX D. XPS ANALYSIS

Appendix D-1 Initial Surface Condition of Nickel Metal

This appendix relates the surface condition of c.p. Ni sheet, as determined using XPS, during various stages of the electrode polishing procedure (§3.1.1). The specimen conditions were:

(i.) as-received, degreased and analysed the same day,
(ii.) ground with 600 grit SiC paper, degreased and analysed the same day,
(iii.) ground and then polished to a 1 µm diamond finished, degreased and analysed the same day,
(iv.) specimen (iii) analysed after sitting one week in a dessicator,
(v.) as (iii) but degreased with analar grade acetone and methanol only.

The Ni 2p peaks of the specimens are shown in Figure D.1 in the order of decreasing oxidation, as determined by the relative intensities of the metallic and oxide Ni 2p$_{3/2}$ peaks at 852.7±0.2 eV and ca. 855-856 eV, respectively. It can be seen that the as-received specimen has the characteristic Ni 2p$_{3/2}$ doublet of NiO, but, although it has the strongest oxide signal of the samples, there is also a strong metallic signal indicating a low oxide thickness. The as-ground and as-polished specimens have profiles with decreased oxide components which did not change after sitting for one week. The as-polished, solvent-rinsed specimen has the lowest oxide component which could be due to the lack of a final water rinse or to variation from the grinding and polishing procedure.

The corresponding O 1s peaks of the Ni specimens are shown in Figure D.2. The peaks of specimens (i) – (iv) exhibit similar shapes with a prominent peak at ca. 531.5 eV and distinct shoulder near ca. 529.5 eV; the peak is intermediate to the O 1s of the NiO and Ni(OH)$_2$ standards. The solvent rinsed specimen is shifted higher to ca. 532.5 eV which, unexpectedly, seems to indicate that there is bound water detected. Because there is such a small Ni 2p oxide signal, the O 1s peak may indicate that there is adsorbed water on top of the very minimal oxide layer.
It is shown that nickel specimens could be produced for electrochemical testing which had minimal surface oxide. Since the electrochemical phenomena are surface and interface dependent, testing took place on essentially Ni, as opposed to Ni oxide, electrodes.

Figure D.1  XPS Ni 2p peaks of c.p. Ni sheet during various stages of polishing, scaled to height.
Figure D.2  XPS O 1s peaks of c.p. Ni sheet during various stages of polishing, scaled to height.

Appendix D-2  Sub-Peak Fitting Parameters

Table D-I gives the XPS fit parameters from Ni and Co standards described in the literature (§2.4.4, Tables 2-VI to 2-VII) that were used as a guideline to fit the experimental spectra sub-peaks in this study for peak deconvolution. The fits in this study followed the literature parameters to ca. ±0.2 eV, which is the accuracy that was attained with the spectrometer for the metallic Ni 2p_{3/2} position. Table D-2 gives the sub-peak fit parameters for the specimens shown in the Section 5 (Figures 5.5, 5.8, 5.9, 5.29, 5.41 and 5.42).
TABLE D-I  XPS fit parameters from literature for Ni and Co materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni 2p_{3/2} (eV)</th>
<th>FWHM (eV)</th>
<th>Δ-sat (eV)</th>
<th>Δ-2p_{1/2} (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>852.5</td>
<td>-</td>
<td>-6.4</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>852.8</td>
<td>-</td>
<td>-6.5</td>
<td>-</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>852.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>852.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>852.8</td>
<td>-</td>
<td>~4.4</td>
<td>17.2</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>852.7</td>
<td>-</td>
<td>-6.3</td>
<td>17.3</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>852.8</td>
<td>-</td>
<td>-</td>
<td>17.5</td>
<td>[94]</td>
</tr>
<tr>
<td>NiO</td>
<td>854.9, 856.8</td>
<td>2.27</td>
<td>6.2</td>
<td>17.9</td>
<td>[94]</td>
</tr>
<tr>
<td>Ni(OH)\textsubscript{2}</td>
<td>855.6</td>
<td>2.9</td>
<td>5.1</td>
<td>17.7</td>
<td>[94]</td>
</tr>
<tr>
<td>Co</td>
<td>778.0</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>CoO</td>
<td>780.0, 782.1</td>
<td>2.7</td>
<td>5.6, 6.4</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>Co(OH)\textsubscript{2}</td>
<td>781.0</td>
<td>3.2</td>
<td>-5.0</td>
<td>-</td>
<td>[86]</td>
</tr>
</tbody>
</table>

