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HOMOGENEOUS CATALYSIS
IN
ALKALINE WATER ELECTROLYSIS

by

Michael C. Stemp

A Thesis submitted in conformity with the requirements for the
Master's degree in Applied Science and Engineering
Department of Metallurgy and Materials Science
University of Toronto

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Homogeneous Catalysis in Alkaline Water Electrolysis  
Master’s of Applied Science and Engineering, 1997  
Michael Colin Stemp  
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University of Toronto

Abstract

The effect of addition of a transition metal salt, chromium, as a homogeneous catalyst, to the electrolyte in alkaline water electrolysis, for the hydrogen evolution reaction (HER) on commercial purity Ni-200 and an amorphous alloy (Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$) was investigated. Chronopotentiometry showed that electrolyte impurities such as Fe lowered the cathode overpotential but in the presence of catalyst additions, Fe reduced the catalyzing effect. An increase in catalyst concentration from 5 to 500 p.p.m. chromium led to a potential drop at the Ni-200 cathode of 160 to 400 mV and at the Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ cathode of 170 to 390 mV. Tafel measurements indicated a change in reaction after catalyst addition although the mechanism is still unclear. An increase in exchange current density from 3.10 mA/cm$^2$ in the absence of catalyst, to 3.74 mA/cm$^2$ after addition of 500 p.p.m. chromium was observed for Ni-200 while for Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ the values were 2.95 mA/cm$^2$ and 4.17 mA/cm$^2$, respectively. After catalyst addition scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX) and x-ray photoelectron spectroscopy (XPS) showed the presence of several chromium species on the cathode surface in the Cr$^0$, Cr$^{3+}$ and Cr$^{6+}$ states. Chromium additions to the electrolyte catalyzed the HER through competing reaction mechanisms.
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List of Symbols / Abbreviations

A  Area
b  Tafel slope in mV/decade
C  Coulombs
F  Faraday's constant, 96,486.7 C/mole
I  current in mA
i  current density in mA/cm²
iₑ  exchange current density in mA/cm²
Kₜ  dissociation constant of water
l  length in mm
M  Molarity in moles/litre
R  gas constant, 8.314 J K⁻¹ M⁻¹
T  temperature in °C or K
SEM  scanning electron microscope
XPS  x-ray photoelectron spectroscopy
HER  hydrogen evolution reaction
OER  oxygen evolution reaction
ppm  parts per million

Greek Symbols

η  overpotential
1.0 Introduction

1.1 Historical Significance of Hydrogen Production

Hydrogen production by water electrolysis was first achieved by Carlisle and Nicholson in 1800 [1.1]. It was over a full century later, however, that water electrolysis was first used on an industrial level by the Oerlikon Engineering Company. Chronologically speaking, an interesting situation occurred during this period in which, as often occurs, art preceded science. In 1874, Jules Verne in his now famous book, *The Mysterious Island*, predicted the use of hydrogen as a fuel, "...water as fuel for steamers and engines! Yes, but water decomposed into its primitive elements and decomposed, doubtless, by electricity, which will by then have become a powerful and manageable force..." [1.2]. Ironically, it was just about one hundred years after this that the OPEC oil crisis of 1973 prompted an explosion of research into non-fossil fuel energy sources, such as hydrogen, lending credence to Verne's prediction. Hydrogen's advantages are many and are now being widely investigated. As an energy source, hydrogen can be ecologically benign (depending on the primary energy source for production), can be transported and stored, can be used as fuel in industry, households and for land and air transportation. The use of hydrogen as a future energy source makes research into the various means of improving hydrogen production more important now than ever before.

1.2 Methods of Hydrogen Production

Today approximately 80 percent of the world's energy demands are met by fossil hydrocarbons; coal, petroleum and natural gas [1.3]. These same hydrocarbons also provide the main source of energy for the production of hydrogen industrially, the other source being water. Through the use of an external energy source, hydrogen can be produced by fossil hydrocarbons, by water alone or through a mixture of both. The energy cost for the production of hydrogen using hydrocarbons is much lower than that of the electrolysis of water, therefore, methods based on fossil hydrocarbons are preferred in industry. The major portion of hydrogen for industrial use is produced by coal, oil and natural gas with a smaller portion being produced
by electrolysis. Despite the higher costs associated with electrolysis, there continues to be an increasing demand for clean, renewable energy sources. In order to meet the demand of this growing market, the economics, and hence technology governing electrolysis are rapidly changing. A comparison of the costs associated with the more commonly used methods of hydrogen production is presented in Table 1.1. A more complete description of each of the processes is given in Appendix-A.

1.3 Objectives

The objectives of this project can be summarized as follows:

i) to elucidate the role of a transition metal addition, chromium, to the electrolyte, in alkaline water electrolysis,

ii) to determine the effect of catalyst concentration on cathodic overpotentials,

iii) to determine the effect of catalyst concentration on the hydrogen evolution reaction,

iv) to propose a reaction mechanism for homogeneous catalysis, and

v) to propose simple procedures to be used on an industrial scale.
<table>
<thead>
<tr>
<th>Process (cont')</th>
<th>Steam Reforming</th>
<th>Partial Oxidation</th>
<th>Gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Natural Gas</td>
<td>Residual Oil</td>
<td>Bit. Coal</td>
</tr>
<tr>
<td>Capital Investment($10^6)</td>
<td>111.82</td>
<td>274.84</td>
<td>425.24</td>
</tr>
<tr>
<td>Annual Operating Cost ($10^3)</td>
<td>91521</td>
<td>138711</td>
<td>189407</td>
</tr>
<tr>
<td>H₂ Product Cost with By-Product Credits ($/GJ)</td>
<td>5.60</td>
<td>9.11</td>
<td>12.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process (cont')</th>
<th>Steam Iron</th>
<th>Water Electrolysis</th>
<th>High Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Coal</td>
<td>Electricity</td>
<td>Electricity</td>
</tr>
<tr>
<td>Capital Investment($10^6)</td>
<td>434.9</td>
<td>175.8</td>
<td>189.3</td>
</tr>
<tr>
<td>Annual Operating Cost ($10^3)</td>
<td>210,692</td>
<td>291,251</td>
<td>224,716</td>
</tr>
<tr>
<td>H₂ Product Cost with By-Product Credits ($/GJ)</td>
<td>10.64</td>
<td>16.87</td>
<td>12.44</td>
</tr>
</tbody>
</table>

Table 1.1: Cost of hydrogen production by various methods. (Production capacity = 33 X 10^9 SCF/YR)
2.0 Background

2.1 Alkaline Water Electrolysis

As was mentioned in §1.0, the first industrial use of alkaline water electrolyzers was at the beginning of this century. During the early years, developments in electrolyzer design focused primarily on improved safety, reliability and user convenience. The first major innovation, marketed in 1948 by Lurgi, was a design that allowed operation at pressure [2.1]. In the 1950's and 60's interest developed in electrolysis as oxygen for life support in submarines. Gradually, new technologies emerged, such as the introduction of the solid polymer electrolyzer by General Electric. These were spawned by a number of factors not the least of which was the 1973 OPEC oil crisis. Since that time developments in water electrolysis have continued unabated.

2.1.1 Types of Electrolyzers

There are basically two types of water electrolyzers; the unipolar and the bipolar. The unipolar, or tank, electrolyzer is comprised of individual cells grouped in parallel that share a common electrolyte. The bipolar, or filter press type electrolyzer, comprises individual cells that are connected in series, each with its own electrolyte. Both types use 25-30 wt% potassium hydroxide as the electrolyte and operate at 70-85 °C.

The main components of an electrolyzer, as well as, their desired characteristics are summarized in the following table:
Table 2.1: Electrolyzer components and their desired properties.

2.1.1.1 Unipolar Electrolyzers

In unipolar electrolyzer design, single cells are placed in a common electrolyte tank known as a module. The anodes and cathodes are connected in parallel such that the overall module voltage is the same as the single cell voltage. Alternate electrodes are surrounded by diaphragms to prevent mixing of the gases. In order to achieve the desired hydrogen production capacity, the modules are connected in series. The advantages and disadvantages of this type of electrolyzer are summarized in Table 2.2.

2.1.1.2 Bipolar Electrolyzers

In filter press type electrolyzers, one electrode acts as both the cathode in one cell and the anode in the adjacent cell. In contrast to the unipolar electrolyzer, bipolar cells are connected in series allowing for a voltage increase proportional to the number of cells. Due to the nature of the cell
configurations, each cell contains its own electrolyte. The advantages and disadvantages of this type of electrolyzer are summarized in Table 2.2 below.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unipolar</th>
<th>Bipolar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Construction</td>
<td>- simple, low degree of precision</td>
<td>- complex, high degree of precision of machined parts</td>
</tr>
<tr>
<td>2) Electrolyte</td>
<td>- common throughout cell bank</td>
<td>- restricted to individual cells</td>
</tr>
<tr>
<td>3) Cell connections</td>
<td>parallel</td>
<td>series</td>
</tr>
<tr>
<td>4) Operating</td>
<td>- high current at low voltage</td>
<td>- lower current with higher voltage</td>
</tr>
<tr>
<td>Characteristics</td>
<td>- need for external busbars</td>
<td>- simplified power conditioning</td>
</tr>
<tr>
<td></td>
<td>- need for DC power conditioner</td>
<td></td>
</tr>
<tr>
<td>5) Service</td>
<td>- high reliability</td>
<td>- cells in series makes maintenance and</td>
</tr>
<tr>
<td>Characteristics</td>
<td>- easy removal of individual cells for repair</td>
<td>repair of individual cells costly</td>
</tr>
</tbody>
</table>

Table 2.2: Comparison of unipolar and bipolar electrolyzers [2.2].

2.1.2 Fundamentals of Alkaline Water Electrolysis

Water electrolysis occurs when a direct current is passed between two electrodes immersed in an aqueous electrolyte. Water decomposition requires a voltage across the two electrodes that is greater than the free energy of formation (decomposition) of water plus voltage to overcome polarization due to ohmic and electrode effects. A schematic illustrating the main components of an electrolysis cell is shown in Figure 2.1.
In alkaline water electrolysis, the key electrode reactions are:

**Cathode (hydrogen evolution)** \[ 4e^- + 4H_2O = 2H_2 + 4OH^- \] \{2.1\}

**Anode (oxygen evolution)** \[ 4OH^- = O_2 + 2H_2O + 4e^- \] \{2.2\}

**Overall reaction** \[ 2H_2O = 2H_2 + O_2 \] \{2.3\}

Figure 2.1: Water electrolysis in alkaline media.

The primary electrochemical parameters of water electrolysis are the cell voltage and the cell current density. The cell voltage is a direct measure of the energy required for electrolysis and is related to the cell's efficiency. The cell current density is a measure of the quantity of hydrogen produced per unit area of the electrode structure within the cell and is thus related to capital cost.
2.1.3 Cell Voltage

The theoretical minimum cell voltage, or reversible cell voltage \( (E_{\text{cell}}) \), is the minimum electric energy that must be supplied to the cell for electrolysis to occur. This energy is given by the decrease in free energy, \( \Delta G \), required to decompose water into its elements.

\[
E_{\text{cell}} = \frac{\Delta G}{nF} \quad \{2.4\}
\]

As with any chemical reaction, a change in heat content \( (\Delta H) \) is associated with water electrolysis. If we assume constant pressure and an isothermal process,

\[
\Delta G = \Delta H - \Delta Q_{\text{rev}} \quad \{2.5\}
\]

where, \( \Delta Q_{\text{rev}} = T\Delta S \)

For electrolysis to occur at practical rates, the voltage applied \( (V) \) must exceed the cell voltage \( (E_{\text{cell}}) \). The difference \( V - E_{\text{cell}} \) is needed to overcome both electric and polarization resistances. The corresponding energy is dissipated within the cell as irreversible heat \( (\Delta Q_{i}) \) according to

\[
V - E_{o} = \frac{\Delta Q_{\text{irrev}}}{nF} \quad \{2.6\}
\]

Combining equations \{2.4\}, \{2.5\} and \{2.6\} yields,

\[
V = -(\Delta H - \Delta Q_{\text{rev}} - \Delta Q_{\text{irrev}}) / nF \quad \{2.7\}
\]

This equation states that the reversible endothermic heat requirement \( (\Delta Q_{\text{rev}}) \) is exactly balanced by irreversible heat \( (\Delta Q_{\text{irrev}}) \) liberated due to cell inefficiency when the applied voltage equals \( -\Delta H/nF \). Under these conditions there is no heat exchange and we refer to this voltage as the thermoneutral voltage. Electrolysis cells operating at a voltage \( E \leq V < \Delta H \) voltage must be supplied heat from an external source. Cells operating above the thermoneutral voltage must be cooled. Most electrolyzers operate at
voltages in excess of the $\Delta H$ voltage and hence require cooling. This also means that they will be operating at an efficiency of less than 100%. In electrolysis, the cell voltage is often expressed by the following equation,

$$V = \Delta E + \Sigma \eta + \Delta V_O$$  \hspace{1cm} [2.8]

where, $\Delta E$ = theoretical cell voltage,
$\Sigma \eta$ = anodic and cathodic overvoltages,
$\Delta V_O = I R_o$,
$I$ = cell current, and
$R_o$ = cell resistance.

The anodic and cathodic overvoltages are due to the kinetic limitations of reactions at the respective electrodes. The cell resistance is caused by a number of factors such as electrolyte conductivity, distance between electrodes, diaphragm conductivity and contact resistance between cell components. The major objective in water electrolysis is to optimize $\eta_c$, $\eta_a$ and $I R_o$ to achieve higher efficiency and to do so subject to installed capital cost constraints.

2.1.4 Cell Current Density

The rate of hydrogen production is proportional to the applied current according to:

$$R_g = 4.4 \times 10^{-4} I$$ \hspace{1cm} [2.9]

where, $R_g =$ rate of hydrogen generation (m$^3$/h)
$I =$ current (amps) [2.3]

By dividing both sides of the equation by area, we can determine the rate of hydrogen production per unit cell area, which is a good indicator of capital cost.

$$R_g/A = 4.4 \times 10^{-4} i$$ \hspace{1cm} [2.10]

where, $i =$ A/m$^2$
2.1.5 Mechanism of Hydrogen Evolution Reaction (HER)

There are few reactions that have been more widely studied than that of hydrogen evolution. Dating from the beginning of this century and throughout its history, countless reaction steps have been proposed as part of the overall reaction.

The mechanism of hydrogen evolution today is well described for both acids and bases. In the case of the latter, the steps are described as, water reduction with hydrogen adsorption (Volmer), followed by two parallel competitive steps, electrochemical (Heyrovsky) and chemical (Tafel) desorption:

Volmer: \[ M + H_2O + e^- = MH_{ads} + OH^- \quad b = 120 \text{ mV/dec} \]  \[ \text{(2.11)} \]

Heyrovsky: \[ MH_{ads} + H_2O + e^- = H_2 + M + OH^- \quad b = 40 \text{ mV/dec} \]  \[ \text{(2.12)} \]

Tafel: \[ 2MH_{ads} = 2M + H_2 \quad b = 30 \text{ mV/dec} \]  \[ \text{(2.13)} \]

If the steps are consecutive and one is the rate determining step (r.d.s.), theory predicts (at 25°C) a Tafel slope of 120 mV/decade for reaction (2.11), of 30 mV for reaction (2.13) and provided the coverage by the intermediate \( H_{ads} \) is small, 40 mV for reaction (2.12).

Lasia et al. have proposed that for the Volmer-Heyrovsky mechanism there are always two equivalent solutions that are generated by exchanging the rate constants \( k_i \leftrightarrow k_2 \) and \( k_{-1} \leftrightarrow k_{-2} \) [2.4]. This leaves the experimental curve unchanged with only the hydrogen surface coverage \( \phi \) changing. In the case where there is a decrease in surface coverage with overpotential the Volmer step is assumed to be rate determining. Assuming the Heyrovsky reaction as the rds physically translates to an increase in surface coverage with overpotential.
2.1.6 Effect of Increased Cell Temperature

Increasing the temperature at which an electrolyzer operates leads to a decrease in the theoretical cell voltage. This same increase also causes slight increases in the ΔH voltage. Therefore at higher temperatures more total energy is required but the amount from electric energy is lower. This can be seen in Figure 2.2 below.

