NICKEL - BASED AMORPHOUS ALLOYS
WITH Cr/V ADDITIONS
FOR THE HYDROGEN EVOLUTION REACTION
IN ALKALINE SOLUTION

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

Department of Metallurgy and Materials Science Engineering
University of Toronto

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Abstract

Alloy compositions of Ni_{55-x}Co_{25}B_{20}Cr_x and Ni_{55-y}Co_{25}B_{20}V_y where x = 1-20 and y = 1-10 were produced using the melt spinning technique. The amorphous nature of the alloys was confirmed by X-ray diffraction and their atomic composition verified by Inductively Coupled Plasma Spectroscopy. Differential Scanning Calorimetry was used to determine their thermal characteristics. The electrocatalytic activity of the alloys was measured using a steady state potentiostatic technique.

Polarization curves yielded data on the exchange current density and the Tafel slope values for the alloys. As the concentration of chromium and vanadium increased in the alloys, from 1 to 20 at.% and 1 to 10 at.%, the exchange current density increased from 4 to 16 x 10^{-5} A/cm^2 and from 3 to 6.6 x 10^{-5} A/cm^2 respectively. Increased Cr and V concentrations increased the Tafel slopes from 155 to 210 mV/dec and from 145 to 165 mV/dec respectively, in the low overpotential range.
Acknowledgements

I would like to thank my supervisors Dr. D.W. Kirk and Dr. S.J. Thorpe for their advice, guidance and patience throughout this project. I would also like to thank Stuart Energy Systems for initiating and funding this research endeavor.

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-Anson Sinanan
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LIST OF SYMBOLS AND ABBREVIATIONS

\( a_x \) = activity of species \( x \)
\( \text{ads} \) = adsorbed
\( b \) = Tafel slope (mV/dec)
\( \text{c.p.} \) = commercially pure
\( \text{Cps} \) = counts per second
\( C_x \) = molar concentration of species \( x \)
\( C_{\text{min}} \) = minimum solute concentration required to form an amorphous phase
\( D \) = effective crystallite dimension (nm)
\( \text{dec} \) = current decade
\( \text{DSC} \) = differential scanning calorimetry
\( e^- \) = electron
\( E \) = potential (V)
\( E_a \) = anode potential (V)
\( E_c \) = cathode potential (V)
\( E^o \) = standard potential of an electrochemical reaction (V)
\( E_{\text{rev}} \) = reversible potential (V)
\( E_{\Omega} \) = ohmic loss, IR (V)
\( \text{EDX} \) = energy dispersive x-ray spectroscopy
\( F \) = Faraday constant (96487 C/mol)
\( \text{GFA} \) = glass forming ability
\( \Delta G^o \) = Gibbs standard free energy change (J)
\( \Delta H \) = change in enthalpy (J/mol)
\( \text{HER} \) = hydrogen evolution reaction
\( i \) = current density (A/cm\(^2\))
\( i_o \) = exchange current density (A/cm\(^2\))
\( I \) = current (A)
\( \text{ICP} \) = inductively coupled plasma spectroscopy
\( k_i \) = rate constant of step \( i \)
\( K_w \) = dissociation constant for water
\( l \)  = length of field (m)
\( m_x \)  = molality of species x (mol/kg)
\( M \)  = metal species
\( M \)  = molarity (mol/L)
\( n \)  = number of electrons transferred
\( \text{OER} \)  = oxygen evolution reaction
\( \text{ppm} \)  = parts per million
\( r \)  = type of rate determining step \((r = 1 \text{ if electron step, } r = 0 \text{ if chemical step})\)
\( r_A \)  = atomic radius of solvent atom
\( r_B \)  = atomic radius of solute atom
\( \text{rpm} \)  = revolutions per minute
\( R \)  = universal gas constant \((8.314 \text{ J/K-mol})\)
\( R \)  = resistance \((\Omega\text{-ohms})\)
\( \text{rds} \)  = rate determining step
\( \Delta S \)  = change in entropy \((\text{J/K-mol})\)
\( \text{SEM} \)  = scanning electron microscope
\( t \)  = amorphous ribbon thickness
\( T \)  = temperature (K)
\( U_w \)  = wheel velocity
\( \Delta V \)  = volume mismatch
\( \text{XRD} \)  = X-ray diffraction
\( Z_e \)  = valence
\( \alpha \) = transfer coefficient

\( \alpha_a \) = anodic transfer coefficient

\( \alpha_c \) = cathodic transfer coefficient

\( \beta \) = symmetry factor (0.5 for electron transfer step)

\( \beta \) = full width at half maximum

\( \phi \) = surface coverage of reactant

\( \Delta \phi \) = potential drop across electrode-electrolyte interface (V)

\( \gamma \) = number of electron step before the rate determining step

\( \gamma_z \) = mean molal activity

\( \eta \) = overpotential (V)

\( \eta_a \) = anodic overpotential (V)

\( \eta_c \) = cathodic overpotential (V)

\( \eta_{250} \) = overpotential at 250 mA/cm\(^2\) (V)

\( \lambda \) = wavelength of X-ray radiation (Cu-K\( \alpha \) = 0.1542nm)

\( \lambda_e \) = limiting equivalent conductivity (m\(^2\)Ω\(^{-1}\)eq\(^{-1}\))

\( \lambda_\sigma \) = atomic size effect (\( \lambda_\sigma \) = 0.10)

\( \mu \) = chemical potential

\( \nu \) = number of times rate determining step (rds) occurs

\( \theta \) = Bragg angle of the maximum intensity peak

\( \rho_x \) = partial pressure of species x

\( \sigma \) = specific conductivity (Ω\(^{-1}\)m\(^{-1}\))

\( \Phi \) = osmotic coefficient

\( \Delta \Psi \) = IR drop (V)
1.0 Introduction

1.1 Toward a hydrogen economy

For generations the global environment has had to cope with the depletion of its natural resources and the absorption of pollutants due to the consumption of fossil fuels. There has been a gradual shift towards finding an acceptable replacement for the world's demand on fossil fuels as the primary source of energy. There have been great strides in this endeavor with the introduction of wind, solar, nuclear and hydroelectric alternatives to the production of electricity. The implementation of these techniques has reduced the world's dependence on fossil fuels but not to the point where it is no longer a threat to the global environment. Hydrogen, an energy carrier, is anticipated to join electricity as the foundation for a globally sustainable energy system.

Scientists have recognized hydrogen as a potential source of fuel since the early 19th century. Hydrogen is a transportable, storable and non-polluting fuel that can be found chemically bound in numerous materials such as natural gas, coal, biomass and water. Hydrogen is the simplest and most common element in the universe. It also has the highest gravimetric energy density of all known fuels.\(^{(1)}\)

The transportation, industrial and residential sectors have used hydrogen for many years. Currently, hydrogen is used industrially for refining petroleum, the production of ammonia and methanol, as a coolant in electrical generators and as a fuel in rocket engines to list a few. Hydrogen can be burned as a liquid or a gas. Motor vehicles can be converted to use hydrogen as a fuel, since hydrogen burns 50% more efficiently than gasoline and produces less air pollution.\(^{(1)}\) When hydrogen is combusted with pure oxygen, the products are heat and pure water. However, it is more likely that hydrogen
will be combusted with air, which contains nitrogen, and will produce small amounts of NOx gases in addition. Hydrogen has a higher flame speed, wider flammability limits, higher detonation temperature, burns hotter and takes less energy to ignite than gasoline. This means that hydrogen burns faster, but carries the danger of pre-ignition and flashback.¹

1.2 Fuel Cells

The use of fuel cells is a very promising alternative to fossil fuel or hydrogen fuel combustion engines. Fuel cells are electrochemical power generation devices. Sir William Grove recognized the value of deriving electric current directly from fuels in 1839, but it wasn’t until the 1960’s that fuel cells were employed in practical situations. The main components of a fuel cell are the anode, where the fuel is supplied, the cathode, where the oxidant is supplied, the electrolyte that permits the flow of ions between the anode and cathode, and a load connected by an external circuit. Different types of fuel cells rely on different ions to carry charge from one electrode to the other and are therefore generally distinguished by their electrolytes. Table 1.1 shows some of the major fuel cell types and their distinguishing features along with the ion responsible for charge transfer. Most fuel cells being developed consume hydrogen or hydrogen rich fuel. However, some fuel cells can directly use fuels such as methane, methanol, carbon monoxide or ammonia. The theoretical operation of fuel cells that use hydrogen is illustrated in Figure 1.1. At the anode, hydrogen fuel is supplied which dissociates into H⁺ ions and generates electrons. These ions migrate through the electrolyte towards the cathode where oxygen molecules combine with the migrating H⁺ ions and consume electrons to produce water. An electric potential is produced between the anode and the
cathode due to the generation of electrons at the anode and the consumption of electrons at the cathode. This potential difference drives current through the external load and is what makes the fuel cell a source of power. Fuel cells can be used to power a large array of appliances including automobiles. Development of fuel cells for stationary power generation is already approaching commercial reality.\(^{(2)}\)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Charge Transfer Ion</th>
<th>Temperature (°C)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline</td>
<td>OH(^-)</td>
<td>70-200</td>
<td>High current and power densities, high efficiency</td>
<td>CO(_2) intolerance</td>
</tr>
<tr>
<td>Proton-exchange membrane</td>
<td>H(^+)</td>
<td>80-110</td>
<td>High current and power densities, long operating life</td>
<td>CO intolerance, water management, noble catalyst</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H(^+)</td>
<td>150-210</td>
<td>Technologically well advanced</td>
<td>Relatively low efficiency, limited lifetime, noble catalyst</td>
</tr>
<tr>
<td>Molten carbonate</td>
<td>CO(_3)(^-)</td>
<td>550-650</td>
<td>High efficiency, internal fuel processing, high grade waste heat</td>
<td>Electrolyte instability, short operating life</td>
</tr>
<tr>
<td>Solid oxide ceramic</td>
<td>O(^+)</td>
<td>1000-1100</td>
<td>Internal fuel processing, high grade waste heat, long operating life, potentially inexpensive</td>
<td>High operating temperature, limited thermodynamic efficiency, relatively low ionic conductivity</td>
</tr>
</tbody>
</table>

Table 1.1 Major Types Of Fuel Cells\(^{(2)}\)
In order to use hydrogen as a fuel, safe and practical storage and transportation systems must be developed. New materials have been developed that allow the storage of hydrogen at extremely high pressures, however the costs of the tanks and compression are high. Hydrogen can be stored as a liquid, but it is a difficult process because the hydrogen must be cooled to -253°C. This requires a significant input of energy along with special materials and handling procedures. A potentially more efficient method of storing hydrogen is in the form of hydrides. Various pure and alloyed metals can combine with hydrogen to form stable metal hydrides, which when heated decomposes.
and releases the hydrogen. Research has been conducted on magnesium hydrides and alloys such as magnesium nickel, magnesium copper and iron titanium. Hydride storage of hydrogen has a higher density than that of compression. Utilization of hydride storage will depend on the identification of a metal alloy with a sufficient hydrogen adsorption capacity and that can operate under a practical temperature range. Hydrogen gas adsorption is another technique of storage. Hydrogen molecules can be adsorbed on activated charcoal (carbon) with storage density approaching that of liquid hydrogen. Another approach is the use of micro spheres, very small glass spheres that can store hydrogen at high pressures. The spheres are charged with hydrogen gas at high temperatures where the gas can pass through the wall of the spheres. At low temperatures the glass is impervious to hydrogen and it is locked in. Customized glass spheres are in development for this purpose. A definitive method of storage for hydrogen is a yet unsolved problem but there are advancements in this field continuously.\(^{(1,3)}\)

### 1.4 Hydrogen production

In order to use hydrogen as a source of fuel in the future, a method of harnessing the energy stored in hydrogen must be developed. This task will most probably be accomplished by the fuel cell technology in the near future. Secondly, a method of storage for this fuel of the future must be developed. The most important task however is the production of the fuel, hydrogen. Hydrogen bound in organic matter and water make up a large percentage of the earth’s surface. The decomposition of water into hydrogen and oxygen allow us to use the hydrogen as a fuel and return it in the same form making it totally recyclable. There are many methods for the production of hydrogen that are currently used, or are under research and development. Most of the hydrogen produced
today is done by natural gas steam reforming. Other methods include biomass gasification and pyrolysis, photobiological, photoelectrolysis, and water electrolysis to list a few. The choice of production methods varies depending on the quantity and the desired purity of hydrogen. Water electrolysis and in particular alkaline water electrolysis is fast becoming one of the most favorable techniques for the production of hydrogen. It is the simplest technology of producing hydrogen from non fossil fuels and because electrolysis cells have no moving parts it is reliable and the least labor-intensive method of producing hydrogen. Hydrogen produced by electrolysis is extremely pure, and electricity from renewable energy sources can be used making it very promising for the future.\textsuperscript{(1,4)}

1.5 Water electrolysis

Water electrolysis is the decomposition of water into hydrogen and oxygen by the passage of an electric current. Nicholson and Carlisle first carried out this experiment in 1800 after the discovery of Volta's pile. Today water electrolysis is performed on an industrial scale in electrolysers. Alkaline water electrolysers are preferred because with an alkaline medium there is less concern about corrosion than with an acidic medium. Also, no specialty materials are required for construction. An electrolyser consists mainly of an anode where oxygen is produced, a cathode where hydrogen is produced, a diaphragm that keeps the hydrogen and oxygen from mixing, and the electrolyte. The electrolyte is an alkaline medium usually potassium hydroxide (KOH) at a concentration of about 25–30 wt. %. A schematic of an alkaline water electrolyser is shown in Figure 1.2.
The reactions that occur at the electrodes are:

<table>
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<th>Reaction</th>
<th>Equation</th>
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<tr>
<td>Cathode</td>
<td>$2H_2O + 2e^- \rightarrow 2OH^- + H_2$</td>
<td>(1.1)</td>
</tr>
<tr>
<td>Anode</td>
<td>$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$</td>
<td>(1.2)</td>
</tr>
</tbody>
</table>

Overall Cell : $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (1.3)

There are basically two types of electrolysers, unipolar (tank type) and bipolar (filter press). In the unipolar design, cells are placed in one tank called a module and the anodes and cathodes are connected in parallel. This arrangement allows the entire module to have the same voltage as each individual cell. The cells are fed from one low voltage power source, which requires high current flow at low voltages as well as transformers and rectifiers. To attain required hydrogen production modules are connected in series. Most electrolysers are of the second type, bipolar design. In this design cells are stacked and connected in series. The electrodes in this type of electrolyser have two polarities. The opposite side of the cathode for one cell is the anode for the other cell. The voltage required to run the electrolyser is the sum of the voltages of the individual cells, which means low voltages are not required and power conditioning is simpler. A series arrangement also means that if one cell fails, the entire module fails. (4)
Figure 1.2  Schematic of an alkaline water electrolysis cell

1.6  The need for new electrode materials

The major operational cost of electrolytic hydrogen is the cost of the electricity, which is approximately 80%. It is therefore very advantageous to commercial electrolysers to reduce the power consumption for the decomposition of water. The cell voltage required for the breakdown of water into hydrogen and oxygen can be represented as:

\[ E = E_{\text{rev}} + \eta_a + \eta_c + E_\Omega \]  

(1.4)

where \( E_{\text{rev}} \) is the theoretical thermodynamic decomposition voltage of water

\( \eta_a \) is the anodic overpotential
\( \eta_c \) is the cathodic overpotential and
\[
E_\Omega \text{ is the ohmic losses (IR) due to electrolyte conductivity}
\]
Cathodic and anodic overvoltages are a substantial fraction of the total cell voltage. Higher temperatures and catalysts increase electrode reaction kinetics and help lower the overvoltage. Reduction of the overvoltages by catalysis without substantial increase in temperature is the ideal goal. To reduce the overvoltages at the anode and cathode require the development of new materials that can effectively catalyze the hydrogen and oxygen evolution reaction. The strong caustic environment has restricted the choice of materials for use as anodes and cathodes due to corrosion. Iron (Fe) and nickel (Ni) are known to be good electrocatalysts in alkaline environments. Nickel is more expensive than iron but because of its superior corrosion resistance and catalytic properties, it is widely used in commercial electrolysers. Catalysts based on noble metals such as platinum and ruthenium are the most active but they are very expensive. A low cost alternative to noble metals, a reduction of the noble metal loading and the improvement of the activity of nickel catalysts are the main goals in this field.

Surface modification of electrodes to increase the actual surface area by various methods have also led to the increase in catalytic activity and a reduction in the electrode overvoltages. Sintered nickel-aluminum or nickel-zinc leached in a caustic solution produces such an increased surface area electrode.\(^5\) The combination of materials that have a synergistic effect have also been shown to improve hydrogen catalysis properties.\(^5\)

The use of amorphous metal alloys is currently being studied for anode and cathode materials. Amorphous metals are produced by a rapid quenching technique and
as such possess unique properties not available in crystalline materials. Amorphous alloys can have very good corrosion resistance and can be produced in a wide variety of compositions. They have also demonstrated good electrode activity and as such are of great interest as electrode materials for the use in electrolyzers.
2.0 Objectives

The objectives of this project can be divided into three phases:

Phase 1: Production of Ni-Co-B-Cr and Ni-Co-B-V amorphous alloys

Phase 2: Characterization of the alloys using various techniques

1. Physical Characterization - SEM & XRD
2. Chemical Characterization - EDX & ICP
3. Thermal Characterization - DSC

Phase 3: (1) Determination of the electrocatalytic activity of the alloys with respect to the hydrogen evolution reaction (HER) in alkaline solution using polarization techniques.

(2) Determine the effect of chromium and vanadium additions as electrocatalytic agents.
3.0 Background And Literature Survey

3.1 Water Electrolysis

Water electrolysis is the electrochemical decomposition of water (H₂O) into its elemental components of hydrogen (H₂) and oxygen (O₂) due to the passage of a voltage between two electrodes in an aqueous conductive electrolyte.

3.1.1 Alkaline Water Electrolysis

When water electrolysis is done using an alkaline electrolyte such as potassium hydroxide, it is referred to as alkaline water electrolysis. The ion responsible for the charge transfer in such a system is the hydroxyl (OH⁻) ion. A schematic of an alkaline water electrolysis cell is shown in Figure 3.1. The reduction of water into hydrogen gas and hydroxyl ions occurs at the cathode, while at the anode the hydroxyl ions are oxidized to form water and oxygen gas. These two electrode reactions are summarized as follows:

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

The overall result is the decomposition of water into hydrogen and oxygen gas. The reaction that occurs at the cathode is called the hydrogen evolution reaction (HER) and similarly the reaction that occurs at the anode is called the oxygen evolution reaction (OER). Both these reactions have been studied for many years but it is the hydrogen evolution reaction that is the primary focus of this study. The hydrogen evolution reaction (HER) will be discussed in more detail in the following section.
3.2 Hydrogen Evolution Reaction

The feasibility of hydrogen production by water electrolysis is dependent upon the other electrode reaction, the evolution of oxygen. The electrochemistry of hydrogen and oxygen are intimately connected. The following sections describe the mechanism by which hydrogen is produced and some of the fundamental thermodynamic and kinetic considerations for the electrolysis of water.

