Electrochemical characteristics of metal hydride electrodes for nickel/metal hydride rechargeable batteries.

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ELECTROCHEMICAL CHARACTERISTICS OF METAL HYDRIDE ELECTRODES FOR NICKEL/METAL HYDRIDE RECHARGEABLE BATTERIES

By

Feng (Peter) Feng

A Dissertation Submitted to the Faculty of Graduate Studies and Research through the Department of Mechanical, Automotive and Materials Engineering Engineering Materials Program in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada

2002
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ABSTRACT

The electrochemical characteristics of LaNi$_{4.7}$Al$_{0.3}$, LaNi$_{4.7}$Al$_{0.3}$ (with Cu-coating), Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ and Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy electrodes are examined in detail. The specific discharge capacity of the cell made using the LaNi$_{4.7}$Al$_{0.3}$, Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ and Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloys maintain 250 mAh g$^{-1}$ at 100-120 mA g$^{-1}$ discharge current density after 20, 40 and 200 cycles respectively. Thus with regard to cycle lifetime the Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ and Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloys are considerably superior to LaNi$_{4.7}$Al$_{0.3}$ alloy. At the same number of cycles, all the electrochemical properties are related to the hydrogen concentration, i.e., depth of discharge (DOD). As the hydrogen concentration decreases, the exchange current density, the apparent activation energy, the hydrogen diffusion coefficient and the symmetry factor increase. The equilibrium potential increases (i.e. becomes more positive) with decreasing hydrogen concentration.

Almost all the electrochemical properties are temperature related. As the temperature increases, both the exchange current density and the symmetry factor increase. The specific discharge capacity reaches a maximum value at room temperature for the Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy. The equilibrium potential decreases with increasing temperature. With increasing number of cycles, the exchange current density, the ratio of $D/a^2$ ($D=$hydrogen diffusivity; $a=$sphere radius) and the equilibrium potential increase with cycles, stabilizing after 30-40 cycles. Cu-coating of the electrode alloys increases the exchange current density and the high-rate dischargeability of the metal hydride electrodes, and decreases the discharge potential, especially for higher discharge.
current densities. The discharge potentials for the Cu-coated electrode showed little change with discharge current density differences, indicating the stabilizing effect of Cu-coating on the battery performance.

A theoretical treatment is derived to account for the two-phase (α-β) region of pressure-composition (P-C) isotherms of hydrogen-absorbing alloys by considering H-H interaction kinetics. Based on electrochemical reaction kinetics, a theoretical model on the relationship between equilibrium potential and hydrogen concentration is established for the equilibrium discharge process of a MH electrode. The relationship between equilibrium potential of a metal hydride electrode reaction and hydrogen pressure in a gaseous hydrogen environment is also derived and thus, $E-C-T$ curves can be accurately transferred to $P-C-T$ curves and vice versa. These theoretical equations are of particular use in evaluating suitable electrode alloys.

A novel and relatively simple electrochemical method, called "Potential Step Chrono-Amperometry (PSCA)" method, is developed to determine the hydrogen diffusion coefficient and its variation with hydrogen concentration. Using this method, the value of the room temperature diffusion coefficient of hydrogen in a LaNi$_{4.7}$Al$_{0.3}$ alloy is found to be in the range of $3.1 \times 10^{-14}$ to $8.6 \times 10^{-13}$ m$^2$ s$^{-1}$, and is comparable with the range of $10^{-10}$ to $10^{-15}$ m$^2$ s$^{-1}$ obtained for various AB$_5$-type alloys by other methods.
To My Parents

and

My Wife
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1: H/M=0.82, -0.9291 → -0.3291 V; 2: H/M=0.51, -0.9188 → -0.3188 V;
3: H/M=0.28, -0.9179 → -0.3179 V; 4: H/M=0.14, -0.9150 → -0.3150 V;
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**NOMENCLATURE**

\( A^* \)  
Surface area of alloy particles \( \text{m}^2 \text{ g}^{-1} \)

\( A_0; A_1 \)  
Constants \( \text{J mol} \text{H}_2 \text{g}^{-1} \)

\( A_2 \)  
Constant \( \text{J (mol} \text{H}_2 \text{K})^{-1} \)

\( a \)  
Radius of an alloy particle sphere; \( \text{m} \)

\( a_{\text{OH}^-} \)  
Activity of \( \text{OH}^- \) \( \text{mol m}^3 \)

\( a_{\text{H}_2\text{O}} \)  
Activity of \( \text{H}_2\text{O} \) \( \text{mol m}^3 \)

\( a_{\text{H}_2} \)  
Activity of \( \text{H}_2 \) \( \text{mol m}^3 \)

\( B; B_1 \)  
Constants \( \text{V} \)

\( B_2 \)  
Constant \( \text{V K}^{-1} \)

\( C(r,t); (C) \)  
Hydrogen concentration in a sphere with respect to radius \( r \) and time \( t \) \( \text{molH m}^3 \)

\( C_0 \)  
Initial hydrogen concentration in a sphere \( \text{molH m}^3 \)

\( C_s \)  
Surface hydrogen concentration of a sphere \( \text{molH m}^3 \)

\( C_{\text{th}} \)  
Specific discharge capacity \( \text{mAh g}^{-1} \)

\( c_H \)  
Hydrogen concentration (H/M-ratio) \( \text{dimensionless} \)

\( c_m \)  
Maximum hydrogen concentration (H/M-ratio) \( \text{dimensionless} \)

\( D \)  
Diffusion coefficient of hydrogen \( \text{m}^2 \text{s}^{-1} \)

\( E_{r,-} \)  
Difference in equilibrium potential between the positive and negative electrodes \( \text{V} \)

\( E \)  
Potential with resect to \( \text{Hg/HgO} \) reference electrode \( \text{V} \)

\( E_r \)  
Reaction potential of an MH electrode \( \text{V} \)

\( E_e \)  
Equilibrium potential with resect to \( \text{Hg/HgO} \) reference electrode \( \text{V} \)

\( E_a \)  
Apparent activation energy \( \text{J mol}^{-1} \)

\( E_{\text{eq}}(\text{H}_2/\text{H}_2\text{O}) \)  
Absolute equilibrium potential of an MH electrode \( \text{V} \)

\( E_{\text{eq}}(\text{HgO/Hg}) \)  
Absolute equilibrium potential of an \( \text{Hg/HgO} \) reference electrode \( \text{V} \)

\( E^0(\text{H}_2/\text{H}_2\text{O}) \)  
Standard potential of an \( \text{H}_2/\text{H}_2\text{O} \) reaction couple \( \text{V} \)

\( E^0(\text{HgO/Hg}) \)  
Standard potential of an \( \text{Hg/HgO} \) reference electrode \( \text{V} \)

\( F \)  
Faraday's constant = 96487 \( \text{C mol}^{-1} \)

\( G^0 \)  
Standard Gibbs free energy \( \text{kJ (mole } \text{H}_2)^{-1} \)

\( \Delta G \)  
Gibbs free energy change per mole \( \text{H}_2 \) \( \text{kJ (mole } \text{H}_2)^{-1} \)

\( \Delta H \)  
Enthalpy change for the \( \alpha/\beta \) transition \( \text{kJ (mole } \text{H}_2)^{-1} \)

\( \Delta H_s; (\Delta H_d) \)  
Enthalpy change for hydrogen absorption (desorption) reaction \( \text{kJ (mole } \text{H}_2)^{-1} \)

\( I_0 \)  
Exchange current density \( \text{A g}^{-1} \)

\( I \)  
Absolute value of the intercept of the plot of \( j(t) \) vs. \( t^{1/2} \) \( \text{A g}^{-1} \)

\( j; j(t) \)  
Applied current density \( \text{A g}^{-1} \)

\( K \)  
Equilibrium constant \( \text{dimensionless} \)

\( k \)  
Boltzmann constant \( \text{dimensionless} \)

\( k_1; k_2; (k_j) \)  
Forward (reverse) specific reaction rate constants \( (j=1 \text{ and } 2) \) \( \text{m s}^{-1} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_j^0, (k_j^0)$</td>
<td>Frequency factor (j=1 and 2)</td>
</tr>
<tr>
<td>$l_j, (l_j)$</td>
<td>Forward (reverse) specific reaction rate constants</td>
</tr>
<tr>
<td>$l_j^0, (l_j^0)$</td>
<td>Frequency factor (j=1 and 2)</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight of an alloy</td>
</tr>
<tr>
<td>$m$</td>
<td>Concentration of KOH</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of metallic atoms per alloy unit</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons involved in the electrode reaction</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Cycle number</td>
</tr>
<tr>
<td>$P_{ce}, (P_{H2})$</td>
<td>Equilibrium (hydrogen) pressure</td>
</tr>
<tr>
<td>$Q_d$</td>
<td>Specific discharge capacity</td>
</tr>
<tr>
<td>$Q$</td>
<td>Storage (remaining) specific capacity</td>
</tr>
<tr>
<td>$R$</td>
<td>Molar gas constant = 8.3144</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Internal resistance of an electrode</td>
</tr>
<tr>
<td>$R_O$</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial distance from the center of a spherical particle</td>
</tr>
<tr>
<td>$S$</td>
<td>Absolute value of the slope of the plot of $j(t)$ vs. $t^{1/2}$</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>Entropy change for the $\alpha/\beta$ transition</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$U$</td>
<td>Voltage of a battery</td>
</tr>
<tr>
<td>$W$</td>
<td>Weight of metal hydride alloy</td>
</tr>
<tr>
<td>$x_0; (y_0)$</td>
<td>Maximum (minimum) solubility of hydrogen in $\alpha$-phase ($\beta$-phase)</td>
</tr>
<tr>
<td>$x_H$</td>
<td>Fractional site occupancy of hydrogen = $c_H/c_m$</td>
</tr>
</tbody>
</table>

*Greek symbols*

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_j; (\varepsilon_j^0)$</td>
<td>Activation energy barrier (for process j)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Interaction coefficient of $H_{abs}-H_{abs}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Interaction coefficient of $H_{ads}-H_{ads}$</td>
</tr>
<tr>
<td>$\gamma_{H2}$</td>
<td>Fugacity coefficient of hydrogen gas</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Proportional coefficient</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
</tr>
<tr>
<td>$\eta_0; (\eta_0)$</td>
<td>Overpotential of a positive (negative) electrode</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Hydrogen surface coverage</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Mass density of an alloy</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Transition time</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Symmetry factor (dimensionless)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Subscripts</td>
<td></td>
</tr>
<tr>
<td>abs; a</td>
<td>absorbed site</td>
</tr>
<tr>
<td>ads; d</td>
<td>adsorbed site</td>
</tr>
<tr>
<td>1,-1</td>
<td>Forward and reverse absorb and adsorb reaction</td>
</tr>
<tr>
<td>2,-2</td>
<td>Forward and reverse charge transfer reaction</td>
</tr>
<tr>
<td>cal</td>
<td>Calculated</td>
</tr>
<tr>
<td>exp</td>
<td>Experimental</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 DEVELOPMENT OF NI/MH BATTERIES

The development of Ni/MH (Metal Hydride) batteries based on MH negative electrodes is one of the more important areas of electrochemical study today. Batteries based on metal hydride materials have several major advantages over the more conventional lead-acid and nickel-cadmium systems [1-3]. The Ni/MH battery is an alkaline storage battery, similar in many aspects to the Ni/Cd (nickel-cadmium) battery, which has been until recently the main workhorse for many electronic devices. Environmental safety concerns regarding the toxicity of cadmium and the safe disposal of Ni/Cd batteries have accelerated the commercialization of Ni/MH batteries. The Ni/MH battery also has higher gravimetric and volumetric energy densities than Ni/Cd batteries by approximately 30-40% for batteries of the same size.

The Ni/MH battery also has the advantage of being able to replace a Ni/Cd battery virtually without a change of the existing power systems for many electronic devices, because they are very similar in physical structure and have similar charge and discharge voltage characteristics. Both battery systems have a 1.2 volt nominal voltage and similar discharge endpoints. Ni/MH batteries are typically connected in parallel first, then in series strings, to give the desired pack voltage and capacity. The charging method used for Ni/Cd batteries is compatible with that for Ni/MH batteries and there is no need to minimize the overcharge of Ni/MH batteries. Ni/MH batteries are environmentally friendly and offer more energy per unit volume or weight than Ni/Cd or lead-acid batteries. At present, they can be considered among the preferred rechargeable batteries
of the future, at least in the field of small portable energy devices. The high energy density, excellent power density, and long cycle lifetime of Ni/MH batteries also make them a leading technology as the battery power source for electric vehicles (EVs), especially in bipolar designs [4]. However, further improvements of the battery are needed for longer cycle lifetime, reduced self-discharge, and optimum operation at an elevated temperature.

The performance of a Ni/MH battery, measured by parameters such as capacity, durability (cycle lifetime) and dischargeability (kinetics), depends closely on the characteristics of the hydride-forming alloy, which is the alloy used as the active material of the anode. These characteristics are quite sensitive to alloy composition. Today, AB₅ [5-16] and AB₂-type [17-25] multicomponent metal hydride alloys are being extensively studied for their commercial use in Ni/MH batteries. The most important electrochemical characteristics of the hydrogen storage compounds used in these batteries include capacity, cycle lifetime, exchange current density, high-rate dischargeability and equilibrium potential. The electrochemical behaviour of such intermetallics depends on their structure, the nature and amount of each element in the intermetallic compound, and the electrochemical process(es) taking place. These electrochemical characteristics can be altered by designing the composition of the hydrogen storage alloy to provide optimum performance of the Ni/MH batteries.

1.2 DESIRED IMPROVEMENTS IN MH ELECTRODES

Although, Ni/MH batteries show considerable advantages compared to conventional batteries, improvements are still required in terms of a higher discharge capacity, longer
cycle lifetimes, better thermodynamic properties (those related to the stability of the electrode), better kinetic behaviour (related to its high-rate charge/discharge ability) and a lower cost. The performance of a Ni/MH battery depends principally on the properties of a metal hydride electrode (i.e. negative electrode in the battery) because the MH alloy can reversibly absorb and desorb only a limited amount of hydrogen. Thus, the selection of MH alloy is very important. Finally, evaluation methods for MH alloys still need to be improved in order to design and select suitable metal hydride alloys to be used in Ni/MH batteries. In order to improve the overall performance of Ni/MH battery, development has been focused on the metal hydride electrode.

1.3 FOCUS OF THIS STUDY

There are many intrinsic factors that influence the performance of a metal hydride electrode, which must be investigated if optimum performance of Ni/MH batteries is to be realized. Also, a detailed knowledge of the mechanisms for the electrochemical reactions that occur at the electrode/electrolyte interface is required, for determining the suitability of specific alloys for use as electrodes. The parameters examined in this study include equilibrium potential, discharge capacity, exchange current density, high-rate dischargeability, apparent activation energy, symmetry factor, hydrogen diffusion coefficient, specific surface area and the hydrogen pressure-equilibrium potential of the electrode. In brief, the main focus of this study is to identify the factors that determine the electrochemical performance of a MH electrode and to improve the electrode performance through their control. The metal hydride electrode alloys studied are limited to four different hydrogen storage alloys.
1.3.1 Hydrogen desorption in a gaseous hydrogen environment

The hydrogen pressure of MH alloys in a gaseous hydrogen environment can be related to the MH-KOH (aqueous) equilibrium, from which the hydrogen-alloy powder reaction mechanisms in the two different environments can be compared. The dependence of hydrogen pressure on the hydrogen concentration and temperature is established by considering the H-H interactions, from which the hydrogen reaction mechanisms in the metal hydride alloys (in a gaseous hydrogen environment) are developed and compared with the electrode reaction mechanism in aqueous KOH environment.

1.3.2 Equilibrium potential of MH electrodes

The voltage of the Ni/MH battery can be described by the following equation [26]:

\[ U = E_{e\text{-ref}} + \eta_+ + \eta_- + jR_i \]  \hspace{1cm} (1.3.1)

where \( E_{e\text{-ref}} \) is a difference in equilibrium potential between the positive and negative electrodes; \( \eta_+ \) and \( \eta_- \) are the polarization over-potentials of the positive and negative electrodes, respectively; \( j \) is the applied current and \( R_i \) is the internal resistance of the battery, which consists of the ohmic resistance of the negative and positive electrodes, the electrolyte, separator and electric collector [27]. For the charge/discharge of a MH electrode, any decrease in the equilibrium potential and polarization overpotential are considered to be an improvement (discharge voltage and high-rate charge/discharge capability) in the charge/discharge performance of the Ni/MH battery.
The equilibrium potential is related to the depth of discharge and temperature. The relationship between equilibrium potential, hydrogen concentration and temperature can be used to predict the progress of Ni/MH batteries during slow discharge process. In this study, the electrochemical reaction kinetics is used to establish this relationship for the first time, and compared to the hydrogen absorption model. A slope-influencing parameter for the discharge curve of an electrode alloy is derived and the variation of equilibrium potential with hydrogen storage capacity at different cycles is measured.