![Figure 2.2: Theoretical electrolysis voltage versus temperature.](image)

More importantly, $\eta_a$, $\eta_c$ and $I_R$ decrease at increasing temperatures. This decrease is almost linear and is due primarily to an increase in conductivity. As a result of the advantages of higher operating temperatures, most electrolyzers work at 70 - 90°C. Operation above this temperature range leads to materials problems such as corrosion and the need to pressurize the cell in order to reduce H₂O loss due to evaporation.
Despite these limitations, an increase in temperature improves performance and decreases cost.

### 2.1.7 Effect of Increased Cell Pressure

Increasing the cell pressure of an electrolyzer is a considerable advantage because the O\textsubscript{2} and H\textsubscript{2} can be delivered at pressure with little energy penalty. In considering the reversible thermodynamics, the minimum energy for pressurization of gases from the following reaction,

\[ 2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2 \tag{2.14} \]

can be calculated from,

\[ \Delta E = (3RT/4F) \ln P \tag{2.15} \]

where, \( \Delta E \) = change in cell voltage due to pressure
\( R \) = gas constant
\( T \) = temperature (K)
\( F \) = Faraday’s constant
\( P_2/P_1 \) = ratio for which \( \Delta E \) applies [2.1]

Using the above formula the voltage increase required to deliver gases at 10 atm of pressure would be 44 mV, while the voltage increase to deliver gases at 100 atm of pressure would be only 88 mV. In practice, the voltage penalty would be even less since the reversible thermodynamics only apply to reversible electrode processes. Therefore, if \( \eta_c \) or \( \eta_a \) is large most of the activation energy would be recovered as pressure volume work. Also, the volume of evolving gas bubbles decreases as the pressure increases leading to a reduction in IR\textsubscript{O}.

Increasing cell pressure is, however, limited by the following problems,

i) difficulties in separating and containing the gases,
ii) materials problems such as hydrogen embrittlement, and
iii) at higher pressures H₂ and O₂ will more rapidly diffuse across the diaphragm and recombine before they leave the system creating inefficiency losses as high as 1-10% of H₂ generated.

2.2 Means of Reduction of Overpotential

2.2.1 Electrocatalysis

As was described in §2.1.3, the voltage, ΔV, applied across an electrolysis cell can be described by the following expression,

\[ ΔV = ΔE + Ση + ΔV_Ω \]  \hspace{1cm} (2.16)

where,  
ΔE = theoretical cell voltage,  
Ση = total overpotential,  
ΔV_Ω = IR_Ω,  
I = cell current, and  
R_Ω = cell resistance.

Electrocatalysis affects that part of η that depends on the electrode material and is only one of several ways of improving the rate of an electrochemical process. Other means of improving this process usually involve the cell as a whole. As with all these methods, the purpose of electrocatalysis is to reduce the voltage applied across the cell, ΔV, in order to reduce the operational cost.

A reduction in ΔV is accomplished by increasing the true surface area of an electrode or by changing the catalytic nature of the overpotential for the HER, i.e. a change in i_0/β. Therefore, evaluation of electrode materials is accomplished by either comparing the apparent current density at a given electrode potential (chronoamperometry) or more commonly by comparing the overpotential at a given current density (chronopotentiometry). This is coupled with steady-state potentiostatic polarization to determine changes in Tafel parameters and hence, kinetics of the catalytic process.

Increasing the surface area can improve electrode performance as much as a reduction in overpotential and this is one of the procedures
adopted in practice to activate cathodes [2.5]. While the reduction of $\Delta V$ related to an increase in surface area has a decisive effect, this can only be considered as an electrocatalytic effect if there is an accompanying variation in the surface active sites. Therefore, two main factors have to be considered when evaluating electrode materials; geometric factors and electronic factors.

2.2.1.1 Electrocatalytic Activity

The hydrogen evolution reaction (HER) is the only reaction for which a complete theory of electrocatalysis has been developed [2.6]. This is primarily due to the limited number of steps involved and the formation of possibly only one type of intermediate. The theory predicts that electrocatalytic activity depends on the heat of adsorption of the intermediate formed on the surface. This gives rise to the well known "volcano" curve shown below.

![Volcano curve for hydrogen generation on metals.](image)

**Figure 2.3** Volcano curve for hydrogen generation on metals.
Predictions based on the volcano curve have been confirmed experimentally and this remains the main predictive basis for activity [2.7]. The volcano curve is based on the performance of simple metals and the heat of adsorption is the main factor which turns out to be responsible for change in the activity from metal to metal.

However, it is difficult to identify the properties of the metals that give rise to the magnitude of the heat of adsorption. A number of correlations have been proposed to explain this based primarily on the different electronic and structural properties. It is seen that metals in the same group occupy the same relative position on the volcano curve. Discovering which factors predominate and their relative contribution to the electronic and chemical properties is of paramount importance.

While correlations do exist for simple metals it becomes much more difficult to make predictions for composite materials. Cathode activation has two aims: to replace active but expensive materials (e.g., Ru, Ir, Pt) with cheaper ones or to enhance the activity of cheaper materials so as to approach the electrocatalytic activity of more expensive ones. For simple metals finding a new material satisfying the above requirements is unlikely since the volcano curve fixes a metal's position. Therefore, activation of pure metals can only be achieved by modifying its surface structure so as to enhance its surface area, change its $\Delta H_{\text{ads}}$ and/or produce a different mechanism for HER.

Composite materials attempt to take advantage of synergetic effects which are described as, effects that are caused by a reciprocal influence between two or more components so as to obtain a material whose activity exceeds that of either of the pure components [2.8]. This effect usually involves intimate electronic interactions between the various components leading to a change in their electronic structures. It has been proposed that a metal deprived of part of its valence electrons may behave as an element on its left in the periodic table [2.9]. While some synergetic effects have been demonstrated on a laboratory scale they have not yet reached industrial applicability [2.10, 2.11, 2.12].
2.2.1.2 Factors of Activity Enhancement

The following is a list of some of the approaches used in trying to increase the electrocatalytic activity of cathodes for the HER. The approaches are fundamentally interesting but also give insight into the factors responsible for the activity of industrial electrodes.

2.2.1.2.1 Surface State

The change in morphology of the surface state of an electrode without the addition of foreign materials can lead to an enhancement in the apparent activity of cathodes. This includes merely increasing the surface area by mechanical means [2.13]. This is also generally the precursor to coating for both activated anodes and cathodes. Alternatively, the metal can be co-deposited with ultrafine particles of silicon carbide to form a rougher surface, as in the case of nickel. The roughening of electrode surfaces is a long established means of increasing electrode activity.

Generally, the effect of roughening corresponds just to an increase in surface area. The investigation of active sites on evaporated films of nickel has shown that the mechanism does not change, with the activity corresponding to the number of active sites [2.14]. However, other observations have been made. In the case of mechanically renewed surfaces, an increase in activity was seen for both catalytic and non-catalytic metals. This increase corresponds to a decrease in activation energy suggesting the M-H adsorption bond is modified by the mechanical treatment.

Although there has been evidence to suggest the reduction of Tafel slopes at low overpotentials for mild steel due to roughening of the surface, no effects of simple roughness (except surface effects) has been observed for the electrocatalytic activity of nickel.

One of the most useful forms of nickel is Raney Ni which is formed by leaching Al or Zn from Ni-Al and Ni-Zn alloys in solution. The resultant properties seem to depend heavily on the nature of the alloy prior to leaching. Raney Ni which can be prepared by a number of methods, such as low pressure plasma spraying, shows lower Tafel slopes suggesting a real catalytic effect [2.15]. On such highly porous Ni it is possible that the
proportion of surface active sites (at the edges and peaks of crystallites) increases considerably.

It has been proposed that different crystallographic orientations might influence the electrocatalytic activity of a material. When comparing crystal faces of various metals, only platinum showed a significant increase in electron work function and hence exchange current density from (111) > (100) > (110) at low surface coverage [2.16]. In the case of nickel [2.17], there is only a minor influence of the crystal structure on the electron work function from (111) > (100) > (110).

Ion implantation is often suggested as a means of enhancing the electrocatalytic activity of a cathode. This is accomplished by either disrupting the surface structure of the catalyst or by placing active atoms on inactive matrix sites. While ion implantation provides a way of introducing small amounts of more expensive materials, for the purposes of observing surface state effects self-implantation or ion beam bombardment is the most appropriate approach. Implantation of Ni on Ni has led to modest enhancement of the surface area but not to electrocatalytic effects [2.18]. Other materials such as platinum, however, have shown an increase in activity for hydrogen evolution.

2.2.1.2.2 In-situ Additions (Adatoms)

Unlike processes such as ion implantation, adatoms can be deposited in-situ on the surface of the electrode at an underpotential. The mechanism of adsorption is dependent on potential and is well documented in the literature [2.19]. The choice of metals to be deposited in-situ is usually limited to the elements that can be deposited in the underpotential region. This restricts the choice of materials to mostly post-transition, sp-metals.

Inactive adatoms on noble metals have little impact on the practical problems of cathode activation, because deactivation is the most common occurrence and adatoms are not stable in the absence of ions in solution where a finite level of precursors must be maintained.
2.2.1.2.3 Crystallites

In terms of electrode surfaces, the transition from adatoms to bulk solids involves two intermediates; crystallites (microcrystals) and thin films. Both of these are widely used to modulate the electrocatalytic properties of cathodes primarily due to the low expenditure of active materials.

When dealing with dispersed catalysts there are two features that are paramount in determining effect on the electrode. These are the particle size effect (degree of dispersion) and the nature of the support (metal-support interaction). Properties of microdeposits, as well as, details about their preparation and characterization have been intensively studied, most notably by Kinoshita [2.20]. All investigations have shown that the properties of the crystallites differ considerably from those of the bulk metal, as well as, adatoms and thin films.

Electrocatalytic effect of the small crystallites has been attributed primarily to metal-support interactions. In precious metals, high electron work functions result in the injection of electrons into the crystallites thus modifying the electron density, which becomes a function of size. As the particle size decreases, the ratio of the number of atoms at the surface to those in the bulk increases with a parallel decrease in the average coordination number for the metal atom, something that is also expected to be a factor in electrocatalysis [2.21].

2.2.1.3 Specific Materials

This section will outline some of the materials that have been used as electrocatalysts for the hydrogen evolution reaction, as well as, some potential materials for future use.

2.2.1.3.1 Nickel

Nickel is the most widely used material for cathodes both in the activated and non-activated states. The mechanism for hydrogen evolution on nickel is well documented [2.22]. The Tafel slope is usually around 120 mV/decade while the surface is heavily covered with adsorbed hydrogen. This corresponds, in alkaline solutions, to the rate determining step (r.d.s.)
being the primary discharge of water (Equation (2.11)). Although for the case of Na-based alkaline solutions it has been proposed that the intermediate of the primary discharge is probably Na_{ads} [2.5]:

\[
\text{Na}^+ + e^- = \text{Na}_{ads}
\]  \hspace{1cm} (2.17)

followed by,

\[
\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H}_{ads}
\]  \hspace{1cm} (2.18)

As was previously discussed in §2.1.5, Lasia et.al. have also proposed that for the Volmer-Heyrovsky mechanism there are always two equivalent solutions that are generated by exchanging the rate constants \(k_1 \leftrightarrow k_2\) and \(k_{-1} \leftrightarrow k_{-2}\) [2.4]. This leaves the experimental curve unchanged with only the surface coverage changing. In the case where there is a decreasing surface coverage of hydrogen with overpotential, the Volmer step is assumed to be rate determining. Assuming the Heyrovsky reaction as the rds physically translates to an increase in surface coverage with overpotential.

The literature values for Tafel slopes and exchange current densities for nickel at a variety of temperatures and electrolyte concentrations are given in Table 2.3 below.

<table>
<thead>
<tr>
<th>Tafel Slope (b) mV/dec</th>
<th>Exchange Current Density (i_0) A/cm²</th>
<th>Temperature (K)</th>
<th>Solution</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>115 ± 9</td>
<td>1.8 ± 1.6 x 10⁻⁶</td>
<td>298</td>
<td>1M NaOH</td>
<td>2.23</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>303</td>
<td>7.6M KOH</td>
<td>2.24</td>
</tr>
<tr>
<td>110</td>
<td>1.26 x 10⁻⁶</td>
<td>298</td>
<td>1M NaOH</td>
<td>2.25</td>
</tr>
<tr>
<td>80</td>
<td>6.0 x 10⁻⁵</td>
<td>301</td>
<td>7.6M KOH</td>
<td>2.26</td>
</tr>
<tr>
<td>79-80</td>
<td>1.4 x 10⁻⁴</td>
<td>325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>4.1 x 10⁻⁴</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>3.55 x 10⁻⁵</td>
<td>303</td>
<td>7.6M KOH</td>
<td>2.27</td>
</tr>
<tr>
<td>111</td>
<td>4.47 x 10⁻⁵</td>
<td>323</td>
<td></td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>7.08 x 10⁻⁵</td>
<td>343</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>1.41 x 10⁻⁴</td>
<td>363</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3: Literature values for HER on nickel.
The activity of smooth nickel cathodes decreases under prolonged cathodic load. This has been primarily linked to hydrogen adsorption into the nickel metal lattice which can reach high levels of concentration [2.28].

As with all transition metals in alkaline solutions nickel forms oxides. The role of surface oxides in the cathodic range of potentials depends primarily on the conditions under which they are formed. It has been shown that a reducible layer of hydroxide \( \text{Ni(OH)}_2 \) or even oxohydroxide \( \text{NiOOH} \) can improve the electrocatalytic activity of the cathode [2.29].

2.2.3.3 Amorphous Alloys

The electronic properties of solids depend strongly on crystal structure. Thus, the transition from a crystalline material to an amorphous one results in a change in both electronic and geometric surface properties. The high electrocatalytic activity of amorphous alloys was first recognized in their catalysis of hydrogenation reactions [2.30]. Studies have also been performed on the recombination reaction, although it is unsure whether or not the amorphous state is responsible for the electrocatalytic activity [2.31].

Amorphous alloys have compositionally homogeneous surfaces with no grain boundaries. They have, therefore, been targeted as ideal surfaces for studying elementary catalytic reactions since they can be produced with controlled electronic properties. Amorphous alloys also have problems associated with them such as,

i) low surface area,
ii) presence of surface oxides, and
iii) tendency to crystallize at high temperatures.

Although amorphous alloys have been recognized for years as unusually corrosion resistant materials, only recently have they been considered for hydrogen evolving electrodes.

Investigations by Lian et al. [2.32] have focused on on number of factors which could influence the electrocatalytic activity of amorphous alloys, such as the effect of metalloids and the Ni/Co ratio. Metalloids are
generally used as glass formers in amorphous alloys and the addition of large quantities of either phosphorus, boron, silicon or carbon is necessary for the formation of the amorphous structure by rapid quenching from the melt [2.33]. While these metalloids have been shown to affect the corrosion rate of amorphous alloys (specifically, Fe-Cr alloys show decreased corrosion rates in the order Si, B, C and P) they have little effect on the electrocatalytic activity as can be seen in Table 2.4. Similarly, the electrocatalytic activity of Ni/Co amorphous alloys shows little dependence on the ratio.