3.2.1 Mechanism

The mechanism of the HER in aqueous solution involves the formation of an adsorbed hydrogen atom intermediate, $M_{ads}$ (Volmer reaction, Equation 3.1), the electroodic desorption of hydrogen into solution (Heyrovsky reaction, Equation 3.2),
and/or a chemical desorption by the combination of two adatoms (Tafel reaction, Equation 3.3).

\[
M + H_2O + e^- \xrightleftharpoons[k_{-1}]{k_1} MH_{ads} + OH^- \tag{3.1}
\]

\[
MH_{ads} + H_2O + e^- \xrightleftharpoons[k_{-2}]{k_2} H_2 + M + OH^- \tag{3.2}
\]

\[
MH_{ads} + MH_{ads} \xrightleftharpoons[k_{-3}]{k_3} 2M + H_2 \tag{3.3}
\]

where \(k_i\) and \(k_j\) are the rate constants of the forward and backward reactions respectively for the \(i\)th step. \(M\) is a free site on the metal surface and \(M_{ads}\) is the metal surface occupied by hydrogen adatoms.\(^{(6)}\)

### 3.2.2 Thermodynamic Considerations

The thermodynamics of the reaction

\[
H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \tag{3.4}
\]

which in electrolysers proceeds in the forward direction and in the reverse direction for fuel cells, has been studied for numerous years. The minimum potential difference that can be applied between the electrodes of an electrolyser is thermodynamically defined in term of the Gibbs energy change for the reaction

\[
E = -\frac{\Delta G}{nF} \quad (n=2) \tag{3.5}
\]

where

\[
\Delta G = \mu_{H_2} + \frac{1}{2} \mu_{O_2} - \mu_{H_2O} \tag{3.6}
\]

and \(\mu\) are the chemical potentials. \(\Delta G\) is a positive value for the reaction. For the alkaline water electrolysis the standard electrode potentials are:
Cathodic Reaction \((1.1)\) \[ E^o = -0.826 \text{ V vs SHE} \]

Anodic Reaction \((1.2)\) \[ E^o = +0.401 \text{ V vs SHE} \]

Overall Reaction \((1.3)\) \[ E_{\text{cell}} = -1.227 \text{ V vs SHE} \]

Rearranging Equations 3.5 and 3.6 gives

\[ -E = \frac{\Delta G^o}{nF} + \frac{RT}{2F} \ln\left(\frac{\rho_{H_2} \cdot \rho_{O_2}^K}{\alpha_{H_2O}}\right) \tag{3.7} \]

\(E\) measures the equilibrium cell potential, which is the difference between the reversible potentials of the anode and cathode. Equation 3.7 demonstrates that \(|E|\) is increased as the pressure is increased; it is also affected by the concentration of the electrolyte through the influence on the activity of water. \(E\) is also affected by temperature due to the dependence of \(\Delta G^o\) on temperature. \(E\) is decreased as the temperature is increased. From these dependence relationships, thermodynamics would suggest that the best conditions for energy savings would be an electrolyser operating at high temperatures and low pressures. This is however impractical due to solvent evaporation under these conditions. Thus the temperature can only be increased under high pressures.

While \(\Delta G\) can be used to calculate the minimum electrical energy required, the energy required to break and form molecular bonds is measured by enthalpy (\(\Delta H\)).\(^{(7)}\)

\[ \Delta G = \Delta H - T\Delta S \tag{3.8} \]

The difference between the free energy and the enthalpy (\(\Delta H\)) is governed by an entropy (\(\Delta S\)) change in the process. The entropy change cannot be converted to electricity, which means it must be supplied or removed as heat. For water electrolysis, the voltage corresponding to the enthalpy change can be calculated to be 1.47 volts under standard conditions. This is referred to as the "thermo neutral" voltage. However, the cell voltage corresponding to the free energy change is only 1.227 volts. This suggests that under
standard conditions water electrolysis performed by the application of 1.47 volts would generate hydrogen and oxygen isothermally, that is 100% thermal efficiency, and no waste heat would be produced. A voltage of 1.227 would also produce hydrogen and oxygen but would absorb heat from the surroundings. Practical electrolyser cells usually operate at voltages greater than 1.47 volts and liberate heat because of a variety of efficiency losses occurring within the cell.

The free energy change voltage, E or the reversible voltage required for the decomposition of water varies with temperature as shown in Figure 3.2. Raising the temperature lowers the voltage required for the breakdown of water, which is beneficial for the operation of electrolyser cells because, at higher temperatures the electrode processes proceed at a faster rate with fewer losses while requiring less energy input. The "thermo neutral" voltage varies very little with increasing temperature as shown in Figure 3.1. There are three regions or conditions that can be identified from this analysis:

1. hydrogen generation is impossible
2. hydrogen generation is performed at apparently greater than 100% efficiency and
3. hydrogen generation is performed at less than 100% efficiency with waste heat being produced
Electricity used to make hydrogen, waste heat evolved

Thermo neutral voltage

Heat and electricity used to make hydrogen

Reversible voltage

Water Thermodynamically Stable

Figure 3.2  Idealized Operating Conditions For Electrolyser\(^{(8)}\)
3.2.3 Kinetic Considerations

The potential difference required to drive reaction (3.4) at a practical rate can be split into several components.

\[ E = E_a + \eta_a - (E_c - \eta_c) + \Omega \]

(3.9)

Where \( \eta_a \) and \( \eta_c \) are the anodic and cathodic overpotentials which represent the surplus electrical energy required to overcome any energy barriers and activate the electrode reactions. \( \Omega \) is the ohmic drop due to electrolyte resistances, electrode structure and connecting circuitry. Both \( \eta \) and \( \Omega \) depend on current density. \( \Omega \) follows a linear relationship

\[ \Omega = IR \]

(3.10)

where \( R \) is the total resistance and \( I \) is current (Ohm's Law).

\[ \eta = \left( \frac{RT}{\alpha_a nF} \right) \ln \left( \frac{i}{i_{a,a}} \right) + \left( \frac{RT}{\alpha_c nF} \right) \ln \left( \frac{i}{i_{a,c}} \right) \]

(3.11)

called the Tafel equation where \( \left( \frac{RT}{\alpha_a nF} \right) = b \) is the Tafel slope.

From Equation 3.11 it follows that \( \eta \) will depend on the practical operating conditions of the electrolyser. Figure 3.3 shows the schematic relationship between applied potential and the obtained current. It can be seen that \( \Omega \) becomes more predominant as \( i \) increases. Energy saving can be accomplished by decreasing \( \eta \) and by minimizing \( \Omega \). The former can be accomplished by electrocatalysis while the latter is a matter of cell engineering. The two parameters are however inter-related, different electrode materials can enable a more convenient cell design.\(^{(9)}\)
Figure 3.3  Dependence of the components of the potential difference applied to an electrolysis cell on the circulation current\(^{9}\)

For an electrochemical reaction, the rate of the reaction, measured by \(i\), can be expressed by the Butler-Volmer equation.

\[
i = i_o (\exp((1-\beta)\eta F/RT) - \exp(-\beta\eta F/RT))
\]  

(3.12)

where  \(\eta\) = overpotential (mV) 
\(\beta\) = symmetrical factor  
\(i_o\) = exchange current density (mA/cm\(^2\))  
F = Faraday's constant (C/mol)  
R = Gas constant (J/mol*K)  
T = Temperature (K)
The term $\beta$ is often assumed to be 0.5 for simplicity and if the reaction contains multiple steps, the transfer coefficient, $\alpha$ is used instead.

$$\alpha_e = \gamma/v + r\beta$$}

(3.13)

$$\alpha_a = \gamma/v + r - r\beta$$}

(3.14)

where $\gamma = \text{number of electron steps before the rate determining step}$

$v = \text{number of times RDS occurs}$

$r = \text{type of RDS, } r=1 \text{ if it is an electron transfer step, } r=0 \text{ if it is a chemical step}$

$\beta = \text{the symmetry factor (usually equal to 0.5)}$

Equation 3.12 thus becomes

$$i = i_0 \exp(\alpha_e \eta F/RT) - \exp(-\alpha_e \eta F/RT)$$}

(3.15)

At high cathodic overpotentials ($\eta < -0.1V$), as is necessary for the production of hydrogen, the anodic term in Equation 3.14 becomes negligible and the equation reduces to the Tafel equation for a cathode:

$$\eta_c = (2.303RT/\alpha_e F)\log(i_{oc}) - (2.303RT/\alpha_e F)\log(i_c)$$}

(3.16)

which is of the form $\eta = a + b \log i$

The exchange current density, $i_0$, and the Tafel slope, $b$, are the most important parameters in evaluating the electrocatalytic activity of electrode materials.\(^{(10)}\)

### 3.2.4 Tafel Analysis

The exchange current density, $i_0$, and the Tafel slope, $b$, are both dependent on the electrode material. The minimization of overvoltage, $\eta$, is a matter of materials selection. According to equation 3.16 the performance of an electrode can be accomplished by either increasing the exchange current density, $i_0$, or by decreasing the Tafel constant, $b$ or both if possible. An examination of some hypothetical Tafel plots (Figure 3.4) show
that more active materials will have higher $i_0$ (curve 3 has the highest $i_0$ and as such is the most active at low $\eta$). Materials with indistinguishable $i_0$ values but with different Tafel values will have different activities. At high $\eta$ the reaction rates will differ and the more active materials can be distinguished by their corresponding current densities. The higher the current density for a given overpotential is indicative of the more active material. As depicted in Figure 3.4 for a given $\eta_0$ curve 2 has a higher activity than curve 1 given that they both have similar $i_0$ values. Similarly, for materials with the same Tafel slopes the higher the current density for a given overpotential the more active the material (Curve 3 is the most active for a given $\eta_0$).

When there is non-linear behavior there can be some uncertainty in the interpretation of the data. Stern and Geary’s analysis of the shape of polarization plots summarized the phenomenon that can cause non-linearity.\(^{11}\) Linear behavior is typical of activation polarization. Deviations from linearity at high overpotentials can result from concentration polarization and/or resistance polarization. Secondary reactions such as corrosion reactions also contribute to non-linear behavior. These cases are depicted in Figure 3.5.
Figure 3.4  Hypothetical cathodic Tafel plots
Figure 3.5 Possible $\eta$-log $i$ phenomena for a non-corroding electrode system
$Z^+ + e^- \leftrightarrow Z$ (line $\cdots\cdots$)\(^{(11)}\)

a) activation polarization
b) activation polarization and concentration polarization with limiting current
c) resistance polarization
d) second electrochemical (corrosion) process $M^+ + e^- \leftrightarrow M$ (line $\cdots\cdots$)
3.3 Catalysis

Catalysis occurs when the presence of a catalyst provides an alternate path of lower activation energy by which the reactants can proceed to form the products. A catalyst lowers the energy of the transition state, or activated complex significantly, while the energies of the reactants and products remain the same. Since a catalyst provides a path that requires lower energy of activation, a much higher proportion of the total molecules will have sufficient energy to react effectively along the catalyzed path than could have reacted along the uncatalyzed path. The rate of reaction can be greatly increased by the presence of a catalyst. However, there is no change in the free energy of the reaction since the catalyst does not affect the energies of the products and reactants. The decrease in activation energy applies to the reverse reaction as well as to the forward reaction, and the position of equilibrium will remain unchanged on the addition of a catalyst because the rates of the forward and reverse reactions would have both been increased. These are important properties of catalysts.\(^{(12)}\)

3.3.1 Types of Catalysis

Catalytic systems can be divided into three distinct categories, homogeneous catalysis, where the reactants and catalysts are present in the same phase, heterogeneous catalysis, where the reactants and catalysts are present in different phases and enzyme catalysis.\(^{(13)}\) Enzyme catalysis is of no relevance to this thesis and will not be elaborated upon.

3.3.2 Homogeneous Catalysis

In homogeneous catalytic reactions, the catalysts and reactants are present in one phase. Although there are some examples of gaseous homogeneous catalytic reactions,
most reactions are in the liquid phase. This creates a major disadvantage since separating the products from the catalysts becomes very difficult. When a homogeneous catalyst is added to a solution system it can either produce metastable complexes or adsorb directly on the electrode surface. This has the effect of lowering the activation energy required for the desired reaction. There are many industrial applications where homogeneous catalysis is used, however there is little information as to the mechanisms for these catalytic reactions.\(^{(14)}\)

### 3.3.3 Heterogeneous Catalysis

Heterogeneous catalytic reaction systems, in which fluid reactants are in contact with a solid catalyst, are at present the most widely used catalytic process. Solid catalysts are classified according to their chemical nature into metals (Pt, Pd, Fe, Ni), semiconductors (NiO, ZnO, Cr\(_2\)O\(_3\), NiS), insulators (Al\(_2\)O\(_3\), MgO) and solid acids (zeolites). With heterogeneous catalytic reactions the following steps usually occur:

1. Diffusion of reactants from the bulk fluid to the surface of the catalytic particle.
2. Adsorption of reactants on the surface of the solid catalyst.
3. Surface catalyzed reaction to form products.
4. Desorption of products.
5. Diffusion of products from the surface of the catalyst particle to the bulk fluid.

Electrocatalysis implies the concept of heterogeneous catalysis at electrode surfaces and therefore the criteria that govern heterogeneous catalysis such as geometric and electronic factors also apply to electrocatalysis. These factors and how they affect the catalytic properties of materials will be elaborated upon in the following sections.\(^{(15)}\)
3.3.4 Electrocatalysis

Electrocatalysis as stated before is essentially heterogeneous catalysis at an electrode surface. The fundamental difference between these two types of catalysis is the activation processes. Heterogeneous catalysis is temperature controlled while electrocatalysis is mainly controlled by an electric potential. A comparison between heterogeneous catalysis and electrocatalysis is shown in Table 3.1.\(^{(16)}\)

<table>
<thead>
<tr>
<th></th>
<th>Heterogeneous Catalysis</th>
<th>Electrocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Dependence</td>
<td>(\exp(-\Delta G^\circ/RT))</td>
<td>(\exp(-\alpha F \Delta \phi/RT))</td>
</tr>
<tr>
<td>Potential Dependence</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Temperature Dependence</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Operating Temperature (°C)</td>
<td>Above 150°C</td>
<td>Below 150°C</td>
</tr>
<tr>
<td>Activation Energy (kJ/mol)</td>
<td>= 40-400</td>
<td>= 30-150</td>
</tr>
</tbody>
</table>

Table 3.1 Comparison between Heterogeneous Catalysis and Electrocatalysis

where

\(\Delta G^\circ\) = the change in standard Gibbs free of a chemical process (J/mol)

\(R\) = the gas constant (J K\(^{-1}\)mol\(^{-1}\))

\(T\) = temperature (K)

\(\alpha\) = transfer coefficient

\(F\) = Faraday’s constant (C mol\(^{-1}\))

\(\Delta \phi\) = potential drop across the electrode–electrolyte interface (V)

The principles of electrocatalytic studies are the enhancement of the reaction rate through the decrease in the activation energy of the desired reaction, either by formation of more favorable adsorption bonds or through the a more convenient sequence of reaction steps.
According to Equation 3.11, the reaction rate depends on both the exchange current density \(i_o\) and the Tafel slope \(b\). Improvement of the performance of an electrode can thus be accomplished by either increasing the exchange current density or by decreasing the Tafel slope.

3.3.4.1 Chemisorption

Electrocatalysis, like heterogeneous catalysis, is a chemisorption process. Chemisorption is a process in which the adsorbate interacts with the adsorbant forming a chemical bond by the re-arrangement of electrons. Chemisorption is a strong, selective process and is a function of surface geometric factors and electronic factors.

3.3.4.2 Geometric Factors

Surface geometric factors include interatomic spacing of crystals (lattice spacing), the presence of coordinatively unsaturated sites (CUS) on the surface and other crystal defects. Bockris and Srinivasan demonstrated that the minimum activation energy of chemisorption occurred at an optimum interatomic spacing. If the lattice spacing were too small, the chemisorption would be weak due to repulsive forces between the adsorbates. If the lattice spacing were too large, the intermediate species would dissociate. As a result specific crystal planes would be more catalytically active than others.\(^{17}\) Khomutov later concluded that for the hydrogen evolution reaction the optimum inter-atomic distance approached that of a water molecule.\(^{18}\)

Coordinately unsaturated sites such as steps, kinks and surface defects act as active sites for the adsorption/desorption processes which occur on the surface. These sites have a lower coordination number (number of atoms surrounding them) and as such are at a high interaction energy state giving them high adsorption activity (the ability to
adsorb atoms). This makes these sites favorable to chemisorption. Crystal defects such as dislocations, have the same low activation energy for chemisorption similar reasons.\(^{(17)}\)

### 3.3.4.3 Electronic Factors

The electronic configurations are another important factor in the determination of the catalytic activity of a material. Catalytic reactions take place via a chemisorption process of one or more reactants on the surface of the electrode, which then changes the electronic and geometric configuration of the reactants thus increasing the reaction rate. Chemisorption can be measured by the heat of adsorption. A correlation between the heat of hydrogen adsorption and catalytic activity give rise to a "volcano curve" relation (Figure 3.6a). The Principle of Sabaties\(^{(19)}\) suggests that the catalysts exhibiting maximum activity will be those having optimum bonding of the surface species and therefore an intermediate heat of formation or adsorption. At low heats of adsorption, the chemisorption will be weak. Only a small area of the surface is covered by the reactants, which is insufficient to sustain the reaction. Desorption of the reactants will occur before any chemical or electrochemical transformation can occur. At higher heats of adsorption there is an increase in the surface coverage of the electrode by the reactants approaching full coverage (\(\phi \to 1\)). When the surface coverage by the adsorbent approaches 100% the catalytic activity is at an optimum. At heats of adsorption in excess of this, the chemisorption will be too strong resulting in the formation of stable species on the surface of the electrode that will inhibit catalytic activity. This is due to the blocking of reaction sites on the surface of the electrode. This relationship is depicted in Figure 3.6 a & b.\(^{(20)}\) Volcano curves have been verified for the case of hydrogen evolution on pure metals. An experimental volcano curve is shown in Figure 3.7.\(^{(21)}\)
Figure 3.6  Theoretical "volcano" curve relationship between heat of adsorption of HER intermediate and activity\textsuperscript{(28)}
Figure 3.7 Exchange current densities for electrolytic hydrogen evolution vs. bonding adsorption strength (enthalpy) of intermediate metal-hydrogen (M-H) bond formed during the electrode reaction itself\textsuperscript{(21)}
The electrocatalytic activity of a metal is a function of its group in the Periodic Table of the Elements. The elements that satisfy the chemisorption criteria are the transition metals. The heat of adsorption and formation (for hydrogen, oxygen etc.) on transition metals decrease from left to right in each period. The elements with the greatest catalytic activity are the Group VIII metals of the transition metals. The electron band theory relates the effect of the d-band electrons overlapping with the higher s-band electrons resulting in some energy levels remaining unfilled in the d-band. These holes act as unpaired electrons, which can form an adsorption bond with the s and p-band electrons of the adsorbate. This theory is only applicable to the Group VIII metals and does not account for the catalytic behavior of the other transition metals.