1.3.3 Correlation between equilibrium potential and hydrogen pressure

The hydrogen absorption and desorption characteristics of metals in gaseous environment are represented by pressure-composition-temperature ($P$-$C$-$T$) curves. Analogous plots for the MH electrodes in KOH solutions are presented by equilibrium potential-composition-temperature ($E$-$C$-$T$) curves. Both curves are related and provide important information on the selection of MH electrode materials employed as the negative electrode [5,28]. The equilibrium potential of the MH electrochemical reaction corresponds to a hydrogen equilibrium pressure in a gaseous hydrogen environment. The theoretical correlation between equilibrium potential and hydrogen pressure is established using reaction thermodynamics and an example of converting equilibrium potential to hydrogen pressure is given to validate the derived equations.

1.3.4 Discharge capacity of MH electrode

The discharge capacity of the metal hydride electrode reflects the stored energy in the metal hydride electrode. It is a key parameter to determine whether the hydride alloy
can be used in Ni/MH batteries. The aim of this study is to investigate the characteristics of discharge capacity, and the factors affecting discharge capacity.

1.3.5 Exchange current density

The exchange current density, a measure of the electrode reaction rate and representative of the reversibility of the electrode reactions, is examined in detail. An increase in the exchange current density of a metal hydride electrode is indicative of improvement in its kinetic properties. In this study, the factors that determine the exchange current density are investigated using polarization measurements.

1.3.6 High-rate dischargeability

High-rate dischargeability is also a kinetic property of metal hydride electrode and one aim of this study is to improve the high-rate dischargeability of metal hydride electrodes. The high-rate dischargeability is determined for both LaNi$_{4.7}$Al$_{0.3}$ and Cu-coated LaNi$_{4.7}$Al$_{0.3}$ electrodes. The reasons for the different high-rate dischargeabilities obtained are examined.

1.3.7 Apparent activation energy

The exchange current density is related to the apparent surface area, the hydrogen content of the electrode, and temperature. However, the apparent activation energy is dependent only on the hydrogen content. Therefore the exchange current density is not sufficient in itself to characterize the catalytic activity of a metal hydride electrode, and the apparent activation energy is also required in characterizing MH electrodes. A high
exchange current density with low apparent activation energy is a measure of enhanced performance of MH electrodes. In this study, the apparent activation energy is measured at different hydrogen concentrations.

1.3.8 Symmetry factor of electrode reaction

The symmetry factor is a parameter that relates to activation energy of a metal hydride electrode reaction, and is an indicator of the reversibility of the electrode reactions. The factors that affect the symmetry factor are investigated in the present study.

1.3.9 Hydrogen diffusion coefficient

The kinetic properties of a metal hydride electrode are influenced significantly by the diffusion behaviour of hydrogen. One of the key parameters, determined in this research, is the diffusion coefficient for hydrogen.

The permeation technique is frequently used to determine diffusion coefficients of hydrogen in metals, which necessitates preparation of thin films (of the order of several μm) of alloys. However, the hydrogen-absorbing alloys are very brittle materials and are very difficult to prepare as thin films. Also, a further difficulty with the permeation method is that the calculated hydrogen diffusion coefficient in the thin film is not equivalent to that in the MH electrode comprised of alloy particles.

In this study, a novel and relatively simple potentiostatic method is developed for the first time, called Potential Step Chrono-Amperometry (PSCA), for determining the hydrogen diffusion coefficient without the need for prior hydrogen concentration and
specific surface area data. The diffusion process, which usually becomes the rate-determining step in an electrode process, is analyzed. The variation of hydrogen diffusivity with hydrogen concentration is also examined.
CHAPTER 2

LITERATURE REVIEW

2.1 METAL HYDRIDE ELECTRODE MATERIALS

Hydrogen reacts with elements from most groups of the periodic system to form hydrides. Although the distinction is not always sharp, these different binary hydrides are usually classified in three categories [29]:

- ionic or saline hydrides: e.g. LiH, MgH₂ and HCl;
- covalent hydrides: the prototype is CH₄, but AlH₃ also belongs to this class;
- metal hydrides: this group comprise the hydrides formed by transition metals.

This study is concerned with metallic hydrides, in particular, alloys capable of absorbing and desorbing hydrogen reversibly in the pressure range around 1 atm and near room temperature, which can be applied to the Ni/MH batteries. The following topics are reviewed in the following sections: fundamentals of hydrogen storage materials; material requirements; and chemical and structural disorder in engineered materials.

2.1.1 Fundamentals of hydrogen storage materials

Early work on hydrogen storage alloys, such as LaNi₅ and MmNi₅, began in the 1970s with the energy crisis that resulted from high oil prices. Hydrogen is considered to be one of the most promising fuels for the future due to its distinctive and unique features such as a very high energy density, abundance in nature, and its non-polluting nature. One method of hydrogen storage that is considered effective and economical is metal hydrides. Hydrogen reacts with the hydrogen storage material, usually an intermetallic compound or alloy, to form a metal hydride where the hydrogen is bonded to the alloy.
Through this reaction, hydrogen is stored in alloy. However, the metal hydride formation reaction can be easily reversed.

The formation reaction for the metal hydride is exothermic, and usually spontaneous, and the hydrogen can be easily recovered by heating the hydride. The hydrides are stable below their dissociation temperature and the self-cooling effect will stop any loss of hydrogen if the reverse reaction happens. Therefore, metal hydrides are classified as a safe method for hydrogen storage.

The absorption and desorption of hydrogen by metals is most conveniently represented by pressure-composition-temperature (P-C-T) curves. The typical P-C-T curve and the various phase regions are described in Fig. 2.1, which comprises the following features:

A small amount of hydrogen gas dissolves in the original metallic host without forming a second phase:

$$M + \frac{x_0}{2} H_2 \xrightarrow{\text{MH}_{x_0}}$$  \hspace{1cm} (2.1.1)

where $x_0$ is the maximum solubility of hydrogen in $\alpha$-phase. The absorbed hydrogen atoms occupy interstitial sites in the metal lattice and their concentration depends strongly on the hydrogen pressure. This hydrogen-poor solid solution is denoted by the $\alpha$-phase. The next stage involves the absorption of hydrogen after the solid solution is saturated:

$$\text{MH}_{x_0} + \frac{y_0 - x_0}{2} H_2 \xrightarrow{\text{MH}_{y_0}}$$  \hspace{1cm} (2.1.2)
where $y_0$ is the minimum solubility of hydrogen in $\beta$-phase. Now, a new solid phase, referred to as the $\beta$-phase, nucleates and grows. This is accompanied by a discontinuous change in the lattice parameters. Ideally, during the $\alpha$/ $\beta$-phase transition the equilibrium pressure remains constant according to Gibbs's phase rule: $F = C - P + 2$. Two components $C$ ($H_2$ and $M$) and three phases $P$ (two solid and one gaseous) are present, so the number of degrees of freedom $F$ is one. Thus, at a given temperature the pressure is fixed. This constant pressure level is often called the plateau pressure. Even if the host metal consists of an intermetallic compound, in this context, it is considered to be only one component because of the immobility of its constituents at low temperatures. However, most $P$-$C$-$T$ diagrams do not exhibit flat, horizontal pressure plateaus. Impurities, inhomogeneities, particle size, stress and H-H attractive interactions may all be factors contributing to this phenomenon.

After the $\alpha$-phase has been completely converted into the $\beta$-phase, further increase of the hydrogen concentration in the metal is accompanied by an increasing equilibrium pressure. Similar to the hydrogen dissolution in the 'empty' host, i.e. the $\alpha$-phase, hydrogen dissolves in the hydrided $\beta$-phase.

The equilibrium hydrogen pressure, $P$ is related to the change in Gibbs free energy ($\Delta G$), which occurs for the reaction between gaseous hydrogen and the hydrogen storage alloy to form the MH. This value can be written as follows, according to the relation of Van't Hoff:

$$\Delta G = \Delta H - T\Delta S = RT \ln P$$  (2.1.3)
Because the entropy term, $T\Delta S$, is small at room temperature, $\Delta H$ largely determines $\Delta G$. Thus, the determination of $P$ provides a measure of $\Delta H$, which is related to the metal-hydrogen bond strength.

Based on the crystal structure, hydrogen storage materials can be classified into five groups: AB, AB$_2$, A$_2$B, AB$_3$, AB$_5$ (including the multi-component alloys based on them). Metal A is assumed to have a stronger affinity for hydrogen than B [30]. Of these, the AB$_2$ (e.g., ZrV$_2$-based alloys) and AB$_5$ (e.g., LaNi$_5$-based alloys) type alloys are the most commonly used because of their attractive characteristics in both gas-phase and electrochemical reactions. AB type compounds (the most studied compound is FeTi) are also important materials for practical application, because of their isotherm characteristics, chemical stability on cycling, and cost. A$_2$B type intermetallic compounds (the most studied compound is Mg$_2$Ni) have been most frequently cited for their high hydrogen storage capacity. AB$_3$ compounds are rarely used as metal hydride electrodes in practical applications because of their electrochemical properties, isotherm characteristics, chemical stability on cycling, and cost.

The properties of the hydrogen storage materials make them attractive for use in various applications, such as hydrogen fuel storage for vehicles [31-33], purification and compression of hydrogen [34-38], energy conversion for thermal transformers, heat pumps and refrigerators [37-45], and metal hydride batteries [29,46]. One of the most promising battery technologies is the Ni/MH battery. Ni/MH batteries have been commercially available since 1990. By 1997, Ni/MH batteries made up 40% of the small rechargeable battery market, accounting for 25% percent of the sales figures for that market [47].
2.1.2 Material requirements

The discharge pressure of a metal hydride should be between 0.1 and 1 atm at room temperature to ensure that the amount of hydrogen stored in the alloy can be completely released. The amount of hydrogen that the MH material can absorb determines the electrochemical storage capacity of the electrode and, consequently, the energy storage capacity of the battery. It is desirable to have a high electrode storage capacity that is electrochemically reversible. The capacity of MH alloy electrodes is related to their stability. It has been shown that the nature of the chemical bond between the constituent atoms (M-M) plays the dominant role in determining the hydride stability of AB (TiFe), AB₂ (ZrMn₂) and AB₅ (LaNi₅ or CaNi₅) systems [48]. The desorption pressure of a MH alloy corresponds to the equilibrium potential of the MH electrode. In the required range of hydrogen desorption pressure (0.1~1 atm), the desorption pressure should be high enough, i.e., the equilibrium potential should be negative enough (close to -0.9324 V vs. Hg/HgO), to ensure that a large amount of hydrogen can be completely released. To ensure reversibility, an important aspect of the MH design is the range of metal-to-hydrogen (M-H) bond strengths, which should be between 25 and 50 kJ mol⁻¹ [49]. If the bond strength is too low, hydrogen will not react with the alloys, and if too high, hydrogen is irreversibly bound.

The materials should exhibit good oxidation and corrosion resistance in an alkaline electrolyte and oxygen gas. The Ni/MH battery operates in a strongly oxidizing medium composed of a high-concentration alkaline electrolyte. Many chemical elements react to form oxides in an alkaline electrolyte, and these elements will oxidize and fail to store hydrogen reversibly. MH electrodes are typically designed for use in totally sealed
batteries where oxygen recombination occurs at their surfaces, especially in the
overcharging process. During overcharging the oxygen evolves at the Ni electrode as
follows:

$$\text{OH}^- \rightarrow \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} + e^- \quad (2.1.4)$$

In this aggressively oxidizing environment, the degree of oxidation and corrosion of
the MH electrode materials is critical, as the cycle lifetimes depend strongly on the
oxidation and corrosion resistance of the MH electrode materials.

Hydrogen diffusivity in the alloy and exchange current density should be high so as
to ensure the high discharge rate of the Ni/MH battery, especially at high discharge
current densities, and these properties are related to the mass and charge transfer
processes. During discharge, hydrogen stored in the bulk metal is brought to the electrode
surface by diffusion, which then reacts with hydroxyl ions at the metal-electrolyte
interface. Thus, hydrogen diffusivity in the alloys and the exchange current density affect
the rate at which energy is stored and released in the Ni/MH battery. Exchange current
density can be influenced by surface properties such as oxide thickness, electrical
conductivity, surface porosity and topology, surface area, and degree of catalytic activity.

For the battery to operate as a sealed system, it must also tolerate the consequences
of chemical reactions that occur during cell overcharge and overdischarge. In overcharge,
oxygen gas is generated at the Ni(OH)$_2$-positive electrode and must recombine with
hydrogen at the MH electrode to form water. In overdischarge, which occurs when a low-
capacity cell in a series-connected string is subjected to reverse polarity, hydrogen is
generated at the Ni(OH)$_2$ electrode and must be recombined at the surface of the MH electrode to form water. In a sealed system, these gas recombination reactions must occur at sufficient rates to avoid pressure buildup. This condition requires adequate electrode area, a thin electrolyte film, and, for the hydrogen absorption process, catalytic activity at the MH electrode surface to promote rapid dissociation of hydrogen.

In summary, the desired properties of intermetallic compounds used for Ni/MH batteries include: an appropriate hydrogen desorption pressure (0.1~1 atm); an appropriate equilibrium potential (close to -0.9324 V vs. Hg/HgO); high corrosion resistance; and fast mass transfer and charge transfer reactions.

2.1.3 Chemical and structural disorder in engineered materials

The diverse properties required for a superior MH battery electrode can be attained by engineering new hydrogen storage materials on the basis of the concepts of structural and compositional disorder [49]. Compositional and structural disorder is designed into the new MH materials on three different length scales using elemental composition and processing techniques of alloys and electrodes. The length scales over which disorder is created can be designated: local (or atomic), which comprises regions with dimensions up to a few nearest-neighbor atomic distances; intermediate range, which comprises regions typically about 10 to 20 nm and extending up to about 100 nm; and long range, which involves regions with a dimension larger than about 100 nm. Disorder on each of these length scales is used to achieve different goals in the engineered alloys.

Compositional and structural disorder on a long-range length scale is used in the bulk of metal hydride alloys to give considerably higher hydrogen storage and better kinetics
than is possible with conventional unprocessed MH alloy structures, which are compositionally ordered and crystalline. The processing of disordered alloys can be optimized to produce a polycrystalline, compositionally multiphase material.

Intermediate-range structural and chemical disorder plays a number of important roles, primarily at interfaces both within the bulk of the MH electrode and at the electrode-electrolyte interface. Formation of the polycrystalline, compositionally multiphase bulk alloy gives rise to a high density of grain boundaries between compositional and structural phases. The intermediate-range disorder that occurs at the grain boundaries increases surface area, which can greatly increase the density of catalytic sites. At the electrode-electrolyte interface, disorder on a length scale of approximately 10 to 100 nm is created during electrode processing and activation by the exploitation of chemical properties that are traceable to the elemental constituents of the MH alloy.

Compositional disorder on the atomic scale is used to increase hydrogen storage capacity and improve catalytic activity through the incorporation of elements into the MH alloy that generate new chemically active sites. These sites offer an increased variety of hydrogen bonding possibilities and enhanced rates as a result of increased catalysis. Incorporation of elements with multidirectional $d$ orbitals increases the range of stereochemical possibilities for bonding hydrogen, as confirmed by the increased amount of hydrogen absorbed and by increased catalytic activity. These effects also occur to a lesser extent with elements containing $f$ orbitals that extend in still more directions than $d$ orbitals, but which are closer to the nucleus of the metal atom and less accessible.
Figure 2.1  The typical $P$-$C$-$T$ curve.
2.2 ELECTROCHEMICAL CHARACTERISTICS OF MH ELECTRODES

2.2.1 Specific discharge capacity

The specific discharge capacity is an important factor in determining whether the electrode can be used as a negative electrode in a Ni/MH battery. The specific discharge capacity is closely related to the cycle times. Over the first 10-20 charge/discharge cycles, the specific discharge capacity increases with number of cycles to a maximum value, beyond which it decreases with additional cycles. The specific discharge capacity reported without reference to the cycles denotes the maximum value for the electrode. The decay rate of the specific discharge capacity (also called discharge capacity, or just capacity) is generally specified in evaluating MH electrodes.

According to Willems [29], the discharge capacity of a LaNi$_5$ electrode decreases drastically owing to the pulverization of the LaNi$_5$ powder that occurs during cycling, a result of the expansion of the lattice (by about 25%) during hydriding, and the inherent brittleness of LaNi$_5$. The capacity decay in the LaNi$_5$ alloy on cycling also results from segregation of nickel and lanthanum at the surface of the MH alloy powder. A multicomponent substitution in this compound was suggested for reducing the lattice expansion and the capacity decay. The capacity decay of LaNi$_5$ and Ti-Ni-based alloys is also attributed to the formation of a passive oxide layer on the surface in the latter, and to the oxidation/decomposition of the alloys to La(OH)$_3$ and nickel in the former. The replacement of Ni with Co has been used to reduce the capacity decay. A La$_{0.8}$Nd$_{0.2}$Ni$_{2.5}$Co$_{2.4}$Si$_{0.1}$ alloy was shown to have a long charge/discharge cycle lifetime, with a capacity decay of only 30% after 1000 cycles [1]. Sakai et al. [50-52] have investigated MmNi$_5$-based alloys (Mm, mischmetal) as a low cost negative battery
electrode. The replacement of nickel by cobalt and coating of nickel on the powder surface were also effective in improving the cycle lifetime, but caused a decrease in both capacity and high rate dischargeability. Sakai et al. reported in their review paper [52] that the decay in capacity of a MH electrode made of MnNi_{3.5}Co_{0.7}Al_{0.8} alloy was only 10% after 2000 cycles. The cylindrical sealed cell also showed a very long cycle lifetime (a capacity decay of 6% after 2000 cycles).