TABLE D-II  XPS fit parameters for Ni and Co materials in this study.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Species</th>
<th>Ni 2p_{3/2} (eV)</th>
<th>FWHM (eV)</th>
<th>Δ-sat (eV)</th>
<th>Δ-2p_{1/2} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Polished c.p. Ni</td>
<td>Ni\textsuperscript{0}</td>
<td>852.5</td>
<td>1.65</td>
<td>6.2</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td>Ni\textsuperscript{2+} (NiO)</td>
<td>854.9, 856.8</td>
<td>2.27</td>
<td>6.1</td>
<td>18.0</td>
</tr>
<tr>
<td>As-Polished Ni\textsubscript{60}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10}</td>
<td>Ni\textsuperscript{0}</td>
<td>852.7</td>
<td>1.6</td>
<td>6.5</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>Ni\textsuperscript{2+} (NiO)</td>
<td>854.9, 856.8</td>
<td>2.27</td>
<td>6.1</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>Co\textsuperscript{0}</td>
<td>778.0</td>
<td>1.6</td>
<td>-</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>Co\textsuperscript{2+} (CoO)</td>
<td>780.0, 782.7</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cathodically Polarized</td>
<td>Ni\textsuperscript{0}</td>
<td>852.6</td>
<td>1.65</td>
<td>6.1</td>
<td>17.1</td>
</tr>
<tr>
<td>c.p. Ni in p.e. KOH</td>
<td>Ni\textsuperscript{2+} (Ni(OH)\textsubscript{2})</td>
<td>856.1</td>
<td>2.85</td>
<td>5.2</td>
<td>17.5</td>
</tr>
<tr>
<td>Cathodically Polarized</td>
<td>Ni\textsuperscript{0}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni\textsubscript{60}Co\textsubscript{25}P\textsubscript{15}B\textsubscript{10} in p.e. KOH</td>
<td>Ni\textsuperscript{2+} (Ni(OH)\textsubscript{2})</td>
<td>855.4</td>
<td>2.8</td>
<td>5.0</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Co\textsuperscript{0}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Co\textsuperscript{2+} (Co(OH)\textsubscript{2})</td>
<td>780.5</td>
<td>3.1</td>
<td>3.6</td>
<td>15.9</td>
</tr>
</tbody>
</table>
Appendix D-3  Calculation of Film Thickness

Surface film thickness was calculated from XPS sub-peak intensities (areas) using Equation (5.2) which yields the following expression for film thickness depth, d:

\[ d = -\lambda/2 \ln[I_{\text{subs}}/I_{\text{film}}] \quad (E.1) \]

where, \( d \) = film thickness  
\( \lambda \) = photoelectron inelastic mean free path  
\( I_{\text{subs}}, I_{\text{film}} \) = measured intensities of substrate, film

The assumptions are that the divalent species detected \( (I_{\text{film}} = I_{M^{2+}}) \) represents a surface film with uniform thickness and coverage, the metallic species \( (I_{\text{subs}} = I_{M^0}) \) represents the substrate and that the mean free path of Ni 2p photoelectrons is the same through metallic nickel and divalent nickel. The areas underneath the sub-peaks were calculated by the ESCATools deconvolution software. The photoelectron inelastic mean free path was estimated from the universal curve (Figure D.3) where the electron energy \( (E_k) \) was estimated from Equation (2.20):

\[ E_k = h\nu - E_b \quad (E.2) \]

where, \( h\nu = E_{\text{Mg K\alpha}} = 1253.6 \text{ eV} \)  
\( E_b \approx E_{(M)2p} \)

Then for Ni 2p\(_{3/2} \) \( (E_{\text{Ni2p}_{3/2}} \approx 853 - 855 \text{ eV}) \):

\[ E_k \approx 400 \text{ eV}, \]  
\[ \lambda_{\text{Ni}} \approx 10 \text{ Å} \]

and for Co 2p\(_{3/2} \) \( (E_{\text{Co2p}_{3/2}} \approx 778 - 781 \text{ eV}) \):

\[ E_k \approx 475 \text{ eV} \]  
\[ \lambda_{\text{Co}} \approx 11 \text{ Å} \]
Figure D.3  Universal curve for electron mean free path (after [9]).