<table>
<thead>
<tr>
<th>System</th>
<th>Tafel Slope (b) mV/decade</th>
<th>Exchange Current Density ( i_0 ) mA/cm(^2)</th>
<th>Temperature (K)</th>
<th>Solution</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}<em>{50}\text{Ni}</em>{22}\text{Si}<em>{15}\text{B}</em>{10} )</td>
<td>174.4 ± 7.4</td>
<td>5.4 ± 0.2</td>
<td>302</td>
<td>1M KOH</td>
<td>2.32</td>
</tr>
<tr>
<td>( \text{Ni}<em>{50}\text{Co}</em>{20}\text{Si}<em>{15}\text{B}</em>{10} )</td>
<td>178.0 ± 6.3</td>
<td>5.7 ± 0.2</td>
<td>302</td>
<td>1M KOH</td>
<td>2.32</td>
</tr>
<tr>
<td>( \text{Ni}<em>{50}\text{Co}</em>{23}\text{P}<em>{15}\text{B}</em>{10} )</td>
<td>144.0 ± 9.8</td>
<td>5.8 ± 0.4</td>
<td>302</td>
<td>1M KOH</td>
<td>2.32</td>
</tr>
<tr>
<td>( (\text{Ni}<em>{90}\text{Pd}</em>{10})<em>{80}\text{P}</em>{20} )</td>
<td>133 ± 7</td>
<td>0.044 ± 0.011</td>
<td>302</td>
<td>7M KOH</td>
<td>2.12</td>
</tr>
<tr>
<td>( (\text{Ni}<em>{95}\text{Pd}</em>{5})<em>{80}\text{P}</em>{20} )</td>
<td>126 ± 13</td>
<td>0.342 ± 0.062</td>
<td>302</td>
<td>7M KOH</td>
<td>2.12</td>
</tr>
<tr>
<td>NiCr(<em>2)P(</em>{20}) *</td>
<td></td>
<td>0.3</td>
<td>302</td>
<td>1M HCl</td>
<td>2.34</td>
</tr>
<tr>
<td>NiCr(<em>3)P(</em>{20}) *</td>
<td></td>
<td>0.15</td>
<td>302</td>
<td>1M HCl</td>
<td>2.34</td>
</tr>
<tr>
<td>NiCr(<em>{10})P(</em>{20}) *</td>
<td></td>
<td>0.1</td>
<td>302</td>
<td>1M HCl</td>
<td>2.34</td>
</tr>
</tbody>
</table>

* Exchange current densities \( \eta_{250} \) calculated from polarization tests at scan rates of 10 mV/minute.

**Table 2.4:** Literature values for HER on various amorphous alloys.
2.3 In-situ Additions/Homogeneous Catalysis

Another means of reduction of the cathodic overpotential is by in-situ additions, of which homogeneous catalysis is an example. In-situ activation can be achieved by dissolving a substance into the electrolyte. As with other activation techniques, the resultant activation is strongly dependent on the precursors. In this case activation will depend on the concentration of the species in solution and on the potential at which the addition is made [2.35]. In-situ activation is especially attractive since it doesn’t require a separate surface activation step which adds considerably to the cost of the electrode. It’s applicability is sensitive to the conditions of electrolysis since the additions might interact with the product gases or might turn out to be unwanted impurities in the electrolyte which would have to be removed from the wastewater at some expense. Although the presence of the additive in solution can prevent deactivation, maintaining the desired concentration could pose a problem. Various species have been proposed for in-situ activation with varying degrees of success. Table 2.5 gives relevant Tafel parameters from in-situ additions found in the literature, as well as, the parameters for materials related to this study.
<table>
<thead>
<tr>
<th>Addition ppm (x10³)</th>
<th>Solution</th>
<th>Temperature (K)</th>
<th>Tafel Slope (b) mV/dec</th>
<th>Exchange Current Density (iₒ) A/cm²</th>
<th>Substrate</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe = 0.014</td>
<td>7.6M KOH</td>
<td>343</td>
<td>79</td>
<td>1.3 x 10⁻⁴</td>
<td>Co</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>1.4 x 10⁻⁴</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>95</td>
<td>2.1 x 10⁻⁴</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75</td>
<td>6.0 x 10⁻⁵</td>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>Mo = 0.024 Fe = 0.024</td>
<td>7.6M KOH</td>
<td>343</td>
<td>151</td>
<td>4.5 x 10⁻⁴</td>
<td>Co</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>154</td>
<td>8.1 x 10⁻⁴</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>182</td>
<td>1.5 x 10⁻³</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>163</td>
<td>7.2 x 10⁻⁴</td>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>NiSO₄ = 80 Na₂MoO₄ = 20</td>
<td>6M KOH</td>
<td>353</td>
<td>112</td>
<td></td>
<td>mild steel</td>
<td>2.38</td>
</tr>
<tr>
<td>NiSO₄ = 80 Na₂WO₄ = 20</td>
<td>6M KOH</td>
<td>353</td>
<td>25</td>
<td></td>
<td>mild steel</td>
<td>2.38</td>
</tr>
<tr>
<td>NiSO₄ = 80 ZnSO₄ = 40</td>
<td>6M KOH</td>
<td>353</td>
<td>50</td>
<td></td>
<td>mild steel</td>
<td>2.38</td>
</tr>
<tr>
<td>NiSO₄ = 80 FeSO₄ = 20</td>
<td>6M KOH</td>
<td>353</td>
<td>25</td>
<td></td>
<td>mild steel</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Table 2.5: HER parameters for chromium and various in-situ additions and related methods.
<table>
<thead>
<tr>
<th>NiSO₄ = 80</th>
<th>6M KOH</th>
<th>353</th>
<th>35</th>
<th>mild steel</th>
<th>2.38</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄ = 20</td>
<td>6M KOH</td>
<td>353</td>
<td>150</td>
<td>mild steel</td>
<td>2.38</td>
</tr>
<tr>
<td>molybdate</td>
<td>5M NaOH</td>
<td>298</td>
<td>80</td>
<td>Pt</td>
<td>2.39</td>
</tr>
<tr>
<td>tris-Co complex</td>
<td>5M NaOH</td>
<td>298</td>
<td>110</td>
<td>Pt</td>
<td>2.41</td>
</tr>
<tr>
<td>Molybdate + tris-Co</td>
<td>5M NaOH</td>
<td>298</td>
<td>100</td>
<td>Pt</td>
<td>2.39</td>
</tr>
<tr>
<td>none</td>
<td>H₂SO₄ + Na₂SO₄</td>
<td>298</td>
<td>120</td>
<td>Cr</td>
<td>2.40</td>
</tr>
<tr>
<td>none</td>
<td>1N H₂SO₄</td>
<td>298</td>
<td>107</td>
<td>Cr</td>
<td>2.41</td>
</tr>
<tr>
<td>none</td>
<td>1N H₂SO₄</td>
<td>298</td>
<td>123</td>
<td>Cr</td>
<td>2.42</td>
</tr>
<tr>
<td>none</td>
<td>1N H₂SO₄</td>
<td>298</td>
<td>126</td>
<td>Cr</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Table 2.5: HER parameters for chromium and various in-situ additions and related methods (cont.).
2.3.1 Role of In-Situ Additions in HER

The first reported electrocatalytic effect for the HER by in-situ activation was made by Jaksic et al. in the mid-seventies [2.44]. This was achieved by the addition of cobalt salts and molybdates in alkaline solution to various substrates (mild steel, nickel, graphite, titanium). Further improvements to the electrocatalytic effect were made with the synergetic Mo-Co pair which became possible through the development of stable cobalt complexes. Specifically, tris-ethylenediamine cobalt (III) chloride which in alkaline solutions precipitates regular Co-ions. The electrocatalytic effect that was obtained by this pair even at small concentrations was remarkable; Tafel lines were shifted to more positive values and the slopes were often less than 30 mV/dec. The specific values are listed in Table 2.5. The theoretical considerations proposed for this activation are based on d-electron effects of the transition metals.

More recently, Huot and Brossard have done extensive research into the effect of molybdate additions on the HER in 30 wt.% KOH at 70°C on various substrates. The Tafel parameters are presented in Table 2.5. Their work has focused on industrial electrolysis applications and their associated parameters and has included the effects of metallic impurities.

The preliminary investigations focused on nickel and its associated deactivation at constant current. Figure 2.4 illustrates the time dependence of the cathode potential both with (line b) and without (line a) molybdate addition.
Figure 2.4: Time dependence of nickel cathode (curve a) and nickel cathode with in-situ addition of molybdate (curve b) [2.45].

The above figure is divided into two distinct regions labelled I and II. The deactivation in region I is associated with $\beta$-hydride formation (hydrogen penetration into the lattice), while region II is associated with the electrodeposition of an iron-rich deposit on the nickel electrode. With an increase in time and iron concentration, the deactivation in region II is followed by a slight reactivation process.

In order to counteract deactivation, molybdate additions were made prior to the deactivation process. Figure 2.4, above, illustrates the activation effect of the molybdates (curve b). This is accomplished through the direct electrodeposition of an active metallic form of molybdenum with mixed metals which arise from the indirect reduction of deposited intermediate oxides by the adsorbed atomic hydrogen during discharge [2.45]
2.3.2 Mechanism of Homogeneous Catalysis

There are two primary types of industrial catalysis, heterogeneous and homogeneous. In heterogeneous catalysis, the reactants and the catalyst are in different phases. Usually, the catalyst is solid and the reactants are either gases or liquids. In homogeneous catalysis, the reactants, products and catalyst are all dispersed in the same phase, usually liquid [2.46].

Homogeneous catalysts when added to solution can:

i) produce either metastable complexes in solution, or
ii) adsorb directly on the electrode surface.

The overall effect of the addition is the lowering of the cell voltage through inhibition of competing reactions.

Little has been reported in the literature to account for the mechanism of homogeneous catalysis. While there exist numerous examples of homogeneous catalysis industrially these are specific processes that are unrelated to the systems being investigated here.

There have, however, been some investigations into the addition of chromates into alkaline solution to improve the corrosion resistance of iron and iron alloys. Specifically, Calvo and Pallotta have proposed mechanisms by which chromates in solution deposit on the electrode surface. Focusing their experiments on voltammetry and XPS they identified two forms of chromium species at the surface of iron electrodes treated in alkaline chromate. On top of the passive film chromic hydroxide was found while deeper chromium centers were found entrapped within the passive layer. The latter was determined to be a permanent modification of the surface while the former chromium species was easily removed anodically from the surface as a soluble chromate. The proposed reaction mechanisms were of the form,

\[ \text{i) } \text{CrO}_4^{2-} \leftrightarrow \text{Cr(III)} \text{ surface} \quad \{2.19\} \]
\[ \text{ii) } \text{CrO}_4^{2-} \leftrightarrow \text{Cr(III)*} \quad \{2.20\} \]
\[ \text{iii) } \text{Cr(III)*} \leftrightarrow \text{Cr(VI)*} \quad \{2.21\} \]
where, * = entrapped in the inner oxide

Reactions \(\{2.19\}\) and \(\{2.20\}\) are parallel reduction reactions. Reaction \(\{2.21\}\) is described as a redox transformation of a stable form of chromium structurally mixed with iron and oxygen in an inner surface layer. The other form of chromium as described by reaction \(\{2.19\}\) would be a more external hydrous Cr(III) precipitate arising from the reductive precipitation of chromate on top of the inner chromium containing layer and requiring a source of chromate in solution to be observed.

2.3.3 Role of Homogeneous Catalysis in HER

Little has been cited in the literature to explain the role of homogeneous catalysis in the HER. The problem lies in the fact that no one has identified homogeneous catalysis as a possible method for catalyzing the HER.

Since homogeneous catalysis is a dynamic process involving metastable ions in solution and surface species its role would be one of inhibiting competing reactions. Specifically, with reference to the work of Calvo and Pallotta, homogeneous catalysis could catalyze the HER through a cyclic reductive precipitation of chromate followed by dissolution of this surface chromium species and the liberation of hydrogen.

2.4 Surface Analysis Techniques

2.4.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states of the chromium on the electrode surface. The following table is a summary of the literature values for the binding energies of chromium. These values were used as a reference for the experimental values that were obtained.
Referencing Material: "*values correspond to metal salts of sodium and potassium"

**Table 2.6: XPS data for the binding energies of chromium.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding Energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr2p 1/2 Cr</td>
<td>588.4*, 589.1, 583.3</td>
<td>2.47, 2.48, 2.49</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>586.7, 585.5</td>
<td>2.48, 2.49</td>
</tr>
<tr>
<td>CrOOH</td>
<td>586.9, 586.2</td>
<td>2.48, 2.49</td>
</tr>
<tr>
<td>CrO3</td>
<td>587.3</td>
<td>2.49</td>
</tr>
<tr>
<td>CrO4 2-</td>
<td>588.5</td>
<td>2.49</td>
</tr>
<tr>
<td>Cr2p3/2 Cr</td>
<td>579.3*, 579.8, 574.1</td>
<td>2.47, 2.48, 2.49</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>576.8, 576.3</td>
<td>2.48, 2.49</td>
</tr>
<tr>
<td>CrOOH</td>
<td>577.0, 577.0</td>
<td>2.48, 2.49</td>
</tr>
<tr>
<td>CrO3</td>
<td>578.1</td>
<td>2.49</td>
</tr>
<tr>
<td>CrO4 2-</td>
<td>579.3</td>
<td>2.49</td>
</tr>
</tbody>
</table>
3.0 Experimental Procedure

3.1 Materials and Sample Preparation

The following is a summary of the preparation of the various materials used for electrochemical testing.

3.1.1 Commercial Ni-200

Commercial Ni-200 was used as the standard testing material for comparison with the amorphous alloy. Small coupons of Ni-200 (~2cm x 1.5cm) were sectioned from a larger sheet to produce the size required to make electrodes. The nominal composition of Ni-200 is given in Table 3.1 below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>99.5</td>
</tr>
<tr>
<td>C</td>
<td>0.08</td>
</tr>
<tr>
<td>Mn</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.13</td>
</tr>
<tr>
<td>Si</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 3.1: Nominal composition of commercial Ni-200 [3.1].

The Ni-200 coupons were progressively ground on 400 and 600 grit SiC paper (Leco GP-25 Grinder-Polisher, model 023-200, serial #3061). The coupons were then polished to a 1 μm diamond paste finish (Buehler Metaserve Grinder-Polisher, model 95c 2345-160, serial #406 GPT 691) using first 6 μm DP-Paste followed by 1 μm MicroMetallurgical diamond paste.

The coupons were then electrically contacted to a copper wire using solder wire (Kester, 3mm wire, 50Pb50Sn). A select area of the copper wire/Ni-200 coupon (now referred to as an electrode) was masked off using Amercoat 90HST™ Epoxy Resin and Cure. This was applied in three thin coatings at 24 hour intervals to allow for curing. The exposed area of the
electrode was measured by image analysis using an Olympus LZ-II Stereo Macrograph with a Leco Video Camera Module (model XC-77, serial #38512) and IA-3001 Image Analysis Software.

3.1.2 Amorphous Alloy

The amorphous alloy used was produced by melt spinning [Keryn Lian, Master's Thesis, 1991]. Its nominal composition was Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$. The alloy came in ribbon form and was sectioned into smaller coupons (~1cm x 2cm x 40 μm thickness). These coupons were polished down to a 1 μm diamond paste finish following the same protocol as for the Ni-200. The coupons were then soldered to a thin nickel wire, far enough away to prevent crystallization of the ribbon and selected areas were masked off following the procedure described for Ni-200. The exposed areas were then measured using image analysis.

3.2 Electrochemical Measurements

3.2.1 Electrochemical Cell

The electrochemical cell used for experimentation was a standard three electrode cell comprised of a reference electrode, a counter electrode and a working electrode. The cell was made of Teflon due to dissolution of silicates from glassware in highly alkaline solutions [3.2]. A diagram of the cell and its components is shown in Figure 3.1.
The reference electrode used was made of Hg/HgO paste in 1M KOH contained in an HDPE tube. Due to the high cell temperatures during testing (70°C) the reference electrode was removed from the cell and connected via a salt bridge. All measured values are reported versus the Hg/HgO reference electrode. The counter electrode was made of a platinum mesh (0.0762 diameter wire, ~10mm x 25mm) spot welded to a platinum wire. The electrode was placed inside a teflon tube (~1/2 inch diameter) in order to reduce oxygenation during testing. The working electrode was the material to be investigated.
3.2.2 Electrolyte

3.2.2.1 Non-electrolyzed Electrolyte

The electrolyte used for electrochemical testing was prepared using Type I water (Nanopure II, 18.3 MΩ-cm, Barnstead) and potassium hydroxide (KOH) pellets (BDH Inc., Analar Grade, Minimum Assay 85.0%). An electrolyte concentration of 8M was used throughout testing.