It has already been noted that Ni/MH battery performance is often better when the metal hydride electrode is a multiphase material. The AB₂ compositions are predominantly hexagonal C14 and cubic C15 Laves phases that generally do not solidify directly into a single phase. As many as five phases have been reported in some hydride electrodes, with specific roles (e.g., hydrogen storage capacity, electrocatalysis, corrosion protection) attributed to each phase [53]. There are several requirements for the electrochemical properties of MH electrode which must be balanced for practical use. The multiple components used in commercial alloys produce the multiphase microstructures that give the diverse properties required for the electrodes.

Generally, the Ni/MH battery is made from replacing the negative Cd electrode of the Ni/Cd battery by the MH electrode, in which the MH alloys break up into micro-sized particles with increasing number of charge/discharge cycles. According to Belkbir’s results [54], the particle size of the LaNi₅ alloy powder decreases greatly in the first 5 cycles and then remains constant (at about 2 μm) with increasing number of cycles. The alloy powder is thus easily oxidized in the early hydrogen absorption/desorption cycles, and then resists further oxidation after the particle size reaches a constant value. Van
Rijswijk suggested that compounds rich in cobalt, nickel or copper would be protected against corrosion by a thermodynamically stable surface layer [29].

The protection against corrosion using cobalt, nickel or copper in alloy compounds is only moderate and is insufficient. The surface layer may possess an open structure and still allow lanthanum to reach the electrode/electrolyte interface. Also, fracturing of the metallic powder may continue, progressively yielding fresh surface area. If the latter occurs, as partly suggested by the activation process, coating of the fine metal particles with a protective layer, e.g., palladium or a passive oxide [29], will not prevent severe deterioration of discharge capacity. To understand and characterize discharge capacity degradation more fully, both the oxidation reaction and the disintegration of the intermetallic compound need further examination.

2.2.2 Cycle lifetime

The cycle lifetime of a metal hydride electrode must be high for it to qualify for use in a practical battery. During charge/discharge cycling, the discharge capacity of the metal hydride electrode decreases gradually due to oxidation, erosion, pulverization, and other effects. The cycle lifetime of a metal hydride electrode is usually measured by the number of cycles for the discharge capacity to decrease to a certain value. The half-life is often used as an evaluation of the cycle lifetime [55]. The number of cycles for the discharge capacity of the electrode to decrease to half of its maximum capacity (usually obtained on the first cycle after activation) is defined as the cycle lifetime of the electrode. This capacity decay upon cycling has been studied by many researchers, and models have been developed to predict the relationship between discharge capacity and
cycle lifetimes for different metal hydride systems [29,55]. Although some metal hydride electrodes, such as LaNi\textsubscript{5} and LaN\textsubscript{4}Cu, have high initial discharge capacities which are very close to their theoretical ones (about 370 mAh g\textsuperscript{-1}), the capacities decrease very quickly. The half-life is only about 150 cycles, which renders these electrodes useless for practical application. The metal hydride material, which is used as the metal hydride electrode in the battery, should have a half-life of at least 1000 cycles. Many multicomponent electrodes with excellent characteristics have now been developed which have sufficiently long cycle lifetimes for commercial battery application.

2.2.3 Polarization behaviour

In an alkaline aqueous solution, the hydrogen atoms produced at the surface of the MH alloy powder are instantly adsorbed and then diffuse into the bulk of the MH alloy. The electrochemical reactions are expressed as follows:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H}_{\text{ad}} + \text{OH}^-
\]  \hspace{1cm} (2.2.1)

and

\[
\text{H}_{\text{ad}} \rightarrow \text{H}_{\text{ab}}
\]  \hspace{1cm} (2.2.2)

where H\textsubscript{ad} and H\textsubscript{ab} denote the hydrogen atoms on the surface of the MH alloy powder and in the bulk of MH alloy, respectively. Reaction (2.2.1) represents the charge transfer process at the interface between the MH alloy powder and the electrolyte, and reaction (2.2.2) the hydrogen transition from an adsorbed to an absorbed state (i.e. surface to the bulk) in the alloy particles.

The electrochemical kinetics of the charge-transfer process are typically determined
by dc polarization methods. The slope of the linear polarization curve represents the 
internal resistance of the electrode \( (R_i) \). The internal resistance of the electrode is 
composed of the ohmic resistance \( (R_\Omega) \) and polarization resistance \( (R_p) \). The polarization 
resistance is mainly determined by the charge-transfer process at the interface between 
the MH electrode and the electrolyte. The charge-transfer process can be described by 
using the exchange current density. The exchange current density can be calculated from 
the polarization resistance in the charge transfer process, as follows:

\[
R_p = \frac{RT}{jF} = \frac{\eta}{j} \quad (2.2.3)
\]

where \( R \) is the gas constant \( (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \); \( T \) is the temperature (K); \( F \) is the Faraday 
constant \( (96487 \text{ C mol}^{-1}) \); \( I_0 \) is the exchange current density \( (A \text{ g}^{-1}) \); \( j \) is current density 
\( (A \text{ g}^{-1}) \) and \( \eta \) is the over-potential (V). Since the magnitude of the ohmic resistance \( (R_\Omega) \) 
is very small compared to the polarization resistance \( (R_p) \), the slope of the linear 
micropolarization curve can generally be used to estimate the exchange current density.

The exchange current density \( (I_0) \) is a dynamic parameter that depends on the state of 
charge (SOC) or discharge (SOD) of the electrode. The discharge efficiency (ratio of 
capacity at \( n \) cycles to the total storage capacity) increases significantly with increasing \( I_0 \) 
[56]. The study of this parameter has partially elucidated the electrochemical processes 
occurring at the metal hydride electrodes.

A study of electrocatalytic activity, as reflected in the exchange current density of the 
MH electrode, is also very important in the application of MH electrodes since it is 
related to such fundamental processes and properties as activation treatment, discharge 
overpotential and high-rate dischargeability, which are the practical parameters for
evaluating MH electrodes. A lower exchange current density leads to a higher overpotential. A larger overpotential leads to a decrease in usable capacity and an increase in anode corrosion, the latter decreasing the cycle lifetime. Iwakura and coworkers [6,57,58] found that the high-rate dischargeability increases asymptotically with increasing exchange current density. The magnitude of the exchange current density is determined principally by the structure of the electrodes and the composition of the hydrogen-absorbing alloys [59], but also by the charge transfer process at the electrode/electrolyte interface.

Although data have been published on the dependence of exchange current density on the SOC (state of charge) for a La_{0.65}Ce_{0.35}Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} hydride alloy [60], no data has been provided on the effects of temperature changes, which data would allow calculation of the apparent activation energy for the discharge process of the MH electrode.

2.2.4 Hydrogen diffusion

One of the most important kinetic properties of the electrochemical processes in the hydrogen storage compounds used in these batteries is the hydrogen diffusion coefficient ($D$).

Different approaches have been proposed for the evaluation of the hydrogen diffusion coefficient in hydrogen storage alloys. These have included nuclear magnetic resonance (NMR) [61-63], quasi-elastic neutron scattering (QNS) [64,65], electrochemical impedance spectroscopy (EIS) [66], and various other electrochemical techniques, including potential-step and current-step methods [67-73]. The diffusion
coefficients of hydrogen measured in various AB₅-type alloys using the different methods can vary up to five orders of magnitude at room temperature (from $10^{-10}$ to $10^{-15}$ m² s⁻¹) [61-73]. These widely varying values of $D$ may be due to differences in alloy composition and structure, artifacts associated with the different experimental methods, and also differences (real or apparent) in the hydrogen concentrations in the various alloys.

The conventional potentiostatic method is widely used to study the hydrogen diffusion coefficient, as it is a simple and convenient method [66,68]. This method requires a sufficiently large time period (greater than about 5000 s) for the measurement, and thus, the calculated hydrogen coefficient represents an average value for the time interval involved. Thus this method cannot be used for determining the diffusion coefficient at a given specific time. The potential intermittent titration technique (PITT) can be used for a fixed-time determination [74,75], and has already been used to study the Li⁺ ion diffusion in a graphite anode of rechargeable lithium batteries [76].

A major difficulty in comparing $D$ values obtained by the different techniques, or with different samples of the same electrode material, is the uncertainty in the true surface area and the hydrogen concentration for the electrode. However, it is expected that when different techniques are used for studying the diffusion process in the same system, the $D$ values obtained would be similar, although this is not always the case in practice, which leads to different interpretations of the equations used for the determination of $D$. The diffusivity depends on the temperature, the nature of the diffusing species, and the nature of the diffusion medium. $D$ may also be dependent on the hydrogen concentration, which is frequently ignored for simplicity of analysis. A new
experimental technique is required for determining accurate and consistent diffusivities in MH electrodes.

2.2.5 Mechanisms of MH electrode reactions

The following important processes are considered to take place in the bulk of the alloys, and at the electrode/electrolyte interface during discharge:

(i) Diffusion of absorbed hydrogen from the bulk to the surface of the electrode. When the static equilibrium state is established, hydrogen is homogeneously distributed in the metal hydride.

(ii) Transition of hydrogen from an absorbed state to an adsorbed state on the surface of the alloy particles.

\[ \text{MH}_{\text{abs}} \leftrightarrow \text{MH}_{\text{ads}} \quad (2.2.4) \]

(iii) Hydrogen atom interactions at the surface of each individual particle of the electrode.

(iv) Electrochemical reaction occurring at the surface of each individual particle of the electrode.

\[ \text{H} + \text{OH}^- \xrightarrow{\text{discharge}} \text{H}_2\text{O} + \text{e}^- \quad (2.2.5) \]

Several mathematical models have been proposed for the electrochemical properties (discharge capacity, cycle lifetime, exchange current density, equilibrium or discharge potential) during discharge, which are related to the discharge state (i.e. hydrogen
concentration) and several alloy parameters [18,77-82]. Yang et al. [83] considered hydrogen transfer through the interface and established a general relationship between the overpotential and the rate of hydrogen diffusion in the electrodes, as well as the kinetic parameters characterizing the transfer from the absorbed to the adsorbed state. Zheng et al. [84] developed a porous electrode theory to estimate the exchange current density, the polarization resistance and the transfer coefficient for a LaNi$_{4.27}$Sn$_{0.24}$ hydride electrode in an alkaline solution. Haran et al. [80] developed a model which indicated that the particle size of the alloy and hydrogen diffusivity are the determining factors affecting the performance of electrodes made with metal hydride particles. However, further study of electrode reactions is necessary as disagreements in the literature are many on the proposed mechanisms.

Yayama et al. [85] studied a TiMn$_{1.5}$ electrode and found that the rate-determining step in the electrode reaction at current densities less than 100 mA·g$^{-1}$ is the diffusion of hydrogen in the solid electrode. Wakao et al. [86] also found hydrogen atom diffusion to be the rate-determining step in the electrode reaction, but reported a higher negative value of $\Delta H$. Iwakura et al. [57] found that the electrode discharge at high discharge rates is controlled both by the electrochemical surface reaction and hydrogen diffusion. Yang et al. [87] studied the activation and concentration overpotentials of a Ti$_{0.35}$Zr$_{0.65}$Ni$_x$V$_{2-x}$Mn$_y$ alloy by using anodic polarization measurements. They found that for small discharge current densities, the charge transfer process is the dominant electrode reaction, and for large discharge current densities, hydrogen diffusion in the bulk MH alloy is the rate-determining step. These different findings might be attributable to differences in
alloy composition, different electrode dimensions and geometries, and/or different methods used for the measurements.

2.3 DEVELOPMENT OF MH ELECTRODES

The most commonly used metal hydride electrode alloys are multi-component alloys rather than pure binary alloys. Multi-component metal hydride electrodes have been in commercial use for a number of years, since they have many advantages over binary alloy electrodes, including: higher capacity, longer cycle lifetime, good structural stability, high charge/discharge rate capacity, good resistance to overcharge or overdischarge, and low cost.

There are two main series of multi-component electrodes that have been developed: the AB₅ and AB₂ type alloys. The AB₅ type alloys include LaNi₅-based alloys, MNI₅-based alloys, MmNi₅-based alloys, and MmBₓ-based alloys, where MI denotes the La-rich mischmetal and Mm the Ce-rich mischmetal. The AB₂ type alloys include the C14 and C15 series of alloys such as the ZrV₂-based, ZrCr₂-based and ZrMn₂-based alloys. Ti-Ni-based alloys have also been developed as metal hydride electrodes and exhibit good electrochemical properties. Also Mg-based alloys are seen as promising metal hydride electrode alloys [88,89], although they are still in the early experimental stage. They show excellent potential in terms of their high capacity and low cost.

In the following sections, two important factors which influence the electrochemical behaviour of a metal hydride electrode are reviewed. The first factor is crystallography, and the second is surface modification.
2.3.1 Effect of crystallography on the electrochemical behavior of MH electrode

Effect of "crystallography" on the electrochemical behavior of metal hydride electrode includes effects of microstructure, structural parameters, type of intermetallic (AB$_5$ and AB$_2$) and alloying elements.

2.3.1.1 Microstructure

It has been found that the electrochemical properties of a multicomponent alloy are improved when the alloy is changed from a single to a multiphase material [49,90,91]. The multiphase materials, which consist of a single-phase hydride forming material of the AB$_5$ or AB$_2$-type and a second or third, highly electrocatalytic phase(s) which is homogeneously distributed upon the powder particles, will improve the discharge efficiency [56]. These multiphase solids with the desired morphology can be relatively easily produced by simply solidifying a melt to a nonstoichiometric composition; i.e. a composition just outside the homogeneity region of either the AB$_5$ or AB$_2$ intermetallics.

Hydrogen storage alloys are usually annealed to obtain a homogeneous composition in the ingots after casting [92]. Generally, annealed samples show flat and wide plateau regions. However, it takes a long time to reach complete homogeneity. Although La$_{0.99}$Ni$_{4.74}$Mn$_{0.27}$ annealed for 36-84 h at 900 °C was reported to be highly homogeneous [92], both LaNi$_{4.8}$Mn$_{0.2}$ [93] and LaNi$_{4.55}$Al$_{0.45}$ [94] annealed for 8 h at 1000 °C and 1050 °C still exhibited precipitation of a Mn-rich phase and an Al-rich phase, respectively. However, the capacity and durability (or cycle lifetime) of a MnNi$_{3.5}$Co$_{0.8}$Mn$_{0.4}$Al$_{0.3}$ electrode was appreciably improved by annealing at 1000-1100 °C for 6 h [95]. Good
homogeneity has also been attained by means of rapid quenching using the melt spinning technique [94].

Annealing hydrogen storage alloys does not always improve the performance of the alloys. Sakai et al. [51,95] reported that a cast ingot of MnNi<sub>3.5</sub>Co<sub>0.7</sub>Al<sub>0.8</sub> exhibited different morphologies depending on the cooling rate. A columnar grain structure (column diameter ~10 μm) was produced by rapid solidification and an equiaxed grain structure (grain size ~50 μm) was produced by slow cooling or annealing. The capacity of the equiaxed-structure sample at the 100th cycle was smaller by 28% than that of the columnar-structure sample. Sakai et al. [51,95] attributed the superior durability of the columnar-structure sample to the higher resistance to pulverization.

2.3.1.2 Structural parameters

The corrosion resistance of AB<sub>5</sub> electrodes has been shown to be determined by two factors: (i) surface passivation due to the presence of surface oxides or hydroxides, and (ii) the molar volume of hydrogen (V<sub>H</sub>) in the hydride phase [1]. An electrode in which V<sub>H</sub> is large and has a high H storage capacity will undergo large volume changes upon cycling, and corrodes relatively rapidly. Therefore it is important to formulate alloy electrodes in which V<sub>H</sub> is minimized. Another consequence of large volume changes is the increased mobility of metal atoms at the moving interface between the metal phase and the hydride phase during the charge-discharge process. This increases the possibility of transport of easily oxidized alloy components to the electrode surface [1]. It has also been found that corrosion and the consequent decay in storage capacity of La<sub>1-x</sub>Ce<sub>x</sub>B<sub>5</sub> electrodes is not solely a function of the volume change per cycle, but also the rare-earth
composition [10]. The presence of a small amount of Ce has been shown to retard corrosion regardless of the lattice expansion/contraction due to hydride formation/decomposition. A possible explanation for this finding lies in the fact that Ce can form a protective oxide film on the metal surface [10].