If sampling depth is taken to be when the substrate produces 95\% of the signal, i.e.

\[ \frac{I_{\text{subs}}}{I_{\text{film}}} \approx 95/5 = 20, \]

then for nickel, the sampling depth is:

\[ d_{\text{max}} \approx 16 \text{ Å} = 0.0016 \text{ µm} \]

---

Sample Calculations:

Given below is a table of data generated from the ESCATools deconvolution of as-polished c.p. Ni sheet (Figure 5.5):

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>#</th>
<th>182</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curve-fit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ni2p3/2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>species</th>
<th>BE/eV</th>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area/ eV²</th>
<th>rel at.prcnt</th>
<th>rel at.prcnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(met)</td>
<td>-852.5</td>
<td>-852.5</td>
<td>1.65</td>
<td>4.78E+04</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>sat.(Ni(met))</td>
<td>-858.7</td>
<td>-858.7</td>
<td>2.75</td>
<td>5.23E+03</td>
<td>6</td>
<td>61</td>
</tr>
<tr>
<td>Ni(2+)</td>
<td>-858</td>
<td>-858</td>
<td></td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ni(2+)</td>
<td>-858</td>
<td>-858</td>
<td></td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>sat.(Ni2+)</td>
<td>-858</td>
<td>-858</td>
<td></td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>sat.(Ni2+)</td>
<td>-858</td>
<td>-858</td>
<td></td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

| Sum       | 8.61E+4 | 100            | 100      |

The relative atomic percentages are the ratio of the sub-peak areas to the total area.

From Equation (E.1), the depth of the film is:

\[ d = -(10^{-10} \text{ m})/2 \ln[55/(22+11)] \]
\[ d = -2.6E-11 \text{ m} \]

(or)

\[ d = -(10^{-10} \text{ m})/2 \ln[(55+6)/(22+11+2+3)] \]
\[ d = -2.4E-11 \text{ m} \]

Thus, the oxide film is ca. 0.00025 μm thick.
APPENDIX E. 'OFF' CURRENT DENSITY DURING MODULATION

The Hokto Denko HA-501G Potentiostat/Galvanostat, when operated in galvanostat mode, allows only pre-set control of the current range. The available current ranges are 1, 10, 100 μA, 1, 10, 100 mA, 1A. The required currents for the 'on' current density of 250 mA/cm² were 50-100 mA, thus requiring selecting the galvanostat 100 mA current range that ranged from 0.0 – 100.0 mA with a current set accuracy of ±0.15%. Thus, the 'off' currents were dictated by the required 'on' current and were 0.0±0.15 mA. Since, the exchange currents measured from the η-log i plots were less than 0.01 mA, there was still an appreciable cathodic current during the 'off' cycles. The controlling software was modified to remotely change the current set range to the 1 μA range during the 'off' cycles, which gave an 'off' current of ca. 0.0000±0.00015 mA.

Figure F.1 shows the response of a freshly polished c.p. Ni cathodes to three different current inputs: cyclic modulations with the two different 'off' conditions described above and a steady 250 mA/cm² hold. It can be seen that when the 'off' current density is 0.0 mA/cm² the 'off' potentials are -1200 to -1300 mV_{Hg/HgO} but when the 'off' current density is 0.0000 mA/cm² the 'off' potential is ca -900 mV_{Hg/HgO}, which is close to the open-circuit potential. It can also be seen that modulation delays the 'on' cycle deactivation compared to the steady state hold condition.
Figure F.1  Effect of 'off' current on potentials during cyclic modulation on freshly polished c.p. Ni sheet.