3.2.2.2 Pre-electrolyzed Electrolyte

The Analar Grade KOH pellets used to make the electrolyte contain impurities (most notably Fe and Mo) which can affect the results of the electrochemical tests being performed [3.3]. In order to remove or minimize the effect of these impurities, a pre-electrolysis technique was used. The electrolyte was subjected, galvanostatically, to a potential of -1700 mV vs. Hg/HgO using platinum mesh electrodes as the working, reference and counter electrodes. The electrodes were removed after a 24 hour period and cleaned in nitric acid. The technique was then applied for a second 24 hours at which point the electrolyte was ready for testing.

3.2.3 Electrochemical Instrumentation

A schematic of the equipment used for electrochemical testing is shown in Figure 3.2.
Figure 3.2: Schematic of experimental setup.

The following is a list of the instruments illustrated above.

Potentiostat/Galvanostat: Hokuto Denko Ltd. HAB-151
Serial #A2737

Data Acquisition System: IOTECH Multiscan 1200
Serial #108776

Data Acquisition Card: IOTECH IEEE488

Software Program: Multiscan/1200 v1.0 (Multiview v1.0)

Immersion Bath Heater: Cole Parmer Polystat
Heater/Circulator (Model #1253-00)

Computer: P133 Intel CPU
The Teflon cell was placed into a Techne water bath which was heated to 70°C. The working, reference and counter electrodes were connected to the potentiostat/gavanostat. The required electrochemical parameters (current for chronopotentiometry and potential step for Tafel) were input manually into the potentiostat/galvanostat. These were then output to the cell and simultaneously recorded by the data acquisition system. The data was directly uploaded to the computer for processing. A minimum of three tests were run at each parameter being investigated to ensure reproducibility and to allow for statistical evaluation of error.

3.2.4 Chronopotentiometry

Chronopotentiometry is defined as, "the basic form of controlled current electrolysis" [3.4]. As the name implies, a current is passed between the working and counter electrodes in solution and the potential of the working electrode is monitored as a function of time. A typical chronopotentiogram is shown in Figure 3.3.

![Figure 3.3: A schematic of a chronopotentiogram.](image)
The current applied during these experiments was dependent on the surface area of the electrodes as a cathodic current density of 250 mA/cm² was chosen in order to best reproduce industry values. Prior to experimentation the cell was deaerated for 1 hour using argon gas. The working electrode was then introduced and the cell was deaerated for a second hour. The electrode was then cathodically cleaned for 2 hours at a potential of -1350 mV vs. Hg/HgO. The required current was then applied and the system was allowed to reach steady state (~ 24 hours). The catalyst was then added in solution form and the system was again allowed to equilibrate. Depending on the specific data being collected, the testing procedure followed one of:

i) Tafel, chronopotentiometry, Tafel,
ii) chronopotentiometry, SEM, or
iii) chronopotentiometry, XPS.

3.2.5 Steady State Potentiostatic Measurements (Tafel)

A Tafel test is a form of steady state potentiostatic measurement. In this test a potential step is applied and the resultant current response is measured. Figure 3.4 below illustrates the typical current decay that occurs at each increase in potential.
Tafel measurements were made both pre- and post-testing for all of the materials being investigated. Before testing, the samples were cathodically cleaned for 2 hours at a potential of -1350 mV versus Hg/HgO to remove any surface oxides. Since the hydrogen evolution reaction (HER) was the reaction of interest, the electrodes were scanned from potentials of -900 to -1500 mV versus Hg/HgO. The scan rate used was limited by the potentiostat to 6 mV/minute. The samples were subjected to a minimum of three cycles and the Tafel data was plotted as log $i_0$ versus cathodic overpotential ($\eta_c$). From this plot it was then possible to calculate the Tafel slope (b) which was used to determine the hydrogen evolution reaction (HER) limiting step. A schematic of a Tafel plot is shown in Figure 3.5.
3.3 Analytical Techniques

3.3.1 Numerical Analysis

In order to determine the error associated with the various tests, the average of at least three tests was used to determine the standard deviations. For calculations that required line fitting, the least squares method of linear regression was used. For the Tafel experiments, the exchange current density \( i_0 \) and the tafel slope \( b \) were calculated using,

\[
\eta = b \log \left( \frac{i}{i_0} \right) \tag{3.1}
\]

where, \( \eta \) is the overpotential.
3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX) was performed on a Hitachi S-2500 scanning electron microscope with a LINK EDX system. The working parameters are given in Table 3.2.

<table>
<thead>
<tr>
<th>Function</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating Voltage</td>
<td>20 keV</td>
</tr>
<tr>
<td>Emission Beam Current</td>
<td>100 μA</td>
</tr>
<tr>
<td>Tilt Angle</td>
<td>15°</td>
</tr>
<tr>
<td>Working Distance</td>
<td></td>
</tr>
<tr>
<td>i) Photomicrographs</td>
<td>15 ± 3 mm</td>
</tr>
<tr>
<td>ii) EDX</td>
<td>30 - 35 ± 5 mm</td>
</tr>
</tbody>
</table>

Table 3.2: Scanning electron microscope settings.

The samples were removed from the cell after testing and were rinsed with Type I water and air dried. They were then mechanically attached to the SEM stage. In order to ensure proper conductivity and in order to reduce charging effects the samples were contacted to the stage using carbon paint.

SEM was used to characterize the electrode surfaces both prior to and post-testing. SEM micrographs were taken in order to determine the surface morphology of the electrodes and EDX was used to determine the elemental composition of the surface and of certain specific surface features.

3.3.3 X-ray Photoelectron Spectroscopy (XPS)

XPS was performed on the samples post-testing to determine the surface state. Low resolution scans were used to determine the surface film constituents and their relative abundance and high resolution scans were used to determine the specific oxidation states of the species present.

X-ray photoelectron spectroscopy was carried out using a Leybold MAX 200 system. Unmonochromatized Mg-Kα radiation (1253.6 eV) was produced at a dual anode X-ray source operating at 15 kV and a 20 mA
emission current. The binding energy scale was calibrated to Ag 3d$_{5/2}$ and Cu 2p$_{3/2}$ peaks 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.
4.0 Results

This section will present the results that were obtained from the experimental procedure which was outlined in § 3.0. In all cases, the electrochemical results from chronopotentiometry and steady-state potentiostatic polarization will be shown first, followed by surface analysis results in the form of SEM micrographs and EDX spectra.

The results for Ni-200 will be presented first and will serve as a standard against which the nickel-based amorphous alloy will be compared. For both cathode materials results for catalyst additions of 100, 50 and 10 p.p.m. will be shown first. Concentrations above and below this range (5 and 500 p.p.m.) will then be presented to confirm the trends that were observed. The results of the effect of the catalyst concentration will then be tabulated.

Results from tests to determine the effect of electrolyte impurities and the effect of the method of addition will include chronopotentiometry data and SEM micrographs with accompanying EDX spectra.

Finally, x-ray photoelectron spectroscopy (XPS) results for the catalyst modified electrode surfaces will be presented.
4.1 Commercial Ni-200

This section will present the results obtained for the Ni-200 samples. Figure 4.1 shows the experimental curves obtained from the steady-state potentiostatic polarization (Tafel) tests. Figure 4.2 shows the standard Tafel plot obtained from this data. The Tafel curve is the average of the three tests shown and the standard deviation is represented by the error bars.

Figure 4.3 shows the SEM micrograph for an as-polished Ni-200 sample with the corresponding EDX spectrum for this sample shown in Figure 4.4.
Experimental Tafel Data for Ni-200

Figure 4.1: Experimental Tafel data (3 tests) for Ni-200 without catalyst addition.
Figure 4.2: Cathodic Tafel plot with error bars for Ni-200 without catalyst addition (average of 3 tests).
Figure 4.3: SEM micrograph showing as-polished Ni-200 sample.

Figure 4.4: EDX spectrum of as-polished Ni-200 sample.
4.1.1 Ni-200 with 100 p.p.m. Catalyst Addition

This section will present the results for an Ni-200 sample with a 100 p.p.m. catalyst addition. Figure 4.5 shows the chronopotentiograms for three separate tests while Figure 4.6 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.7 shows the experimental curves generated from the Tafel testing and Figure 4.8 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.9 and 4.10 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 100 p.p.m. catalyst addition.
Figure 4.5: Chronopotentiograms of Ni-200 (3 tests) with 100 p.p.m. catalyst addition.
Figure 4.6: Chronopotentiogram of Ni-200 with error bars for 100 p.p.m. catalyst addition (average of 3 tests).
Figure 4.7: Experimental Tafel data showing the averages of each of the first three cycles for a 100 p.p.m. catalyst addition.
Figure 4.8: Cathodic Tafel plot showing the averages of each of the first three cycles for a 100 p.p.m. catalyst addition.
Figure 4.9: SEM micrograph showing electrode surface after 100 p.p.m. catalyst addition.

Figure 4.10: EDX spectrum of electrode surface after 100 p.p.m. catalyst addition.
4.1.2 Ni-200 with 50 p.p.m. Catalyst Addition

This section will present the results for an Ni-200 sample with a 50 p.p.m. catalyst addition. Figure 4.11 shows the chronopotentiograms for three separate tests while Figure 4.12 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.13 shows the experimental curves generated from the Tafel testing and Figure 4.14 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.15 and 4.16 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 50 p.p.m. catalyst addition.
Figure 4.11: Chronopotentiograms of Ni-200 (3 tests) with 50 p.p.m. catalyst addition.
Figure 4.12: Chronopotentiogram of Ni-200 with error bars for 50 p.p.m. catalyst addition (average of 3 tests).
Figure 4.13: Experimental Tafel data showing the averages of each of the first three cycles for a 50 p.p.m. catalyst addition.
Figure 4.14: Cathodic Tafel plot showing the averages of each of the first three cycles for a 50 p.p.m. catalyst addition.
Figure 4.15: SEM micrograph showing electrode surface after 50 p.p.m. catalyst addition.

Figure 4.16: EDX spectrum of electrode surface after 50 p.p.m. catalyst addition.
4.1.3 Ni-200 with 10 p.p.m. Catalyst Addition

This section will present the results for an Ni-200 sample with a 10 p.p.m. catalyst addition. Figure 4.17 shows the chronopotentiograms for three separate tests while Figure 4.18 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.19 shows the experimental curves generated from the Tafel testing and Figure 4.20 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.21 and 4.22 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 10 p.p.m. catalyst addition.
Chronopotentiometry of Ni-200 with 10 p.p.m. Catalyst Addition

Figure 4.17: Chronopotentiograms of Ni-200 (3 tests) with 10 p.p.m. catalyst addition.
Figure 4.18: Chronopotentiogram of Ni-200 with error bars for 10 p.p.m. catalyst addition (average of 3 tests).
Figure 4.19: Experimental Tafel data showing the averages of each of the first three cycles for a 10 p.p.m. catalyst addition.
Figure 4.20: Cathodic Tafel plot showing the averages of each of the first three cycles for a 10 p.p.m. catalyst addition.
Figure 4.21: SEM micrograph showing electrode surface after 10 p.p.m. catalyst addition.

Figure 4.22: EDX spectrum of electrode surface after 10 p.p.m. catalyst addition.
4.1.4 Ni-200 with 5 and 500 p.p.m. Catalyst Additions

This section will present the results for an Ni-200 sample with additions of 5 and 500 p.p.m. respectively. Since these concentrations were chosen to confirm trends already observed, only one test was performed at each.

**Figure 4.23** shows the chronopotentiogram for Ni-200 with a 5 p.p.m. catalyst addition. **Figure 4.24** shows the experimental Tafel results while **Figure 4.25** shows these results as a standard Tafel plot. **Figures 4.26 and 4.27** show the SEM micrograph and the corresponding EDX spectrum of the electrode surface after 5 p.p.m. catalyst addition.

**Figure 4.28** shows the chronopotentiogram for Ni-200 with a 500 p.p.m. catalyst addition. **Figure 4.29** shows the experimental Tafel results while **Figure 4.30** shows these results as a standard Tafel plot. **Figures 4.31 and 4.32** show the SEM micrograph and the corresponding EDX spectrum of the electrode surface after 500 p.p.m. catalyst addition.
Figure 4.23: Chronopotentiogram of Ni-200 with 5 p.p.m. catalyst addition.
Figure 4.24: Experimental Tafel data of the first three cycles for a 5 p.p.m. catalyst addition.
Figure 4.25: Cathodic Tafel plot of the first three cycles for a 5 p.p.m. catalyst addition.
Figure 4.26: SEM micrograph showing electrode surface after 5 p.p.m. catalyst addition.

Figure 4.27: EDX spectrum of electrode surface after 5 p.p.m. catalyst addition.
Figure 4.28: Chronopotentiogram of Ni-200 with 500 p.p.m. catalyst addition.
Figure 4.29: Experimental Tafel data of the first three cycles for a 500 p.p.m. catalyst addition.
Cathodic Tafel Plot for Ni-200 (500 p.p.m.)

Figure 4.30: Cathodic Tafel plot of the first three cycles for 500 a.p.m. catalyst addition.
Figure 4.31: SEM micrograph showing electrode surface after 500 p.p.m. catalyst addition.

Figure 4.32: EDX spectrum of electrode surface after 500 p.p.m. catalyst addition.
4.1.5 Effect of Concentration

This section will summarize the results of the varying catalyst additions (5, 10, 50, 100, 500 p.p.m.) with a Ni-200 cathode material. Figure 4.33 shows chronopotentiograms at all 5 concentrations and Figure 4.34 shows the effect of the catalyst concentration on the cathode potential. Figure 4.35 shows Tafel plots for all 5 concentrations while Figure 4.36 shows SEM micrographs of the electrode surfaces after the catalyst addition.
Figure 4.33: Effect of catalyst concentration on cathode potential.
Figure 4.34: Effect of catalyst concentration on potential drop.
Effect of Catalyst Concentration on Electrode Activity

Figure 4.35: Cathodic Tafel plot for Ni-200 with various catalyst additions.
Figure 4.36: SEM micrographs of the Ni-200 surface after various catalyst additions.
4.1.6 Effect of Impurities

This section will present the results from the tests using both treated and non-treated electrolyte. The treated electrolyte was prepared as outlined in §3.0. Figure 4.37 shows the chronopotentiograms using both types of electrolytes with a 100 p.p.m. catalyst addition. Figures 4.38 and 4.39 show the SEM micrograph and the corresponding EDX spectrum of the electrode surface after catalyst addition using the treated electrolyte. Figures 4.40 and 41 show the SEM micrograph and corresponding EDX spectrum of the electrode surface after catalyst addition using the non-treated electrolyte.
**Figure 4.37:** Chronopotentiometry of Ni-200 with treated and non-treated electrolyte.
Figure 4.38: SEM micrograph showing electrode surface using treated electrolyte.

Figure 4.39: EDX spectrum of electrode surface using treated electrolyte.
Figure 4.40: SEM micrograph showing electrode surface using non-treated electrolyte.

Figure 4.41: EDX spectrum of electrode surface using non-treated electrolyte.
4.1.7 Effect of Method of Addition

This section will present the results from the single and multiple addition tests. For the multiple addition test, 10 additions of 10 p.p.m. were made at twenty minute intervals for a total concentration of 100 p.p.m., which is the same concentration that was used in the single addition. Figure 4.42 shows the chronopotentiograms that were produced and Figure 4.43 shows the effect of the additions on the cathode potential for both methods of addition.

Figures 4.44 and 4.45 show the SEM micrograph and corresponding EDX spectrum of the electrode surface after a single 100 p.p.m. catalyst addition. Figures 4.46 and 4.47 show the SEM micrograph and corresponding EDX spectrum of the electrode surface after the multiple additions.
Effect of Method of Addition

Figure 4.42: Chronopotentiometry of Ni-200 showing effect of method of addition.
Figure 4.43: Effect of method of addition on the cathode potential.
**Figure 4.44:** SEM micrograph showing electrode surface after single 100 p.p.m. catalyst addition.