2.3.1.3 Type of intermetallics (AB$_5$ and AB$_2$)

AB$_5$-based (A=rare earth elements, especially La; B=transition metals, primarily Ni) and AB$_2$-based (A=Mg, Zr and Ti; B=Ni, V, Cr and Mn) intermetallic compounds have been successfully applied as negative electrode materials in Ni/MH rechargeable batteries. The AB$_5$-type alloys were the first generation to be used as electrode materials, and have an hexagonal or orthorhombic lattice structure of the CaCu$_5$-type shown in Fig. 2.2 [96]. The AB$_2$-type alloys mainly form one of two structures, either the cubic C15 structure or the hexagonal C14 structure [97,98]. These crystal structures are shown in Fig. 2.3 [98]. The AB$_2$ hydrogen storage intermetallic compounds have been investigated extensively because of their potential application in high capacity negative electrodes for Ni/MH batteries [99]. Many studies have concentrated on the compositional substitution of metallic elements in ZrMn$_2$, ZrCr$_2$ and ZrV$_2$ Laves phases, to improve the hydrogen absorbing/desorbing kinetics and to increase the electrochemical capacity [100].

It is recommended that a highly electrocatalytic alloy or a pure metal, which are homogeneously distributed throughout the powder particles, be used as catalytic materials to generate both good hydrogen storage levels and electrocatalytic activity. The Brewer intermetallic bonding model [101] suggests that whenever metals in the left-side of the transition series, which have empty or half-filled d-orbitals, are alloyed with metals in the
right-side of the transition series, which have internally paired d-electrons not available for bonding in the pure metal, the alloying proceeds with a definite charge transfer and there is a marked synergism in electrocatalysis for the hydrogen evolution reaction (h.e.r.), which often exceeds the individual catalytic effects of the precious metals by themselves or in combination (the synergism phenomenon) and approaches reversible behaviour over a wide range of current density. These alloys include some stoichiometric Laves compounds (mainly AB₃ type) such as MoCo₃, MoNi₃, WNi₃ [56], ZrPt₃, HfPt₃ [102], WPt₃, HfPd₃, MoIr₃, MoPt₃ and MoPd₃ [103] and other types of compounds such as Ti₂Ni and TiNi [104] or Ni [105]. Such catalytic alloys and metals (Ni or Pt) may be formed either by metallurgical preparation or by coating the MH alloy particles. Recently, it has been found that amorphous Ti₂Ni and TiNi alloys, prepared by rapid quenching of the metal and subsequently treated with HF, were very electrocatalytically active for the h.e.r. The high activity of Ti₂Ni and TiNi alloys for the h.e.r. was attributed to the selective dissolution of TiO₂, which left a porous and electrocatalytically active Ni layer. The porous and electrocatalytically active Ni layer can significantly increase the electrode surface area and activity. For crystalline alloys, such selective dissolution of the oxide layer is difficult to achieve [103,104].

Table 2.1 presents typical electrochemical properties for selected AB₂ and AB₅-based intermetallic compounds at room temperature. In Table 2.1, the bracketed number following the maximum capacity represents the current density for the determination; n* is the number of cycles to decrease the capacity to one-half the maximum capacity; Jₒ is the exchange current density after activation and at fully charged state; and Eₑ is the equilibrium potential (vs. Hg/HgO reference electrode) at fully charged state. The
superscript "a" refers to data estimated from the results given in the references, and the "b" superscript refers to the average equilibrium potential obtained at half the full capacity. Compacting powders are used to improve the electronic conductivity and catalysis of MH electrodes. It can be seen that the AB$_2$-type alloys exhibit higher discharge capacities than AB$_3$-type alloys. However, the cycle lifetime and exchange current density of AB$_2$-type alloys are lower than that of AB$_3$-type alloys, i.e. the hydrogen absorbing/desorbing kinetics still need to be improved.

Table 2.1 Electrochemical properties for AB$_2$ and AB$_3$ intermetallics.

<table>
<thead>
<tr>
<th>Alloy Powder</th>
<th>Compacting Powder</th>
<th>Max. cap ($I_{\text{dc}}$) (mAh g$^{-1}$) (mA g$^{-1}$)</th>
<th>$n'$</th>
<th>$i_0$ (mA g$^{-1}$)</th>
<th>$E_c$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(V$<em>{0.2}$Ni$</em>{0.8}$)$_2$</td>
<td>Ni</td>
<td>285(12)</td>
<td></td>
<td>120$^a$</td>
<td>80</td>
<td>-0.905 [106]</td>
</tr>
<tr>
<td>Zr(V$<em>{0.2}$Ni$</em>{0.8}$)$_2$</td>
<td>Cu</td>
<td>285(12)</td>
<td></td>
<td>370$^b$</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Zr$<em>{0.5}$Ti$</em>{0.5}$V$<em>{0.5}$Ni$</em>{1.1}$Cr$_{0.2}$</td>
<td>Cu</td>
<td>300(50)</td>
<td></td>
<td>—</td>
<td>104</td>
<td>—</td>
</tr>
<tr>
<td>Zr$<em>{0.5}$Ti$</em>{0.2}$V$<em>{0.8}$Mn$</em>{0.1}$Ni$<em>{0.8}$Fe$</em>{0.2}$</td>
<td>Cu</td>
<td>350(50)</td>
<td></td>
<td>19.8</td>
<td>-0.933</td>
<td>[25]</td>
</tr>
<tr>
<td>Zr$<em>{0.5}$Ti$</em>{0.2}$V$<em>{0.8}$Mn$</em>{0.2}$Pd$<em>{0.1}$Ni$</em>{0.8}$Fe$_{0.2}$</td>
<td>Cu</td>
<td>346(50)</td>
<td></td>
<td>$&gt;600^a$</td>
<td>19.8</td>
<td>-0.933 [25]</td>
</tr>
<tr>
<td>Zr$<em>{0.5}$Ti$</em>{0.2}$V$<em>{0.6}$Mn$</em>{0.2}$Pd$<em>{0.1}$Ni$</em>{0.8}$Fe$_{0.2}$</td>
<td>Cu</td>
<td>372(50)</td>
<td></td>
<td>250$^a$</td>
<td>21.2</td>
<td>-0.932 [25]</td>
</tr>
<tr>
<td>LaNi$<em>{14.7}$Sn$</em>{0.3}$</td>
<td>Carbon black</td>
<td>308(10)</td>
<td></td>
<td>$&lt;300^a$</td>
<td>88</td>
<td>—</td>
</tr>
<tr>
<td>La$<em>{0.9}$Y$</em>{0.1}$Ni$<em>{14.7}$Sn$</em>{0.3}$</td>
<td>Carbon black</td>
<td>287(10)</td>
<td></td>
<td>$&gt;300^a$</td>
<td>53</td>
<td>—</td>
</tr>
<tr>
<td>La$<em>{0.9}$Y$</em>{0.2}$Ni$<em>{14.5}$Sn$</em>{0.3}$</td>
<td>Carbon black</td>
<td>268(10)</td>
<td></td>
<td>—</td>
<td>52</td>
<td>—</td>
</tr>
<tr>
<td>La$<em>{0.7}$Y$</em>{0.3}$Ni$<em>{14.4}$Sn$</em>{0.3}$</td>
<td>Carbon black</td>
<td>198(10)</td>
<td></td>
<td>—</td>
<td>52</td>
<td>—</td>
</tr>
<tr>
<td>La$<em>{0.7}$Y$</em>{0.3}$Ni$<em>{14.4}$Sn$</em>{0.3}$Co$_{0.1}$</td>
<td>Carbon black</td>
<td>221(10)</td>
<td></td>
<td>—</td>
<td>41</td>
<td>—</td>
</tr>
<tr>
<td>La$<em>{0.9}$Zr$</em>{0.1}$Ni$<em>{14.5}$Al$</em>{0.5}$</td>
<td>Cu</td>
<td>289(93)</td>
<td></td>
<td>580</td>
<td>—</td>
<td>-0.907$^b$ [5]</td>
</tr>
<tr>
<td>La$<em>{0.8}$Zr$</em>{0.13}$Ni$<em>{14.5}$Al$</em>{0.5}$</td>
<td>Cu</td>
<td>271(93)</td>
<td></td>
<td>690</td>
<td>—</td>
<td>-0.911$^b$ [5]</td>
</tr>
<tr>
<td>La$<em>{0.8}$Zr$</em>{0.2}$Ni$<em>{14.5}$Al$</em>{0.5}$</td>
<td>Cu</td>
<td>254(93)</td>
<td></td>
<td>810</td>
<td>—</td>
<td>-0.905$^b$ [5]</td>
</tr>
<tr>
<td>LaNi$<em>{14.0}$Al$</em>{0.3}$</td>
<td>Cu+Ni</td>
<td>290(120)</td>
<td></td>
<td>—</td>
<td>300</td>
<td>-0.925 [109]</td>
</tr>
<tr>
<td>Mn$<em>{0.95}$Ti$</em>{0.05}$Ni$<em>{0.83}$Co$</em>{0.43}$Mn$<em>{0.35}$Al$</em>{0.33}$</td>
<td>Ni</td>
<td>276(120)</td>
<td></td>
<td>230</td>
<td>—</td>
<td>-0.925 [109]</td>
</tr>
<tr>
<td>Mn$<em>{0.95}$Ti$</em>{0.05}$Ni$<em>{0.83}$Co$</em>{0.43}$Mn$<em>{0.35}$Al$</em>{0.33}$ (Pd-coated)</td>
<td>Ni</td>
<td>275(120)</td>
<td></td>
<td>255</td>
<td>—</td>
<td>-0.932 [110]</td>
</tr>
<tr>
<td>La$<em>{0.6}$Ce$</em>{0.35}$Ni$<em>{0.75}$Co$</em>{0.7}$Mn$<em>{0.4}$Al$</em>{0.3}$</td>
<td>Pt</td>
<td>278(27.8)</td>
<td></td>
<td>20</td>
<td>-0.935</td>
<td>[60]</td>
</tr>
<tr>
<td>La$<em>{0.2}$Mn$</em>{0.8}$Ni$<em>{1.8}$Al$</em>{0.3}$Co$<em>{0.3}$Mn$</em>{0.4}$Al$_{0.3}$</td>
<td>Cu</td>
<td>300(—)</td>
<td></td>
<td>70</td>
<td>—</td>
<td>[111]</td>
</tr>
</tbody>
</table>
2.3.1.4 Alloying elements

The elements used for alloy formation in MH electrode materials are Li, C, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Sn, La, W, and Re, of which Mg, Ti, V, Zr, Nb, and La can increase the number of hydrogen atoms stored per metal atom. Other elements adjust the metal-hydrogen bond strength (V, Mn, and Zr), or provide catalytic properties to ensure sufficient charge and discharge reaction rates and gas recombination (Al, Mn, Co, Fe, and Ni), or impart desirable surface properties such as oxidation and corrosion resistance, improved porosity, and electronic and ionic conductivities (Cr, Mo, and W). The wide range of physical and chemical properties that can be produced in these alloys allows performance optimization of the Ni/MH battery.

Mn, Ni, Cu, Cr, Al, Co and Sn

Previous studies have shown that modifications to the LaNi5 alloy affect the cycle lifetime and hydrogen absorption capacity of AB5 metal hydride electrodes, but the reasons for these effects are not well understood [112-115]. The effects of various ternary substitutions for Ni in LaNi5 have been studied, and the results show that cycle lifetime improves with the amount of ternary alloy substitution in the order Mn < Ni < Cu < Cr < Al < Co [112], i.e. Co has the optimum effect. The positive effect of Co substitution has been attributed both to a reduction in the volume changes upon hydrogen absorption and desorption, and to a surface passivation mechanism (i.e. oxide formation) [113]. Ratnakumar et al. [112,114,115] detailed the advantages associated with using Sn as a ternary substituent, as compared to either In, Ge, Si, and Al. The addition of small amounts of Sn improves cycle lifetime and the kinetics of hydrogen absorption and
desorption, with only a slight reduction in specific capacity. In other studies, Sakai et al. [51] showed that substituting either Ce or Nd for La also enhances the cycle lifetime. In all the above ternary alloys, the improvement in the cycle lifetime is accompanied, unfortunately, by a decrease in the hydrogen absorption capacity, longer activation, or slower kinetics [116].

Fe and Co

Long cycle lifetime may be obtained by Co substitution for part of the Ni in LaNi$_5$-type alloys. However, Co can also decrease the capacity at high discharge current density. The effect of the Co content on the exchange current density and high-rate dischargeability has been examined for the alloy MmNi$_{4.0-x}$Mn$_{0.75}$Al$_{0.25}$Co$_x$ (0≤x≤0.6) [117]. Both the exchange current density and the high-rate dischargeability decrease with an increase in Co content because of the decrease in effective surface area, based on the reduced level of disintegration which results from the decreased volume expansion, and also because of the decrease in catalytic activity of the 'Ni-poor' surface (see Fig. 2.4). However, the stability of the hydride increases with increasing Co content of the alloys [117]. An alloy containing Fe also shows a similar feature, i.e., a long cycle lifetime [118]. In addition, Fe addition promotes activation and low polarization during discharge. The attractive features of both Fe and Co were obtained in the MmNi$_{5-w}$Al$_x$Co$_y$Fe$_z$ alloy [118].

2.3.2 Effect of surface modification on the electrochemical behaviour of MH electrode
CHAPTER 2  LITERATURE REVIEW

Surface modification of the metal hydride electrodes can be very effective for improving their electrochemical performance, such as specific discharge capacity, high-rate discharge capacity, cycle lifetime and activation, etc. Surface modification methods include micro-encapsulation, solution pretreatment, and ultrasound treatment. These are discussed in more detail in the following sections.

2.3.2.1 Micro-encapsulation of alloy powders

One of the most significant improvements in electrochemical performance was realized by microencapsulation of the hydrogen storage alloy powder in various kinds of electroless coatings, e.g. Cu, Ni-P and Ni-B [58,119-121]. Microencapsulation provides complete coverage of the intermetallic alloy to prevent corrosion or oxidation. Metals such as Cu and Ni are softer and less brittle than intermetallics, and thus provide both the necessary contact between alloy powders, and good electrical and thermal conduction [119]. Microencapsulation has been shown to be effective in improving the cycle lifetime and in generating a high dischargeability [58,120-122].

A simple method of electroless copper plating for the preparation of metal hydride electrodes has been reported by Park and Kirchheim [123]. Copper is plated on (RE)Ni$_5$ (RE: rare earth) or Mg$_2$Ni when the alloy is immersed in an acidic bath containing only CuSO$_4$ and H$_2$SO$_4$. The coating is easy to apply and the process is rapid and takes less than 5 minutes without any pretreatment being required for air-exposed alloys. Chemical analysis showed that the coating mechanism involved ion exchange between Cu$^{2+}$ ions and the alloy constituents. This method can be applied to only rare earth (RE)-nickel-
based alloys, but not to other alloys such as TiFe and the Laves phase alloys because of their inability to reduce copper ions and dissolve in the plating solution [123].

2.3.2.2 Solution treatment

It has been found that an alkaline or acid solution treatment of the metal hydride electrode can greatly improve the electrochemical properties.

2.3.2.2.1 Alkaline solution treatment

In this type of treatment, the metal hydride alloy is immersed in an alkaline solution for a set period of time. Suitable alkaline solutions include aqueous solutions of KOH and sodium borohydride (NaBH₄) [124], or a solution of KOH containing fluoride [125]. Treatment of a MnNi₃-based alloy with KOH and NaBH₄ improves the charge/discharge characteristics. The sodium borohydride solution formed a thin nickel metal layer exhibiting electrocatalytic activity. It also formed a thin layer of oxide which retarded the growth of La(OH)₃ needle crystals that degrade the activity of the alloy [124].

ZrNi₂-based alloys have poor activation behaviour. A Zr(V₀.₂₅Ni₀.₇₅)₂ alloy electrode treated with a KOH solution containing HF showed a much larger initial capacity than the untreated one, and the activation (charge-discharge process) time was greatly reduced [125].

2.3.2.2.2 Acid solution treatment

The poor electrocatalytic activity and activation performance of ZrNi₂-based alloys can also be improved by pretreatment with an HF acid solution or an HF+H₂O₂ solution
[126,127]. The electrochemical performance of HF-treated Zr(V_{0.4}Ni_{0.6})_2 and Zr(V_{0.2}Mn_{0.2}Ni_{0.6})_2 alloy electrodes is dramatically improved. This treatment procedure results in changes in the surface state of the alloy powder, such as a change from a Zr-rich to a Ni-rich surface layer. These changes lead to accelerated activation and improved surface electrocatalytic activity and hydrogen adsorption for the alloy electrode [126].