The valence-band theory is more applicable to the transition metals. It states that transition metals have two types of electron orbitals, a dsp hybrid orbital and which overlap to form metallic bonds and an atomic orbital which contains unpaired electrons and an unfilled d-orbital. The percentage d-band character describes the amount that the d-band electrons participate in the dsp hybridization, which reflects the extent to which the d shells are filled. Metals that have more unpaired electrons in their d shells have a lower percentage d-band character. This allows for the unpaired d-band electrons in the metal to pair with unpaired s- or p-band orbital electrons from H or other donating atoms or molecule, which results in chemisorption. The percentage d-band character of each transition metal can be determined and shows that the group VIII metals have the optimum percentage d-band character. The Group VIII metals also have intermediate heat of adsorptions that correspond to high catalytic activity, hence a relationship between d-band character and catalytic activity can be inferred. Experimental work
performed on the electrocatalytic HER process show excellent agreement between the high d-band character and high catalytic activity for the Group VIII metals such as Ni, Pd, Rh, Pt etc.\textsuperscript{(23)} Electronic configuration theories are however not conclusive on the behavior of electrocatalytically active transition metals. Studies of the HER on Ag-Pd alloys claimed that there was no correlation between electrocatalysis and electronic configurations.\textsuperscript{(24)} Similar conclusions were made on studies of Ni-Mo\textsuperscript{(25)} and Ni-Mo/Co.\textsuperscript{(26)}

3.4 **Amorphous Alloys**

Amorphous alloys, also called metallic glasses are a unique class of materials that are composed primarily of metallic elements but have the atomic structure of a glass. Amorphous alloys exhibit some remarkable physical and chemical properties. The metallic glasses reported in literature to date fall into well defined categories as follows;

1) late transition metal + metalloid

2) early transition metal + late transition metal or group IB metals

3) earth alkali metal + group IB metal

4) early transition metal + alkali metal and

5) actinide + early transition metal

Amorphous alloys of categories (1) and (2) are exclusively used in catalysis research.\textsuperscript{(27)}

3.4.1 **Production and Properties of Amorphous Alloys**

The production of amorphous alloys is dependent upon two primary factors; the cooling rate of the alloy and the concentration of the constituents, which affect the glass forming ability (GFA) of the alloys. There are many different techniques that can be
used to prepare amorphous alloys. The different techniques each have their advantages and disadvantages and produce different types of materials, the most common of which are thin films, foils and ribbons. Some of the more commonly used methods of producing amorphous alloys are listed in Table 3.2

<table>
<thead>
<tr>
<th>Production Technique</th>
<th>Type of material produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Evaporation</td>
<td>Thin Film</td>
</tr>
<tr>
<td>Sputtering</td>
<td>Thin Film</td>
</tr>
<tr>
<td>Glow-discharge Decomposition</td>
<td>Thin Film</td>
</tr>
<tr>
<td>Chemical Vapor Deposition</td>
<td>Thin Film</td>
</tr>
<tr>
<td>Melt Quenching</td>
<td>Flakes, ribbons, wires, rods</td>
</tr>
<tr>
<td>Gel Desiccation</td>
<td>Bulk material</td>
</tr>
<tr>
<td>Electrolytic Deposition</td>
<td>Thick Film</td>
</tr>
<tr>
<td>Reaction Amorphization</td>
<td>Thin Film</td>
</tr>
<tr>
<td>Irradiation</td>
<td>Thin surface layers</td>
</tr>
<tr>
<td>Pressure Induced Amorphization</td>
<td>Powders</td>
</tr>
<tr>
<td>Solid State Diffusional Amorphization</td>
<td>Bulk Material</td>
</tr>
<tr>
<td>Mechanical Alloying</td>
<td>Bulk Material</td>
</tr>
</tbody>
</table>

Table 3.2 Techniques for the production of amorphous alloys

Although most of the known preparation methods can be used for the production of metallic glasses, the most frequently used technique is a form of melt quenching called melt spinning.

Not all metals or alloy combinations can be produced in an amorphous state. As previously mentioned, the two main factors that influence the formation of an amorphous state are the cooling rate and the concentration of the constituents. Different substances can produce an amorphous state by applying an appropriate cooling rate. Determination of this cooling rate is critical to the formation of an amorphous phase. Certain easy glass
formers such as \( \text{B}_2\text{O}_3 \) will form an amorphous phase under conditions of very slow cooling (1K/s), whereas other materials such as metallic glasses require very high cooling rates. Typical cooling rates of \( 10^2 - 10^3 \) K/s produce materials with a thickness of up to 10mm, rates of \( 10^5 - 10^8 \) K/s for a thickness up to 0.1 mm and \( 10^9 \) for a thickness up to 0.1 \( \mu \)m. Cooling rates of \( 10^6 \) K/s or higher are typically required to produce metallic glasses.\(^{29}\) The melt spinning process achieves a cooling rate in the range of \( 10^6 - 10^8 \) K/s and as such is ideal for the production of metallic amorphous alloys.

There are three methods used to attain the high rates of cooling required to produce an amorphous phase,

a) by imposing high under-cooling prior to solidification

b) by imposing a high velocity of advance of the solid/liquid interface during continuous solidification and

c) by imposing a high cooling rate during solidification

Imposing high under-cooling prior to solidification is a process in which a material is super-cooled to a certain temperature at which the latent heat released during solidification is entirely dissipated within the solidifying volume before being transferred to the environment. The re-heating of a solidifying body is termed recalescence.

Imposing a high velocity of advance of the solid/liquid interface during continuous solidification can be achieved by withdrawal of a thin layer of material at a high velocity through a steep temperature gradient that constrains solidification to advance with a high front velocity causing all the heat to be dissipated radially.

Imposing a high cooling rate during solidification can also cause a high solidification front velocity depending on the rate of heat removal. The same result can
be achieved indirectly by first under-cooling the melt sufficiently to promote rapid solidification during recalescence.\(^{(30)}\)

The concentrations of the constituents directly affect the glass forming ability (GFA) of an alloy. The most important factors affecting the glass forming ability of an alloy include the atomic size ratio, alloy crystallization temperature and melting point, heat of formation, the number of components in the alloy and the chemical affinity of the neighboring constituents in the alloy\(^{(31, 32)}\). Of all the factors listed that affect the glass forming ability, the atomic size ratio is the most important. An empirical equation for the minimum solute concentration \(C_{B}^{\text{min}}\) using the criteria of volume mismatch to estimate the GFA is given by,

\[
\lambda_{o} = C_{B}^{\text{min}} \left| \frac{\Delta V_{AB}}{V_{A}} \right| \quad \text{where} \quad \frac{\Delta V_{AB}}{V_{A}} = \frac{r_{A}^{3} - r_{B}^{3}}{r_{A}^{3}} \quad (3.17)
\]

\(
\lambda_{o} \quad \text{= the atomic size effect of constituent elements on glass formability in binary systems (} \lambda_{o} = 0.10\)
\)

\(\frac{\Delta V_{AB}}{V_{A}}\) = the volume mismatch where A is the solvent and B is the solute

\(C_{B}^{\text{min}}\) = the minimum solute concentration necessary to form an amorphous phase

\(r_{A}\) = the atomic radius of the solvent atom

\(r_{B}\) = the atomic radius of the solute atom

The expression can be expanded for ternary alloys and beyond as

\[
\lambda'_{o} = C_{B}^{\text{min}} \left| \frac{\Delta V_{AB}}{V_{A}} \right| + C_{B}^{\text{min}} \left| \frac{\Delta V_{AB}}{V_{A}} \right| + ... \quad (3.18)
\]
The terms $\lambda_0$ and $\lambda'_0$ usually attain a constant value of 0.10 for glass formation. This value is related to the elastic strain energy surrounding an atom.\(^{(31)}\) The presence of metalloids such as B, P and Si tend to increase the glass forming ability of an alloy.

Amorphous alloys have significantly different properties compared to their corresponding crystalline structures. The typical characteristics of amorphous alloys are listed in Table 3.3.\(^{(33)}\) Many of the enhanced properties of amorphous alloys are due to their structure and composition.

<table>
<thead>
<tr>
<th>Mechanical</th>
<th>High Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Toughness</td>
</tr>
<tr>
<td></td>
<td>High Tensile Strength</td>
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<tr>
<td></td>
<td>High Deformability</td>
</tr>
<tr>
<td></td>
<td>High Fracture Strength</td>
</tr>
<tr>
<td></td>
<td>Small temperature dependence of linear expansion</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>High Corrosion resistance</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Soft Magnetism</td>
</tr>
<tr>
<td></td>
<td>Low loss factor</td>
</tr>
<tr>
<td></td>
<td>Ideal square loops in B-H hysteresis</td>
</tr>
<tr>
<td>Electrical</td>
<td>Small temperature coefficients of electrical resistivity</td>
</tr>
<tr>
<td></td>
<td>Super-conducting behavior</td>
</tr>
<tr>
<td>Other</td>
<td>Very low sound velocity and attenuation</td>
</tr>
<tr>
<td></td>
<td>Resistance to radiation damage</td>
</tr>
</tbody>
</table>

**Table 3.3 General Properties of Amorphous Alloys\(^{(33)}\)**

The major disadvantage associated with amorphous alloys is their thermodynamic stability. Amorphous alloys are metastable materials and will form stable phases when heated above their crystallization temperature. The crystallization temperature varies for the types of alloys but is generally in the range of 400°C to 500°C.
3.4.2 Motivation for using Amorphous Alloys As Electrocatalysts

The motivation to use amorphous alloys as catalytic surfaces, initially as heterogeneous catalyst and then as electrocatalyst originated from their unique properties which some are listed as follows

1. ideally the surface of amorphous materials should be devoid of any long range ordering of the constituents and exhibit a high density of low coordination sites and defects. The important role of low coordination sites such as terraces, steps and kinks was previously mentioned and was demonstrated by Somorjai$^{(34)}$ on crystalline materials

2. glassy metals should posses high flexibility with regard to fine tuning of the electronic properties mainly because thermodynamic constraints are less stringent in super-cooled liquids than in crystalline materials$^{(35)}$

3. glassy metals are ideally chemically homogeneous and structurally isotropic

4. glassy metals are highly reactive due to their metastable structure and undergo solid-state reactions more easily than their crystalline counterparts. This property is of importance in their use as catalysts precursors

5. glassy metals exhibit good conductivity for electricity and heat. These properties paired with excellent corrosion resistance make them particularly interesting for application in electrocatalysis

6. glassy metals prepared by melt-quenching exhibit planar morphology ideal for structural investigation

7. their manufacturing as foils and ribbons may facilitate the design of new reactor concepts.
Table 3.4 lists some amorphous alloys that have been used in catalytic studies of certain reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Amorphous Alloys</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenation of CO</td>
<td>Fe₄₀Ni₄₀P₁₆B₄</td>
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</tr>
<tr>
<td></td>
<td>Fe₂₀Ni₆₀P₂₀</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Fe₉₀Zr₁₀</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Fe₈₁B₁₃₅Si₃₅C₂</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Ni₆₇Zr₃₃</td>
<td>40</td>
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<td>Pd₃₅Zr₆₅</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Au₂₅Zr₇₅</td>
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<tr>
<td></td>
<td>Rh₂₅Zr₇₅</td>
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<tr>
<td></td>
<td>Pt₂₅Zr₇₅</td>
<td>42</td>
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<tr>
<td></td>
<td>Pd₂₅Zr₇₅</td>
<td>42</td>
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<tr>
<td></td>
<td>Os₂₅Zr₇₅</td>
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<tr>
<td></td>
<td>Ir₂₅Zr₇₅</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Fe₈₂₂B₁₇₈</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Fe₈₀B₂₀</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Fe₄₀Ni₄₀B₂₀</td>
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</tr>
<tr>
<td></td>
<td>Ni₇₈P₁₉La₃</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Ni₈₁P₁₉</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Cu₇₀Zr₃₀</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Cu₆₀Ti₄₀</td>
<td>46</td>
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<tr>
<td></td>
<td>Cu₆₄Hf₃₆</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Cu-Ce-Al</td>
<td>47</td>
</tr>
<tr>
<td>Hydrogenation of CO₂</td>
<td>Cu₇₀Zr₃₀</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Pd₃₅Zr₆₇</td>
<td>49</td>
</tr>
<tr>
<td>Hydrogenation of</td>
<td>Fe₄₄₋ₓNi₅₇CrₓP₁₃B₄ (x&lt;10)</td>
<td>50</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Pd₈₀Si₂₀</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Pd₇₇Ge₂₃</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Ni₈₁P₁₉</td>
<td>53</td>
</tr>
<tr>
<td>Process</td>
<td>Alloy</td>
<td>Activity</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Ammonia synthesis</td>
<td>Fe$_9$Zr$_9$</td>
<td>57</td>
</tr>
<tr>
<td>Reduction of NO</td>
<td>Ni$_9$Zr$_9$</td>
<td>58</td>
</tr>
<tr>
<td>Oxidation of CO</td>
<td>Pd$<em>{35}$Zr$</em>{67}$</td>
<td>60</td>
</tr>
<tr>
<td>Hydrogenation of methanol</td>
<td>Cu$<em>{67}$Ti$</em>{33}$</td>
<td>61</td>
</tr>
<tr>
<td>Decomposition of formic acid</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>62</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>Ni$<em>{62}$B$</em>{38}$</td>
<td>63</td>
</tr>
<tr>
<td>Cycloamination</td>
<td>Cu$<em>{70}$Zr$</em>{30}$</td>
<td>64</td>
</tr>
<tr>
<td>Hydrogen evolution in acid solution</td>
<td>Fe-Zr</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Ni-Zr</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Co-Zr</td>
<td>65</td>
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<tr>
<td></td>
<td>Ni-Nb</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Cu-Ti</td>
<td>66</td>
</tr>
<tr>
<td>Hydrogen evolution in alkaline solution</td>
<td>Cu-Zr</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Fe-Co-Si-B</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Co-Ni-Si-B</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 3.4  Amorphous alloys used in catalytic studies

For some instances the amorphous alloys used exhibited higher activity than their crystalline counterparts and even exceeded the best known catalysts. An example of this were demonstrated for the hydrogen evolution reaction in alkaline solution by Fe$_{60}$Co$_{20}$Si$_{10}$B$_{10}$ which showed higher activity than Pt and Ni. Although not all
amorphous alloys have high catalytic activity, they can be activated by chemical and electrochemical methods. These activation techniques usually result in a surface modification of the material. Chemical activation usually involved the immersion of the alloy in a strong acid such as HF to increase the surface area by the selective dissolution of a particular component.\(^{(68)}\) Electrochemical activation involved steady-state and dynamic electrochemical oxidation to modify the surface of the alloy in order to increase the activity.\(^{(69)}\)

### 3.5 Nickel Based Materials for Water Electrolysis

Cathodic and anodic overvoltages constitute a substantial fraction of the total cell voltage, particularly at low temperatures. Both higher temperature and suitable catalysts favor electrode reaction kinetics and help in lowering overvoltages. Reduction of overvoltages by catalysis without a substantial increase in temperature is an ideal approach in electrolyser improvement. While materials evaluation is an essential task of electrocatalysis, materials selection is not only based on electrocatalysis. Very often an electrode material must meet the following requirements in order to be of technological interest,

1) good electrocatalytic properties
2) good electric conduction
3) large specific surface area
4) enhanced selectivity
5) long term stability
6) minimized gas bubble problems
7) good mechanical properties
8) low cost and large availability
9) health safety

Corrosive alkaline electrolytes have essentially restricted the choice to Ni-based catalysts in alkaline electrolysers. A search for low-cost substitutes for noble metal catalysts or reduction of noble metal catalyst loading and improvement of the activity of nickel catalysts are the primary development goals. \(^{70,71}\)

The following sections give a general review of nickel and nickel-based electrode materials that have been studied for the HER in alkaline solutions.