**Figure 4.45:** EDX spectrum (spot analysis) of white particle after single 100 p.p.m. catalyst addition.
Figure 4.46: SEM micrograph showing electrode surface after multiple 10 p.p.m. catalyst additions (total concentration 100 p.p.m.).

Figure 4.47: EDX spectrum (spot analysis) of large white agglomerate particle after multiple additions.
Figure 4.48: XPS spectrum of Ni-200 after catalyst addition showing O 1s peak.

Figure 4.49: XPS spectrum of Ni-200 after catalyst addition showing Cr 2p peaks (1=Cr⁰, 2=Cr³⁺, 3=Cr³⁺, 4=Cr⁵⁺, 5=Cr⁶⁺).
Figure 4.50: XPS spectrum of Cr 2p3/2 identifying the valence states.

Peak 1
Oxidation State = Cr
Chemical Species = Cr

Peak 2
Oxidation State = Cr³⁺
Chemical Species = Cr₂O₃

Peak 3
Oxidation State = Cr³⁺
Chemical Species = CrOOH

Peak 4
Oxidation State = Cr⁶⁺
Chemical Species = CrO₃

Peak 5
Oxidation State = Cr⁶⁺
Chemical Species = CrO₄²⁻
4.2 Amorphous Alloy (\(\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}\))

This section will present the results obtained for the \(\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}\) amorphous alloy without catalyst addition. Figure 4.51 shows the experimental curves obtained from the steady-state potentiostatic polarization (Tafel) tests and Figure 4.52 shows the standard Tafel plot obtained from this data. The Tafel curves are the average of the three tests shown and the standard deviation is represented by the error bars.

Figures 4.53 and 4.54 show the SEM micrograph and corresponding EDX spectrum for the as-polished \(\text{Ni}_{50}\text{Co}_{25}\text{P}_{15}\text{B}_{10}\) amorphous alloy.
Figure 4.51: Experimental Tafel data (3 tests) for amorphous alloy without catalyst addition.
Figure 4.52: Cathodic Tafel plot of the first three cycles for amorphous alloy without catalyst addition.
4.2.1 Amorphous Alloy with 100 p.p.m. Catalyst Addition

This section will present the results for an Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ amorphous alloy sample with a 100 p.p.m. catalyst addition. Figure 4.55 shows the chronopotentiograms for three separate tests while Figure 4.56 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.57 shows the experimental curves generated from the Tafel testing and Figure 4.58 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.59 and 4.60 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 100 p.p.m. catalyst addition.
Figure 4.55: Chronopotentiograms of amorphous alloy (3 tests) with 100 p.p.m. catalyst addition.
Chronopotentiometry of Amorphous Alloy with 100 p.p.m. Catalyst Addition

Figure 4.56: Chronopotentiogram of amorphous alloy with error bars for 100 p.p.m. catalyst addition (average of 3 tests).
**Figure 4.57:** Experimental Tafel data for 100 p.p.m. catalyst addition to amorphous alloy.
Figure 4.58: Tafel plot for 100 p.p.m. catalyst addition to amorphous alloy.
Figure 4.59: SEM micrograph showing amorphous alloy with 100 p.p.m. catalyst addition.

Figure 4.60: EDX spectrum of amorphous alloy with 100 p.p.m. catalyst addition.
4.2.2 Amorphous Alloy with 50 p.p.m. Catalyst Addition

This section will present the results for an Ni_{50}Co_{25}P_{15}B_{10} amorphous alloy sample with a 50 p.p.m. catalyst addition. Figure 4.61 shows the chronopotentiograms for three separate tests while Figure 4.62 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.63 shows the experimental curves generated from the Tafel testing and Figure 4.64 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.65 and 4.66 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 50 p.p.m. catalyst addition.
Figure 4.61: Chronopotentiograms of amorphous alloy (3 tests) with 50 p.p.m. catalyst addition.
Figure 4.62: Chronopotentiogram of amorphous alloy with error bars for 50 p.p.m. catalyst addition (average of three tests).
Figure 4.63: Experimental Tafel data showing the averages of each of the first three cycles for a 50 p.p.m. catalyst addition.
Figure 4.64: Cathodic Tafel plot showing the averages of each of the first three cycles for a 50 p.p.m. catalyst addition.
Figure 4.65: SEM micrograph showing amorphous alloy with 50 p.p.m. catalyst addition.

Figure 4.66: EDX spectrum of amorphous alloy with 50 p.p.m. catalyst addition.
4.2.3 Amorphous Alloy with 10 p.p.m. Catalyst Addition

This section will present the results for an Ni_{50}Co_{25}P_{15}B_{10} amorphous alloy sample with a 10 p.p.m. catalyst addition. Figure 4.67 shows the chronopotentiograms for three separate tests while Figure 4.68 shows the average of the three tests with the standard deviation represented by the error bars.

Figure 4.69 shows the experimental curves generated from the Tafel testing and Figure 4.70 shows the standard Tafel plot for these curves with the standard deviation represented by the error bars.

Figures 4.71 and 4.72 show the SEM micrograph and the corresponding EDX spectrum for the electrode surface after the 10 p.p.m. catalyst addition.
Figure 4.67: Chronopotentiograms of amorphous alloy (3 tests) with 10 p.p.m. catalyst addition.
Figure 4.68: Chronopotentiogram of amorphous alloy with error bars for 10 p.p.m. catalyst addition (average of 3 tests).
Figure 4.69: Experimental Tafel data showing the averages of each of the first three cycles for a 10 p.p.m. catalyst addition.
Figure 4.70: Cathodic Tafel plot showing the averages of the first three cycles for a 10 p.p.m. catalyst addition.
Figure 4.71: SEM micrograph showing amorphous alloy with 10 p.p.m. catalyst addition.

Figure 4.72: EDX spectrum of amorphous alloy with 10 p.p.m. catalyst addition.
4.2.4 Amorphous Alloy with 5 and 500 p.p.m. Catalyst Additions

This section will present the results for an Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$ amorphous alloy sample with additions of 5 and 500 p.p.m. respectively. Since these concentrations were chosen to confirm trends already observed, only one test was performed at each.

**Figure 4.73** shows the chronopotentiogram for the amorphous alloy with a 5 p.p.m. catalyst addition. **Figure 4.74** shows the experimental Tafel results while **Figure 4.75** shows these results as a standard Tafel plot. **Figures 4.76 and 4.77** show the SEM micrograph and the corresponding EDX spectrum of the electrode surface after 5 p.p.m. catalyst addition.

**Figure 4.78** shows the chronopotentiogram for the amorphous alloy with a 500 p.p.m. catalyst addition. **Figure 4.79** shows the experimental Tafel results while **Figure 4.80** shows these results as a standard Tafel plot. **Figures 4.81 and 4.82** show the SEM micrograph and the corresponding EDX spectrum of the electrode surface after 500 p.p.m. catalyst addition.
Figure 4.73: Chronopotentiogram of amorphous alloy with 5 p.p.m. catalyst addition.
Experimental Tafel Data for Amorphous Alloy (5 p.p.m.)

Figure 4.74: Experimental Tafel data of the first three cycles for a 5 p.p.m. catalyst addition.
Figure 4.75: Cathodic Tafel plot of the first three cycles for a 5 p.p.m. catalyst addition.
Figure 4.76: SEM micrograph showing amorphous alloy with 5 p.p.m. catalyst addition.

Figure 4.77: EDX spectrum of amorphous alloy with 5 p.p.m. catalyst addition.
Figure 4.78: Chronopotentiogram of amorphous alloy with 500 p.p.m. catalyst addition.
Figure 4.79: Experimental Tafel data of the first three cycles for a 500 p.p.m. catalyst addition.
Figure 4.80: Cathodic Tafel plot of the first three cycles for a 500 p.p.m. catalyst addition.
Figure 4.81: SEM micrograph showing amorphous alloy with 500 p.p.m. catalyst addition.

Figure 4.82: EDX spectrum of amorphous alloy with 500 p.p.m. catalyst addition.
4.2.5 Effect of Concentration

This section will summarize the results of the varying catalyst additions (5, 10, 50, 100, 500 p.p.m.) to the amorphous alloy cathode material. Figure 4.83 shows chronopotentiograms at all 5 concentrations and Figure 4.84 shows the effect of the catalyst concentration on the cathode potential. Figure 4.85 shows Tafel plots for all 5 concentrations while Figure 4.86 shows SEM micrographs of the electrode surfaces after the catalyst addition.
Figure 4.83: Effect of catalyst concentration on amorphous alloy cathodic potential.
Figure 4.84: Effect of catalyst concentration on amorphous alloy potential.
Figure 4.85: Cathodic Tafel plot for amorphous alloy with various catalyst additions.
Figure 4.86: SEM micrographs of the amorphous alloy surface after various catalyst additions.
Figure 4.87: XPS spectrum of amorphous alloy after catalyst addition showing O 1s peak.

Figure 4.88 (a): XPS spectrum of amorphous alloy after catalyst addition showing Cr 2p peaks (1=Cr⁰, 2=Cr³⁺, 3=Cr⁵⁺, 4=Cr⁶⁺, 5=Cr⁷⁺).
Figure 4.88(b): XPS spectrum of Cr 2p3/2 for amorphous alloy identifying the valence states.

Peak 1
Oxidation State = Cr
Chemical Species = Cr

Peak 2
Oxidation State = Cr\textsuperscript{3+}
Chemical Species = Cr\textsubscript{2}O\textsubscript{3}

Peak 3
Oxidation State = Cr\textsuperscript{3+}
Chemical Species = CrOOH

Peak 4
Oxidation State = Cr\textsuperscript{6+}
Chemical Species = CrO\textsubscript{3}

Peak 5
Oxidation State = Cr\textsuperscript{6+}
Chemical Species = CrO\textsubscript{4}\textsuperscript{2-}
5.0 Discussion

This section will discuss the results that were obtained in §4.0 following the procedure outlined in §3.0. The discussion is divided into five sections. The first section, §5.1, will discuss the electrochemical and surface properties of the two electrode materials, Ni-200 and the amorphous alloy (Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$) in the absence of any catalyst addition. These will serve as standards against which the catalyst modified electrodes discussed in §5.2 and §5.3 will be compared. Section 5.4 will discuss the reaction mechanisms which have been proposed to explain the catalyzing effect of the addition on the HER and finally, §5.5 will discuss some practical considerations of homogeneous catalysis on an industrial scale. This final section will address the effect of electrolyte impurities on the cathode and the possibility of optimizing the effect of the catalyst through different means of addition.

5.1 Electrochemical and Surface Properties of the Electrode Materials

5.1.1 Commercial Ni-200

This section will discuss the results from §4.0 for the experimentation performed on Ni-200. These results will be used as a standard against which the catalyst modified electrodes will be compared.

5.1.1.1 Steady State Potentiostatic Measurements (Tafel)

In order to evaluate the kinetics of HER on Ni-200, Tafel measurements were performed and compared to literature values. The HER in alkaline media is very well described [2.23, 2.26, 2.25], and is believed to follow the steps outlined in §2.1.4. These are described as, water reduction with hydrogen adsorption (Volmer), followed by two parallel competitive steps, electrochemical (Heyrovsky) and chemical (Tafel) desorption:

Volmer: \[ M + H_2O = MH_{\text{ads}} + OH^- \quad b = 120 \text{ mV/dec} \quad \{5.1\} \]
It has been reported [2.24] that in highly alkaline solutions the Tafel slope for nickel is 120 mV/dec. This corresponds to an electrode discharge pathway that is represented by reactions 5.1 and 5.2, where reaction 5.2 is the rate determining step for an electrode covered by adsorbed hydrogen.

The above Tafel slopes are for experiments conducted at 298 K. For experiments at 343 K, Huot [2.22] reported a value of 138 mV/dec for a simple discharge reaction (atom-ion desorption) on a surface fully covered by adsorbed hydrogen. This value is in keeping with the theoretical expectation which is governed by the relation $2.3 \times RT/\beta F$.

The above Tafel slopes also don't take into account electrolyte impurities which are present in varying quantities. The effect of these impurities was investigated by Huot, who found that at low overpotentials, Fe (one of the main electrolyte impurities) electrodeposition is a possible parallel reaction. It was proposed that the electrodeposition of dissolved ferric ions comprised two consecutive steps: reversible reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ close to the reversible hydrogen potential, followed by reduction of $\text{Fe}^{2+}$ to metallic iron close to -200 mV hydrogen overpotential. These reduction steps could be responsible for the observed changes in Tafel slope.

The experimental results for Ni-200 presented in §4.1 give a Tafel slope of $203 \pm 24$ mV/dec. This value lies higher than the literature values using comparable electrolyte concentrations and temperatures. Possible reasons for this are, the different scan rates and the electrolyte impurities.

In order to determine the effect of the scan rate, steady state potentiostatic tests using a comparable electrolyte and electrode but a different scan rate were performed independently. The results using a scan rate of 2 mV/min produced a Tafel slope of $140 \pm 20$ mV/decade [D. Anthony, Master’s Thesis, University of Toronto]. This value lies intermediate to the literature values and the values presented here. Therefore, it can be seen that scan rate does have an influence on the Tafel behaviour of this system.

Heyrovsky: $\text{MH}_{\text{ads}} + \text{H}_2\text{O} + e^- = \text{H}_2 + \text{M} + \text{OH}^- \quad b = 40 \text{ mV/dec} \quad \{5.2\}$

Tafel: $2\text{MH}_{\text{ads}} = 2\text{M} + \text{H}_2 \quad b = 30 \text{ mV/dec} \quad \{5.3\}$
The presence of Fe on the electrode surface post-testing indicates that at the lower overpotentials it could be reduced following the reactions proposed by Huot. Further, the deviation of the Tafel slope from the simple discharge process value indicates the potential for an HER mechanism controlled by mixed rate-determining reactions. Although the present study did not vary the temperature, Huot et al. using the temperature dependence of log (i_p) calculated an apparent heat of activation at the reversible potential of 21 kJ/mol. This value is slightly less than reported values for alkaline solutions and the difference was attributed to the KOH metallic impurities and electroosorbed hydrogen [2.37].

The values cited for the exchange current density for hydrogen evolution on nickel varied considerably from author to author. Values range from 4.1 x 10^{-4} to 1.8 x 10^{-7} A/cm^2 [2.25, 2.23]. The present study found a value of 3.1 ± 0.97 x 10^{-4} A/cm^2. This value lies at the high end of the literature values but the exchange current density is extremely sensitive to data point selection and experimental parameters.

5.1.1.2 Scanning Electron Microscopy

The scanning electron micrograph shown in Figure 4.3 illustrates the state of the as-polished electrode surface. The surface is featureless except for scratches from the polishing. This sample was simply intended for use as a standard for comparison. The accompanying EDX spectrum, Figure 4.4, shows prominent peaks for nickel only. As was mentioned in §3.1.1 there are several impurities associated with Ni-200. The presence of these could not be confirmed by EDX due to their low concentrations. Of these impurities, only Fe is reported to have an effect on the HER in this concentration range (≤ 1 p.p.m.). Iron impurities in low concentrations can catalyze the HER through the formation of crystallites on the electrode surface as proposed by Huot by the mechanisms discussed in §2.2.1.2.3.

5.1.2 Amorphous Alloy (Ni_{50}Co_{25}P_{15}B_{10})

This section will discuss the results from §4.2 for the experimentation performed on the Ni_{50}Co_{25}P_{15}B_{10} amorphous alloy without catalyst addition.
This will serve as a standard against which the catalyst modified electrodes will be compared.

5.1.2.1 Steady State Potentiostatic Measurements

Steady state potentiometric measurements (Tafel) were performed in order to determine the kinetics of the hydrogen evolution reaction on the amorphous electrode and to compare these to literature values.

The HER is well defined for many crystalline materials in alkaline solutions with most Tafel slopes being above 100 mV/decade. Typically, the Tafel slope is \(-120 \text{ mV/decade}\) corresponding to the r.d.s. being the water discharge step \(5.2\).