2.3.2.3 Ultrasound treatment

It has been found that surface modification using an ultrasound pretreatment can improve the electrochemical performance of metal hydride electrodes. Dou et. al. [128] reported that the surface modification of a Mg_{1.9}Y_{0.1}Ni_{0.9}Al_{0.1} alloy electrode with an ultrasound pretreatment significantly improved the electrocatalytic activity of the electrode. This reduced the over-potential for charging/discharging, thus resulting in a significant increase in electrode capacity and high-rate discharge capacity, but had little influence on the cycle lifetime.
Figure 2.2  The \( \text{AB}_3 \) structure in both the hexagonal or trigonal (right) and the orthorhombic (left) lattices. Also shown are tetrahedral \((\bullet)\) and octahedral \((\square)\) sites and their possible degeneracies for hydrogen favourable occupancy \((\Delta)\) [96].
Figure 2.3  The cubic (C15) and hexagonal (C14) Laves phase structures are shown. A atoms are represented by open circles, while B atoms are represented by solid ones. The possible interstitial sites for hydrogen occupancy are also shown: a) B4 site, b) AB3 site and c) A2B2 site [98].
Figure 2.4 Relationship between high-rate dischargeability and exchange current density for MmNi_{4.0-x}Mn_{0.75}Al_{0.25}Co_{x} (0 ≤ x ≤ 0.6) [114].
2.4 NI/MH BATTERIES

2.4.1 Reaction characteristics of the Ni/MH battery

In a Ni/MH battery, the positive electrode is the same as the Ni electrode (sintered or porous) in a Ni/Cd battery, and the negative electrode is the metal hydride. The electrochemical reaction process for the positive and negative electrodes of the Ni/MH battery is shown schematically in Fig. 2.5.

Therefore, the overall battery reaction is:

\[
M + x\text{Ni(OH)}_2 \xrightarrow{\text{charge}} \text{MH}_x + x\text{NiOOH} \quad (2.4.1)
\]

where \(M\) and \(\text{MH}_x\) stand for the hydride forming compound and metal hydride, respectively. The subscript \(x\) indicates the hydrogen content (H/M) in the hydrogen storage alloy. From Eq. (2.4.1) it can be seen that in the Ni/MH battery, the \(\text{H}_2\text{O}\) content remains the same during the charge/discharge process. The electrochemical reaction in the Ni/MH battery is different from the reaction in the Ni/Cd battery where water is produced in the discharge process and is consumed in the charge process. The electrochemical reaction in the Ni/Cd battery is described as follows:

\[
2\text{NiOOH} + \text{Cd} + 2\text{H}_2\text{O} \xrightarrow{\text{charge}} 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2 \quad (2.4.2)
\]
Thus in the manufacturing process of a sealed Ni/MH battery, it is important that the water content in the battery remains at a constant level over the long charge/discharge cycle lifetimes.

For both electrodes in Ni/MH batteries, the charge/discharge mechanism does not involve the intermediate formation of a dissolved metal ion species. Instead, charging and discharging occur via a solid state transition mechanism, which results in a high structural stability of both electrodes. During operation of the battery, there is neither a net generation, nor consumption, of the electrolyte species, such as \( \text{OH}^- \) and \( \text{H}_2\text{O} \). This permits a simple and compact construction. As illustrated in Fig. 2.5, charging and discharging of a Ni/MH battery can be viewed as a mere shuttle bus of protons from one electrode to the other. This implies that such a cell is capable of being charged and discharged at high rates, and with a high degree of utilization of the active material. The power density is therefore expected to be considerably larger than that of a Ni/Cd battery [29]. In a Ni/MH battery, the storage capacity of the MH electrode exceeds that of the Ni electrode [29]. Oxygen, evolved at the Ni electrode during over-charging, will be reduced to form water at the MH electrode. The hydrogen gas evolved at the Ni electrode during over-discharging, has no negative effect on the battery performance since it will be absorbed by, and oxidized at, the MH electrode. As a consequence, a hazardous high gas pressure is not built up during over-charging or over-discharging. Therefore both over-charging and over-discharging are permitted for Ni/MH batteries. Furthermore, Ni/MH batteries do not contain the poisonous heavy metals cadmium and mercury. This is particularly important for the widespread use of small batteries.
The potential of the negative electrode vs. Hg/HgO is about -0.93 V and the potential of positive electrode vs. Hg/HgO is about +0.39 V. Thus the electromotive force (EMF), $E_0$, of the Ni/MH battery is $E_0=0.39-(-0.93)=1.32$ V. This value is almost the same as the nominal voltage of 1.2 volt of the Ni/Cd battery. As a result, the Ni/MH battery has the advantage of being able to replace a Ni/Cd battery virtually without a change of the existing power systems for many electronic devices.

### 2.4.2 Design and testing of metal hydride batteries

The design of a sealed Ni/MH battery is different from that of a test cell. In a test cell, in order to determine the characteristics of the MH electrode (negative electrode), the electrochemical capacity of the positive electrode is designed to be higher than that of the negative electrode. However, in a sealed Ni/MH battery, in order to allow overcharging of the battery, the storage capacity of the MH electrode must exceed that of the positive electrode. Willems [29] analysis of the design of the battery is summarized as follows: during overcharging, oxygen evolution starts at the positive electrode at the end of charging, while the negative electrode is still storing hydrogen. As the oxygen which is formed subsequently, reacts at the hydride electrode, the state of charge of both electrodes remains constant. However, the excess storage capacity of the MH electrodes will decrease during cycling owing to the corrosion of the MH alloy. Failure of the sealed battery is expected when the storage capacities of both electrodes become equal. If cycling is still continued, the pressure in the battery gradually increases and ultimately exceeds the level at which the safety valve opens (about 20 atm). Thus, the durability is primarily determined by the excess of the active mass (i.e. the hydrogen storage alloy).
and the corrosion rate of the MH electrode. A schematic diagram of a sealed cylindrical battery is shown in Fig. 2.6.

The capacity of a Ni/MH battery is usually tested at a low discharge rate. The high rate discharge capacity, which is the important parameter for the battery, also needs to be tested at high discharge rates. Usually the high rate capacity is smaller than the low rate capacity because of kinetic reasons.

2.4.3 Overcharging of Ni/MH batteries

Sakai [122] has provided a detailed description of the overcharging of a Ni/MH battery, which is now briefly summarized. During overcharging of the Ni/MH battery, the oxygen evolved at the Ni electrode (as per Eq. 2.1.4), is rapidly consumed at the MH electrode (as per Eq. 2.4.3 and Eq. 2.4.4 or the reverse reaction of Eq. 2.1.4).

Positive electrode reaction:

\[
\text{OH}^- \rightarrow \frac{1}{4} O_2 + \frac{1}{2} H_2O + e^- \quad (E_0 = +0.401 V) \quad (2.1.4)
\]

Negative electrode reactions:

\[
M + xH_2O + xe^- \rightarrow MH_x + xOH^- \quad (E_0 = -0.828 V) \quad (2.4.3)
\]

\[
\frac{x}{4} O_2 + MH_x \rightarrow M + \frac{x}{2} H_2O \quad (2.4.4)
\]
Hydrogen evolution is a side reaction at the MH electrode, as shown in Eq. 2.4.5, which leads to a lower charging efficiency. The consumption rate of hydrogen, as per Eq. 2.4.6, is not high enough such that a significant increase in cell pressure is brought about. Thus, it is very important for the sealed battery to prevent the side reaction for hydrogen evolution.

Negative electrode reaction:

$$\text{H}_2\text{O}+e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \quad (E_0 = -0.828 \, V)$$  \hspace{1cm} (2.4.5)

Positive electrode reaction:

$$\frac{1}{2}\text{H}_2 + \text{NiOOH} \rightarrow \text{Ni(OH)}_2$$  \hspace{1cm} (2.4.6)

It was found that the micro-encapsulation of the alloy with copper or nickel can reduce the pressure rise greatly, since the surface covered by the copper or nickel prevents the release of hydrogen gas, thus facilitating the diffusion of hydrogen into the electrode, and thus, improving the charging efficiency.

2.4.4 **Self-discharge of a Ni/MH battery**

Self-discharge of a Ni/MH battery leads to a capacity loss during storage in the open-circuit condition. The capacity loss is divided into two parts [121], namely the reversible and irreversible losses.
The reversible capacity loss has been attributed to the desorption of hydrogen from the MH anode, which occurs when the cell-inner pressure drops to a pressure lower than the hydrogen pressure of the anode. This drop is a result of the reaction of hydrogen with the nickel cathode with the consumption of hydrogen, as follows:

\[
\frac{1}{2} H_2 + \text{NiOOH} = \text{Ni(OH)}_2
\] (2.4.7)

Other researchers believe that the reversible capacity loss results from the self-decomposition of the positive electrode as shown in Eq. 2.4.8 [129].

\[
\frac{1}{2} H_2O + \text{NiOOH} \rightarrow \text{Ni(OH)}_2 + \frac{1}{4} O_2
\] (2.4.8)

The irreversible capacity loss has been attributed to the deterioration of the hydrogen-absorbing alloy by such means as the chemical or electrochemical oxidation of the active material of the MH electrode [121].

There are many factors that influence the self-discharge rate, such as the gaseous environment, the electrolyte composition, storage time, temperature and nitrogen impurities [129,130].

The micro-encapsulation of the alloy with copper can usually prevent the chemical reaction of hydrogen with the nickel cathode, or trap all the nitrogen impurities present in the battery. Thus, micro-encapsulation has been used to improve the self-discharge characteristics of the Ni/MH batteries [121,129,130].
2.4.5 Comparison with other battery types

Although conventional storage batteries such as Ni/Cd and lead-acid batteries have been improved in design and packaging in recent years, further improvement is required in performance and power density. The innate toxicity of cadmium and lead has also come under scrutiny. Although Ni/MH batteries have superior specific energy than the other two aqueous electrolyte systems (lead-acid and Ni/Cd batteries), they remain greatly inferior to the new rechargeable lithium (Li-ion) batteries [131]. However, lithium batteries are much more expensive to produce. It has estimated [132] that the approximate cost (per Wh) for Ni/Cd, Ni/MH and Li-ion batteries are in the ratio of 1:1.35:2~3, respectively. In addition, lithium batteries can not be operated for safety reasons without electronic control of each individual battery. The typical characteristics of rechargeable batteries, including cell voltage, specific energy and cycle lifetime are given in Table 2.2 [131].

The need for high energy density storage batteries has been growing in recent years. The advent of electric vehicles, portable computers, cellular telephones and new cordless appliances and tools has made this need even more urgent. With the advantages of no pollution to the environment, a high energy density, a long cycle lifetime, a high rate capacity, a lower temperature capability and an absence of memory effect (no loss of capacity following incomplete discharge) [29,133], Ni/MH batteries have been developed to replace the traditional batteries, such as Ni/Cd and lead-acid batteries.
Table 2.2 Cell voltage, specific energy and cycle lifetime of rechargeable batteries.

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Electrode</th>
<th>Cell voltage (V)</th>
<th>Specific energy (Wh/kg)</th>
<th>Cycle lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Positive</td>
<td>Negative</td>
<td>Theo.</td>
<td>Prac.</td>
</tr>
<tr>
<td>Lead-Acid</td>
<td>PbO₂</td>
<td>Pb</td>
<td>2.1</td>
<td>175</td>
</tr>
<tr>
<td>Nickel-Cadmium</td>
<td>NiOOH</td>
<td>Cd</td>
<td>1.2</td>
<td>210</td>
</tr>
<tr>
<td>Nickel-Metal Hydride</td>
<td>NiOOH</td>
<td>MH</td>
<td>1.2</td>
<td>220(AB₂)</td>
</tr>
<tr>
<td></td>
<td>(AB₂₅; AB₂)</td>
<td></td>
<td></td>
<td>230(AB₂)</td>
</tr>
<tr>
<td>Lithium Ion</td>
<td>CoO₂</td>
<td>NiO₂</td>
<td>4.0</td>
<td>455</td>
</tr>
<tr>
<td></td>
<td>Mn₂O₄</td>
<td>Li₅C₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium-Nickel Chloride (ZEBRA)</td>
<td>NiCl₂</td>
<td>Na</td>
<td>2.5</td>
<td>788</td>
</tr>
<tr>
<td>Sodium-Sulfur</td>
<td>S</td>
<td>Na</td>
<td>2.1</td>
<td>635~760</td>
</tr>
<tr>
<td>Zinc-Air</td>
<td>O₂</td>
<td>Zn</td>
<td>1.4</td>
<td>1085</td>
</tr>
</tbody>
</table>

2.4.6 A Ni/MH battery for electric vehicles (EVs)

Electric vehicles (EVs) include pure electric vehicles (PEV), hybrid electric vehicles (HEV) and fuel cell electric vehicles (FCEV). Pure electric vehicles (PEV) have employed Ni/MH batteries. These include models by Toyota, Honda, Mitsubishi, Mazda, Subaru, Suzuki, Nissan, and Daihatsu [47]. Maximum driving ranges, battery storage energy, and speeds vary between the developed models, with driving range per charge ranging from about 55 km to about 240 km. PEV cost more than twice the price of a regular gasoline car [47].

Another use of Ni/MH batteries is in hybrid electric vehicles (HEV). These vehicles use the battery for starting and low speeds, and a gasoline engine for higher speeds. They
are less expensive than PEVs, and have significantly lower emissions and higher gas mileage than standard gasoline vehicles. Toyota currently has a version on the market, and other companies have HEVs in development [47].

Fuel cells (FC) operate at an efficiency of about 60%, twice that of an internal combustion engine. A FCEV has been developed by Daimler-Benz that operates solely on a FC system, and Toyota has developed a hybrid FCEV with a FC system and a Ni/MH battery, as has Mazda. FC vehicles are expected to be the wave of the future, but are currently not available to the public [47].

If PEV, HEV, and FCEV become more popular, as a result of environmental concern or the desire for greater fuel efficiency, Ni/MH batteries could become the major power source for automobile transportation.
Figure 2.5  Schematic diagram of the electrochemical reaction process of a Ni/MH battery. For the charge process, the hydrogen atom dissociates from Ni(OH)$_2$ and is absorbed by the MH alloy. For the discharge process, the hydrogen atom dissociates from the MH alloy and joins with NiOOH to form Ni(OH)$_2$.
Figure 2.6  The schematic diagram of a sealed cylindrical battery.
CHAPTER 3

EXPERIMENTAL DETAILS

3.1 MATERIALS AND MATERIALS CHARACTERIZATION

3.1.1 MATERIALS

Four different hydrogen storage alloys were used for the electrochemical studies:

1. LaNi$_{4.7}$Al$_{0.3}$ alloy, known as Hy-Stor Alloy 207, obtained from Ergenics Division, MPD Technology Corporation, Wyckoff, NJ, U.S.A. The LaNi$_{4.7}$Al$_{0.3}$ alloy is used for these studies since it is representative of the commercial multicomponent AB$_5$-type alloys that are presently used as MH electrodes in rechargeable batteries.

2. Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy (where Mm denotes Mischmetal, comprising 43.1 wt.% La, 38.9 wt.% Ce, 13.3 wt.% Pr and 3.5 wt.% Nd), which was obtained from Central Iron and Steel Research Institute, Beijing, China, where it was prepared by induction melting and rapid cooling. The as-received cast alloy is annealed at 1173 K for 10 hours in vacuum.

3. Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy (where Mm denotes Mischmetal, comprising 54.6 wt.% La, 30.0 wt.% Ce, 4.0 wt.% Pr and 11.3 wt.% Nd) which was obtained from Rhodia Inc., AZ, U.S.A. The as-received cast alloy is annealed at 1173 K for 10 hours in vacuum.

4. A 9.0 Cu %-coated LaNi$_{4.7}$Al$_{0.3}$ alloy, prepared using alloy 1 with an electroless coating deposit. The LaNi$_{4.7}$Al$_{0.3}$ alloy was first mechanically pulverized to a particle size of around 40–60 μm before plating. The copper plating is done by immersing the alloy powder in an aqueous acid bath containing only CuSO$_4$ (0.16 g ml$^{-1}$) and H$_2$SO$_4$
(PH=4~5). The coating is easy to apply without the need for any pretreatment of air-exposed alloys.

3.1.2 Materials characterization

Scanning electron microscopy (SEM) using a JEOL JSM-5800 LV Microscope was used to measured the average particle size and determine the surface morphology of copper-coated alloy particles. Double sided tape was placed on a SEM stub and then the powder was sprinkled on the tape. The specimens were coated with gold to increase the conductivity. The samples were viewed and photographed in the SEM at magnifications ranging from 75× to 20,000×. The accelerating voltage used was 15 kV, while images were recorded on the floppy discs and on the 11×14 cm sheet photograph papers. Average particle sizes were measured directly from the recorded photographic papers.

3.2 ELECTRODE PREPARATION

3.2.1 Preparation of negative electrodes

The hydrogen storage alloy ingots were first mechanically pulverized and sieved to a mean particle size of around 45-53 μm using 325 mesh and 270 mesh sieves (W. S. Tyler, Inc. U.S.A.).

The negative electrode without Cu-coating was made by first mixing the alloy powder (about 0.1 g) with nickel powder in a ratio of 1:1. The mixing of the nickel powder with the metal hydride alloy powders increases the electrical conductivity and increases reaction kinetics.
The negative electrode with the Cu-coated powders was made by mixing the 70.00 mg of Cu-coated alloy powder (containing 63.70 mg of LaNi$_{4.7}$Al$_{0.3}$) with 63.70 mg of nickel powder, keeping the weight ratio of active material to nickel powder 1:1. A polytetrafluoroethylene (PTFE) dispersion (4 wt%) was added to the mixture as a binder. The powder mixture was filled into a porous nickel mold with the diameter of 10.0 mm and was then pressed into a sheet of 0.6 mm thickness at a pressure of 500 MPa for 2 min. This was used as the negative electrode in the experimental cells. The cylindrical press and several negative electrodes are shown in Fig. 3.1.