### 3.5.1 Crystalline Nickel and Nickel-based Electrode Materials

Table 3.5 gives a partial list of some crystalline nickel and nickel based materials for which polarization data has been reported with respect to the hydrogen evolution reaction (HER). Table 3.5 lists the material, the solution in which it was tested, the exchange current density, \(i_0\), and the Tafel slope \(b_c\). Some materials have two Tafel slope values because they exhibited two Tafel regions during their polarization tests. From Table 3.5 it can be observed that the reported Tafel values for nickel and the nickel-based electrodes vary amongst the different references. Even when the conditions reported are similar, there are discrepancies between the reported values. The discrepancies between the reported values may be due to the pre-treatments that the electrodes under-went prior to polarization testing. Reported cathodic pre-treatments ranged from 30 minutes to 3 hours at overpotentials ranging between 300 and 400 mV, while others performed no pre-treatments. Since the exchange current density, \(i_0\) is an extrapolation of the Tafel slope there are similar discrepancies between reported values. The nickel-based electrode
materials are alloyed with other elements using various production techniques such as electroplating, powder pressing and Raney produced structures. These materials tend to produce exchange current density values that are superior to that of nickel. This is due in part to the fact that the real surface areas of these materials are much greater than that of the geometric surface area of nickel. However their Tafel slope values are comparable to those of nickel. There may be other factors that contribute to the discrepancies amongst reported Tafel slope values that are not forthcoming.
<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>Exchange Current Density, $i_0$ (mA/cm²)</th>
<th>Tafel slope, $b_c$ (mV/dec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1M KOH</td>
<td>30</td>
<td>0.006</td>
<td>96, 148</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.100</td>
<td>146</td>
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<td></td>
<td></td>
<td>30</td>
<td>0.032</td>
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<td>159</td>
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<td>0.126</td>
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<td></td>
<td></td>
<td>90</td>
<td>0.126</td>
<td>147</td>
<td>67</td>
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<td>73</td>
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<td></td>
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<td>80, 167</td>
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<td>0.010</td>
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<td>25</td>
<td>37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ni-Mo
Ni-Zn
Ni-Co
Ni-W
Ni-Fe
Ni-Cr
Ni-Mo-Fe
Ni-Mo-Cu
Ni-Mo-Zn
Ni-Mo-W
Ni-Mo-Co
Ni-Mo-Cr
Ni (99.99)
90Ni/10Zn
70Ni/30Zn
50Ni/50Zn
50Ni/50Zn
Raney Ni
Table 3.5  Polarization data for nickel and nickel-based electrode materials for HER in alkaline solution

<table>
<thead>
<tr>
<th>Pressed Powder:</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50Ni/50Al</td>
<td>&quot;</td>
<td>25</td>
<td>14</td>
<td>121</td>
</tr>
<tr>
<td>50Ni/50Al</td>
<td>&quot;</td>
<td>70</td>
<td>35</td>
<td>62</td>
</tr>
<tr>
<td>70Ni/30Al</td>
<td>&quot;</td>
<td>70</td>
<td>31</td>
<td>103</td>
</tr>
<tr>
<td>50Ni/50Al</td>
<td>30% NaOH</td>
<td>70</td>
<td>23</td>
<td>146</td>
</tr>
</tbody>
</table>

3.5.2 Amorphous Nickel-based Cathode Materials

Amorphous alloys have generally been studied for their corrosion resistance behavior. More recently they have gained recognition as potentially viable electrocatalytic materials for use as electrodes in many electrochemical processes, particularly for the HER and OER in alkaline water electrolysis. Table 3.6 lists the polarization data for some of the nickel-based amorphous alloys along with some Fe- and Co- based amorphous alloys that have been studied as potential electrode materials for the HER.

As previously mentioned not all amorphous alloys exhibit high catalytic activity in their as-spun states. Lian et al.\(^{(87)}\) produced Ni-Co-B-(P, Si) based amorphous alloys that showed inferior catalytic activity compared to crystalline nickel and cobalt for the HER, however after surface treatment of the amorphous alloys, their electrocatalytic activity surpassed that of their crystalline counterparts. This increase in activity was partially attributed to the increase in surface area of the amorphous alloys but it was not the only contributing factor. Suzuki et al.\(^{(26)}\) investigated the effect of Co/Mo ratios in amorphous Ni-(Co-Mo)-B alloys for the HER. Initially the amorphous alloys had inferior activity to that of crystalline nickel but after voltammetric potential cycling, the exchange current density of the Ni-(Co-Mo)-B amorphous alloys had increased when
compared to their as-polished states. Also, crystalline nickel exhibited signs of attack while the amorphous alloys were stable. There are amorphous alloys that have superior activity to crystalline Ni for the HER, namely Fe_{60}Co_{20}Si_{10}B_{10} and Fe_{46}Ni_{46}B_{20} which were studied by Kreysa and Hakansson.\(^{(67)}\) Although these alloys exhibited higher activity for the HER they had low corrosion resistance.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>Exchange Current Density, (i_0) (mA/cm^2)</th>
<th>Tafel slope, (b_c) (mV/dec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{50}Co_{25}Si_{15}B_{10}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.002</td>
<td>110, 178</td>
<td>72</td>
</tr>
<tr>
<td>Surface-treated</td>
<td>1M KOH</td>
<td>30</td>
<td>0.0003</td>
<td>90</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>0.00003</td>
<td>127</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>0.0001</td>
<td>113</td>
<td>67</td>
</tr>
<tr>
<td>Ni_{50}Co_{25}P_{15}B_{10}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.0016</td>
<td>101, 144</td>
<td>72</td>
</tr>
<tr>
<td>Surface-treated</td>
<td>1M KOH</td>
<td>30</td>
<td>0.0040</td>
<td>111, 166</td>
<td>72</td>
</tr>
<tr>
<td>Co_{50}Ni_{25}Si_{15}B_{10}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.004</td>
<td>124, 174</td>
<td>72</td>
</tr>
<tr>
<td>Surface-treated</td>
<td>1M KOH</td>
<td>70</td>
<td>0.00003</td>
<td>127</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.008</td>
<td>110, 172</td>
<td>72</td>
</tr>
<tr>
<td>Ni_{58}Co_{20}Si_{10}B_{12}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.001</td>
<td>140</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.02</td>
<td>146</td>
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<td></td>
<td></td>
<td>70</td>
<td>0.02</td>
<td>155</td>
<td>67</td>
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<td></td>
<td></td>
<td>90</td>
<td>0.05</td>
<td>145</td>
<td>67</td>
</tr>
<tr>
<td>Co_{58}Ni_{10}Fe_{5}Si_{11}B_{16}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.025</td>
<td>174</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.003</td>
<td>119</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>0.004</td>
<td>120</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>0.005</td>
<td>128</td>
<td>67</td>
</tr>
<tr>
<td>Fe_{60}Co_{20}Si_{10}B_{10}</td>
<td>1M KOH</td>
<td>25</td>
<td>0.001</td>
<td>95</td>
<td>88</td>
</tr>
<tr>
<td>Material</td>
<td>30% KOH</td>
<td>1M KOH</td>
<td>1M KOH</td>
<td>1M KOH</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>Anodically oxidized</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$<em>{70}$Mo$</em>{20}$Si$_{15}$B$_5$</td>
<td>30</td>
<td>0.063</td>
<td>128</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.050</td>
<td>140</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.200</td>
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<td></td>
<td>70</td>
<td>1.000</td>
<td>132</td>
<td>67</td>
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<td></td>
<td>75</td>
<td>0.251</td>
<td>150</td>
<td>88</td>
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</tr>
<tr>
<td></td>
<td>90</td>
<td>2.000</td>
<td>166</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.400</td>
<td>138</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1.0 - 2.5</td>
<td>71-99</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Ni$<em>{78}$Si$</em>{18}$B$_{14}$</td>
<td>30</td>
<td>0.079</td>
<td>165</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.158</td>
<td>106</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.251</td>
<td>276</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{39}$Ni$</em>{39}$Mo$<em>2$Si$</em>{12}$B$_8$</td>
<td>30</td>
<td>0.010</td>
<td>123</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.016</td>
<td>150</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.013</td>
<td>173</td>
<td>67</td>
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<td></td>
<td>90</td>
<td>0.013</td>
<td>167</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{40}$Ni$</em>{40}$B$_{20}$</td>
<td>25</td>
<td>0.001</td>
<td>140</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.0008</td>
<td>102</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.050</td>
<td>150</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.040</td>
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<tr>
<td></td>
<td>70</td>
<td>0.013</td>
<td>130</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.158</td>
<td>125</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.040</td>
<td>148</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{78}$Si$</em>{11}$B$_{11}$</td>
<td>25</td>
<td>0.126</td>
<td>174</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.158</td>
<td>184</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.050</td>
<td>230</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1.000</td>
<td>188</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{78}$Si$</em>{11}$B$_{11}$</td>
<td>30</td>
<td>0.016</td>
<td>137</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.158</td>
<td>187</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.318</td>
<td>225</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.126</td>
<td>134</td>
<td>67</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.6  Polarization data for nickel-based amorphous electrode materials for HER in alkaline solution

<table>
<thead>
<tr>
<th>Composition</th>
<th>Electrolyte</th>
<th>Potential</th>
<th>Temperature</th>
<th>Overpotential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{66.5}Mo_{23.5}B_{10}</td>
<td>0.5M NaOH</td>
<td>25</td>
<td>0.0025</td>
<td>120</td>
</tr>
<tr>
<td>Ni_{66.5}Mo_{23.5}Fe_{10}B_{10}</td>
<td>0.5M NaOH</td>
<td>25</td>
<td>0.005</td>
<td>100</td>
</tr>
<tr>
<td>Ni_{66.5}Mo_{23.5}Cr_{10}B_{10}</td>
<td>0.5M NaOH</td>
<td>25</td>
<td>0.01</td>
<td>135</td>
</tr>
<tr>
<td>Ni_{72}Co_{8}Mo_{2}B_{20}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.01</td>
<td>147</td>
</tr>
<tr>
<td>Ni_{72}Co_{4}Mo_{4}B_{20}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.0006</td>
<td>110, 132</td>
</tr>
<tr>
<td>Ni_{72}Co_{2}Mo_{6}B_{20}</td>
<td>1M KOH</td>
<td>30</td>
<td>0.001</td>
<td>114</td>
</tr>
</tbody>
</table>

3.6  Chromium and Vanadium as catalytic agents

As previously mentioned, one of the ways of lowering the electrical energy consumption in alkaline water electrolysis is to reduce the hydrogen evolution reaction overpotential. Catalysis is one of the best-known techniques used to lower the HER overpotential. There are many elements or combinations of elements that have been used in an attempt to reduce the HER overpotential. The addition of metallic ions to act as a catalyst has long been studied. Metallic ions can be added to the electrolyte resulting in homogeneous catalysis of the reaction. They can also be deposited on the surface of a substrate material or incorporated directly into the electrode material, which would constitute heterogeneous catalysis or electrocatalysis. Due to the fact that most commercial alkaline water electrolyzers frequently have iron impurities, there have been extensive studies conducted on the effect of iron additions to the electrolyte.\cite{76, 92-94}  It was found that the iron deposited on the surface of the cathodes and had a favorable effect on the electrocatalytic activity of the electrodes towards the HER. Cobalt and molybdates are also well-characterized in situ additions that have resulted in favorable electrocatalytic behavior.\cite{76, 95}  It has been reported that most transition metals tend to
improve the hydrogen evolution reaction depending on the concentration of the ion present.\textsuperscript{(94)}

This study is primarily interested in the effect of chromium and vanadium additions to the electrode material with respect to electrocatalytic activity for the HER in alkaline solution. The use of chromium as a catalyst has been studied for both homogeneous and heterogeneous catalysis. Stemp et al.\textsuperscript{(96)} conducted a study on the catalytic effect of in situ additions of chromium ions to the electrolyte on the HER for nickel and amorphous Ni-Co-P-B alloy electrodes. It was found that increasing concentrations of chromium ions lowered the HER overpotential on nickel 160 to 400 mV and on the amorphous alloy 170 to 390 mV. It also increased the exchange current densities of the electrodes. A Ni-Cr binary alloy study showed a favorable electrocatalytic effect for the HER in alkaline solution.\textsuperscript{(97)} Lasia and Borodzinski conducted a study of amorphous nickel boride electrodes doped with transition metals and showed that amorphous nickel boride doped with chromium exhibited improved electrocatalytic activity with respect to plain nickel boride. The alloys also demonstrated good mechanical and physical properties with long term stability.\textsuperscript{(98)}

Law et al.\textsuperscript{(99)} studied the use vanadium as a catalyst for the HER as a homogeneous addition to the electrolyte on nickel and an amorphous Ni-Co-P-B alloy electrodes. The addition of vanadium ions to the electrolyte lowered the HER overpotential on both the nickel and the amorphous Ni-Co-P-B alloy. Gala et al.\textsuperscript{(100)} studied the effect of various Ni-Mo-V electrodeposited alloys for hydrogen evolution reaction. It was shown that the hydrogen overvoltage decreased for the electrodeposited alloys compared to nickel. The overvoltage values for the Ni-Mo-V alloys were in the range of 63 to 82 mV as compared
to 300 mV for nickel when the cathodic current density was 2000 A/m². The effect of vanadium was further verified by testing a Ni-Mo alloy, which exhibited overvoltages 40 to 60 mV higher than the alloys with vanadium additions.\(^{(100)}\)
4.0 Experimental

This chapter is divided into three main sections. The first section describes the production of the amorphous alloy systems using the rapid quench planar flow casting or melt spinning technique. The second section deals with the physical and chemical characterization of the produced amorphous alloys. The third section focuses on the electrochemical testing of the alloys.

4.1 Production of Amorphous Alloys

The production of an amorphous alloy using the melt spinning technique can be divided into two major processes. The first is the preparation of a melted block of the alloy in the form of a slug that can be charged into the melt spinner crucible. This step was termed “pre-melting”. Once the alloy slug is prepared, it is then used for the second stage, which is the actual production of the amorphous alloy. This is called the melt spinning process.

4.1.1 Materials

The composition of the alloys that were targeted is listed in Table 4.1.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Co</th>
<th>B</th>
<th>Cr</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>25</td>
<td>20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>25</td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>25</td>
<td>20</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>25</td>
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</tr>
<tr>
<td>54</td>
<td>25</td>
<td>20</td>
<td>1</td>
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</tr>
<tr>
<td>50</td>
<td>25</td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>25</td>
<td>20</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Target compositions of alloys
Discrete increments in the chromium and vanadium concentrations were used in order to get a good representation of the range of the alloys. In order to achieve the targeted composition with high accuracy, elemental powders of high purity were used in the production of the alloys. The constituent materials used are listed in Table 4.2

<table>
<thead>
<tr>
<th>Material</th>
<th>Size and Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>-100+200 mesh, 99.9%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-100+325 mesh, 99.8%</td>
</tr>
<tr>
<td>Boron</td>
<td>≤ 1 mm, 99.5%</td>
</tr>
<tr>
<td>Chromium</td>
<td>-100 mesh, 99%</td>
</tr>
<tr>
<td>Vanadium Boride</td>
<td>1-5 μm, 99.8%</td>
</tr>
</tbody>
</table>

Table 4.2 Constituent materials

4.1.2 Premelting

The production of the alloy slug to be used for the melt spinning process involved two melting steps. Firstly, the material was melted in a vacuum arc furnace and again in a quartz crucible using a RF coil in the melt spinner. A slug of 30g was determined to be adequate for the process. The constituent materials were weighed out in 30 ± 0.05g batches keeping the atomic percentage ratios as shown in Table 4.1. The powders were pressed into small blocks using a stainless steel mould and a hydraulic press. This process was necessary in order to be able to melt the alloy in the vacuum arc furnace. Because of the nature of the vacuum arc furnace the powders must be pressed into a cohesive block to prevent dispersion during the melting process. The pressed blocks of material are placed in a grooved chamber on a copper hearth that is water cooled from the bottom. The chamber was evacuated and purged with argon gas twice to remove as much air as possible. The chamber was then filled with argon gas to maintain an inert environment. A stinger with a tungsten tip was used to melt the material by striking an
arc with the stinger using a high voltage power source. The melting process takes approximately 30 seconds, after which the melted slug is allowed to cool and removed from the chamber. A picture of the vacuum arc furnace is shown in Figure 4.1.

The alloy slug is then crushed and remelted in a quartz tube using the RF coil in the melt spinning apparatus. The remelting of the slug is necessary to produce an alloy slug of the required size that can be used for the melt spinning process.

![Vacuum Arc Furnace](image)

**Figure 4.1 Vacuum Arc Furnace**

### 4.1.3 Melt Spinning Apparatus

The melt spinning apparatus consisted of:

- **Melt Spinner**: D-7400 Tübingen, manufactured by Edmund Bühler of Germany
- **Induction Heater**: Toccotron 2EG 103, The Ohio Crankshaft Co., USA

The melt spinner comprises a vacuum chamber connected to the ribbon collector and a control unit as shown in Figures 4.2 and 4.3. The vacuum chamber of the melt spinner
houses the copper wheel, crucible holder and the copper induction coil. It is also connected to a vacuum pump and a turbo molecular pump used for the evacuation of the chamber. An argon cylinder is also connected to the vacuum chamber and pressure accumulators, used for purging the chamber and ejection of the molten material respectively. The induction coil is connected to the induction heater and closed loop water circulator that supplied the cooling water during operation. The setup of the melt spinner is shown in Figures 4.2 and 4.3.

The alloy slug that was produced by the vacuum arc melting process was remelted using the melt spinner as mention previously. A quartz crucible as shown in Figure 4.4, with an inner diameter of 19 mm was used. The quartz crucible was filled with the crushed alloy fragments and mounted in the crucible holder of the vacuum chamber. It was lowered into the center of the induction coil a few centimeters above the copper wheel. The chamber was then purged with argon gas and evacuated to a pressure of ca. $5 \times 10^{-4}$ torr ($6.7 \times 10^{2}$ Pa). The induction heater was then used to melt the alloy, resulting in a bullet shaped slug of the proper dimensions as shown in Figure 4.5.

During the two melting processes, there were inevitably mass losses, which resulted in the slugs being of lower weight than originally intended. The starting weight of all the alloy slugs was ca. 30.0g, however final slug weights ranged from 28.5 - 29.5g.
Figure 4.2  Schematic of Melt Spinner

Figure 4.3  Picture of Melt Spinner
Figure 4.4  (a) Schematic and (b) Picture of Quartz Crucible

Figure 4.5  Pre-melted Alloy Slug
4.1.4 Melt Spinning

The melt spinning of the alloy slugs into amorphous ribbons was performed using the melt spinning apparatus and a slit nozzle boron nitride crucible as shown in Figure 4.6. The slit nozzle at the bottom of the boron nitride crucible measured 0.5 X 10 mm. Polishing of the copper wheel was necessary to reduce surface imperfections of the amorphous alloy. The wheel was polished using an abrasive paste and cleaned with methanol prior to each melt spin. The prepared alloy slug was then placed in the boron nitride crucible and fixed in the crucible holder of the chamber. The crucible was lowered into the center of the induction coil at a distance of 0.5 mm from the surface of the copper wheel. The setup of the crucible in the chamber was as shown in Figure 4.7. The chamber was then purged with argon gas and evacuated in the same manner as done for the premelting procedure. The induction heater was then used to heat the alloy slug beyond its melting temperature to a predetermined temperature. The temperature was measured using an optical pyrometer through a quartz window at the top of the chamber. When the material was at the required temperature, the molten mass was then ejected through the slit nozzle at the bottom of the boron nitride crucible onto the spinning copper wheel using a small argon gas pressure. The copper wheel was rotated counterclockwise at approximately 2000 rpm which resulted in a tangential linear velocity of 21 m/s. The molten material was ejected using argon gas stored in the accumulators at a pressure of ca. 300 mbar and fed through at the top of the boron nitride crucible. Upon ejection of the molten material from the crucible, the amorphous ribbon material was quenched on the surface of the copper wheel and thrown to the end of the
collection tube. A summary of the conditions used for the melt spinning of the various alloys as listed in Table 4.1 is given in Table 4.3.