For amorphous alloys, the HER isn’t as well defined. For Tafel slopes above 120 mV/decade there aren’t well defined mechanisms with accompanying rate determining steps. Literature values for the Tafel slope and exchange current density have been reported for this amorphous alloy by K. Lian \([2.32]\) to be \(144.0 \pm 9.8 \text{ mV/decade}\) and \(0.043 \pm 0.008 \text{ mA/cm}^2\), respectively.

The corresponding values from this study are \(213 \pm 19 \text{ mV/decade}\) and \(2.95 \pm 0.6 \text{ mA/cm}^2\). While these values appear high this is again due to the high scan rate which was discussed in \(5.1.1\) and the electrolyte which was pre-electrolyzed 8M KOH. In the case of Lian, the tests were run at lower scan rates with a 1M KOH electrolyte that wasn’t pre-electrolyzed. The impurities (such as Fe) found in the electrolyte could serve to lower the Tafel slope.

5.1.2.2 Scanning Electron Microscopy (SEM) with EDX

The scanning electron micrograph shown in Figure 4.54 is representative of the as-polished electrode state. Since the surface was given a 1 µm diamond paste finish little is seen in the way of morphology except for small depression in the surface which appear darker than their surroundings. Also visible on the surface are scratches from the polishing process. The accompanying EDX spectrum, Figure 4.55, shows the presence of nickel, cobalt and phosphorus with the absence of boron. While
all four of these elements should be present the lack of a detectable peak for boron is due to the resolution limit of the microscope.

5.2 Electrochemical Properties Catalyst Modified Electrodes

5.2.1 Ni-200

This section will discuss the results presented in §4.1.1 through §4.1.5 concerning the effect of catalyst addition on the chronopotentiometry and steady state potentiostatic polarization measurements of Ni-200.

5.2.1.1 Chronopotentiometry

As described in §3.2.4, chronopotentiometry was performed at various catalyst concentrations using cathodic currents corresponding to a nominal -250 mA/cm² current density.

Sections §4.1.1 to §4.1.4 show the experimental chronopotentiograms generated with various catalyst additions, and the corresponding chronopotentiograms representing the average of three curves with standard deviation represented by the error bars. All the chronopotentiograms show three well defined regions.

The first region is defined by a rapid increase in potential over a very short time frame. Prior to the chronopotentiometric testing, the sample is held at a potential of -1350 mV vs. Hg/HgO in order to remove air-formed oxides. Once the current is applied there is a rapid increase from this initial potential to a maximum value of ~2050 mV. This rise is mainly due to the imposed current but there are also several theories which have been reported to account for increases in cathodic overpotential on nickel with time. These are i) loss of electrocatalytically active material from the cathode, ii) slow reduction of nickel hydroxide to nickel, which has lower kinetics for the HER than Ni(OH)₂, iii) deposition of impurities from the electrolyte, and iv) the absorption of atomic hydrogen into the lattice of the nickel cathode [5.1].

The second region is marked by a gradual decrease in potential from the maximum value to a steady-state. It is the decrease in overpotential in this region that indicates that the absorption of atomic hydrogen into the nickel lattice was indeed responsible for the recoverable initial increase. This
is due primarily to the lack of recovery mechanisms for theories i) to iii) which is further supported in the literature [2.45, 5.2]. The nickel containing hydrogen can exist in one of two forms. The α-hydride is a solid solution of hydrogen atoms in the octahedral interstices of nickel and is characterized by a H/NI ratio of 0.03. Above an atomic ratio of 0.06 the β-hydride phase exists. This phase acts as a diffusion barrier to hydrogen and leads to the increase in overpotential. The subsequent decrease in overpotential is due to the instability of this hydride phase.

The third region corresponds to the rapid potential drop associated with the addition of the catalyst. It is the potential drop in this region that is unique to each catalyst concentration. The rapid drop is caused by reactions involving the homogeneous catalysis addition of chromium which compete with the HER reactions on nickel and serve to catalyze the overall HER. The full reaction mechanisms and their justification will be presented in Section 5.3.

5.2.1.2 Steady-State Potentiostatic Polarization (Tafel)

This section will discuss the Tafel results at the various catalyst concentrations as presented in the results sections §4.1.1 to §4.1.4. These results will be discussed in terms of the effect of catalyst concentration and compared to the Ni-200 sample without catalyst addition previously discussed in §5.2.1 and literature values for both nickel and chromium.

A literature value for the Tafel slope on pure chromium could not be found in a highly alkaline medium. It is more commonly documented in 1N H₂SO₄ and is given as ~120 mV/dec [2.40]. This value is at 25 °C and corrected to 70 °C corresponds to 138 mV/dec.

Despite the different electrolyte, some information is offered into the hydrogen discharge. Specifically, the value for the Tafel slope indicates that either reaction 5.1 (with electrode coverage φ = 0) or reaction 5.2 (with electrode coverage φ = 1) will be the rate determining step (r.d.s.). Since chromium is a good catalyst for adsorbing hydrogen [5.3], it is likely that the HER would proceed on an electrode covered by adsorbed hydrogen, indicating reaction 5.2 as the r.d.s.

More specific to this study is the Tafel data reported by Raj et. al. [2.38] for an Ni-Cr binary alloy co-deposit in 6M KOH at various
temperatures. The physical characteristics of the deposit are listed in Table 5.1 below.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>80 g p l</td>
</tr>
<tr>
<td>CrO₃</td>
<td>20 g p l</td>
</tr>
<tr>
<td>K₃C₆H₅O₇·H₂O</td>
<td>50 g p l</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Excess</td>
</tr>
<tr>
<td>pH</td>
<td>10.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>301 K</td>
</tr>
<tr>
<td>Current Density</td>
<td>10 mA/cm²</td>
</tr>
<tr>
<td>Duration</td>
<td>90 min</td>
</tr>
<tr>
<td>Agitation</td>
<td>250 r p m</td>
</tr>
<tr>
<td>Weight of Deposit</td>
<td>5-6.0 mg/cm²</td>
</tr>
<tr>
<td>Thickness of Deposit</td>
<td>5-7 μm</td>
</tr>
<tr>
<td>Colour of Deposit</td>
<td>Bright White</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Very Good</td>
</tr>
</tbody>
</table>

Table 5.1: Operating conditions for electrolytic deposition.

At 343 K, the Tafel slope is reported to be 150 mV/dec. The authors do not propose a reaction mechanism for the HER, nor do they attempt to elucidate the role of chromium.

The Tafel slopes that were measured at the various catalyst concentrations and the exchange current densities are shown in Table 5.2.
Table 5.2: Experimental Tafel data for Ni-200 at various catalyst concentrations.

<table>
<thead>
<tr>
<th>Catalyst Addition (p.p.m.)</th>
<th>Exchange Current Density $i_0(\eta_{250})$, mA/cm$^2$</th>
<th>Tafel Slope (b) mV/decade lower/upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>3.10 ± 0.9</td>
<td>203 ± 24</td>
</tr>
<tr>
<td>5</td>
<td>3.38</td>
<td>186 ± 7</td>
</tr>
<tr>
<td>10</td>
<td>3.48 ± 0.26</td>
<td>210 ± 7</td>
</tr>
<tr>
<td>50</td>
<td>3.54 ± 0.09</td>
<td>219 ± 13</td>
</tr>
<tr>
<td>100</td>
<td>3.72 ± 0.03</td>
<td>316 ± 56</td>
</tr>
<tr>
<td>500</td>
<td>3.74</td>
<td>311 ± 16</td>
</tr>
</tbody>
</table>

The Tafel slope remained constant up to 50 ppm but increased with catalyst concentration above that. Due to the lack of proposed mechanisms for Tafel slopes above 120 mV/decade it was impossible to determine the probable reactions. The change in slope does not necessarily indicate that a change in reaction occurred. The Tafel curves for the catalyst modified electrodes showed a less linear trend than for the Ni-200 without catalyst addition. The curvature was due to concentration polarization effects and the presence of adsorbed species. This also accounts for the increase in slope with increasing concentration. Deviation from the observed trends could simply be an anomaly or could be a function of the time between catalyst addition and Tafel testing. Huot et al. have demonstrated a marked change in Tafel parameters, with the slope and exchange current density increasing with time [2.35]. This accounts for the large error associated with some of the samples.

5.2.2 Amorphous Alloy (Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$)

5.2.2.1 Chronopotentiometry

Chronopotentiometry was performed with various catalyst additions at a current corresponding to the nominal current density of -250 mA/cm$^2$. Catalyst additions of 5, 10, 50, 100 and 500 p.p.m. were made to the
electrolyte and the resultant curves are shown in Figures 4.56, 4.62, 4.67, 4.73 and 4.78. As with Ni-200, the chronopotentiograms for the amorphous alloy show three distinct regions. These regions are described in §5.2.1. The only differences that were observed between the amorphous alloy and the Ni-200 were with respect to the initial and final potentials. In the case of the amorphous alloy, the initial potential was approximately 80 mV lower than that of Ni-200. When one takes into account the experimental error associated with each, the difference becomes much less significant. The primary cause is the greater surface roughness of the amorphous alloy as seen in the micrographs. This increase in surface area is primarily due to the dissolution of phosphorus from the alloy. This has been reported in alkaline solutions by Lian et al. The lower final potential associated with the amorphous alloy is again a result of the greater surface area. The larger surface provides more sites for the adsorption of chromium species according to the reactions proposed in §5.4.

As with the Ni-200 electrodes, the amorphous samples showed a potential drop with a logarithmic dependence. This phenomenon is a function of the chromium concentration as it relates to the Nernst equation and is described in §5.4.

5.2.2.2 Steady State Potentiostatic Measurements

Steady state potentiostatic measurements (Tafel) were made for all the catalyst concentrations on the amorphous alloy electrode. The results are shown in §4. The Tafel slopes and exchange current densities are given in Table 5.3 below.
There appears to be a decreasing trend in the Tafel slopes with an increase in catalyst concentration. In all cases, except for the 10 p.p.m. addition, the slope was lower than for the amorphous alloy without addition. When the experimental error is taken into account the difference is much less significant. The reason for the anomalous behaviour of the 10 p.p.m. samples could be due to physical differences within the amorphous ribbon. Since tests were run consecutively by catalyst concentration, it is conceivable that a variation in the amorphous ribbon could be seen only in one set of tests.

The change in Tafel slopes from the non-catalyst modified electrodes indicates that there is a change in the reaction mechanism. The decreasing trend in the Tafel slope is in stark contrast to what was observed for the Ni-200 samples whose Tafel slopes increased with increasing catalyst concentration. This is due in part to the means of data acquisition used in both cases. For the Ni-200, a data acquisition system was used. For the amorphous alloy a chart recorder was used. As the catalyst concentration increased, the data points at lower current densities became harder to resolve from the chart recorder. This led to some anomalous features at lower concentrations, as well as, lower Tafel slopes as determined by the line fitting.

The exchange current densities showed an increasing trend with respect to catalyst concentration. In all cases, the exchange current density was higher than for the samples without catalyst addition. This was due to

<table>
<thead>
<tr>
<th>Catalyst Addition</th>
<th>Exchange Current Density (i_o(\eta_{250})) mA/cm(^2)</th>
<th>Tafel Slope (b) mV/decade</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>2.95 ± 0.16</td>
<td>213 ± 19</td>
</tr>
<tr>
<td>5</td>
<td>3.09</td>
<td>191 ± 23</td>
</tr>
<tr>
<td>10</td>
<td>3.28 ± 0.36</td>
<td>265 ± 33</td>
</tr>
<tr>
<td>50</td>
<td>3.55 ± 0.34</td>
<td>172 ± 16</td>
</tr>
<tr>
<td>100</td>
<td>4.02 ± 0.23</td>
<td>150 ± 1</td>
</tr>
<tr>
<td>500</td>
<td>4.17</td>
<td>109 ± 3</td>
</tr>
</tbody>
</table>

Table 5.3: Tafel parameters for various catalyst additions to amorphous alloy.
the HER catalyzing reactions involving chromium that are described in §5.4. By increasing the catalyst concentration more chromium becomes available for the reactions.

5.3 Surface Characterization of Catalyst Modified Electrodes

5.3.1 Commercial Ni-200

5.3.1.1 Scanning Electron Microscopy

The micrographs and corresponding EDX spectra for the electrode surfaces at each catalyst concentration are presented in §4.1.5. All of the micrographs show two distinct regions; a surface film (<1 μm) and spherical white particles. EDX analysis of the surface film showed the presence of strong peaks for nickel, and smaller peaks for iron and chromium. The presence of nickel was from the Ni-200 substrate while the chromium was from the catalyst addition. The presence of iron could be from the electrolyte (small amounts that weren’t removed during pre-electrolysis) or from the catalyst salt addition where it can also be found as an impurity (< 0.005%). EDX spot analysis of the white particles showed relatively smaller peaks corresponding to nickel and iron, with much larger chromium peaks. These particles are absent on the electrode surface prior to catalyst addition and are attributed to the chromium salt.

As the concentration of the catalyst is increased, a greater number of white particles is observed on the electrode surface. Although some larger particles were observed (10-15 μm) the small size of the majority of the particles (1-3 μm) relative to the surface area of the electrode, made it impossible using EDX to resolve the amount of chromium on the surface at each catalyst addition concentration. It is, therefore, difficult to determine whether or not the particles are solely responsible for the catalytic effect.

In order to further elucidate this question a test was run in which the catalyst was added to the electrode and the system was allowed to equilibrate. The electrode was then removed and placed in an electrolyte without chromium. The resultant rise in potential was accompanied by a loss of surface film. Using EDX it was possible to identify the presence of
chromium in the film indicating the particles don’t represent the only form of chromium on the surface.

This parallels the work of Calvo and Pallotta previously described in §2.3.2. They demonstrated that two distinct forms of chromium were found on iron electrode surfaces after chromate additions. The first, stable form of chromium was structurally mixed in the inner oxide layer and was referred to as "entrapped". This corresponds in the present study to the EDX signals for chromium from the surface film. The second chromium species was described as a more external hydrous Cr(III) precipitate on top of the chromium-containing layer that required a source of chromate in solution to be observed. This is thought to correspond in the present study to the observed white particles.

In order to determine whether or not these particles were capable of independently supporting the required current density associated with the potential drop, rough calculations were made from the micrographs and can be found in Appendix-E. The calculations show that the current density would have to be in the order of 34 A/cm². This value is too high to be supported by the particles alone, indicating that the chromium present in the film must also participate in the catalyzing reactions.

**5.3.1.2 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy of the catalyst modified Ni-200 electrode showed the presence of a number of species. For the purposes of this investigation, however, high resolution scans were limited to chromium (Cr 2p1/2, Cr 2p3/2) and oxygen (O 1s) in order to determine the state of the catalyst on the surface post-testing. The corresponding spectra are shown in Figures 4.48 to 4.50. The binding energies of the respective valence states of chromium and oxygen and their associated chemical species are given in Table 5.4.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding Energy (eV)</th>
<th>Valence State</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>574.1</td>
<td>0</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>576.2</td>
<td>+3</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td></td>
<td>577.0</td>
<td>+3</td>
<td>CrOOH</td>
</tr>
<tr>
<td></td>
<td>578.1</td>
<td>+6</td>
<td>CrO₃</td>
</tr>
<tr>
<td></td>
<td>579.3</td>
<td>+6</td>
<td>CrO₄²⁻</td>
</tr>
<tr>
<td>Oxygen</td>
<td>530.0</td>
<td>+2</td>
<td>oxides</td>
</tr>
<tr>
<td></td>
<td>531.3</td>
<td>+2</td>
<td>hydroxides</td>
</tr>
<tr>
<td></td>
<td>532.9</td>
<td>+2</td>
<td>water</td>
</tr>
</tbody>
</table>

Table 5.4: Experimental binding energies for chromium species (Cr 2p3/2) for catalyst modified Ni-200 and amorphous alloy.