3.2.2 Preparation of positive electrodes

The positive electrodes in the cell are (before charging) sintered Ni(OH)$_2$/NiOOH plates with dimensions of 1.5 cm × 4 cm × 0.07 cm, which are obtained from the Central Iron and Steel Research Institute, Beijing, China. A positive electrode is shown in Fig. 3.2.

3.3 EXPERIMENTAL CELL SETUP

The electrochemical cell was equipped with three compartments. The negative electrode (working electrode) was placed in the central compartment and two positive electrode plates (Ni(OH)$_2$/NiOOH) were placed on either side. The emphasis of these charge/discharge tests of the cells was on the electrochemical stability of the negative electrode. Thus, the capacity of the positive electrode was designed to be sufficiently higher than that of the negative MH electrode to avoid cathode limitation. The MH electrode and counter electrodes were separated by a porous frit to prevent the chemical
reaction of gaseous hydrogen with the nickel cathode, and to trap any gaseous nitrogen impurities present in the cell. However, OH\(^-\) can freely pass through this separator. The experimental apparatus was set in a water bath at controlled (±0.5 K) temperatures to maintain a practically constant temperature during each kinetic run. The electrolyte was a 6M KOH aqueous solution. A Hg/HgO/6MKOH electrode was used as the reference electrode. A Luggin capillary tube, which was connected to the reference electrode and working electrode, was placed close to (about 0.5 mm) the working electrode in order to minimize the ohmic drop across the electrolyte solution. The experimental cell and the testing device setup for the electrochemical measurements are shown schematically in Fig. 3.3.

3.4 APPARATUS FOR ELECTROCHEMICAL MEASUREMENTS

The charge/discharge and potentiostatic tests of the experimental cells were conducted using a Solartron 1285 Potentiostat with CorrWare software for Windows. The testing resolution of the potential, current and time is 0.1mV, 0.1mA and 0.1s, respectively. A photograph of the experimental setup is shown in Fig. 3.4.

3.5 METHODS OF ELECTROCHEMICAL MEASUREMENTS

The electrochemical measurements in this study include constant-current charge/discharge polarization curves, and potential step. Through these electrochemical measurements, the characteristics of the metal hydride electrodes can be calculated. The Solartron 1285 Potentiostat, was set-up to give anodic polarization currents and over-potentials as positive values.
3.5.1 Constant current charge/discharge measurements

In this study, the constant current charge/discharge measurements were carried out as follows: the experimental cells were charged at a current of 120 mA g\(^{-1}\) for 3 hrs, and then discharged at a current of 120 mA g\(^{-1}\) to an end-of-discharge-potential of -0.6 V. The curves of negative electrode potential versus time were recorded, and used to calculate the specific discharge capacity and hydrogen concentration for specific cycle lifetimes.

3.5.2 Polarization curve measurements

Polarization curve measurements were carried out after the activation treatments of the metal hydride electrodes, which involved about ten charge/discharge cycles at constant currents. The measurements of the polarization curves were performed under potentiodynamic conditions at a scan rate of 1 mV s\(^{-1}\). The polarization curve was determined at the state of full charge/discharge and also at different depths of discharge (DOD). The polarization curve was measured after the open-circuit potential (i.e. equilibrium potential) was stabilized (i.e. the variation in the potential was less than 1 mV for 1 hour). The measurements were carried out at temperatures of 273, 298, 308 and 318 K, and at different depths of discharge. The scan range was set as -20 mV to +20 mV versus equilibrium potential. The exchange current density, symmetry factor, apparent activation energy and electrode resistance (ohmic resistance and polarization resistance) were then obtained from the polarization curves.

3.5.3 Potential step measurements
A newly developed potential step technique (or transient voltammetry) for working electrode was used to measure the hydrogen diffusion coefficients of electrode alloy powders. It is a most effective voltammetry method for studying the electrode behaviour for a transient process.

The electrochemical discharge process was carried out at the room temperature, and at different constant potentials. The measurement process was as follows: after the open-circuit potential was stabilized, the positive potential was set to be from +0.2 to +0.6 V with reference to the open-circuit potential. At each potential level, the thermodynamic force (i.e. $E_{\text{applied}}-E_{\text{eq}}$) for the metal hydride electrode reaction remains constant. Thus, the current will have a sudden increase to a peak value, and then begin to decrease gradually with time, and finally reach a stable value. The decrease in discharge current was monitored as a function of time at each potential level, in order to control the discharge and to determine the exact amount of hydrogen removed. Before each potential step, a small current density (5 mA g$^{-1}$) was applied to partially remove the adsorbed hydrogen on the particle surface.

The key requirement for obtaining accurate values of the diffusion coefficient, is the application of a sufficiently high potential step (e.g. larger than +0.2 V vs. Hg/HgO at room temperature) so that the amount of charge injected into the electrode during the step is always much higher than the parasitic charge related to the residual current (the current for removing the surface oxide and the adsorbed hydrogen). Since hydrogen diffusion does not become the rate-determining process immediately after the application of a positive potential step, there is a time lapse, which depends on the applied potential and discharge state, before the hydrogen diffusion coefficient can be determined (for the
saturated state, this is approximately 40-70 s). Thus, in determining the dependence of the hydrogen diffusion coefficient on hydrogen concentration, the potential step was always kept larger than +0.6 V vs. Hg/HgO, so as to make more steps available. After discharging for 25 s at each potential step, the discharge process was terminated until the open-circuit (i.e. equilibrium potential) became stabilized (i.e. the change of the potential was less than 0.1 mV for 1 min). This procedure was used to ensure that each subsequent potential step was also applied after equilibrium had been reached for the preceding step.

3.6 MEASUREMENT OF ELECTROCHEMICAL PARAMETERS FOR MH ELECTRODES

The characteristics of a metal hydride electrode, such as specific discharge capacity, hydrogen concentration, equilibrium potential, exchange current density, symmetry factor, apparent activation energy and diffusion coefficient, can be obtained from the measured electrochemical parameters.

3.6.1 Specific discharge capacity

Using the constant current charge/discharge method, the specific discharge capacity for any cycle, $C_{th}$ (mAh g$^{-1}$) can be calculated from the product of the current density and the discharge time given by

$$C_{th} = \frac{j \cdot t}{W} \quad (3.6.1)$$
where \( t \) is the discharge time (hr) and \( W \) is the weight (g) of metal hydride alloy. Where it is not specifically mentioned, the values of specific discharge capacity were measured at a discharge current density of 120 mA g\(^{-1}\) at 298 K, after the electrodes were fully charged at a current density of 120 mA g\(^{-1}\) for 3 hours.

3.6.2 Hydrogen concentration

Hydrogen concentration in the metal hydride electrode can be calculated at various discharge states according to Faraday's law. There are two kinds of discharge: at constant current density and at constant potential.

For the constant current discharge, the discharged capacity is equal to the product of current density and discharge time. The electrochemical absorption and release of hydrogen by the intermetallic compound can be represented by the redox equation:

\[
M + xH_2O + xe^- = MH_x + xOH^- \quad (3.6.2)
\]

This equation shows that each absorbed hydrogen atom corresponds to the storage of one electron. This results in a simple relation that allows calculation of the theoretical (mol ratio) hydrogen concentration \( c_H (H/M) \) in the hydride electrode using Faraday’s law [29]:

\[
c_H = \frac{3.6MQ}{FN} \quad (3.6.3)
\]
where \( Q \) is the remaining specific capacity of the hydride alloy (mAh g\(^{-1}\)); \( M \) is molecular weight of the alloy; and \( N \) is the number of metallic atoms per alloy unit (for AB\(_5\)-type alloy, \( N=6 \)).

For the constant potential discharge (i.e. potentiostatic measurements), the discharged capacity is equal to the integrated value of the \( j(t) \) vs. \( t \) (time) plot. Thus the remaining specific capacity (\( Q(C \ g^{-1}) \)) of the metal hydride alloy after the \( i^{th} \) step discharge can be estimated as follows:

\[
Q = \int_{t_1}^{t} j(t)dt + \int_{t_2}^{t} j(t)dt + \cdots + \int_{t_i}^{t} j(t)dt + \cdots + \int_{t_n}^{t} j(t)dt - \int_{t_1}^{t} j(t)dt \tag{3.6.4}
\]

where \( t_1, t_2, \ldots, t_i, \ldots, t_n \) are the discharge times for every discharge step.

The hydrogen concentration in a metal hydride electrode is then calculated as follows:

\[
c_H = \frac{MQ}{FN} \tag{3.6.5}
\]

### 3.6.3 Equilibrium potential

The equilibrium potential of a metal hydride electrode can be considered as the open-circuit potential. It is measured as follows: after the open-circuit potential of a metal hydride electrode (fully charged first and then discharged) is stabilized (holding until potential change is less than 0.1 mV/min), the open-circuit potential measured is the equilibrium potential of the electrode with respect to its charge/discharge state.
In order to obtain an $E$-$C$-$T$ curve (equilibrium potential vs. hydrogen concentration at a temperature of $T$), the equilibrium is measured at different depths of discharge. Following an activation treatment ($\sim$10 charge/discharge cycles), the MH electrode is charged at a constant current (60 mA g$^{-1}$) until the hydrogen concentration is saturated. All data points for the $E$-$C$-$T$ curves are obtained for constant discharging current (30 mA g$^{-1}$) for 1 hour. Each equilibrium potential was measured after every 30 mAh g$^{-1}$ of discharge to the stabilized open-circuit potential (OCP), i.e. the change of the potential was less than 1 mV for 1 h. The above procedure was repeated until the electrode was discharged to the potential of -0.6 V vs. the Hg/HgO reference electrode to give the $E$-$C$-$T$ curves.

3.6.4 Exchange current density

The polarization curves were used to obtain the exchange current density, the symmetry factor and the over-potential of a metal hydride electrode. From the polarization curve, the exchange current density can be obtained by using Eq. 2.2.3. The over-potential is the difference between the equilibrium potential and the polarization potential. Since the polarization curves are all with reference to the open-circuit potential (equilibrium potential), the over-potential is obtained directly from the polarization curves.

3.6.5 Apparent activation energy
The apparent activation energy for dehydriding is calculated from the plot of exchange current density at constant hydrogen concentration vs. $I/T$ using the following equation [134]:

$$E_a = -R \left[ \frac{\partial \ln I_0}{\partial \left( \frac{1}{T} \right)} \right]$$  \hspace{1cm} (3.6.6)

where $E_a$ is the apparent activation energy (J molH$^{-1}$). The unit of $E_a$ used is J molH$^{-1}$ because the product of the MH-KOH electrochemical reaction is one H atom. A plot of $\ln I_0$ vs. $1/T$ should produce a straight line assuming a constant activation energy, and from the slope of this line the apparent activation energy is calculated.

The dependence of apparent activation energy on hydrogen concentration was measured.

3.6.6 Symmetry factor

The polarization curves were also used to obtain the symmetry factor of the electrode reaction at specific hydrogen concentrations and temperatures. The symmetry factor ($\zeta$) can be calculated using another form of the Butler-Volmer equation [135]:

$$\eta = \frac{RT}{\zeta F} \ln I_0 - \frac{RT}{\zeta F} \ln \left[ \frac{j}{\exp(F\eta/RT)} - 1 \right]$$  \hspace{1cm} (3.6.7)
A plot of \( \eta \) vs. \( \ln[\exp(\eta/RT)-1] \) should give a straight line assuming a constant symmetry factor, with a slope of \( RT/\xi F \). The symmetry factor is dependent on the hydrogen concentration and temperature.

### 3.6.7 Diffusion coefficient

The potential step method developed in this work (described in detail in section 3.5.3) was used to determine the diffusion coefficient of hydrogen in a metal hydride electrode. In this procedure, a potential step from +0.2 to +0.6 V (with reference to the open-circuit potential) is applied to the metal hydride electrode for specific DOD level. The applied current as a function of time is recorded, and from a plot of the applied (diffusion) current density \( j(t) \) vs. \( t^{1/2} \), which gives a straight line for constant \( D \), the absolute values of intercept and slope for this line give \( I \) (A g\(^{-1}\)) and \( S \) (A g\(^{-1}\) s\(^{1/2}\)), respectively. The diffusion coefficient of hydrogen is given by

\[
D = \left( \frac{I}{S} \right)^2 \cdot \frac{a^2}{\pi} \quad (3.6.8)
\]

where \( D \) is an average (or integral) diffusion coefficient of hydrogen (m\(^2\) s\(^{-1}\)); and \( a \) is the radius of the particle sphere (m).

The calculation of hydrogen diffusion coefficients does not need any prior knowledge of either the hydrogen concentration or the surface area.

### 3.7 Measurement of Equilibrium Pressure: Gaseous Hydrogen Test (P-C-T Determination)
Hydriding-dehydriding experiments for $P$-$C$ isotherms are conducted in a conventional Sieverts-type apparatus [136,137]. The first sample in section 3.1.1 (LaNi$_{4.7}$Al$_{0.3}$ alloy) was used in this investigation. In the procedure the alloy is first mechanically pulverized to a particle size of about 50 $\mu$m. About 3 grams of the sample, which is weighed to $\pm$1 mg, is placed in the reactor. A shielded K-type thermocouple is sealed into the reactor and its tip is located in the centre of sample powder, thus eliminating errors arising from the temperature difference between the thermocouple and the sample if the thermocouple is not inserted in sample powder. This also enables the thermocouple to monitor the sudden change of the sample temperature upon hydrogen absorption or desorption with a fast time response. The reactor is immersed in a thermostatted water bath which allowed the temperature to be controlled within $\pm$ 0.1 K. The system is evacuated to a residual pressure of $1.33 \times 10^{-3}$ Pa (i.e. $10^{-5}$ torr) and then bled with ultra-high purity argon gas. This procedure is repeated several times until the final evacuation.

High purity hydrogen gas is admitted from the inlet pressure vessel into the reactor at pressures above the equilibrium pressure. The $P$-$C$ isotherms are obtained after an activation treatment, which involved four hydriding-dehydriding cycles. The equilibrium hydrogen pressures are measured using pressure transducers and recorded using a chart recorder at 300, 313 and 333 K. The pressure transducer has a pressure measurement range of 0-4,000 kPa with an accuracy of $\pm$0.5% full scale. Absorption isotherm measurements are started with a completely desorbed sample. An aliquot (dose) of hydrogen ($\Delta$(H/M)=0.1, i.e., $2.13 \times 10^{-3}$ mol gas hydrogen) is introduced into the reactor. The pressure change is measured by pressure transducer and recorded in the chart
recorder. Two hours is allowed for equilibrium pressure to be obtained. Additional aliquots are then added and the same procedure repeated. Desorption isotherms are obtained by essentially reversing the absorption isotherm procedure. During desorption P-C isotherm measurements, the fully hydrided sample is gradually dehydrided by releasing aliquots hydrogen gas from the reactor and the data points obtained, which corresponded to equilibrium periods of 2 hours. The procedures for P-C isotherm determination for hydriding-dehydriding are also described in detail in refs [136,137].
Figure 3.1  Cylindrical presses and negative electrodes (LaNi$_{4.7}$Al$_{0.3}$).
Figure 3.2  A Ni(OH)$_2$/NiOOH positive electrode.
Figure 3.3  Schematic diagram of the experimental setup for the electrochemical measurements.
Figure 3.4  The electrochemical measurement system (Soltron 1285) used in the present study
CHAPTER 4

RESULTS AND DISCUSSION

4.1 HYDROGEN ABSORPTION IN A GASEOUS HYDROGEN ENVIRONMENT

The hydrogen absorption process for the metal hydride/H₂ (gas) system has some features that apply for hydrogen absorption in the metal hydride/aqueous KOH system, and a study of the former is useful in developing a model for the hydrogen reaction mechanism in alloy powders. The relationships connecting the thermodynamic properties of the electrode materials to the electrochemical reaction kinetics are obtained principally from analysis of the alloys' P-C-T plateaus.

4.1.1 Theoretical model

The P-C isotherms are plots of the incremental changes in the alloy's hydrogen concentration (H/M) resulting from the corresponding incremental changes in the hydrogen pressure exerted on the experimental system. Local (microscopic) equilibrium is assumed to exist at any point in the alloy during hydrogen transport (diffusion), i.e. the process is a dynamic equilibrium hydriding-dehydriding reaction, and thus can be regarded as being steady-state at all times. This assumption of local equilibrium (at a microscopic level) in a macroscopic system under a concentration gradient can be shown to be a valid one [138], which permits the reaction kinetics to be determined at any desired point (hydrogen concentration) in the alloy.
The plateau region of \( P-C \) isotherms is controlled by the reversible \( \alpha = \beta \) phase transition (\( \alpha \) and \( \beta \) are the solid solutions of \( H \) in hydrogen storage alloys and hydrides respectively). The transition from the \( \beta \)-phase to the \( \alpha \)-phase proceeds in three steps [83]:

(i) Diffusion of hydrogen atoms through the \( \beta \)-phase hydride. When an equilibrium state is established, hydrogen is homogeneously distributed in the \( \beta \)-phase hydride. The site occupation quota of absorbed hydrogen is denoted by \( x_H \).