<table>
<thead>
<tr>
<th>Distance of crucible from wheel</th>
<th>0.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle of impingement</td>
<td>12°</td>
</tr>
<tr>
<td>Pre-melted alloy weight</td>
<td>28.5-29.5 ± 0.05 g</td>
</tr>
<tr>
<td>Vacuum chamber pressure</td>
<td>&lt; 5 X 10^-4 torr (6.6661 X 10^-2 Pa)</td>
</tr>
<tr>
<td>Wheel rotation speed</td>
<td>2007 rpm or 21 m/s</td>
</tr>
<tr>
<td>Temperature</td>
<td>1280 ± 2°C</td>
</tr>
<tr>
<td>Ejection Pressure</td>
<td>300 mbar (30 kPa)</td>
</tr>
</tbody>
</table>

Table 4.3 Operational conditions for melt spinning

Figure 4.6 (a) Schematic (b) & (c) Pictures of boron nitride slit nozzle crucible
4.2 Physical and Chemical Analysis

A number of qualitative and quantitative techniques were used to characterize the structure, composition and thermal properties of the amorphous alloys produced.

4.2.1 Scanning Electron Microscope (SEM)

Scanning electron microscopy was used to examine the surfaces of the amorphous alloys. A Hitachi S-2500 scanning electron microscope was used for the examination. An accelerating voltage of 20keV and an emission beam current of 100µA with a tilt angle of 15°. The lower detector of the SEM was used for low magnification imaging, while the upper detector was used for high magnification.
4.2.2 Energy Dispersive X-ray (EDX)

Attached to the Hitachi S-2500 scanning electron microscope was a LINK energy dispersive x-ray (EDX) system with a Si X-ray detector. This system was used to perform elemental chemical analysis of the alloys. The condition for the EDX analysis was a working distance of 30 – 35 mm, with a tilt angle of 15° and a count time of 100 seconds.

4.2.3 X-ray Diffraction (XRD)

X-ray diffraction is a technique used to determine the crystalline phases present in a material and to measure structural properties. X-ray diffraction was used to determine the degree of crystallinity of the alloy ribbons produced. Samples strips measuring approximately 2 cm of the melt-spun ribbons were used for the x-ray analysis. The sample strips were cleaned with acetone, methanol and deionized water prior to the x-ray diffraction analysis. The chemicals used are listed as follows.

Acetone : 99.5% Min. Assay (Caledon)

Methanol : 99.8% Min. Assay (Caledon)

Deionized Water : 18MΩ-cm, Nanopure II system (Barnstead)

In addition to the ribbons, samples of crystallized fragments were also analyzed. Crystallized fragments of the 20 atomic percent chromium and the 10 atomic percent vanadium alloys were used as representative crystalline samples. These crystallized fragments were obtained from the material that did not successfully melt spin into ribbon and was primarily in the form of brittle flakes. The crystallized fragments had the same composition as the corresponding ribbon material. Because of the nature of the x-ray diffraction technique, to avoid preferential diffraction, the crystallized fragments of
material had to be ground into a fine powder. This was done in an alumina crucible and the powder placed on the diffractor slide. X-ray diffraction was also performed on the pure source elemental powders of nickel, cobalt, boron, chromium and vanadium as listed in Table 4.2 for comparison.

The x-ray diffractions were performed using a Siemens D5000 0/20 Diffractometer with Cu-Kα source operating at 50kV and 35mA. The secondary beam is monochromatized by a Kevex Solid State Detector. The data was processed by Diffrac AT™ software. The conditions used for the scans are listed in Table 4.4.

<table>
<thead>
<tr>
<th>Scan Mode</th>
<th>Step Size</th>
<th>Cps time</th>
<th>Slits, mm</th>
<th>Range θ, 2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step</td>
<td>0.02°</td>
<td>1.5 seconds</td>
<td>2.0/0.6</td>
<td>20-70</td>
</tr>
</tbody>
</table>

Table 4.4 Conditions for x-ray diffraction

4.2.4 Inductively Coupled Plasma Spectroscopy (ICP)

Inductively Coupled Plasma Spectroscopy (ICP) is a method of determining the elemental concentrations with sensitivities of ppb (parts per billion) levels. The ICP spectrometer utilizes plasma to excite elemental electrons, which produce photons unique to each element. The solution is introduced to the plasma, and is ionized allowing elemental concentration comparisons to known concentration curves. Using stoichiometric techniques elemental concentrations can be converted into molecular weight percentages.

The alloy ribbons prepared using the melt spinning technique were analyzed using the ICP technique to determine the exact composition of the alloys produced. The analysis was necessary because there was some material loss during the preparation of the alloys for spinning and as such the composition of the alloys may have been affected.
This test was also used to test for compositional changes along the length of the produced ribbon.

Sections of ribbon from the beginning, middle and end of each composition were used for the analysis. The ICP technique requires that the material be dissolved in an aqueous matrix solution for introduction into the plasma stream as an aerosol. The matrix solution was 5 weight percent nitric acid solution. Approximately 0.02g of each sample of amorphous ribbon was weighed and dissolved in 2ml of aqua regia (75% HCL & 25% HNO₃). The solution was then diluted to 100ml with 5% nitric acid. This resulted in a solution with elemental concentrations in the range of 10 – 200 ppm.

Solutions of commercially available nickel, boron and a multi-element standard (which contained Co, Cr and V) were also prepared for the calibration of the ICP machine and to determine the presence of any interference. A blank solution containing 2ml of aqua regia diluted to 100ml with 5% nitric acid was used as the standard for zero calibration.

The major elements that were analyzed were Ni, Co, B, Cr and V. The chemicals used for the preparation of the ICP solutions are listed as follows.

- **Nitric Acid**: 68.0-70.0% Assay (Fisher Scientific)
- **Hydrochloric Acid**: 36.5-38% Assay (Fisher Scientific)
- **Nickel Calibration Standard**: 10000µg/ml Ni (Ni in 5% HNO₃) (Specpure Alfa Aesar)
- **Boron Calibration Standard**: 10000µg/ml B (H₃BO₃ in 1% NH₄OH) (Specpure Alfa Aesar)
- **Multi-element Calibration Standard**: Calibration QC Standard 1 (5% HNO₃) – Detailed elemental composition listed in Appendix A
4.2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a technique used to study the behaviour of materials when they are heated. Thermal transition data of a material can be assessed using this technique. A reference sample and the material of interest are heated separately but in parallel according to a linear temperature program. The two heaters maintain the two samples at identical temperatures. The power supplied to the two heaters to achieve this is monitored and the difference between them plotted as a function of reference temperature, which gives the specific heat as a function of temperature. As the reference temperature is increased or decreased and the sample material approaches a transition, the amount of heat required to maintain the temperature will increase or decrease depending on whether the transition is endothermic or exothermic.

The thermal characteristics of the produced amorphous alloys were determined using a heat flux differential scanning calorimeter (DuPont 910 DSC cell). The cell was calibrated for enthalpy and temperature using the melting of high purity indium and zinc. A sample of the amorphous alloy weighing approximately 4-7 mg was used for the test. The sample was placed in an aluminum pan with an empty pan as the reference. The test was performed in an argon environment maintained by a flow rate of 30ml/min. The heating rates used were 2.5 to 40 K/min. The data was analyzed using the software supplied by DuPont.

4.2.6 Melting Point Determination

During the melt spinning process the temperature of the alloy is monitored using an optical pyrometer, however the temperature recorded is the top surface of the alloy in
the crucible so that the transition from solid to liquid is not very well defined. A simple experiment was performed to determine more accurately the melting temperatures of the alloys produced and to determine the alloys' thermal characteristic properties. The melting point of the alloy was determined by using a vacuum furnace with an induction-heating coil that housed a small alumina crucible. The vacuum furnace was equipped with a cromel-alumel thermocouple that was connected to an external voltmeter. A 30g pre-melted slug of the alloys was placed in the alumina crucible and placed in the induction coil. The thermocouple, which had an alumina sheath for protection from attack, was also placed in the crucible. The chamber was then evacuated and the alloy slug melted using the induction furnace. The alloys were taken beyond their melting points and then allowed to cool in the vacuum chamber. When the alloy had solidified, it was remelted. The voltage readings from the thermocouple were monitored and converted to temperatures using a conversion chart for that particular type of thermocouple. Prolonged periods of constant voltage (temperature) were recorded as the solidification or melting temperatures.

4.3 Electrochemical Testing

The electrochemical behavior of the produced amorphous alloys was investigated using a steady state polarization technique. Commercial nickel 200 was also tested as a comparison reference for the alloys. Testing was performed in an alkaline environment to simulate the conditions used in a commercial alkaline water electrolysis unit. This section will describe the material preparations and experimentation technique used in the determination of the electrochemical characteristics of the amorphous alloy systems.
4.3.1 Electrode Materials

The materials that were electrochemically evaluated were the amorphous alloys that were produced using the melt spinning technique. This consisted of eight distinct amorphous alloys with nominal compositions as listed in Table 4.1. Samples of c.p. Nickel 200 were also tested. The nominal chemical composition of the c.p. Nickel 200 was as listed in Table 4.5.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% (max.)</td>
<td>99.5</td>
<td>0.08</td>
<td>0.18</td>
<td>0.005</td>
<td>0.18</td>
<td>0.13</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 4.5 Nominal chemical composition of c.p. Nickel 200

4.3.2 Electrode Preparation

The working electrodes used were prepared from the c.p. Nickel 200 and the amorphous ribbons using sections of approximately 1cm X 1cm. The c.p. Nickel samples were ground using 600 grit SiC grinding paper followed by 6μm and 1μm diamond paste polishing. The shiny side of the amorphous alloys was polished with a 1μm diamond paste. The samples were then cleaned with acetone, methanol and deionized water. The polished samples were then soldered to a length (ca. 20cm) of insulated copper wire (14AWG) using 50-50 Pb-Sn solder and flux. The solder joints were then cleaned using acetone and deionized water. A specific area of the polished surfaces of the samples was designated as the test area and the remainder was masked with a non-conductive chemically resistant epoxy coating (Amercoat 90HS). The already polished areas that were to be masked with the epoxy were roughened with 320 grit SiC paper in order to assure adherence of the epoxy. The back surfaces, solder joint and exposed copper wire were also coated with the epoxy. The epoxy coating was performed three times at 24-
hour intervals to ensure good insulative integrity. When prepared, the samples appeared as depicted in Figure 4.8.

The exposed polished areas of the samples were measured using a LECO IA-3001 V1.20 based image analysis software and an Olympus SZ-11 stereo microscope attached to a LECO/Sony XC-77 video camera CCD module as shown in Figure 4.9. The exposed sample areas ranged from $0.30 \pm 0.05 \text{ cm}^2$. 
Figure 4.8  Picture of sample electrode

(a) Olympus SZ-11 stereo microscope  (b) LECO IA-3001
4.3.3 Electrolyte

The electrolyte used for the tests was an 8 molar potassium hydroxide solution (8M KOH). The electrolyte solution was prepared by dissolving AnalaR grade KOH pellets in 18MΩ deionized water. An 8M KOH solution required approximately 449g of KOH per liter of solution. Due to the impurities present in the KOH pellets, pre-electrolysis of the electrolyte was necessary to remove the metallic impurities before using the electrolyte for testing purposes. The pre-electrolysis was done using two platinum electrodes to electroplate out the metallic impurities. Electrolysis was done under galvanostatic control at a current that produced a voltage of ca. 2000mV between the electrodes. The solution was electrolyzed for 24 hours after which the impurities on the platinum electrodes were cleaned using concentrated nitric acid and electrolysis repeated for another 24 hours.

4.3.4 Electrochemical Cell and Apparatus

Due to the highly corrosive nature of the 8M KOH electrolyte, Teflon cells were used for the electrochemical testing. The Teflon cell was a three electrode test cell, which consisted of the working electrode, a platinum counter electrode and a Hg/HgO reference electrode connected externally via a salt bridge and luggin. The reference electrode was external because of the temperature at which the tests were performed. The Teflon cell was also equipped with gas inlets and outlets. The gas inlet was connected to a cylinder of industrial grade argon gas controlled by a flowmeter. The gas outlets were connected to a condenser tube to minimize loss of water due to evaporation from the electrolyte. The Teflon test cell can be seen in Figures 4.10-11. The test cell was placed in a water bath where the temperature was maintained at 70 ± 0.1°C by a
Cole-Parmer Polystat model 1253-00 water heater-circulator. The electrodes of the test cell were connected to a Hokuto-Denko HA 501G potentiostat/galvanostat via a controller relay box. A PC computer using an IEEE data acquisition card and a specifically designed software program was used to operate the potentiostat/galvanostat. Data was logged and stored using the computer and program. The experimental setup was as depicted in Figures 4.12-13.
Figure 4.10  Teflon Test Cell

Figure 4.11  Three Electrode Setup inside Teflon Test Cell
Figure 4.12  Schematic of Polarization Test Setup

Figure 4.13  Picture of Polarization Test Setup
4.3.5 Steady State Polarization
The electrocatalytic activity of the amorphous alloys and cp. Nickel 200 was determined using a quasi-steady state polarization test. The Teflon test cell was filled with the pre-electrolysed 8M KOH solution, connected to the reference electrode via the salt bridge and placed in the water bath. The water circulator was set to maintain a temperature of 70°C. The electrolyte was then deaerated with argon gas at a flowrate of ca. 30ml/min for 1 hour prior to the insertion of the working electrode. Argon flow was maintained during testing. The working electrodes were ultrasonically cleaned and degreased in acetone, methanol and deionized water before being placed into the test cell. The electrodes were connected to the potentiostat/galvanostat and the test program initiated via the computer interface program. The working electrode was held at a potential of -1300mV vs. Hg/HgO electrode for a period of 3 hours to electrochemically clean the surface of the electrode. The potential was then swept through the range of -1500 to -1100 mV vs. Hg/HgO reference. The potential sweep rate was maintained at 2 mV/min and three cycles were performed. The polarization sweep is shown in Figure 4.14. The applied potential and current response for the electrodes was recorded and Tafel plots generated for the sample materials. Polarization tests were performed a minimum of 5 times on each material to assess the reproducibility of the results. IR compensation was not performed during the polarization testing of the samples. The samples after testing were examined using SEM and EDX to determine any changes in surface morphology or bulk compositional changes.
Figure 4.14   Graph of potential sweep cycle
5.0 Results And Discussion

The results and discussion chapter will be divided into three sections as was outlined in the experimental section. The first section will deal with the production of the amorphous alloys where the conditions and the difficulties that were encountered are discussed. The second section deals with the physical, chemical and thermal properties of the alloys. The final section will focus on the electrochemical behavior of the alloys as cathodes.

5.1 Amorphous Alloy Production

The production of the amorphous alloys was carried out using the melt spinning technique as described in Section 4.1. The following section outlines the parameters pertaining to the melt-spinning process and how they affect production.

5.1.1 Melt Spinning

The first objective of this thesis was the successful production of a system of nickel based amorphous alloys. The targeted composition of the alloys to be produced is listed in Table 4.1 (Ni$_{55-x}$Co$_{25}$B$_{20}$Cr$_{x}$ (x = 1, 5, 10, 15 & 20) and Ni$_{55-y}$Co$_{25}$B$_{20}$V$_{y}$ (y = 1, 5 & 10)). The melt spinning process has many parameters that have to be taken into account when attempting to produce amorphous ribbons. Table 4.3 lists some of the parameters and the values that were used to successfully produce the amorphous alloys. Other factors that can affect the process include the wheel material and the surface finish of the wheel. Each of the parameters listed has the ability to affect the outcome of a melt-spin.

The melt spinning process is dependent upon the rapid removal of heat from the molten material by an appropriate heat sink, i.e. the wheel. The wheel material is
therefore important to the process, since different materials have different heat transfer coefficients. Common materials used for wheels in the melt spinning process are copper (Cu), copper-beryllium alloy (Cu-Be) and stainless steel. The surface finish of the wheel is also important since imperfections on the wheel surface can act as disruptions for the formation of a stable “melt puddle” on the surface of the wheel which is important for the production of a uniform ribbon as pointed out by Kavesh.\(^{(101)}\) The distance of the crucible from the wheel and the angle of impingement of the crucible also affect the formation of a stable “melt puddle”.

The mass of the alloy being processed affects the outcome of the melt spin operation, in that due to the nature of the heating via an RF coil, there exists a temperature profile within the alloy melt. Since the temperature is measured from the top surface of the molten mass, variance in the alloy mass can translate into significant temperature differences between the top surface and the bulk of the alloy. This difference is important because the temperature of the melt before ejection is one of the most important control parameters of the process. The temperature affects the viscosity of the melt, which determines how the material will flow from the crucible and the formation of the “melt puddle”.

The wheel rotation speed is the main factor that determines the thickness the produced ribbon. Hillmann and Hilzinger showed a relationship between ribbon thickness and velocity of the substrate wheel.\(^{(102)}\) They predicted a relationship based on a purely momentum transport mechanism that was verified experimentally. A relationship of \(t \propto U_w^{-0.8}\) was developed, where \(t\) = ribbon thickness and \(U_w\) = wheel velocity. The wheel rotation speed also can also affect the ductility of the ribbon
produced. Variation of the wheel speed for a given set of conditions can produce ribbons ranging from brittle to very ductile. It was also shown that an ejection pressure that was too high would cause the produced ribbons to be brittle while they would be ductile at lower ejection pressures. The vacuum pressure is mainly to prevent oxidation and the entrapment of any gases during the process.