The binding energies for each of the sub-peaks corresponded well with literature values, specifically with those of Clayton et al. Further, these species are in agreement with the Pourbaix diagram in the experimental pH and potential range. The high level of hydroxide present in the O 1s peak is in contradiction with the Cr 2p peaks which show a higher level of oxides. This indicates that the surface is not covered by a homogeneous chromium-based film. The strong hydroxide peak is likely from Ni(OH)₂.

5.3.2 Amorphous Alloy (Ni₅₀Co₂₅P₁₅B₁₀)

5.3.2.1 Scanning Electron Microscopy (SEM) with EDX

The micrographs and corresponding EDX spectra for the electrode surfaces at each catalyst concentration are given in §4.2. As with the Ni-200 samples, the amorphous alloy samples all show two distinct regions on the surface; a surface film and spherical white particles. EDX of the surface film
showed strong peaks for each of the elements present in the alloy (Ni, Co, P but not B due to resolution limits) and smaller peaks for Cr and in some cases Fe. The presence of chromium was from the catalyst addition, while the presence of Fe could be attributed to impurities in the electrolyte (what wasn’t removed by pre-treatment) or in the catalyst salt addition.

EDX spot analysis of the white particles identified them as chromium-based and their absence prior to the catalyst addition indicates they arise from the catalyst salt. The number of surface particles increases with increasing catalyst concentration, however, it is unlikely they are solely responsible for the catalyzing effect on the HER (see Appendix E). The size of the particles ranges from 1-15 μm with the majority being in the 1 μm range. The reason for this size variation appears to be random.

5.3.2.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy of the catalyst modified amorphous alloy showed the presence of a number of surface species. As with the Ni-200 sample, the high resolution scans for the amorphous alloy were limited to chromium and oxygen species. The experimental binding energies were identical to those found for the Ni-200 samples indicating no effect from the different substrates (Table 5.4). The only difference apparent between the two substrates was a relative change in intensity between the species present. This was limited to the Cr\(^{3+}\) peaks which correspond to Cr\(_2\)O\(_3\) and CrOOH. The difference could be attributable to the amount of time between the end of the electrochemical testing and the XPS. As CrOOH is simply a hydrated form of Cr\(_2\)O\(_3\) a small change in water content could significantly alter the relative amounts of each.

5.4 Proposed Reaction Mechanisms for Catalysis of the HER

The reaction mechanisms that have been proposed to explain the catalyzing effect were produced by determining the stable chromium species from a Pourbaix diagram (Figure 5.1, below) and from the XPS results that were presented in §5.3.1.2 and §5.3.2.2.
Figure 5.1: Potential-pH diagram for chromium.

The calculation of the pH of the solution which was used for identification of the appropriate region on the Pourbaix diagram is shown in Appendix-A.

The reaction mechanisms that have been proposed are as follows:
1. \[ \text{Cr}_2\text{O}_7^{2-} + 2(\text{OH}^-) = 2 \text{CrO}_4^{2-} + \text{H}_2\text{O} \] \{5.5\}

2. \[ 2 \text{CrO}_4^{2-} + 5 \text{H}_2\text{O} + 6\text{e}^- = \text{Cr}_2\text{O}_3 + 10(\text{OH}^-) \] \{5.6\}

3. \[ 2 \text{Cr}_2\text{O}_3 + 8 \text{H}_2\text{O} + 14\text{e}^- = 4 \text{CrO}_3^{3+} + 2(\text{OH}^-) + 7 \text{H}_2 \] \{5.7\}

4. \[ \text{CrO}_3^{3+} + 2(\text{OH}^-) = \text{CrO}_4^{2-} + \text{H}_2\text{O} + 3\text{e}^- \] \{5.8\}

These reactions are self sustaining after the initial catalyst addition (reaction \{5.5\}) and reaction \{5.7\} is the prime generator of hydrogen. As was shown in the results section, §4.0, an increase in the catalyst concentration led to an increase in the potential drop. This can be explained by referring to the chromium species in the above equations and applying LeChatelier's Principle. This demonstrates that an increase in chromium content leads to an increased hydrogen production. This could be limited at higher concentrations by concentration polarization effects.

Further, in §4.1.5 it was demonstrated that the potential drop associated with an increase in catalyst concentration followed a logarithmic relationship. The potential can be represented by:

\[
E = E^\circ - 2.303 \frac{RT}{nF} \log \frac{[\text{products}]}{[\text{reactants}]} \] \{5.9\}

where, \(E\) is the cell potential, \(E^\circ\) is the reversible cell potential, \(R\) is the gas constant, \(T\) is the temperature in Kelvin, \(F\) is Faraday's constant, and products and reactants refer to the appropriate reaction species. Again, making reference to the proposed reaction mechanisms it can be seen that as the concentration of the chromium species increases, the corresponding decrease in potential following equation \{5.9\} is logarithmic.
5.5 Practical Considerations of Homogeneous Catalysis

This section will address some of the practical considerations of homogeneous catalysis with respect to industrial alkaline water electrolysis. The first section, §5.5.1, will discuss the effect of electrolyte impurities on electrode performance. Although impurities such as iron can be minimized on a laboratory scale they are always present industrially. The second section will discuss the effect of method of catalyst addition and the potential for optimization of this process.

5.5.1 Effect of Pre-electrolysis of Electrolyte

This section will discuss the results that were presented in §4.1.6. The first section, §5.5.1.1 will contrast the effect of electrolyte impurities on the electrode under constant current. The second section, §5.5.1.2 will compare the electrode surface post-testing to determine the state of the electrode and how it is affected by metallic impurities.

5.5.1.1 Chronopotentiometry

The results from chronopotentiometry testing for both types of electrolyte are presented in Figure 4.37. There are three major differences between the the two based on the presence of metallic impurities. The differences are;

i) the initial potential before catalyst addition is 150 mV lower in the case of the non-treated electrolyte when compared to the treated electrolyte,

ii) the potential drop associated with catalyst addition for the treated electrolyte is 200 mV greater than for the non-treated electrolyte, and

iii) the final potential for the treated electrolyte is 50 mV lower than for the non-treated electrolyte.

All of these differences are the result of metallic impurities in the electrolyte. In the case of the non-treated electrolyte, Fe is the major
impurity present. This was confirmed by EDX analysis of the platinum electrodes which were used to pre-electrolyze the solutions. In all cases, the appearance of a black film corresponding to Fe was observed.

The difference between the initial potentials is due to the Fe impurities in solution. As was discussed in section §2.3.1, nickel when subjected to constant current deactivates. This is a two phase process that is due initially to β-hydride formation (hydrogen penetration into the lattice), followed by a second phase which is controlled by the concentration of metallic impurities such as Fe. When the concentration of Fe exceeds ~0.5 ppm the effect is one of activation, marked by the growth of crystallites on the electrode surface which reduce the overpotential. This is accompanied by a reduction in the Tafel slope. Huot and Brossard have shown that the crystallites increase in size with time and that specifically for a 14 p.p.m. addition of Fe the effect of activation is of the order of a 70 mV reduction in overpotential [2.37]. This value is taken at overpotentials far anodic to the ones obtained in the present study but does serve to illustrate the general effect of Fe.

The difference in the potential drop associated with catalyst addition is due primarily to the difference in initial potential (which for the treated electrolyte is higher) but also to the mechanism of catalysis of the HER. This is influenced by the presence of Fe on the electrode surface which in turn affects the final potential.

The final potential of the treated electrolyte is lower than that for the non-treated electrolyte. This is due to the Fe present on the electrode surface. The mechanism of homogeneous catalysis with respect to the HER was presented in §5.4, and was shown to be a series of reactions involving chromium ions in solution and solid surface species. It was also previously shown that an increase in chromium concentration led to an increase in potential drop. Huot and Brossard have shown that molybdenum will co-precipitate in the presence of metallic impurities such as Fe [3.3]. While this hasn't been confirmed for chromium in the literature, there is evidence to suggest this will occur, as will be discussed in §5.5.1.2. This co-precipitation with Fe means that in the non-treated electrolyte, some of the chromium from the catalyst addition will be bound with Fe. As a result, less electrode surface area will be available for the formation of Cr₂O₃, effectively
reducing the concentration and the potential drop, and increasing the final potential.

5.5.1.2 Scanning Electron Microscopy (SEM)

The results from the SEM and EDX analysis for both the treated and non-treated electrolytes are presented in Figures 4.38 to 4.41. The main differences that are observed are a direct result of the pre-treatment. In the case of the treated electrolyte, the presence of both white particles and a background surface film is observed. EDX spot analysis confirmed the particles were chromium-based. Chromium is also present in the film as is a small amount of Fe.

For the non-treated electrolyte, the electrode surface has the same particles and surface film but there is the presence of a darker region underlying the chromium-based particles. EDX of the surface confirmed a higher relative level of Fe when compared with the treated electrolyte. Although the resolution of EDX was insufficient to determine the nature of the darker regions, the increased level of Fe coupled with the previously mentioned co-precipitating effect of Fe on molybdenum would suggest that there is a co-precipitation of chromium with Fe.

5.5.2 Effect of Means of Addition

This section will discuss the results presented in §4.1.7. The first section will address the effect of means of addition on the constant current potential for both single and multiple addition tests. The second section will contrast the electrode surfaces based on the two distinct means of addition.

5.5.2.1 Chronopotentiometry

Figure 4.42 shows the chronopotentiograms for two distinct types of catalyst addition. The first type was used throughout the entire experimentation phase and consisted of a single addition of catalyst at a specified concentration. The second type consisted of multiple additions at given increments of lower concentrations (20 additions of 5 p.p.m. each).
The number of additions was chosen to produce a final catalyst concentration equal to that of the single addition.

The three distinguishing features of the chronopotentiogram are,

i) the initial potential,
ii) the potential drop associated with catalyst addition, and
iii) the final potential.

While the first two features are independent, the final potential is a function of the initial potential and the potential drop.

The means of addition had little effect on any of these features. The initial potential, potential drop and final potential were all the same and independent of the two contrasting techniques. The only difference lay in the time to reach the final potential. In the case of the multiple additions, a longer period of time was required. This was simply because physically additions themselves took longer resulting in an increased time to reach the same concentration of catalyst.

The fact that there is no change in potential dependence at constant current between these techniques is reflected in the reaction mechanisms of catalysis that were proposed in §5.4. Since both provided the same concentration of chromium species for the reactions there is no driving force for one to be more catalytic than the other.

The logarithmic dependence that was observed for varying catalyst concentrations is again seen in the case of multiple additions. Figure 4.43 illustrates these effects for both types of additions. In the case of multiple additions the final potentials at lower concentrations lie anodic to those for the single addition. This is because the additions were made before a steady-state was reached (each addition was made at 10 minute intervals). If the system had been allowed to reach steady-state before the next addition was made the potential changes would be the same.

5.5.2.2 Scanning Electron Microscopy (SEM)

Scanning electron micrographs and their corresponding EDX spectra for both the single and multiple addition tests are shown in Figures 4.44 to 4.47.
In the case of the single addition, the micrograph and EDX spectrum for the electrode surface after catalyst addition are consistent with the previous findings that were discussed in §5.3.1.

In the case of the multiple addition the electrode surface shows a markedly different morphology. The chromium-based particles instead of being dispersed on the surface agglomerated into larger (10-15 μm) particles. This indicates that after the first addition, the chromate from each subsequent addition found it energetically more favourable to adsorb onto itself than onto the background film. There are two possible reasons for this.

The first is directly related to surface energy. It is energetically more favourable for the chromium to form one large spherical particle than to exist as a number of smaller ones. This doesn't take into account the effect of the applied current or local potentials on the electrode surface.

The second possibility is that locally where chromium has been deposited on the surface in the form of Cr₂O₃ there exists a lower current. Since chromium was proposed as depositing as Cr₂O₃, areas with lower currents and potentials would be favoured (according to the Pourbaix diagram).
6.0 Conclusions

1) The addition of a homogeneous catalyst of a transition metal, chromium, to the electrolyte lowers the cathodic overpotential for the HER.

2) The magnitude of the potential drop is dependent on the catalyst concentration and follows a logarithmic dependence.

3) The presence of iron alters the surface structure of the electrode. Fe lowers the electrode overpotential in the absence of a catalyst addition but in the presence of a chromium catalyst does so to a lesser degree.

4) The method of addition of the catalyst has no effect on the electrode overpotential, but does significantly affect the surface morphology.

5) The addition of chromium leads to the formation of oxides and hydroxides that catalyze the HER.
References

Introduction


1.2 J. Verne, "The Mysterious Island", 1874.


Background


**Experimental Procedure**


**Discussion**


Appendix-A


A.4 Ibid.


METHODS OF HYDROGEN PRODUCTION

A.1 Hydrogen Production from Fossil Hydrocarbons

A.1.1 Steam Reforming of Natural Gas

Steam reforming has been the most efficient, economical and hence widely used method for the production of hydrogen for the past several decades [A.1]. In this process, hydrocarbons and steam are catalytically converted to hydrogen and carbon oxides. This process only applies to hydrocarbons ranging from natural gas to naptha and light fuel oil since these can be completely vaporized without elemental carbon formation. The hydrocarbons react with steam in an endothermic reaction to form carbon monoxide and hydrogen. The process consists of three main steps:

i) Synthesis gas generation,
ii) Water gas shift, and
iii) Gas purification.

The efficiency of the process defined as the ratio of heating value of hydrogen produced to the energy input as raw material (ie. fuel, electricity) is 65 -75%. The price of the hydrogen produced is defined according to the following terms:

i) The time frame is mid-1987 (adjusted to 1997 dollars)
ii) The base plant capacity is $100 \times 10^6$ SCF/D
iii) The project life is 20 years
iv) The operating factor is 328 D/Y [A.2]

The full economic criteria are listed in §1.2, Table 1.1. With natural gas as the feedstock at a price of $4.10$/GJ, and allowing for a credit for the by-product steam of $6.70/10^3$ lb, the hydrogen production cost is $8.36$/GJ.
A.1.2 Partial Oxidation of Heavy Oil

The process of partial oxidation (POX) of heavy oil is very similar to the steam reforming process. The process uses various hydrocarbon feedstocks that range from methane to naptha when a catalyst is used, to feedstocks that are heavier than naptha in the absence of a catalyst. The preferred feedstocks are heavy residues from petrochemical processes which yield hydrogen and carbon monoxide rich gases. Again, there are three main steps:

i) Synthesis gas generation,
ii) Water gas shift reaction, and
iii) Gas purification.

The shift reaction and the gas purification, either by conventional wet scrubbing or by pressure swing adsorption are similar to those used in steam reforming. In the synthesis gas generation step the hydrocarbon feedstock is now partially oxidized with oxygen and the carbon monoxide that is produced is shifted with steam to carbon dioxide and hydrogen. The efficiency of the partial oxidation process is approximately 50%. The cost, assuming oil availability at $3.88/GJ is in the range of $13.73/GJ [A.3]. The credit for sulphur by-products such as H₂S from POX is too small to influence the overall hydrogen production economics.

A.1.3 Coal Gasification

This process is defined by pulverized coal being converted into gaseous products. The coal is fed into a gasification reactor, is heated and undergoes pyrolysis reactions to produce gases, volatile tar components and char. Contrary to the name the coal itself isn't gasified, it's the pyrolysis products and char. High purity oxygen (>95%) is used at high temperatures and pressures to produce hydrogen or hydrogen-rich products. The gasification reactions are:

\[ 2C + O_2 = 2CO + \text{heat} \]  \hspace{1cm} \text{(A.1)}
\[ C + H_2O + \text{heat} = CO + H_2 \] \hfill (A.2)

where, \( C \) = the pyrolysis products

The coal gasification process is complicated by the need of handling solid fuels and removal of large amounts of ash, which in turn is reflected in the cost. Using a price for coal of $2.57/GJ, the price of hydrogen production would be $18.78/GJ \[^{[A.4]}\]. Once again, the credit for the sulphur product would have a negligible effect on the overall economics.