(ii) Transition of hydrogen from the absorbed sites to adsorbed sites on the particle surface, represented by the reaction

\[
\text{MH}_{y_0, \text{abs}} \xrightarrow{k_1} \text{MH}_{y_0, \text{ads}} \xleftarrow{k_{-1}} \text{MH}_{y_0, \text{abs}} \quad (4.1.1)
\]

(iii) Desorption reaction of hydrogen at the \( \beta \)-phase particle surface, represented by the reaction

\[
\text{MH}_{y_0, \text{ads}} \xrightarrow{k_2} \text{MH}_{x_0} + \frac{y_0 - x_0}{2} \text{H}_2 \xleftarrow{k_{-2}} \text{MH}_{y_0, \text{ads}} \quad (4.1.2)
\]

where \( k_1 \) and \( k_2 \) are the forward specific rate constants for reactions (4.1.1) and (4.1.2); \( k_{-1} \) and \( k_{-2} \) are the reverse specific rate constants for reactions (4.1.1) and (4.1.2); \( x_0 \) is the maximum solubility of hydrogen in \( \alpha \)-phase; and \( y_0 \) is the minimum solubility of hydrogen in \( \beta \)-phase, to give \((y_0 - x_0)\) as the length of the plateau region for the \( P-C-T \) curve. The values of \( x_0 \) and \( y_0 \) vary markedly with temperature (see Fig. 4.1).

In order to develop analytical expressions for the \( P-C \) isotherms in the two-phase region, the following assumptions are made: both transition of hydrogen (Eq. 4.1.1) and desorption (Eq. 4.1.2) reactions may be the rate-controlling steps, and first-order kinetics
applies to the rate equations. As the data points on the \( P-C \) isotherms represent a dynamic equilibrium state, and they involve three consecutive steps, the equilibrium conditions for reactions (4.1.1) and (4.1.2) require that the overall reaction rates be zero, i.e. the forward overall rates and reverse overall rates for each reaction be equal.

Thus for first order reaction kinetics, the dynamic equilibrium condition for the reactions give

\[
k_1 x_H (1 - \theta) = k_{-1} \theta (1 - x_H) \tag{4.1.3}
\]

\[
k_2 \theta = k_{-2} (1 - \theta) P_e^{(y_0 - x_0)/2} \tag{4.1.4}
\]

Where \( \theta \) is the fraction of \( \beta \) particle surface covered with hydrogen, and \( P_e \) is the equilibrium hydrogen pressure. \( x_H = c_H / c_m \), where \( c_m \) is the maximum hydrogen concentration stored in metal. It is assumed that all the rate constants in Eqs. 4.1.1 and 4.1.2 (designated as \( k_j \)) follow an Arrhenius-type dependence, i.e.

\[
k_j = k_j^0 \exp \left( - \frac{\varepsilon_j}{RT} \right) \tag{4.1.5}
\]

where \( k_j^0 \) is a frequency factor (\( j = 1, -1, 2 \) and \( -2 \)), and \( \varepsilon_j \) is the activation energy barrier (for process \( j \)).

It has been suggested that an "effective" H-H interaction consisting of both electronic (at the surface) and elastic (in the bulk) components must be considered in modeling \( P-C \)
isothers [30,139,140] (Fig. 4.2). This feature could be accounted for by introducing an excess term in the chemical potentials of both \( H_{\text{abs}} \) (absorbed hydrogen in the bulk) and \( H_{\text{ads}} \) (adsorbed hydrogen on the surface). The interaction may also be included by replacing the Langmuir isotherm by a Temkin isotherm: the constant activation energies in the rate constants \( k_1, k_{-1} \) and \( k_2 \) are replaced by activation energies containing an interaction term which depends linearly on concentration [141]. Thus, the H-H interaction in the bulk will affect \( k_1 \), whereas the interaction at the surface should influence \( k_{-1} \) and \( k_2 \); thus, \( k_1, k_{-1} \) and \( k_2 \) should be replaced by

\[
k_1' = k_1 \exp\left(\frac{\gamma H}{RT}\right)
\]

\[
k_{-1}' = k_{-1} \exp\left(\frac{\gamma_s \theta}{RT}\right)
\]

\[
k_2' = k_2 \exp\left(\frac{\gamma_s \theta}{RT}\right)
\]

where \( \gamma \) and \( \gamma_s \) are the interaction coefficients for \( H_{\text{abs}}-H_{\text{abs}} \) and \( H_{\text{ads}}-H_{\text{ads}} \) respectively.

With \( k_1', k_{-1}' \) and \( k_2' \) replacing \( k_1, k_{-1} \) and \( k_2 \) respectively, and equating the \( \theta \) terms in Eqs. 4.1.3 and 4.1.4 gives

\[
RT \ln P_e = \frac{2}{y_0 - x_0} \left[ RT \ln \left( \frac{k_1 k_2}{k_{-1} k_2} \right) + RT \ln \left( \frac{x_H}{1-x_H} \right) + \gamma_H \right]
\]
or, if written in terms of $c_H$

$$RT \ln P_e = \frac{2}{y_0 - x_0} \left[ RT \ln \left( \frac{k_1 k_2}{k_{-1} k_{-2}} \right) + RT \ln \left( \frac{c_H}{c_m - c_H} \right) + \frac{\gamma c_H}{c_m} \right]$$

(4.1.10)

The $\gamma$ term has disappeared in Eq. 4.1.10 due to its roles in adsorption and desorption counterbalancing. However, the H-H interaction term may become important at large $x_H$ values, in the concentration range corresponding to the two phase ($\alpha$ and $\beta$) region.

Using Eq. 4.1.5, Eq. 4.1.10 becomes:

$$RT \ln P_e = \frac{2}{y_0 - x_0} \left[ (\varepsilon_{-1} + \varepsilon_{-2} - \varepsilon_1 - \varepsilon_2) + RT \ln \left( \frac{k_1^0 k_2^0}{k_{-1}^0 k_{-2}^0} \right) + RT \ln \left( \frac{c_H}{c_m - c_H} \right) + \frac{\gamma c_H}{c_m} \right]$$

(4.1.11)

or

$$RT \ln P_e = \frac{2}{y_0 - x_0} \left[ A + RT \ln \left( \frac{c_H}{c_m - c_H} \right) + A_0 \cdot c_H \right]$$

(4.1.12)

where

$$A = A_1 + A_2 T \quad \text{and} \quad A_0 = \frac{\gamma}{c_m}$$

(4.1.13)

and

$$A_1 = \varepsilon_{-1} + \varepsilon_{-2} - \varepsilon_1 - \varepsilon_2 \quad \text{and} \quad A_2 = RT \ln \frac{k_1^0 k_2^0}{k_{-1}^0 k_{-2}^0}$$

(4.1.14)
The first term ($A_1$) in Eq. 4.1.12 is assumed to be constant at a given temperature, and the second term ($RT\ln(c_{H_2}/(c_{m-H_2}))$) is the configurational entropy, as originally suggested by Griessen [139]. The third term ($A_0 c_H$) is ascribed to the excess chemical potential of the protons in the non-ideal M-H$_2$ system, which Lacher [142] and Brodowsky [143-145] attribute to an H-H attractive interaction. The increase in hydrogen concentration in the hydride with hydrogen pressure, above that given by Sievert's law, and the associated increase in hydride specific volume, is the result of the attractive energy term for H-H interaction in the hydride.

4.1.2 Fitting the model to experimental data

To test the validity of Eq. 4.1.12 requires determination of $x_0$ and $y_0$, i.e. the maximum and minimum hydrogen solubilities in the $\alpha$ and $\beta$ phases respectively. It is assumed Sievert's law applies, and the solubility is proportional to the square root of the hydrogen gas pressure. To determine $x_0$ and $y_0$, the straight line segments in $\alpha$ and $\beta$ regions of the $P$-$C$-$T$ curve are extended, and the tangent points to the curve are taken to represent the maximum and minimum solubilities (see Fig. 4.1).

Eq. 4.1.12 is used to calculate the $P$-$C$ isotherms for absorption and desorption for a LaNi$_{4.7}$Al$_{0.3}$ alloy represented by the solid curves in Fig. 4.3. The experimental determinations are shown by the open and closed circles for absorption and desorption respectively. The values of the fitted parameters (from Eq. 4.1.12) and the hysteresis factors are summarized in Table 4.1. Hysteresis factor is defined as follows:
\[ \text{Hysteresis Factor} = RT \ln \frac{P_{e,a}}{P_{e,d}} \] (4.1.15)

where \( P_{e,a} \) and \( P_{e,d} \) are absorption and desorption equilibrium pressures at some value of H/M in the plateau region.

It is evident that parameter \( A_0 \) is the same for the absorption and desorption reactions but varies with temperature, whereas parameter \( A \) displays a dependence on both temperature and absorption/desorption reaction.

Table 4.1 Fitted parameters to Eq. 4.1.12 for the two-phase region from absorption and desorption data for \( P-C \) isotherms of a LaNi\textsubscript{4.7}Al\textsubscript{0.3} alloy.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Abs./Des.</th>
<th>( c_m )</th>
<th>( y_0-x_0 )</th>
<th>( A ) kJ molH\textsubscript{2}\textsuperscript{-1}</th>
<th>( A_0 ) kJ molH\textsubscript{2}\textsuperscript{-1}</th>
<th>( RT\ln(P_{e,a}/P_{e,d}) ) kJ molH\textsubscript{2}\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>333 Abs.</td>
<td>1.00</td>
<td>0.892</td>
<td>-17.4</td>
<td>-24.94</td>
<td></td>
<td>0.332</td>
</tr>
<tr>
<td>333 Des.</td>
<td>1.00</td>
<td>0.892</td>
<td>-18.0</td>
<td>-24.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313 Abs.</td>
<td>1.03</td>
<td>0.930</td>
<td>-19.3</td>
<td>-20.77</td>
<td></td>
<td>0.416</td>
</tr>
<tr>
<td>313 Des.</td>
<td>1.03</td>
<td>0.930</td>
<td>-19.8</td>
<td>-20.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 Abs.</td>
<td>1.08</td>
<td>0.985</td>
<td>-19.7</td>
<td>-17.96</td>
<td></td>
<td>0.524</td>
</tr>
<tr>
<td>300 Des.</td>
<td>1.08</td>
<td>0.985</td>
<td>-20.5</td>
<td>-17.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Eq. 4.1.12 can be compared with empirical equations for \( P-C \) isotherms obtained by Brodowsky and Poeschel [145], who investigated \( P-C \) isotherms of the Pd-Ag-H system using an alternative thermodynamic analysis, to give the following relationship between hydrogen pressure, hydrogen content and temperature:
\[ P_{e}^{1/2} = K \cdot \frac{x_{H}}{1 - x_{H}} \cdot \exp\left(\frac{E_{x_{H}}}{RT}\right) \cdot \exp\left\{ \frac{F(x_{H} - 0.52)}{RT} \right\} \]  

(4.1.16)

where \( x_{H} \) (mol H/mol Pd) is the hydrogen concentration in the Pd alloys, and \( K \) is the equilibrium constant for the hydrogen adsorption reaction. The first term is the ideal configurational term which yields Sievert's law \( (P_{H_{2}}^{1/2} = Kx_{H}) \). Sievert's law is valid at only very low hydrogen concentrations. The second term \( \exp(E_{x_{H}}/RT) \) is ascribed to the excess chemical potential of the protons which is caused by the increasing size of the interstices \( (E \) is the activation energy of hydrogen solution reaction). The third term \( \exp\{F(x_{H} - 0.52)/RT\} \) is ascribed to a steep rise in the Fermi energy which occurs after the 4d-band of the metal is filled by electrons from the dissolved hydrogen, and additional electrons enter the 5s-band.

The enthalpy for the dehydriding reaction is given by

\[ \Delta H_{d} = \Delta H_{1} + \Delta H_{2} = (\varepsilon_{1} - \varepsilon_{-1}) + (\varepsilon_{2} - \varepsilon_{-2}) = -A_{i} \]  

(4.1.17)

where \( \Delta H_{1} \) and \( \Delta H_{2} \) are the enthalpies for reactions (4.1.1) and (4.1.2), respectively. The activation energies (kinetic) and the enthalpies (thermodynamic) are shown in the potential energy vs. reaction coordinate plot of Fig. 4.4.

Similarly, for the absorption reaction

\[ \Delta H_{a} = A_{i} \]  

(4.1.18)
From the linear relationship between parameter $A$, enthalpy $A_1$ and temperature $T$ given in Eq. 4.1.13, the value of the enthalpies for the complete process (reactions (4.1.1) and (4.1.2)) of hydriding (and dehydriding) are obtained, from the intercept of the plot of parameter $A$ vs. $T$ (Fig. 4.5). Because the hydride alloy in reaction 4.1.2 releases $(v_0-x_0)/2$ mole $H_2$, the fitted values of $A$ and $A_0$ in Eq. 4.1.12 are divided by this amount of hydrogen to obtain the unit of $kJ \text{ mol} H_2^{-1}$ in Fig. 4.5, which gives $\Delta H_a =43.2 \text{ kJ mol} H_2^{-1}$ and $\Delta H_d =-41.0 \text{ kJ mol} H_2^{-1}$ in the two-phase region ($H/M=0.02-0.9$) for the LaNi$_{4.7}$Al$_{0.3}$ alloy ($R=8.314 J (\text{ mol K})^{-1}$ and the unit of $P$ is Pa when fitting Eq. 4.1.12).

The larger absolute value for $\Delta H_d$ is consistent with the predictions of Flanagan and Clewely [146]. The results are also in good agreement with Sinha and Wallace [147], who found a similar behaviour for ZrMn$_{1.22}$Fe$_{1.1}$ and ZrMn$_{1.1}$Fe$_{1.22}$-H$_2$. It has been shown that the energy difference, $|\Delta H_d| - |\Delta H_a|$, is close to the computed values for the elastic strain energy in the lattice in the (Nb$_x$Fe$_{1-x}$)$_{1-x}$Cr$_x$ ($x=0.05, 0.07$)-H$_2$ system [148]. This implies that the strain energy induced in the lattice on hydriding is largely transformed to additional surface energy (due to pulverization of the alloy grains), and thus the system does not return to the same ground state on the P.E. vs. r.c. diagram (cf. Fig 4.4).

4.1.3 Applications of the model

From Eq. 4.1.12, the slope of the plateau for the $P$-$C$-$T$ curve, a hysteresis factor and H-H interaction factor can be obtained.

4.1.3.1 Calculation of hysteresis factor
Hysteresis, which is the lag in the desorption cycle vs. the absorption cycle in the \( P-C-T \) curves, occurs with most hydride forming materials and is an important property with respect to hydride device design. In almost all practical cases, a minimum hysteresis is desired. The relation of hysteresis to hydrogen concentration and temperature can be modeled using Eq. 4.1.12 for both absorption and desorption.

Assuming the plateau length for the absorption and desorption \( P-C \) isotherms remains the same, it can be seen from Table 4.1 that the hysteresis factor (Eq. 4.1.15) will decrease with increasing temperature. This variation in hysteresis is due to a change in parameter \( A \), not the change in parameter \( A_0 \), i.e., the H-H interactions.

### 4.1.3.2 Analysis of the slope of \( P-C \) isotherms in the two-phase region

The plateau slope is not constant all along the plateau, and can be related to changes in other properties. Taking the derivative of Eq. 4.1.12 (at constant temperature) gives

\[
\frac{dP_e}{dc_H} = P_e \cdot \frac{2}{R(y_o - x_o)} \left[ \frac{A_0}{T} + R \cdot \frac{c_m}{c_H(c_m - c_H)} \right]
\]

which shows the slope \( (dP_e/dc_H) \) of the \( P-C \) isotherm is dependent on the parameter \( A_0/T \), i.e. on the H-H interaction and temperature. The decrease of \( A_0 \) with temperature increase is shown in shown in Table 4.1, and agrees with the less-sloped plateaus obtained at higher temperatures [149-152].
Figure 4.1 $P$-$C$ isotherm for the solid solution of hydrogen ($\alpha$-phase) and hydride formation ($\beta$-phase). The region of coexistence of the two phases is characterized by the flat plateau that begins at $x_0$ and ends at $y_0$. 
Figure 4.2 Simplified model for the dissociation of molecular hydrogen at an interface, and the solution of hydrogen atoms in the bulk.
Figure 4.3  The absorption and desorption $P$-$C$ isotherms of LaNi$_{4.7}$Al$_{0.3}$ alloy. The points are the experimental data and the solid curves are fitted to Eq. 4.1.12.
Figure 4.4  Schematic representation of the potential energy versus reaction coordinate curve for M-H$_2$ reaction.
Figure 4.5 Parameter $A$ vs. temperature, $T$, for the hydrogen absorption and desorption processes in a LaNi$_{4.7}$Al$_{0.3}$ alloy.
4.2 EQUILIBRIUM POTENTIAL OF MH ELECTRODES

The relationship of the equilibrium potential to the hydrogen concentration and temperature is established using the kinetic expressions for the hydrogen absorption model, and a comparison of the calculated and experimental equilibrium potential is a measure of the accuracy of the absorption model used in this study.