For the purposes of this thesis, a copper wheel was used as the substrate. Formerly proven conditions of crucible height, angle of impingement and ejection pressure were adopted from previously produced alloys. The mass of alloy was determined so as not to extend much over the position of the RF coil. The determination of the appropriate speed and temperature that would successfully produce an amorphous structure was accomplished by much trial iteration. Refinement of the conditions was based on the type of material produced from the failed melt spinning runs. If the temperature of the melt were a too high, pellet and brittle small flakes would be the result. If the temperature were too low, the result would be very brittle sections of ribbons with a very uneven surface that would crumble upon handling. A final set of conditions was determined as listed in Table 4.3. These conditions successfully produced ribbons for both the chromium and vanadium series of alloys. It is however conceivable that these may not be the only conditions that will produce an amorphous structure for these alloys. Manipulation of the given parameters may yield other favorable processing conditions.
<table>
<thead>
<tr>
<th>Distance of crucible from wheel</th>
<th>0.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle of impingement</td>
<td>12°</td>
</tr>
<tr>
<td>Pre-melted alloy weight</td>
<td>28.5-29.5 ± 0.05 g</td>
</tr>
<tr>
<td>Vacuum chamber pressure</td>
<td>&lt; 5 X 10^{-4} torr (6.6661 X 10^{-2} Pa)</td>
</tr>
<tr>
<td>Wheel rotation speed</td>
<td>2007 rpm or 21 m/s</td>
</tr>
<tr>
<td>Temperature</td>
<td>1280 ± 2°C</td>
</tr>
<tr>
<td>Ejection Pressure</td>
<td>300 mbar (30 kPa)</td>
</tr>
</tbody>
</table>

Table 4.3  Operational conditions for melt spinning

5.1.2  Macroscopic Examination of Amorphous Alloy Ribbons

Figure 5.1 and 5.2 are examples of the appearance of the as-spun amorphous alloy ribbons. The produced ribbons had a shiny and a dull surface. The shiny surface was produced by the material exposed to the vacuum while melt-spinning. The dull surface was produced from the exposure of the material to the surface of the copper wheel. The amorphous alloy ribbons were produced in varying lengths ranging from a few centimeters to approximately 3 meters continuous. The width and thickness of the produced ribbons are listed in Table 5.1. As previously described, the thickness is mainly influenced by the velocity of the wheel. The widths of the ribbons are related to the viscosity of the materials when molten at the predetermined temperature. The maximum width of the ribbons is set by the width of the slit-nozzle crucible, which is 10mm. The viscosity of the material is dependent on the composition of the alloy. The increasing concentrations of chromium and vanadium do not show any discernable trends with respect to width and thickness. It is however obvious that the differences in alloy composition produce ribbons with different dimensions. This reinforces the notion that width and thickness are dependent on composition.
Figure 5.1  As-spun Amorphous Alloy Ribbon

Figure 5.2  Long Section of Amorphous Ribbon

<table>
<thead>
<tr>
<th>Nominal Amorphous Alloy Composition</th>
<th>Average Width (±0.01mm)</th>
<th>Average Thickness (±0.1μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{54}$Co$</em>{25}$B$_{20}$Cr$_1$</td>
<td>9.59</td>
<td>20.3</td>
</tr>
<tr>
<td>Ni$<em>{50}$Co$</em>{25}$B$_{20}$Cr$_5$</td>
<td>8.08</td>
<td>30.0</td>
</tr>
<tr>
<td>Ni$<em>{45}$Co$</em>{25}$B$<em>{20}$Cr$</em>{10}$</td>
<td>7.66</td>
<td>36.9</td>
</tr>
<tr>
<td>Ni$<em>{40}$Co$</em>{25}$B$<em>{20}$Cr$</em>{15}$</td>
<td>7.55</td>
<td>25.5</td>
</tr>
<tr>
<td>Ni$<em>{35}$Co$</em>{25}$B$<em>{20}$Cr$</em>{20}$</td>
<td>9.25</td>
<td>27.3</td>
</tr>
<tr>
<td>Ni$<em>{54}$Co$</em>{25}$B$_{20}$V$_1$</td>
<td>7.75</td>
<td>19.8</td>
</tr>
<tr>
<td>Ni$<em>{50}$Co$</em>{25}$B$_{20}$V$_5$</td>
<td>9.57</td>
<td>20.5</td>
</tr>
<tr>
<td>Ni$<em>{45}$Co$</em>{25}$B$<em>{20}$V$</em>{10}$</td>
<td>8.55</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Table 5.1  Dimensions of Produced Amorphous Alloy Ribbons
5.2 Characterization of Produced Amorphous Alloy Ribbons

This section deals with the characterization of the produced amorphous alloys. The characterization process was divided into three stages:

1. Physical which included microscopic examination and X-ray diffraction analysis
2. Chemical which was elemental EDX analysis and compositional ICP analysis
3. Thermal which included DSC studies in conjunction with melting point determination tests

5.2.1 Physical Characterization

5.2.1.1 Microscopic Examination

Typical scanning electron micrographs of the shiny surface and dull surface of the produced amorphous alloys are illustrated in Figure 5.3. The shiny surface is relatively featureless and unremarkable. As expected, there is no evidence of any crystalline features such as grain boundaries. The dull surface, which was exposed to the surface of the wheel, has a rougher texture with longitudinal furrows. The roughness of this surface is due to the contact with the wheel surface. The imperfections on the surface of the wheel are reproduced on the surface of the ribbons. The longitudinal furrows that are present on the surface have been reported to be caused by the entrainment of residual inert gas between the wheel surface and the ribbon during the solidification process.\(^{(104)}\)
5.2.1.2 X-ray Diffraction (XRD) Analysis

All of the produced alloys were subjected to X-ray diffraction analysis to determine their degree of crystallinity. Amorphous structures are known to have X-ray diffraction patterns depicted by a broad peak in the spectrum with no prominent narrow peaks indicating the presence of crystalline phases. Figures 5.4 to 5.11 show the X-ray diffraction patterns of the produced alloy ribbons. It is evident that they are all characteristic of the typical amorphous structure. The only deviation from the amorphous structure pattern is detected in the X-ray pattern for Ni$_{54}$Co$_{22}$B$_{20}$V$_{10}$ where there are the small peaks at approximately 45 and 52 theta degrees. Figures 5.12 and 5.13 depict the X-ray diffraction patterns of crystalline samples of Ni$_{54}$Co$_{22}$B$_{20}$Cr$_{20}$ and Ni$_{54}$Co$_{22}$B$_{20}$V$_{10}$ respectively with the amorphous patterns of the same composition overlain. The overlay
patterns for Ni$_{54}$Co$_{23}$B$_{20}$V$_{10}$ show that the two small peaks detected in the amorphous pattern may be the initial stages in the formation of the corresponding crystalline phases. The peaks at approximately 45 and 52 degrees correspond to the formation of a crystalline nickel phase as is evident by the diffraction pattern of the pure nickel (Appendix B1) used to produce these alloys. The pattern is however still typical of an amorphous structure. The detection of Al$_2$O$_3$ peaks in the X-ray diffraction pattern of the crystalline sample was due to the grinding process performed on the material in order to achieve the powdered form required for the process. X-ray diffraction patterns of the other constituent materials are also given in Appendix B1.

The X-ray diffraction patterns also yielded information about the effective crystallite dimension, which is an index calculated to evaluate the largest potential size of crystal embryos present in the structure.$^{(106)}$ Amorphous structures have small crystallite dimension values usually in the range of 1-5nm. Larger values than this tend to indicate nanocrystalline materials. The effective crystallite dimension is calculated by:

$$D = (0.91 \lambda)/(\beta \cos \theta)$$

(5.1)

where

- $D$ = effective crystallite dimension (nm)
- $\lambda$ = wavelength of the Cu-K$_\alpha$ radiation (0.1542nm)
- $\beta$ = denotes the full width at half the maximum intensity of the spectrum
- $\theta$ = the Bragg angle of the maximum intensity peak

The effective crystallite dimensions were calculated for each of the produced alloy ribbons and the results listed in Table 5.2. Determination of the crystallite size from the X-ray diffraction patterns is demonstrated in Appendix B2.
From the crystallite sizes for the different alloys, it is noticeable that as the concentration of chromium increases there is also an increase in the crystallite size. This is also true for the case of increasing vanadium. For the specific case of the Ni₅₄Co₂₅B₂₀Cr₁ alloy, it has the largest crystallite size, which was expected due to the presence of the small peaks in its X-ray diffraction pattern. The increasing trend in the crystallite size is due mainly to the fact that as the chromium/nickel and vanadium/nickel concentration ratios increase, the tendency to form intermetallic phases increases as is evident from the Ni-Cr and Ni-V phase diagrams shown in Appendix C. This was also the primary reason for not continuing to increase the chromium and vanadium concentrations in the alloys.

<table>
<thead>
<tr>
<th>Amorphous Alloy Composition</th>
<th>Peak Maximum Position (2θ)°</th>
<th>Full Width at Half Maximum Intensity β°</th>
<th>Effective Crystallite Dimension (D) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅₄Co₂₅B₂₀Cr₁</td>
<td>44.87</td>
<td>6.7589</td>
<td>1.29</td>
</tr>
<tr>
<td>Ni₅₀Co₂₅B₂₀Cr₁</td>
<td>45.31</td>
<td>5.6911</td>
<td>1.53</td>
</tr>
<tr>
<td>Ni₄₅Co₂₅B₂₀Cr₁₀</td>
<td>45.45</td>
<td>5.6892</td>
<td>1.53</td>
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<tr>
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<td>45.71</td>
<td>5.5637</td>
<td>1.57</td>
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<tr>
<td>Ni₃₅Co₂₅B₂₀Cr₂₀</td>
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<td>5.5058</td>
<td>1.58</td>
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<td>Ni₅₄Co₂₅B₂₀V₁</td>
<td>46.04</td>
<td>7.0813</td>
<td>1.23</td>
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<td>Ni₅₀Co₂₅B₂₀V₅</td>
<td>44.79</td>
<td>5.6713</td>
<td>1.53</td>
</tr>
<tr>
<td>Ni₄₅Co₂₅B₂₀V₁₀</td>
<td>44.85</td>
<td>2.2380</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Table 5.2 Effective Crystallite Dimensions
Figure 5.4  XRD of 1 at.% Cr amorphous alloy

Figure 5.5  XRD of 5 at.% Cr amorphous alloy
Figure 5.6  XRD of 10at.% Cr amorphous alloy

Figure 5.7  XRD of 15 at.% Cr amorphous alloy
Figure 5.8  XRD of 20 at.% Cr amorphous alloy

Figure 5.9  XRD of 1 at.% V amorphous alloy
Figure 5.10  XRD of 5 at.% V amorphous alloy

Figure 5.11  XRD of 10 at.% V amorphous alloy
Figure 5.12  XRD of Crystalline and Amorphous 20 at.% Cr alloy

Figure 5.13  XRD of Crystalline and Amorphous 10 at.% V alloy
5.2.2 Chemical Characterization

5.2.2.1 Energy Dispersive X-ray (EDX) Analysis

Along with the SEM analysis of the surfaces of the produced amorphous ribbons, an EDX analysis was also conducted. EDX was performed to determine the elemental composition of the alloys and also to detect, within the detection limits of the EDX equipment the presence of any contamination due to processing. The EDX scans of each of the produced alloy ribbons are shown in Figures 5.14 to 5.21. From the scans it is clear that the element boron (B) is not detected. Due to the limitations of the EDX analysis technique boron is essentially undetectable due to its very small atomic radius. As a result, complete determination of the composition of the alloys is not possible from the EDX scans. However, the scans show that the other elements namely nickel, cobalt chromium and vanadium are present at the surface, and show a corresponding increase in concentration for the respective alloys. The scans do not detect other elemental contaminants in the alloys within the detection limits of the EDX. This compositional knowledge aided in the refinement of the method used for the quantitative ICP analysis of the ribbons.
Figure 5.14   EDX of 1 at.% Cr amorphous alloy

Figure 5.15   EDX of 5 at.% Cr amorphous alloy
Figure 5.16   EDX of 10 at.% Cr amorphous alloy

Figure 5.17   EDX of 15 at.% Cr amorphous alloy
Figure 5.18  EDX of 20 at.% Cr amorphous alloy

Figure 5.19  EDX of 1 at.% V amorphous alloy
Figure 5.20  EDX of 5 at.% V amorphous alloy

Figure 5.21  EDX of 10 at.% V amorphous alloy
5.2.2.2 Inductively Coupled Plasma Spectroscopy (ICP) Analysis

To accurately determine the chemical composition of the produced alloys was important in order to determine whether the targeted compositions were achieved and/or their variability. It was also necessary for the subsequent electrochemical testing, to accurately follow the effect of increasing chromium and vanadium concentrations in the alloys. The alloys were digested in nitric acid diluted to a 5% solution and ICP analysis performed as outlined in Section 4.2.4. An element analysis of each ribbon composition was calculated in mg/L which was then converted to atomic percentages of the metal alloy. The ICP data and conversions are given in Appendix D. Multiple samples of each ribbon produced by the melt spinning process were examined in order to achieve a representative compositional analysis for the entire alloy. The average composition for each of the produced alloys is given in Table 5.3.

<table>
<thead>
<tr>
<th>Targeted Composition</th>
<th>Actual Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅₄Co₂₅B₂₀Cr₁</td>
<td>Ni₅₄₅₅Co₂₄₃₆B₁₉₄₂Cr₁₀₅</td>
</tr>
<tr>
<td>Ni₅₀Co₂₅B₂₀Cr₅</td>
<td>Ni₅₀₄₈Co₂₅₅₂B₁₉₃₃Cr₅₂₁</td>
</tr>
<tr>
<td>Ni₄₅Co₂₅B₂₀Cr₁₀</td>
<td>Ni₄₅₃₁Co₂₄₇₇B₁₉₂₇Cr₉₈₉</td>
</tr>
<tr>
<td>Ni₄ₐCo₂₅B₂₀Cr₁₅</td>
<td>Ni₄₀₇₃Co₂₄₇₇B₁₉₃₅Cr₁₅₁₃</td>
</tr>
<tr>
<td>Ni₃₅Co₂₅B₂₀Cr₂₀</td>
<td>Ni₃₅₃₁Co₂₄₆₃B₁₉₃₄Cr₂₀₁₁</td>
</tr>
<tr>
<td>Ni₄₅Co₂₅B₂₀V₁</td>
<td>Ni₄₅₂₁Co₂₄₉₇B₁₉₃₉Vo₉₂</td>
</tr>
<tr>
<td>Ni₅₀Co₂₅B₂₀V₅</td>
<td>Ni₅₀₂₃Co₂₄₉₁B₁₉₄₃Vo₇₈</td>
</tr>
<tr>
<td>Ni₄₅Co₂₅B₂₀V₁₀</td>
<td>Ni₄₅₄₁Co₂₄₅₈B₁₉₇₀Vo₉₈</td>
</tr>
</tbody>
</table>

Table 5.3 Average composition of Amorphous Ribbons from ICP analysis

The actual compositions of the alloys are in good agreement with the targeted compositions. The data listed in Appendix D also shows that there maximum standard deviation of ±0.63 atomic percent difference in the compositions within the same ribbons.
The amorphous ribbons can thus be considered homogeneous through out their length. There does however exist some nickel enrichment and boron depletion in the alloys. Deviations in the elemental atomic percentages are small, with a maximum of ±0.73 atomic percent. The most probable cause for the deviations in composition are due losses during the preparation of the slug used for the melt spinning process.

5.2.3 Thermal Characterization

5.2.3.1 Differential Scanning Calorimetry (DSC) Analysis

The thermal characteristics of the produced amorphous alloys were determined using a heat-flux differential scanning calorimeter. Linear heating rates of 2.5 to 40 K/min were used and the data interpreted using manufacturer’s software.

Firstly due to the nature of the material, it is expected that there would be a glass transition temperature. However, from the results of the DSC scans, glass transition temperatures were only detected for two of the alloys, namely Ni50Co25B20Cr5 and Ni35Co25B20Cr20. The glass transition temperature is depicted by a peak in the DSC trace, but it is sometimes difficult to detect, as was the case in this series of alloys. The glass transition temperatures detected for Ni50Co25B20Cr5 and Ni35Co25B20Cr20 were approximately 361°C and 450°C respectively. Following the glass transition temperature there is usually a large main peak that is indicative of the crystallization temperature of the material. In some cases, the main peak was divided into two or had an attached shoulder. Beyond the crystallization temperature, there is usually the detection of the melting point of the material. Due to the limitations of the DSC equipment used (maximum temperature of approximately 600 °C), the melting points of the alloys could
not be detected. A melting point determination of the alloys was done by another method
and is discussed later.

The crystallization temperature of an amorphous alloy is also a measure of the
stability of the alloy in terms of its resistance to crystallization. The higher the
crystallization temperature the more stable the alloy. The crystallization temperatures of
the alloys at a heating rate of 20K/min are plotted in Figure 5.22. Similar trends are
observed at other heating rates. From the crystallization temperature graph, it is seen that
as the chromium and vanadium content of the alloys increase, there is a direct correlation
with the crystallization temperature, which also increases. This indicates that the addition
of chromium and vanadium to the alloy increases its stability. For the chromium and
vanadium alloys tested, there was little difference in the crystallization temperatures
(maximum of 27°C difference) for ≤10 atomic percent additions. At higher
centrations there is no comparison alloy DSC trace.

The dependence of the crystallization temperature on the minor metal addition at
low concentrations, the gradual leveling off at higher temperatures and its relative
insensitivity to the minor metal identity was predicted by Graydon et al.\(^{(109)}\) The basic
assumption was that the crystallization temperature of an amorphous alloy is controlled
by the diffusion of the smaller species. Hence, in a binary alloy, the smaller atom
diffuses while in a ternary alloy; the two smallest atoms must migrate. In the case of the
alloys produced, they can be considered to be ternary alloys. The Ni-Co phase diagram
shows that they form essentially ideal liquid and solid solutions above the hcp ε-Co phase
at 420°C. Since the atomic parameters for Ni and Co are virtually identical, they can be
considered to be equivalent to each other. Under this assumption the alloys can thus be
considered to be ternary alloys of $(\text{Ni,Co})_{80-x}B_{20}Cr_x$ and $(\text{Ni,Co})_{80-y}B_{20}V_y$, where $x = 1, 5, 10, 15 & 20$ and $y = 1, 5 & 10$. Chromium and vanadium both have larger molecular volumes than nickel while boron has the smallest. This means that in order for crystallization to occur, both boron and nickel must migrate in both the series of alloys. It is for this reason that the increase in the amount of chromium and vanadium respectively increases the crystallization temperature. The diffusion of boron is impeded and it forces the diffusion of nickel to occur in order for crystallization to occur. The fact that nickel must migrate, accounts for the very similar crystallization temperatures observed in the two alloy series at the lower concentrations of chromium and the vanadium. In both cases due to the small fraction that the chromium and vanadium occupy and their large volume compared to nickel results in very similar crystallization temperatures. However, at higher concentrations of chromium this linear trend dissipates as the chromium becomes a significant part of the matrix and has additional influence on the diffusion properties of the atoms.

The enthalpy of crystallization was also determined and was the same for each of the alloys for each of the heating rates. Since the crystal structure after crystallization is the same for each alloy, it is independent of heating rate. The enthalpy of crystallization for each of the alloys is plotted in Figure 5.23. From the plot it is seen that as the amount of chromium is increased in the alloy, the enthalpy of crystallization decreases. The opposite relation is evident for increasing vanadium concentration. Other independent studies showed that the addition of aluminum to one of the chromium-containing alloy significantly increased the enthalpy of crystallization. Conversely, the addition of molybdenum to a similar amorphous alloy composition decreased the enthalpy of
crystallization. The enthalpy of crystallization is dependent upon the initial state of the amorphous alloy and the final phase composition after crystallization. From the data shown it is evident that it depends on the chemical properties of the element added. Prediction of the behaviour based on elemental properties is not yet possible.