A.1.4 Coke Oven Gas

The production of hydrogen from coke oven gas was the major source of hydrogen in the first half of this century \[^{[A.5]}\]. However, new iron production techniques in which iron oxide is reduced with synthesis gas need no metallurgical coke. The decrease in demand for metallurgical coke in turn led to decreased production of coke oven gas. Coke oven gas still remains an important and convenient source of hydrogen in areas where it is available. Coke oven gas leaves the coke oven batteries at 750-850 °C. The gas is cooled to ambient temperatures and oil and naphthalene fractions and hydrogen cyanide, ammonia and sulphur compounds are separated. The hydrogen content in the pre-treated gas is 50-60%. The separation of hydrogen from the gas is generally performed using the low temperature condensation method. Condensation of methane, ethylene and other higher boiling point compounds is carried out at 60-70 K. The hydrogen produced is approximately 95% pure. Further purification can be obtained using a nitrogen scrubber to remove methane, carbon monoxide and oxygen.

A.1.5 Steam Iron Process

The steam iron process is one of the oldest ways of producing hydrogen. It basically involves reacting steam with hot iron to produce a hydrogen-rich gas and iron oxide. Although a coal based process, hydrogen is obtained from the interaction of steam with iron oxide. The process consists of four main steps:

\[ \begin{align*} 
\text{i) Coal gasification, } \\
\text{ii) Iron regeneration, } 
\end{align*} \]
iii) Hydrogen generation, and
iv) Purification.

Effluent from a steam iron reactor contains 37% hydrogen and 61% steam, with small amounts of nitrogen and carbon oxides. The condensation of steam leads to an increase in the hydrogen concentration up to 96%. The cost of production using coal at $2.57/GJ is $20.85 GJ. However, the credit for by-product electric power at $0.03/kwh significantly reduces the hydrogen production cost to $15.88/GJ.

A.2 Hydrogen Production from Non-Fossil Hydrocarbons

A.2.1 Water Thermolysis

Theoretically, the simplest method of producing hydrogen is the direct thermal cleavage of water. Water can be thermally divided at temperatures above 2000 K. However, appreciable quantities of hydrogen can only be obtained at temperatures significantly higher than 2000 K. The overall thermal dissociation reaction of water can be represented as follows:

\[
H_2O = aH_2(g) + bOH(g) + cH(g) + dO(g) + eH_2(g) + gO_2(g) \quad \{A.3\}
\]

The thermolysis product of water is a mixture of gases dependent on the reaction temperature and pressure. The main problems associated with thermolysis are those related to the materials needed at very high temperatures. As well, recovery or separation of the hydrogen from the hot mixture can be problematic. Economically, this process is poor due to the recombination of the reaction products at high temperatures.

A.2.2 Water Radiolysis

Water can also be split by high energy radiation. The overall reaction for water radiolysis is:

\[
H_2O = aH + bOH + cH_2 + dH_2O_2 + eOH^- (aq) + g H^+ (aq) \quad \{A.4\}
\]
The energy from nuclear sources is in the form of high energy photons, gamma-rays or high speed particles. The rate of energy transfer to the medium is called linear energy transfer (LET). The yield value, G, is measured as the number of molecules converted per 100 eV absorbed energy. The G-value of hydrogen is greatly affected by the state of the medium and its chemical composition. The irradiation of liquid water using gamma-rays from a $^{60}$Co source gives $G(H_2) = 0.45$ [A.6].

A.2.3 Water Photolysis

The photolytic production of hydrogen is done by cleaving water by solar energy. The net photochemical reaction can be summarized:

\[ H_2O (l) + h\nu = H_2 + \frac{1}{2} O_2 \]  \hspace{1cm} \{A.5\}

The theoretical energy required to split the H-O bond in water is 1.229 eV. Therefore, a single photon with an energy of 2.458 eV is sufficient to split the water molecule. The necessary energy can be obtained from solar radiation, but the process must be made in several stages using several light quanta. Since this process is only on a laboratory scale a proper estimate of its potential cost is impossible.

A.2.4 Thermochemical Systems

Hydrogen is produced by chemical cleavage at temperatures lower than those used in thermolysis, by a series of cyclical chemical reactions which release hydrogen at a certain step. Thermochemical considerations have shown that in the range of 300-1000 K at least 3 chemical steps are needed to dissociate water. Further, modeling has shown that efficiency decreases with an increase in the number of reaction steps. Some 2000-3000 potential thermochemical cycles have been investigated, however, only 20-30 have remained practical for large scale hydrogen production. Some of the more investigated cycles are:

i) Sulphuric acid-iodine cycle,
ii) Hybrid sulphuric acid cycle, and
iii) Calcium bromide-iron oxide cycle.

The average efficiencies are 40-50% for the above cycles. These processes are not economical due to the required mass transport of materials to produce a small amount of hydrogen.

A.3 Unconventional Sources

A.3.1 Hydrogen Sulphide

A possible source of hydrogen is from hydrogen sulphide which is recovered in large amounts from desulphurizing processes in synthesis gas/natural gas production and in refineries. Hydrogen sulphide is an abundant resource that can be converted to elemental sulphur by means of the Claus process or by other oxidizing reactions. Recovery of hydrogen and sulphur from waste hydrogen sulphide is an interesting alternative to production of sulphur alone. Efforts to produce both have been attempted in recent years through various technologies [A.7].

A.3.2 Conversion of Biomass

Hydrogen production from biomass would involve accumulation, transportation and preparation of the biomass for the pyrolysis/gasification process. Biomass would first be heated up to high temperatures under pressure in a reactor. This would decompose and partially oxidize the biomass producing a gas product abundant in carbon dioxide, carbon monoxide, nitrogen, methane and hydrogen. This gas stream goes to a high temperature shift reactor, is converted to a product of hydrogen and minor amounts of carbon oxides and is purified by a pressure swing adsorption unit to produce high purity hydrogen.
A.4 Water Electrolysis

A.4.1 High Temperature Electrolysis

Increasing the temperature at which water electrolysis is performed decreases the theoretical voltage required. However, the voltage corresponding to ΔH, the thermoneutral voltage, increases slightly. Therefore, slightly more energy is needed at higher temperatures but the minimum requirement of electric energy is lower. More importantly, the voltage loss terms $\eta_A$, $\eta_C$ and $I R_o$ decrease considerably with an increase in temperature. Doped ZrO$_2$ or some other rare-earth oxides are known as lattice defect conductors and are used as the electrolyte. They become oxygen ion conductors at temperatures in excess of 800 °C. These materials are usually in the form of thin membranes (~ 0.5 mm) in order to reduce electrical resistance. Porous electrodes are placed on the surface of the membrane. The cathode, ZrO$_2$, is coated with nickel which acts as a hydrogen reaction catalyst. The anodes are mixed perovskite structures. Approximately 1.3 V is applied between the electrodes and 4 A/m$^2$ current densities are obtained in a typical water vapour electrolyzer operating at 900 °C.

A.4.2 Solid Polymer Electrolyte Electrolysis

A proton conducting ion exchange material (such as Nafion) is used to make a thin film diaphragm which acts in place of the electrolyte as a charge carrier. Charge is transferred by means of hydrated hydrogen cations of the sulphonic acid group of this polymer. The cathode is usually made of graphite with platinum acting as the catalyst. The anode is either sintered nickel or titanium with RuO$_2$ acting as catalyst. In solid polymer electrolyte electrolysis, water is added both to hydrate the hydrogen and to cool the system. The volume of this system is greatly reduced compared to an alkaline water electrolyzer due to the absence of an aqueous electrolyte. Extremely high current density values in the range of 20000 A/m$^2$ can be achieved in such systems.
APPENDIX-B

REFERENCE ELECTRODE CALCULATION

This appendix will summarize the calculations required to arrive at the reference electrode potential. Pertinent data have been extracted from, or extrapolated from referenced sources.
Density of water at 70°C: 0.99 g/cm³
Molecular weight of water: 18.015 g/mol
Molecular weight of KOH: 56.11 g/mol
Dissociation constant of water at 70°C: 1.53 X 10⁻¹³

pH Calculation

Zaytzev reported in Properties of Aqueous Solutions of Electrolytes that the mean molal ionic activity coefficient of 8M KOH is:

\[ \gamma_{\text{KOH}} = 2.679 \]

Following the procedure adopted by Suzuki, given the ion size parameters of K⁺ and OH⁻ are equal at 0.3, if the finite ion size modification of the Debye-Huckel limiting law is utilized, values for the molal activity coefficients of both K⁺ and OH⁻ will be the same due to equivalent ion size parameters. Further, it is assumed that the ionic molal activities of K⁺ and OH⁻ are the same.

\[ a_{\text{OH}^-} = (a_{\text{KOH}})^{0.5} = \gamma_{\text{KOH}} (m_{\text{OH}^-})^{0.5} \]

where \( a_{\text{OH}^-} \) is the molal ionic activity of hydroxide ion, \( a_{\text{KOH}} \) is the activity of KOH and \( m_{\text{OH}^-} \) is the molality of hydroxide ion assuming complete dissociation of KOH. For the present case,

\[ a_{\text{OH}^-} = 2.679 \times (1.0)^{0.5} = 2.679 \]

pH can be calculated from \( a_{\text{OH}^-} \) and the dissociation constant for water, \( K_w \).
\[ \text{pH} = -\log a_{\text{H}^+} = -\log \frac{K_w}{a_{\text{OH}^-}} = -\log 1.513 \times 10^{-13}/2.769 = 13.24 \]

**Hg/HgO Reference Electrode Potential**

Longhi [Longhi, P., J. Appl. Electrochem., 17, pp. 505 (1987)] established an empirical expression for the standard potential which incorporates the temperature dependence:

\[ E^\circ_{\text{Hg/HgO}} (\text{mV vs. SHE}) = 992.74 - 0.180807 T - 0.000129576 T^2 \]

where, \( E^\circ_{\text{Hg/HgO}} \) is the standard potential of Hg/HgO referred to SHE and \( T \) is the absolute temperature. Using a value of \( T \) of 343.15 K, \( E^\circ_{\text{Hg/HgO}} \) is 0.915 V vs. SHE.

In 8M KOH solution at 70°C, the potential of the Hg/HgO reference electrode is given by:

\[ E_{\text{Hg/HgO/8M KOH}} = -2.303(R/T/F) \times \text{pH} \]

where, \( R \) is the universal gas constant, \( T \) is the absolute temperature and \( F \) is Faraday's constant. The pH as previously calculated is 13.24. Finally, the reference electrode potential is obtained by:

\[ E_{\text{Hg/HgO/8M KOH}} = 0.915 - 2.303 \times (8.3143 \times 343.15/96486.7) \times 13.24 \]

\[ = 0.084 \text{ V VS. SHE} \]
APPENDIX-C

EQUILIBRIUM REDOX REACTION POTENTIAL

This appendix will deal with the calculation of the reversible hydrogen potential for an 8M KOH solution at 70°C. All calculations will be based on the standard potential and then converted to the potential in 8M KOH solution at 70°C. Pertinent data are listed below.

pH : 13.24
Temperature : 343.15 K
Hg/HgO reference electrode potential : + 0.084 vs. SHE
Gas Constant : R = 8.3143 J/K mole
Faraday's constant : F = 96486.7 C/mole
Dissociation constant for water at 70°C : Kw = 1.513 X 10^{-13}; pKw = 12.82

The reversible hydrogen potential defines the equilibrium between hydrogen gas and water. At this potential, the exchange current density of the reversible hydrogen redox reactions is measured.

2H2O + 2e^- = H2 + 2OH^-

E_{H2/H2O/ OH^-} = -0.827 - 2.303(RT/F) (pH - pKw - log aw)

where, Kw is the dissociation constant of water and aw is the activity of water. The activity of water was extrapolated from data given in Properties of Aqueous Solutions of Electrolytes. However, this value does not greatly affect the calculated potential.

E_{H2/H2O/ OH^-} = -0.827 - 2.303(8.3143(343.15)/96486.7)(13.24 - 12.82 - log(0.4236))

= -0.882 vs. SHE

C-1
The reversible hydrogen potential is thus,

\[ E_{\text{H}_2/\text{H}_2\text{O}^0/\text{H}^+} = -0.882 \text{ vs. SHE} \]

\[ = -0.966 \text{ vs. Hg/HgO} \]
APPENDIX-D

IR-DROP

Ohmic polarization (IR-drop) is of primary concern during electrochemical measurements in a high potential field. The IR-drop is due to the resistivity of the electrolyte, contact resistances in the leads and resistivity of the surface film. Quantification of the IR-drop is of concern in order to properly characterize electrode materials which may themselves have different inherent resistivities.

The definition of specific conductivity, $\sigma$, of an electrolytic solution allows for the calculation of IR-drop due to solution resistivity, $\Delta\psi$, by the following expressions:

$$E \ (V/m) = I/\sigma A = \Delta\psi/l$$

$$\Delta\psi \ (V) = I \ (l/\sigma A)$$

where, $E$ is the field strength, $I$ is the current, $A$ is the area through which the current flows, and $l$ is the length. Specific conductivity can also be expressed as:

$$\sigma = \sigma_{KOH} + \sigma_{H_2O}$$

$$\sigma_i = Z_i C_i \lambda_i$$

where, $\sigma_{KOH}$, $\sigma_{H_2O}$ and $\sigma_i$ are the specific conductivities of KOH, water and arbitrary chemical species, respectively. $Z_i$ is the valence, $C_i$ is the molar concentration and $\lambda_i$ is the limiting equivalent conductivity of a given species. Pertinent data were extrapolated or extracted directly from the CRC Handbook of Chemistry and Physics, 73rd Ed., CRC Press, 1992-1993.

$\sigma_{H_2O}$ at 25°C: $7.127 \times 10^{-6} \ (\Omega^{-1} m^{-1})$

$\lambda_{KOH}$ in 8M KOH solution at 70°C: $30 \times 10^{-4} \ (m^2\Omega^{-1}\text{eq}^{-1})$

$C_{KOH}$ of 8M KOH solution: 8000 (moles/m$^3$)
Using a value of 2mm for l, the IR-drop can be calculated at several current densities. Using a general current density, $I \text{ mA/cm}^2$,

$$\Delta \psi = I(2 \times 10^{-3} \text{ m})/(1 \text{ eq/mole})(8000 \text{ moles/m}^3)(30 \times 10^{-4} \text{ m}^2\Omega^{-1}\text{eq}^{-1})$$

$$= 0.0833 \ (I) \text{ mV}$$

The IR-drop for several current densities are calculated in Table D.1 below.

<table>
<thead>
<tr>
<th>$\Delta \psi \text{ (mV)}$</th>
<th>$I \text{ (mA/cm}^2\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.833</td>
<td>1</td>
</tr>
<tr>
<td>8.33</td>
<td>10</td>
</tr>
<tr>
<td>83.3</td>
<td>100</td>
</tr>
<tr>
<td>208.25</td>
<td>250</td>
</tr>
<tr>
<td>416.5</td>
<td>500</td>
</tr>
</tbody>
</table>

Table D.1: Ir-drop for several current densities.
APPENDIX-E

Calculation of Current Density Required to Meet Potential Drop

Data taken from test MNCP19:

Catalyst Addition = 100 p.p.m.
Potential Drop = 340 mV
Electrode Surface Area = 0.25 cm²

Data from SEM micrograph:

Area of micrograph = 11.5 cm x 10 cm = 115 cm²
Number of particles = 3
Diameter of particles = 2 μm
Scale of micrograph = 1 cm/2.85714 μm

Calculations:

Area of micrograph = 115 cm² (2.85714 μm²/cm²) = 938.78 μm²
Area of electrode = 0.25 cm² (10¹² μm²/cm²) = 2.5 x 10¹² μm²
Total number of particles = (2.5 x 10¹² μm²/938.78 μm²) x 3 = 7.989 x 10⁹
Surface area/particle = 4πr² = 4π(1 μm)² = 12.6 μm² = 1.26 x 10⁻¹² cm²
Total surface area of particles = 7.989 x 10⁹ (1.26 x 10⁻¹² cm²) = 0.01 cm²

Assuming R is constant, then V = IR, V = I = 340 mA

Current density = 340 mA/0.01 cm² ~ 34 A/cm²

Surface coverage of particles = 0.01 cm²/0.25 cm² x 100 ~ 4%