The activation energy \( Q \) (kJ/mol), can be determined from the shift in the exotherm temperature with change in the heating rate, \( r \) (K/min). Kissinger's method was used to determine the activation energies of the alloys over a range of heating rates from 2.5 K/min to 40 K/min. The activation energies of the alloys are plotted in Figure 5.24. The activation energy increases for both the addition of chromium and vanadium, however the addition of vanadium only increases the activation energy slightly. The addition of chromium increases the activation energy significantly more. There is evidence of an inverse relationship between the activation energies and the enthalpy of crystallization for the alloys. As the chromium concentration increases and the activation energies also increase, the enthalpy of crystallization decreases. The trend is not seen for the addition of vanadium but the activation energies for the vanadium alloys is almost constant while the corresponding enthalpies show an increasing trend. Also, the same inverse trend was observed for the addition of molybdenum.

**5.2.3.2 Melting Point Determination**

Due to the temperature restrictions of the DSC equipment, the melting temperatures of the alloys were not able to be determined using that method. A basic melting point determination procedure as described in Section 4.2.5 was performed on the alloys. The solidification/melting temperatures of the alloys were measured using the thermocouple. Due to the nature of the test, the melting point determination could not be
very accurate. The tests resulted in the determination of a melting/solidification range for the two series of alloys. All of the chromium alloys melted/solidified in a temperature range of $1040^\circ C \pm 10^\circ C$ while the vanadium alloys melted/solidified in the range of $1070^\circ C \pm 10^\circ C$.

The data from the DSC scans in conjunction with the melting temperatures of the alloys give a final full thermal profile of each of the alloys. This completed the characterization profile of the alloys in terms of physical appearance, chemical composition and thermal properties.

![Diagram](image.png)

**Figure 5.22** Crystallization Temperature vs. Composition for Amorphous Alloys
Figure 5.23  Enthalpy of Crystallization vs. Composition for Amorphous Alloys

Figure 5.24  Activation Energy of Crystallization vs. Composition for Amorphous Alloys
5.3 Electrochemical Measurements

5.3.1 Potentiostatic Testing

The electrocatalytic activity of the produced amorphous alloys was measured using a potentiostatic polarization technique. Electrodes made from the alloys were held at -1300mV vs. Hg/HgO reference electrode for a duration of 3 hr. The polarization tests were performed using a potential sweep rate of 2 mV/min. between -1100mV and -1500mV vs. Hg/HgO reference electrode in a pre-electrolysed 8M KOH solution at 70°C as described in Section 4.0. The amorphous alloys were compared against c.p. Ni-200 which served as a reference for the hydrogen evolution reaction. Figure 5.25 shows the data from a typical potentiostatic experiment. The upper graph traces the current response of the electrode material through the potential cycle traced by the lower graph. From the potentiostatic data collected for each of the electrode materials, polarization curves (η vs. log i) were constructed for the electrode materials. Figure 5.26 shows the polarization curves for the series of amorphous alloys containing chromium with respect to Ni-200. Figure 5.27 shows the polarization curves for the amorphous alloys containing vanadium with respect to Ni-200. The polarization curves shown in Figures 5.26 and 5.27 depict the average of at least five (5) sample runs. The current variation within each sample test is small at low overpotentials and increases at higher overpotentials as shown in Appendix F, Figure F1. Between different samples, the variation is larger and the error analysis for each material shown in Appendix F. The polarization curves shown in Figures 5.26 and 5.27 represent data that has been IR-compensated. The IR-compensation was performed on the data after polarization testing was completed. Figure 5.28 shows a comparison between the polarization curves for a
sample with and without IR correction. Calculation of the IR-compensation is demonstrated in Appendix E. From the polarization plots in Figures 5.26 and 5.27, the exchange current density ($i_0$) and the Tafel slopes ($b_v$) of the materials can be determined. All of the polarization plots can be divided into three distinct sections based on the changes in the slopes. Each of these three sections of the polarization plots generates a different Tafel value for the particular electrode material in that potential range. Table 5.4 summarizes the Tafel parameters for all of the amorphous alloys and nickel.

In order to evaluate the kinetics of the HER on the various electrode materials, measurements were performed on c.p. Nickel and compared with published values. The HER in alkaline solution is well characterized and is based on the following three steps and associated Tafel values at 298K\(^{110}\):

\[
\text{Volmer: } M + H_2O + e^- \rightleftharpoons MH_{\text{ads}} + OH^- \quad b = 120 \text{ mV/dec} \quad (5.2)
\]

\[
\text{Heyrovsky: } MH_{\text{ads}} + H_2O + e^- \rightleftharpoons H_2 + M + OH^- \quad b = 40 \text{ mV/dec} \quad (5.3)
\]

\[
\text{Tafel: } MH_{\text{ads}} + MH_{\text{ads}} \rightleftharpoons 2M + H_2 \quad b = 30 \text{ mV/dec} \quad (5.4)
\]

The HER process begins as water reduction with hydrogen adsorption (Volmer) followed by the competitive reactions of electrochemical (Heyrovsky) and/or chemical (Tafel) hydrogen desorption. In alkaline solution, the Tafel slope for nickel is about 120 mV/dec\(^{111}\). This indicates that the Volmer reaction is the rate-determining step under these conditions. However, as stated the above reactions were for experiments performed at 298K. The polarization plot of nickel (Figure 5.26 or 5.27) displays a Tafel slope of 155 mV/dec in the low overpotential range (Table 5.4). This value is in the general range of the theoretical value of 138 mV/dec corrected for a temperature of 343K based on the
relation $2.3RT/\beta F$. Similar experimental Tafel values for nickel under similar conditions were reported by D. Anthony $(b = 154 \text{ mV/dec}, i_o = 0.035 \text{ mA/cm}^2)^{(112)}$, and M. Stemp $(b = 203 \text{ mV/dec}, i_o = 0.031 \text{ mA/cm}^2)^{(96)}$.

There are several factors that contribute to the differences in Tafel values at low overpotentials. Firstly, the length of time that the electrodes are exposed to cathodic polarization has been shown to have an effect on the Tafel slopes. The longer the electrodes are polarized, the higher the Tafel slopes. Also the scan rates at which the polarization experiments were performed can also affect the reported values. Potentiostatic scan rates for this work was 2 mV/min, same as D. Anthony, while M. Stemp used a rate of 6mV/min. The higher Tafel slope of Stemp can be partially attributed to the faster scan rate. Finally, the effect of electrolyte impurities must be considered. Huot, reported that there was a parallel electrodeposition of metallic impurities in concentrated alkaline solution at moderate overpotentials which could account for the change in Tafel slope.$^{(76)}$ A large percentage of this deposit was found to be iron. It was determined that the electrodeposition of dissolved ferric ions in the alkaline solution may comprise two consecutive steps: reversible reduction of Fe$^{3+}$ to Fe$^{2+}$ close to the reversible hydrogen electrode potential followed by reduction of Fe$^{2+}$ to metallic iron close to $-200$ mV hydrogen overpotential.$^{(113)}$ Iron is known to be electrocatalytically beneficial for the hydrogen evolution reaction and the presence of iron on the surface of the electrodes may influence the electrocatalytic activity of the electrodes. The presence of iron on the surface of the amorphous alloy electrodes was confirmed when SEM and EDX analysis was performed on the electrodes after testing and will be elaborated upon in the following section.
The Tafel slope for nickel at moderate overpotentials was determined to be 103 mV/dec and is consistent with other published values as listed in Table 3.5. This can be attributed in part to the quasi-independent relationship of the Tafel slope with temperature. Figure 5.29 shows the temperature dependence of the transfer coefficient for the HER on a nickel electrode at moderate overpotentials.\(^{(114)}\) From this plot the transfer coefficient at 343 K is approximately 0.64 which when applied to the theoretical relation \(2.3RT/\beta F\) gives a Tafel value of 106 mV/dec which is very close to that obtained in this study.

The final section of the polarization curve is in the high overpotential range and cannot be rigorously considered a Tafel slope. The degree of scatter in the high overpotential range and the possibility that there may be other contributing reactions other than the hydrogen evolution reaction make the Tafel values extracted in this region doubtful. The major reason for reporting the Tafel data in this region is because most commercial alkaline water electrolysers operate at these higher overvoltages. It is typical for electrolysers to operate at a current density \(\geq 250\) mA/cm\(^2\) and for this reason the "Tafel" slopes are useful in determining the hydrogen overvoltage at such current densities. The extrapolated values for nickel and the amorphous alloys are listed in Table 5.4. The polarization curves for the amorphous alloys also exhibit the three distinct regions as displayed for nickel and their Tafel parameters are summarized in Table 5.4.

5.3.1.1 Exchange Current Density

The exchange current density, \(i_0\), is a fundamental characteristic of electrode behaviour. There is no theoretical method for accurately determining the exchange current density of a material. It must be determined experimentally. The magnitude of
exchange current density is a function of (i) the metal composition, (ii) the surface roughness, (iii) the soluble species concentration, (iv) the surface impurities and (v) the temperature. The exchange current density determined for nickel was $4.0 \times 10^{-5}$ A/cm$^2$ and was consistent with other published values for nickel in similar environments. Figure 5.30 shows a plot of the exchange current density against the composition of the amorphous alloys. For the graph it is seen that the exchange current density increases in both series of the amorphous alloys as the concentration of chromium/vanadium increases. For the lowest concentration (1 at. %), the exchange current density for the amorphous alloy containing chromium is very similar to that of nickel. This similarity is likely to be due to the fact that the amorphous alloy did not contain a sufficient amount of chromium to affect a change with respect to the nickel matrix. The comparable (1 at. %) vanadium alloy displays a marginally lower exchange current density but was within the same range and the difference was not considered significant. As the concentration of chromium and vanadium increases they both display a similar increase in their exchange current density up to the maximum vanadium concentration of 10 atomic percent. The exchange current densities of the chromium containing alloys continue to increase with increasing concentration as depicted in Figure 5.30. As stated above the exchange current density is dependent upon five major factors, since all tests were performed under the same conditions and samples were polished to a similar surface finish, as shown in Figures 5.33 and 5.34, the contribution of the latter factors can be neglected. Thus the changes in exchange current density should reflect the difference in the composition of the amorphous alloys. This is an inherent property of the material due to its composition and structure. The similar trend and values observed for the additions of chromium and
vanadium suggest that the effect of substituting chromium or vanadium for nickel has very similar effect on the amorphous alloy. Chromium and vanadium are different in their atomic radii compared to nickel and there are also differences in their percentage d-band character as listed in Table 5.4. Thus the changes in the exchange current densities ($i_c$) could be due to either structural or electronic modifications of the nickel substrate. Increasing concentrations of chromium and vanadium increases the exchange current density of the nickel-based amorphous alloys. This increasing trend in exchange current density with chromium was also observed by Stemp with the in-situ addition of chromium using nickel and a nickel-based amorphous alloy. Borodzinski and Lasia also reported an increase in the exchange current density for chromium doped amorphous nickel boride electrode over the un-doped electrode. Gala et al reported a similar effect for an increasing Mo/V ratio on electrolytic coatings. This increase in the exchange current density is beneficial to the overall goal of reducing the hydrogen overvoltages. Increasing the exchange current density has the effect of lowering the overvoltages required to attain a desired operating current density (typically 250 mA/cm$^2$).

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radius (nm)</th>
<th>Percentage d-band Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.125</td>
<td>40</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.130</td>
<td>39</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.136</td>
<td>35</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.125</td>
<td>39.7</td>
</tr>
<tr>
<td>Boron</td>
<td>0.098</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 5.4 Atomic radii and percentage d-band character of elements
5.3.1.2 Tafel Slopes

The Tafel slope of the materials is another important parameter that is extracted from the polarization curves. Other factors being equal, the lower the Tafel slope is for a material, the better it will perform for the hydrogen evolution reaction. This is because for a given increase in the overvoltage, the material with the lower Tafel slope value will produce a greater increase in current density, which translates into higher activity and more hydrogen production. Thus the overvoltages required to attain an operating current density of 250 mA/cm² is smaller, which means an operational cost savings.

The alloys and nickel tested in this study all displayed three polarization regions. Nickel was used as a reference to judge the performance of the produced amorphous alloys and has been described previously. The Tafel slopes for the first region or low potential region for the amorphous alloys are plotted against their composition in Figure 5.31. At the low concentrations (1 at. %) the Tafel slope is similar to that of the reference nickel. The Tafel slope increases with the increasing chromium concentration. The same increasing trend is also present in the vanadium containing series of alloys. Experiments performed by Stemp demonstrated an increase of Tafel slope for in-situ chromium additions on a nickel electrode while a decrease in Tafel slope was observed for an amorphous alloy electrode. Law demonstrated that in long-term polarization tests the electrolyte addition of vanadium species lowered the Tafel slopes for both nickel and an amorphous alloy electrode. The Tafel values obtained by Stemp and Law are summarized in Table 5.5. Because of the lack of proposed mechanisms for Tafel slopes above 120mV/dec, it is difficult to interpret the mechanism(s) for this potential range. However, it was noted previously, that the length of cathodic polarization time tends to
increase Tafel slope values. Polarization time can increase the Tafel slope and may be a contributing factor to the high Tafel slopes. Since all samples were cathodically polarized for the same duration prior to testing, it does not explain the effect of concentration on the Tafel slope values. It is well known that chromium and vanadium form oxide layers, which are passive and could partially account for the increasingly less active Tafel slopes. Chromium, especially forms an adherent protective oxide, for example in stainless steels, and is used for corrosion protection. Vanadium is also used to enhance the corrosion resistance of materials and may have a similar passivation effect on the material. As the concentration of chromium and vanadium increases in the amorphous alloys, more of the exposed surface would be expected to be protected by the oxide layer and hence passivated by the chromium and vanadium. This oxide layer could act as a barrier and impede the rate of the hydrogen evolution reaction by blocking the active sites on the electrode surfaces. This could be partially responsible for the high Tafel slopes and the increasing trend in the low overpotential region.

In the moderate overpotential region, it is seen from Table 5.6 of the Tafel parameters that they all exhibit the same or similar Tafel values to that of nickel in that range. The nickel Tafel slope of 103 mV/dec is consistent with published values based on the temperature dependent correction for the transfer coefficient. The Tafel value for nickel in the moderate potential range is consistent with the Volmer rate determining step (Equation 5.2) for the hydrogen evolution reaction in this range of overpotential. The fact that all of the chromium and vanadium containing amorphous alloys also exhibit the same Tafel slopes in this potential range would tend to suggest that hydrogen adsorption is slow for the amorphous alloys. The change in Tafel slope cannot be definitively
determined based on polarization data. It is possible that as the potential is cathodically increased, the passivity layer on the surface of the amorphous alloys may break down, leaving more active surface available for the HER. However, the concentration effect is not simple since as the concentration of chromium and vanadium increases, the concentration of nickel decreases correspondingly. Hence, the Tafel values obtained cannot strictly be ascribed to that of nickel. Chromium and vanadium must also be contributing to the overall activity of the amorphous alloys, thus supporting their role as catalytic agents for the HER. Further investigation is required in order to quantify the role of chromium and vanadium for the produced alloys in this potential range.

The last region of the polarization curves is the high overpotential range. The Tafel slopes for the materials are plotted against their composition in Figure 5.32. From the plot, a significant variability can be seen in this potential range. This current variability is high due to the vigorous hydrogen bubbling and the current response to changing surface area contacted by electrolyte with gas formation on the electrode surface. The Tafel slopes appear to increase with chromium and vanadium concentration. The 5 atomic percent chromium alloy shows an anomalously low Tafel value as it also did in the low overpotential region. Most electrolysers operate at a current density $\geq 250$ mA/cm$^2$ and as such the Tafel slopes of the tested materials were extrapolated to determine the overpotential required to attain a current density of 250 mA/cm$^2$. The extrapolated values are listed in Table 5.6. From the values listed in Table 5.6, all of the chromium alloys have overpotentials in the range of 500 – 520 mV, similar to that of nickel (506 mV). The vanadium series of alloys displayed lower overpotentials in the
range of 480 – 490 mV, and as such would reduce the operating cost of a commercial electrolyser.

<table>
<thead>
<tr>
<th>Material</th>
<th>Catalyst Addition (ppm) - Cr</th>
<th>Tafel Slope (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel 200</td>
<td>None</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>311</td>
</tr>
<tr>
<td>Amorphous (Ni$<em>{50}$Co$</em>{25}$P$<em>{15}$B$</em>{10}$)</td>
<td>None</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>265</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>109</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Catalyst Addition (ppm) - V</th>
<th>Tafel Slope (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel 200</td>
<td>None</td>
<td>140, 311</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>84, 286</td>
</tr>
<tr>
<td>Amorphous (Ni$<em>{50}$Co$</em>{25}$P$<em>{15}$B$</em>{10}$)</td>
<td>None</td>
<td>350, 173</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>347, 133</td>
</tr>
</tbody>
</table>

Table 5.5 Tafel values from literature for Cr$^{(96)}$ and V$^{(99)}$ electrolyte additions to Ni and Amorphous Ni$_{50}$Co$_{25}$P$_{15}$B$_{10}$
Figure 5.25  Typical Polarization Sweep Data

Figure 5.26  Polarization Curves for Ni and Ni-based chromium containing amorphous alloys
Figure 5.27  Polarization Curves for Ni and Ni-based vanadium containing amorphous alloys

Figure 5.28  Comparison of as-tested and IR compensated polarization curves
<table>
<thead>
<tr>
<th>Material</th>
<th>Exchange Current Density ($10^2$ A/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Extrapolated Hydrogen Overpotential* (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-200</td>
<td>4.0</td>
<td>b$_c$, low 155</td>
<td>b$_c$, moderate 103</td>
</tr>
<tr>
<td>Ni$<em>{54}$Co$</em>{25}$B$_{20}$Cr$_1$</td>
<td>4.0</td>
<td>153</td>
<td>105</td>
</tr>
<tr>
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Table 5.6 Tafel parameters for Ni and Ni-based amorphous alloys

b$_c$, low = <260 mV hydrogen overpotential

b$_c$, moderate = 260 – 420 mV hydrogen overpotential

b$_c$, high = >420 mV hydrogen overpotential

* = linear Tafel slope extrapolation from high overpotential region
Figure 5.29  Theoretical temperature dependence of the transfer coefficient for the HER

Figure 5.30  Plot of exchange current density vs. composition for amorphous alloys
Figure 5.31  Plot of Tafel slope vs. composition for amorphous alloys in the low potential range

Figure 5.32  Plot of Tafel slope vs. composition for amorphous alloys in the high potential range
This section presents the SEM and EDX analysis of the surfaces of the samples after polarization testing was completed. Figures 5.33 and 5.34 shows the typical initial state of the nickel and the amorphous alloys for testing. The following figures show the post potentiostatic testing surfaces of the materials along with EDX spectra for the surface. From Figures 5.33 and 5.34 it can be seen that the prepared surfaces were highly polished and planar, with very small polishing marks. The post polarization SEM and EDX figures shown in Figures 5.35 to 5.52 all have one common feature, the presence of iron on the surface of the samples (quantified by the accompanying EDX scans). Despite the pre-electrolysis of the electrolyte, the deposition of iron occurred even in the low overpotential tests and may have contributed to the change in the Tafel slopes of the materials. From the figures, it is also noticeable that there are some crystalline deposits on the surfaces of the samples. These are salts from residual KOH electrolyte on the surfaces of the sample. The chromium containing series of amorphous alloys show almost no degradation or surface change due to the dissolution of any of the elemental constituents after polarization testing. This can be verified by the fact that the scratch marks that were present prior to testing are still visible in the post tested samples. The vanadium series of amorphous alloys however do show signs of surface roughness. This surface roughness is especially noticeable in the vanadium alloy containing 1 atomic percent vanadium. The surface is roughened as depicted by the darker surface and the presence of a dimpled structure. The surface roughening is less apparent in the other vanadium alloys. The change in surface roughness however, was not significant enough to change the composition of the alloy to be detected in the EDX spectra. This surface
roughness may however have contributed to the lower overpotentials exhibited by the vanadium containing alloys over that of the chromium containing alloys and nickel. The roughness was not progressive with the alloy concentration increase or significant for concern with long term stability of the alloy.
Figure 5.33  SEM of polished nickel

Figure 5.34  SEM of a polished amorphous alloy
Figure 5.35  SEM of surface of nickel after testing

Figure 5.36  EDX of nickel after testing
Figure 5.37  SEM of surface of 1 at.% Cr amorphous alloy after testing

Figure 5.38  EDX of 1 at.% Cr amorphous alloy after testing
Figure 5.39  SEM of surface of 5 at. % Cr amorphous alloy after testing

Figure 5.40  EDX of 5 at.% Cr amorphous alloy after testing
Figure 5.41 SEM of surface of 10 at.% Cr amorphous alloy after testing

Figure 5.42 EDX of 10 at.% Cr amorphous alloy after testing
Figure 5.43  SEM of surface of 15 at.% Cr amorphous alloy after testing

Figure 5.44  EDX of 15 at.% Cr amorphous alloy after testing
Figure 5.45 SEM of surface of 20 at.% Cr amorphous alloy after testing

Figure 5.46 EDX of surface of 20 at.% Cr amorphous alloy after testing
Figure 5.47  SEM of surface of 1 at.% V amorphous alloy after testing

Figure 5.48  EDX of 1 at.% V amorphous alloy after testing
Figure 5.49 SEM of surface of 5 at.% V amorphous alloy after testing

Figure 5.50 EDX of 5 at.% V amorphous alloy after testing
Figure 5.51  SEM of surface of 10 at.% V amorphous alloy after testing

Figure 5.52  EDX of 10 at.% V amorphous alloy after testing
6.0 Conclusions

1. The amorphous alloy systems of Ni$_{55-x}$Co$_{23}$B$_{20}$Cr$_x$ and Ni$_{55-y}$Co$_{23}$B$_{20}$Cr$_y$ where (x = 1, 5, 10, 15 & 20 and y = 1, 5 & 10) were able to be successfully produced using the melt spinning technique.

2. The atomic structure of the produced alloys was confirmed as being amorphous using X-ray Diffraction (XRD) techniques.

3. The precise atomic composition of the alloys was determined using Inductively Coupled Plasma Spectroscopy (ICP) and confirmed that the alloys were within 1 at.% of the targeted composition. Compositional gradients within the ribbons were also confirmed to be less than ±0.63 at.%.

4. The thermal behaviour of the produced amorphous alloys was analyzed by Differential Scanning Calorimetry (DSC). The crystallization temperatures ranged from 345°C to 542°C for the chromium containing alloys and from 352°C to 428°C for the vanadium containing alloys.

5. All of the produced alloys were electrocatalytically active with respect to the Hydrogen Evolution Reaction in 8M KOH solutions.
6. The increasing additions of chromium to the amorphous alloy system served to increase the exchange current density from 4 to \(16 \times 10^{-5}\) A/cm\(^2\). It also increased the Tafel slopes of the alloys in the low overpotential range.

7. Increasing vanadium additions to the amorphous alloys increased the exchange current density from 3 to \(6.6 \times 10^{-5}\) A/cm\(^2\). The Tafel slopes of the vanadium containing alloys were not significantly altered.

8. All of the amorphous alloys and nickel displayed similar Tafel slopes in the moderate overpotential range corresponding to the Volmer rate-determining step.

9. The vanadium and chromium containing alloys all had comparable activity with respect to nickel with the chromium alloys showing no degradation with use.
7.0 Recommendations

1. Long term testing of the produced amorphous alloys to determine their structural stability and activity in a more industrial environment.

2. AC impedance testing may reveal more detail about the electrocatalytic activity of the alloys.

3. X-ray photoelectron spectroscopy (XPS) studies of the surface species after polarization tests to determine the residual species present, in an attempt to determine the reaction mechanism(s) at work. Cyclic voltammetry of the alloys may also provide some insight into the reaction mechanism(s) at work.

4. Increased surface area is known to increase the activity of electrodes with respect to the HER. Surface treatment of the alloys to yield a higher actual surface area may enhance also their electrocatalytic performance. Techniques commonly used to modify surfaces are exposure to strong acids, thermal treatments and long-term cyclic polarization.

5. The incorporation of an easily removed (leachable) element such as zinc or aluminum into the alloy(s), which when removed will create a high surface area material that may prove to increase the activity of the material.
6. The production of an alloy(s) containing both chromium and vanadium may have synergistic effects that may result in an improved catalytically active material. In conjunction with surface enhancement techniques, the activity of the alloy(s) may increase considerably.

7. The production of an amorphous coating on a substrate material (nickel or steel) using the alloys in a powder form, maintaining their amorphous structure will increase the exposed surface area available as reaction sites considerably, thus increasing the overall activity of the electrode.
8.0 References


10. F.R. Foulkes, Electrochemistry Course Notes, 1999, Chapter 21


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108. J.W. Graydon, "Thermal Analysis of (Ni, M)55Co25B20 Amorphous Alloys where M is V, Cr and Cr+Al, and Comparison with Ni72(Mo,Co)3B20", Dept. Chemical Engineering, University of Toronto, 2001


### 9.0 Appendices

#### Appendix A

**Composition of ICP Calibration QC Standard 1**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
<th>Element</th>
<th>Concentration (ppm)</th>
<th>Element</th>
<th>Concentration (ppm)</th>
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<tbody>
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<td>100.4</td>
<td>Se</td>
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*Table A1 Composition of ICP Calibration QC Standard 1*
Appendix B1

X-ray Diffraction Patterns of Constituent Materials

Figure B1  X-ray Diffraction Pattern of Nickel

Figure B2  X-ray Diffraction Pattern of Cobalt
Figure B3  X-ray Diffraction Pattern of Boron

Figure B4  X-ray Diffraction Pattern of Chromium
Figure B5  X-ray Diffraction Pattern of Vanadium Boride
Appendix B2

Determination of Crystallite Size from X-ray Diffraction Pattern

The background is calculated as a straight line from points BG1 to BG2.

The Full Width at Half Maximum (FWHM) is determined by fitting parabolas or straight lines from 20% to 80% of the maximum (net height) at both sides of the peak and then taking the horizontal distance between the lines at 50% of the net height of the fitted peak.

FWMH = Full width at half maximum

T = Top of peak

BG1 = First point used to fit the background

BG2 = Second point used to fit the background

BG = Background intensity at the top position
The effective crystallite dimension is calculated by:

\[ D = \frac{(0.91 \lambda)}{(\beta \cos \theta)} \]  

(B1)

where

- \( D \) = effective crystallite dimension (nm)
- \( \lambda \) = wavelength of the Cu-K\(\alpha\) radiation (0.1542 nm)
- \( \beta \) = denotes the full width at half the maximum intensity of the spectrum (radians)
- \( \theta \) = the Bragg angle of the maximum intensity peak

Example using data for Ni\textsubscript{54}Co\textsubscript{23}B\textsubscript{20}Cr\textsubscript{1} from Table 5.2:

FWHM = 6.7589° = 0.118 rad

\[ 2\theta = 44.87^\circ \]

\[ D = \frac{(0.91 \times 0.1542 \text{ nm})}{(0.118 \text{ rad} \times \cos(22.435^\circ))} \]

\[ = 0.140322 \text{ nm}/0.109 \]

\[ = 1.29 \text{ nm} \]
Appendix C

Figure C1  Nickel-Chromium Binary Phase Diagram
Figure C2  Nickel-Vanadium Binary Phase Diagram
Figure C3  Nickel-Boron Binary Phase Diagram
Figure C4  Nickel-Cobalt Binary Phase Diagram
Appendix D

Calculation of Atomic Concentrations from ICP Data

<table>
<thead>
<tr>
<th>Element</th>
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<tr>
<td>Vanadium</td>
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</table>

Table D1 Atomic Mass of Elements

The ICP data was returned in concentration units of mg/L and was converted to atomic percentages as follows for Ni in a chromium containing alloy.

\[
\text{At.\%}_{\text{Ni}} = \frac{(\text{At.}_{\text{Ni}} \times M_{\text{Ni}}) + (\text{At.}_{\text{Co}} \times M_{\text{Co}}) + (\text{At.}_{\text{B}} \times M_{\text{B}}) + (\text{At.}_{\text{Cr}} \times M_{\text{Cr}}) \times \frac{\text{ICP}_{\text{Ni}}}{10000 \times \text{Mass}}}{M_{\text{Ni}}} * 100
\]

where

\( \text{At.}_{x} \) = Theoretical Atomic Weight Fraction of Element X
\( M_{x} \) = Molar Mass of Element X (g/mol)
\( \text{ICP}_{x} \) = ICP concentration data for Element X (mg/L)
\( \text{Mass} \) = Mass of Alloy used

The factor of 10000 is used for the conversion from mass in grams diluted in 100ml to milligrams diluted in 1 liter (1L).
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### Table D2 ICP Data and Conversions to Atomic Percentages

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Table D2 ICP Data and Conversions to Atomic Percentages

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### Table D3 Statistical Analysis of ICP Data

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<th>Element</th>
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<th>Difference from Target</th>
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</thead>
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<td>5 Ni 50.23 Co 24.91 B 19.45 V 4.78</td>
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<td>0.23 Ni 0.09 Co 0.55 B 0.22</td>
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<td>Ni 45  25 20</td>
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<td>0.41 Ni 0.48 Co 0.30 B 0.02</td>
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<table>
<thead>
<tr>
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<tr>
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<td>0.33 Ni 0.23 Co 0.13 B 0.18</td>
<td>0.31 Ni 0.35 Co 0.66 B 0.11</td>
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Table D3 Statistical Analysis of ICP Data
**Appendix E1**

**Calculation of IR Drop**

IR drop is due to resistive losses when electrochemical measurements are performed in a high potential range in an electrolyte, contact resistance of leads and the resistance of surface films on the electrode surface.

IR drop due to solution resistivity, $\Delta \Psi \ (V)$ is related to the specific conductivity, $\sigma$ ($\Omega^{-1} m^{-1}$) of the electrolyte by the following expression:

$$E = I/\sigma A = \Delta \Psi / l$$  \hspace{1cm} (E1)

$$\Delta \Psi = I(l/\sigma A)$$  \hspace{1cm} (E2)

where

- $E = \text{field strength (V/m)}$
- $I = \text{current (A)}$
- $\sigma = \text{specific conductivity (}\Omega^{-1} \text{m}^{-1})$
- $A = \text{area (m}^2\text{)}$
- $l = \text{length of field (m)}$

Specific conductivity, $\sigma$ is also defined as:

$$\sigma = \sigma_e + \sigma_w$$  \hspace{1cm} (E3)

$$\sigma_e = Z_e C_e \lambda_e$$  \hspace{1cm} (E4)

where

- $\sigma_e, \sigma_w = \text{specific conductivity of electrolyte and water respectively}$
- $Z_e = \text{valence}$
- $C_e = \text{molar concentration}$
- $\lambda_e = \text{limiting equivalent conductivity}$
Data for 8M KOH electrolyte

\[ \sigma_w (25^\circ C) = 7.127 \times 10^{-6} \text{ (}\Omega^{-1}\text{m}^{-1}) \]

\[ \lambda_{\text{KOH}} (70^\circ C) = 183 \times 10^{-4} \text{ (}\text{m}^2\text{\Omega}^{-1}\text{eq}^{-1}) \]

\[ C_{\text{KOH}} = 8000 \text{ (moles/m}^3\text{)} \]

Using an average field length (distance from sample surface to center of salt bridge luggin) of \( l = 3\text{mm} \), and ignoring the effects of \( \sigma_w \) because of its very small value:

\[ \Delta \Psi = I^* (l/\sigma A) = I^* (l/Z_c C_e \lambda_e) \]

(E5)

\[ \Delta \Psi = I^* ((3 \times 10^{-3})/[1(\text{eq/mol}) \times 8000(\text{mol/m}^3) \times 183 \times 10^{-4}(\text{m}^2\text{\Omega}^{-1}\text{eq}^{-1})]) \]

This relation is plotted in Figure D1 for various current densities.

![Figure D1](image)

**Figure D1** Plot of IR Drop vs. Current Density for 8M KOH electrolyte at 70°C
Appendix E2

Electrolyte and Electrode Calculations

pH Calculation:

Activity of KOH:

\[ a_{OH^-} = f(a_{KOH}) \]  \hspace{1cm} (E6)

\[ KOH \rightarrow K^+ + OH^- \] \hspace{1cm} (E7)

The ion size parameter of K\(^+\) and OH\(^-\) are both 0.3, therefore

\[ a_{KOH} = a_{K^+} \cdot a_{OH^-} = (a_{OH^-})^2 \] \hspace{1cm} (E8)

Since K\(^+\) and OH\(^-\) both have the same ion size parameter, they will have the same molal ionic activity coefficients hence the same molal concentration, therefore:

\[ a_{KOH} = \gamma_z^2 m_{KOH} \cdot m_{OH^-} = \gamma_z^2 (m_{OH^-})^2 \] \hspace{1cm} (E9)

where

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

Combining E8 and E9:

\[ (a_{OH^-})^2 = \gamma_z^2 (m_{OH^-})^2 \] \hspace{1cm} (E10)

\[ a_{OH^-} = \gamma_z m_{OH^-} \] \hspace{1cm} (E11)

8M KOH = 9.18m KOH

\textit{mean molal ionic activity, } \gamma_z \text{ for } 8M \text{ KOH}\(^1\):

\(^1\) Table 1.890, Properties of Aqueous Solutions of Electrolytes, 1992, p.1323
@ 25°C, $\gamma_2 = 5.7$ \quad \therefore a_{OH} = (5.7)(9.18 \text{ kg/mol}) = 52.3

@ 70°C, $\gamma_2 = 3.37$ \quad \therefore a_{OH} = (3.37)(9.18 \text{ kg/mol}) = 30.94

\textit{Dissociation constant of water, }K^2:\

@ 25°C, $K_w = 10^{-14}$ \quad \therefore - \log K_w = 14.0

@ 70°C, $K_w = 1.513 \times 10^{-13}$ \quad \therefore - \log K_w = 12.8

\[ \text{H}_2\text{O} \Rightarrow \text{H}^+ + \text{OH}^- \]

\[ K_w = a_w = a_{H^+}a_{OH^-} \]

\[ \therefore a_{H^+} = K_w/a_{OH^-} \]

\[ \text{pH} = - \log a_{H^+} = - \log (K_w/a_{OH^-}) \]

\text{pH of 8M KOH:}

@ 25°C, \quad \text{pH} = 14 + \log(52.3) = 15.7

@ 70°C, \quad \text{pH} = 12.8 + \log(30.9) = 14.3

\textit{Activity of Water}

\text{Osmotic Coefficient (}$\mathcal{O}$$\text{) of KOH@ 25°C:}

\[ \mathcal{O} = 2.095 \]

\[ \mathcal{O} = -1000 \ln(a_w)/(vmM_w) \]

\[ 2.095 = -1000 \ln(a_w)/[(2)(9.0)(18.015)] \]

\[ a_w = 0.507 \]

\[ ^2 \text{CRC Handbook of Chemistry and Physics, 55th Ed., 1974} \]

\[ ^3 \text{V.M. Lobo, Handbook of Electrolyte Solutions, 1989, p. 1089} \]
Hg/HgO Reference Electrode Potential

\[
\text{HgO}(s) + H_2O + 2e^- \leftrightarrow \text{Hg}(II) + 2OH^- \tag{E17}
\]

\[
E_{\text{Hg/HgO}} = E^\circ_{\text{Hg/HgO}} - (RT/F)\ln[a_{OH^-}/\sqrt{a_w}] \tag{E18}
\]

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

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

Hydrogen Evolution Reaction Equilibrium Potential

\[
2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \tag{E19}
\]

\[
E_{\text{H}_2/\text{H}_2O} = 0.000 - 2.303(RT/F)pH \tag{E20}
\]

\[
= 0.000 - 0.973
\]

\[
= -0.973 \text{ V}_\text{SHE}
\]

\[
= -972 \text{ mV}_{\text{Hg/HgO}}
\]
Figure F1  Typical Polarization Curve for an amorphous alloy sample
Figure F2  Polarization Curve for Ni200

Figure F3  Polarization Curve for 1 at.% Cr amorphous alloy
Figure F4  Polarization Curve for 5 at.% Cr amorphous alloy

Figure F5  Polarization Curve for 10 at.% Cr amorphous alloy
Figure F6  Polarization Curve for 15 at.% Cr amorphous alloy

Figure F7  Polarization Curve for 20 at.% Cr amorphous alloy
Figure F8  Polarization Curve for 1 at.% V amorphous alloy

Figure F9  Polarization Curve for 5 at.% V amorphous alloy
Figure F10  Polarization Curve for 10 at.% V amorphous alloy