4.2.1 Theoretical model

Hydrogen desorption in a hydride electrode in an alkaline solution occurs in three consecutive steps [83]:

Step 1. Diffusion of absorbed hydrogen from the bulk to the surface of the electrode. When equilibrium is established for a given $E_0$, hydrogen is homogeneously distributed in the metal hydride with a bulk concentration $c_H$ and the site occupation quota of absorbed hydrogen is denoted by $x_H$.

Step 2. Transition of hydrogen from an absorbed state to an adsorbed state on the surface of the alloy particles, as given by Eq. 4.1.1 (p.71)

$$\text{MH}_{y_0,\text{abs}} \xleftrightarrow[l_1]{l_{-1}} \text{MH}_{y_0,\text{ads}}$$ (4.1.1)

Step 3. Electrochemical reaction occurring at the surface of each individual particle of the electrode in an alkaline solution. This reaction can be represented by
\[
\frac{1}{y_0 - x_0} \text{MH}_{y_0, \text{ads}} + \text{OH}^- \xrightleftharpoons[l_2]{l_1} \frac{1}{y_0 - x_0} \text{MH}_{x_0} + \text{H}_2\text{O} + e^- \quad (4.2.1)
\]

where \( l_1 \) and \( l_1 \) are the forward and reverse specific rate constants for reaction (4.1.1); \( l_2 \) and \( l_2 \) are the forward and reverse specific rate constants for reaction (4.2.1).

For small constant discharge current, assuming first-order kinetics for both transfer and desorption reactions, and no interaction between H atoms (absorbed and adsorbed), the local equilibrium condition requires equal forward and reverse overall reaction rates for reactions (4.1.1) and (4.2.1), which for reaction (4.1.1) is given by Eq. 4.1.3 (p.72) [83,153]

\[
l_1 x_H (1 - \theta) = l_1 \theta (1 - x_H) \quad (4.1.3)
\]

and

\[
l_2 a_{\text{OH}^-} \theta \exp\left[\frac{\zeta F (E_e + f(c_H))}{RT}\right] = l_2 a_{\text{H}_2\text{O}} (1 - \theta) \exp\left[\frac{(1 - \zeta) F (E_e + f(c_H))}{RT}\right] \quad (4.2.2)
\]

where \( \zeta \) is the charge-transfer coefficient (symmetry factor); \( E_e + f(c_H) \) represents a reaction potential of the electrode alloy. \( f(c_H) \) can be simplified as a linear function of the hydrogen concentration \( f(c_H) = \lambda \cdot c_H \) (\( \lambda \) is a constant and a first-order electrochemical reaction is assumed). \( a_{\text{OH}^-} \) and \( a_{\text{H}_2\text{O}} \) are the activities of \( \text{OH}^- \) and \( \text{H}_2\text{O} \) respectively, and can be regarded as constant values for small changes in temperature. The potentials on
the surface of an alloy powder electrode are shown schematically in Fig. 4.6 [153]. Eq. 4.2.2 is another expression of the Nernst equation and indicates that the reaction current density for the forward reaction of the electrode at equilibrium is equal to that for the reverse reaction.

From Eqs. 4.1.3 and 4.2.2, the equilibrium potential $E_e$ is obtained

$$E_e = \frac{RT}{F} \ln \left( \frac{l_{1,2} \alpha_{H_2O}}{l_{1,2} \alpha_{OH^-}} \right) + \frac{RT}{F} \ln \left( \frac{1 - x_H}{x_H} \right) + \lambda \cdot c_H \quad (4.2.3)$$

It is assumed that the rate constants have Arrhenius-type dependence on activation energy as in Eq. 4.1.5 (p.72)

Eq. 4.2.3 can be written as

$$E_e = B - \frac{RT}{F} \ln \left( \frac{c_H}{c_m - c_H} \right) + \lambda \cdot c_H \quad (4.2.4)$$

where

$$B = B_1 + B_2 T \quad (4.2.5)$$

$$B_1 = \frac{\varepsilon_1^* + \varepsilon_2^* - \varepsilon_{-1}^* - \varepsilon_{-2}^*}{F} \quad (4.2.6)$$

and
where the $\varepsilon^*$s represent the activation energies for the respective forward and reverse specific rate constants for the reactions.

The first term, $B$ of Eq. 4.2.4, represents a potential that is dependent on the composition of the MH alloy and temperature, and is independent of the hydrogen concentration in the MH alloy. The second term represents a variation of potential with the $\alpha$-$\beta$ phase transformation, and thus is a function of the hydrogen concentration. Under equilibrium conditions, a layer of chemically adsorbed hydrogen is present, which gives rise to a potential difference ($\lambda c_h$) that is proportional to the hydrogen concentration (see Fig. 4.6).

4.2.1.1  Fitting the model to the experimental data

The variation of the equilibrium potential of the LaNi$_{4.7}$Al$_{0.3}$ alloy electrode with the amount of hydrogen in the hydride alloy and temperature is shown in Fig. 4.7. The curves are similar to the $P$-$C$-$T$ curves, and like the $P$-$C$-$T$ curves have three phase regions, $\alpha$, $\alpha+\beta$, and $\beta$ regions. The equilibrium potential of the electrode changes rapidly with hydrogen concentration for $H/M \leq 0.1$, i.e. the solid solution $\alpha$ phase [154]. The plateau region represents the two-phase region where $\alpha$ and $\beta$ (hydride phase) coexist. When the hydrogen concentration $H/M \geq 0.6$, only $\beta$ phase exists and the equilibrium potential decreases (increases negatively) rapidly with an increase in hydrogen concentration in this region. The equilibrium potential decreases with increasing temperature, there is
about 5 mV change in potential for a 20°C temperature change. The constants \( c_m, B \) and \( \lambda \) obtained by fitting the calculated curves (Eq.4.2.4) to the experimental points are given in Table 4.2. The fitting results are shown in Fig. 4.7.

Table 4.2 Calculated values of \( c_m, B \) and \( \lambda \) for the LaNi_{4.7}Al_{0.3} alloy at various temperatures.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>( c_m ) (H/M)</th>
<th>( B ) (V)</th>
<th>( \lambda ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.750</td>
<td>-0.9650</td>
<td>0.1289</td>
</tr>
<tr>
<td>298</td>
<td>0.726</td>
<td>-0.9762</td>
<td>0.1479</td>
</tr>
<tr>
<td>308</td>
<td>0.699</td>
<td>-0.9805</td>
<td>0.1587</td>
</tr>
<tr>
<td>318</td>
<td>0.685</td>
<td>-0.9842</td>
<td>0.1671</td>
</tr>
</tbody>
</table>

The constants \( B \) and \( \lambda \) are independent of hydrogen concentration (\( c_H \)) and can be expressed as linear equations of temperature:

\[
B = -0.8476 - 0.0004T \quad (4.2.8)
\]

and

\[
\lambda = -0.1043 + 0.0009T \quad (4.2.9)
\]

4.2.1.2 Plateau slope of the equilibrium potential vs. hydrogen concentration curve

The plateau slopes of the plots \( E_c \) vs. \( c_H \) curves in Fig. 4.7 are given by
\[
\frac{d(-E_s)}{dc_H} = \frac{RT}{F} \cdot \frac{c_m}{c_H(c_m - c_{H})} - \lambda
\] (4.2.10)

Eq. 4.2.10 shows that the larger the value of \( \lambda \), the flatter the plateau region of the discharge curve. The reaction surface potential results from the adsorbed hydrogen atoms and increases with hydrogen concentration in the electrode. The measured potential includes the true electrode potential and the reaction surface potential (see Fig. 4.6).

4.2.2 Variation of equilibrium potential with hydrogen storage capacity at various cycles

The equilibrium potential is a measure of the \( \mathbf{H}^+ \) activity at the electrode/electrolyte interface. The equilibrium potential of the \( \text{Mm(Ni}_{0.71}\text{Co}_{0.14}\text{Al}_{0.08}\text{Mn}_{0.06})_{5.02} \) alloy as a function of the number of cycles and hydrogen storage capacity is shown in Fig. 4.8. The equilibrium potential does not change with increasing number of cycles for hydrogen storage capacities greater than 60 mAh g\(^{-1}\). However, at hydrogen storage capacities less than 60 mAh g\(^{-1}\), the equilibrium potential increases with increasing number of cycles. The instability of the equilibrium potential at a lower hydrogen storage capacity could lead to instability for Ni/MH batteries after a large number of cycles.

4.2.3 Equilibrium potential and charge/discharge cycles

The equilibrium potential of the electrodes as a function of number of cycles is shown in Fig. 4.9. It can be seen from Fig. 4.9 that the equilibrium potential increases 7 mV up to 20 cycles and then remains constant with increasing the number of cycles for both \( \text{Mm}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \) and \( \text{LaNi}_{4.7}\text{Al}_{0.3} \) alloy electrodes. The similar
equilibrium potentials for both alloy electrodes indicate that the equilibrium potential of the MH electrode is independent of the composition of MH alloy at the fully charged state.
Figure 4.6 Schematic diagram of a difference of the measured potential and real reaction potential on the surface of the electrode alloy powder.
Figure 4.7 The equilibrium potential of the MH electrode as a function of both the hydrogen concentration in the LaNi$_{4.7}$Al$_{0.3}$ hydride alloy and the temperature. The symbols are the experimental data and the full lines are the fitted results.
Figure 4.8 Equilibrium potential of Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.08})_{5.02} electrode vs. hydrogen storage capacity at varying number of charge/discharge cycles.
Figure 4.9 Variation of equilibrium potential of LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrodes with number of charge/discharge cycles for the fully charged state.
4.3 **CORRELATION BETWEEN EQUILIBRIUM POTENTIAL AND HYDROGEN PRESSURE**

The hydrogen absorption and desorption characteristics of metals are represented by pressure-composition-temperature \((P-C-T)\) curves. Analogous plots for the MH electrodes of the Ni/MH batteries are charge/discharge curves and these plots show the variations of the MH electrode equilibrium potential \((E_e)\) with hydrogen concentration (i.e. the state of charge) and temperature \(T\), i.e., \(E-C-T\) curves. The \(P-C-T\) curve is related to the \(E-C-T\) curve and both provide important information for the selection of MH electrode materials [5,28]. The equilibrium potential of the MH electrochemical reaction is related to the hydrogen pressure in an equilibrated MH alloy/hydrogen gas system. The connection between equilibrium potential and hydrogen pressure is established through the activity relationship in the equilibrium constants for the electrochemical reactions.

### 4.3.1 Theoretical procedure

The electrochemical reactions occurring at an MH electrode are given by

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

(4.3.1)

and

\[
\frac{1}{x}\text{M} + \text{H} = \frac{1}{x}\text{MH}_x
\]  

(4.3.2)

to give the overall equation

\[
\frac{1}{x}\text{M} + \text{H}_2\text{O} + e^- = \frac{1}{x}\text{MH}_x + \text{OH}^-
\]  

(4.3.3)
Eq. 4.3.1 determines the potential of the MH electrode, which using the Nernst equation as given by

$$E_e(H_2O/H) = E^0(H_2O/H) + \left( \frac{RT}{F} \right) \ln \frac{a_{H_2O}}{a_H \cdot a_{OH^-}} \quad (4.3.4)$$

where $E_e$ is the equilibrium potential and $E^0$ is the standard potential.

In KOH solution, the following reactions take place

$$H_2O + e^- = \frac{1}{2}H_2 + OH^- \quad (4.3.5)$$

and

$$\frac{1}{2}H_2 = H \quad (4.3.6)$$

which gives the same overall reaction as 4.3.1. Since the final states are the same, the standard Gibbs free energies are related, thus

$$G^0(1) = G^0(5) + G^0(6) \quad (4.3.7)$$

It follows (for unit ionic activities)

$$-FE^0(H_2O/H) = -FE^0(H_2O/H_2) - RT \ln K \quad (4.3.8)$$
where $G^0(1)$, $G^0(5)$ and $G^0(6)$ are the standard Gibbs' free energies for reactions (4.3.1), (4.3.5) and (4.3.6), respectively. $K$ is the equilibrium constant for reaction (4.3.6).

Combining Eqs. 4.3.4 and 4.3.8 gives

$$E_e(H_2O/H) = E^0(H_2O/H_2) + \left(\frac{RT}{F}\right)\ln K + \left(\frac{RT}{F}\right)\ln \frac{a_{H_2O}}{a_H \cdot a_{OH^-}} \quad (4.3.9)$$

$$= E^0(H_2O/H_2) + \left(\frac{RT}{F}\right)\ln \frac{a_{H_2O}}{(a_{H^2})^{1/2} \cdot a_{OH^-}}$$

where the $a$'s are the activities of the reactants and products.

If the mercury oxide electrode is used as the reference electrode for measuring hydrogen voltage during water electrolysis, the individual electrode reaction and the potential of standard electrode (Hg/HgO) in KOH solution is given by

$$HgO + H_2O + 2e^- = Hg + 2OH^- \quad (4.3.10)$$

$$E_e(HgO/Hg) = E^0(HgO/Hg) + \left(\frac{RT}{2F}\right)\ln \left(\frac{a_{H_2O}}{a_{OH^-}}\right) \quad (4.3.11)$$

Thus, the potential difference between the hydrogen electrode (Eq. 4.3.9) and the mercury oxide reference electrode (Eq. 4.3.11) is

$$E_e(H_2O/H) - E_e(HgO/Hg) = E^0(H_2O/H_2) - E^0(HgO/Hg) + \left(\frac{RT}{2F}\right)\ln \frac{a_{H_2O}}{a_{H^2}} \quad (4.3.12)$$
Using the relation for non-ideal gases

\[ a_{H_2} = \gamma_{H_2} \cdot P_{H_2} \]  

(4.3.13)

the equilibrium hydrogen pressure is given by

\[ \ln P_{H_2} = \ln a_{H_2,O} - \ln \gamma_{H_2} - \left( \frac{2F}{RT} \right) \left[ E_e(H_2O/H) - E_e(HgO/Hg) \right] - \left[ E^0(H_2O/H_2) - E^0(HgO/Hg) \right] \]  

(4.3.14)

where \([E_e(H_2O/H)-E_e(HgO/Hg)]\) and \([E^0(H_2O/H_2)-E^0(HgO/Hg)]\) are the measured potential and the standard potential differences respectively, \(a_{H_2,O}\) is the activity of water, \(\gamma_{H_2}\) is the fugacity coefficient for hydrogen, and \(P_{H_2}\) is the hydrogen partial pressure. The values for the above parameters are obtained from the following [155]

\[ E^0(HgO/Hg) = 1.18041 - (4.4666 \times 10^{-3} - 6.93606 \times 10^{-5} \ln T)T - 1.0788 \times 10^{-6} T^2 \]

\[ + 4.512 \times 10^{-10} T^3 - 5.232/T \]  

(4.3.15)

\[ \log a_{H_2,O} = -0.0225 m + 0.001434 m^2 + \left( 1.38 m - 0.9254 m^2 \right)/T \]  

(4.3.16)

\[ \ln \gamma_{H_2} = \left( 20.5 T - 1857 \right) p/(83.1447 T^2) + \left( -351 T^2 + 12760 T^{1.5} - (20.5 T - 1857)^2 \right) p^2/(1.4009 \times 10^4 T^4) \]  

(4.3.17)
The total pressure (atm units) must be used in Eq. 4.3.17. In most cases \( p=1 \text{atm} \) is chosen as the standard pressure. \( m \) is the concentration of the KOH solution (mol (kg electrolyte\(^{-1}\))), which in this study \( m=6 \) (mol kg\(^{-1}\)). \( E^0(\text{H}_2\text{O}/\text{H}_2)=0; R=8.314 \text{ J (mol K)}^{-1}; F=96500 \text{ J (mol V)}^{-1} \).

### 4.3.2 An example of converting equilibrium potential to hydrogen pressure

It is possible to obtain an electrochemical \( P-C-T \) curve by converting the equilibrium potential \( (E_e) \) to hydrogen pressure \( (P_{\text{H}_2}) \) at constant temperatures using Eqs. 4.3.14 and 3.6.3. The hydrogen concentration is calculated from the storage specific capacity of the MH alloy given by Eq. 3.6.3 (p.59). To test the validity of Eqs. 4.3.1-4.3.17, the electrochemical \( P-C-T \) curve is derived from electrochemical \( E-C-T \) curve and compared with the measured \( P-C-T \) curve. The values of the parameters calculated from Eqs. 4.3.15-4.3.17 are listed in Table 4.3.

Table 4.3 The value of standard potential of an Hg/HgO reference electrode \( (E^0(\text{HgO}/\text{Hg})) \), the base-10 logarithm value of the activity of water \( (\log a_{\text{H}_2\text{O}}) \), the natural logarithm value of fugacity coefficient for hydrogen gas \( (\ln \gamma_{\text{H}_2}) \) in 6 M KOH solutions at 298 K.

<table>
<thead>
<tr>
<th>( E^0(\text{HgO}/\text{Hg})/V )</th>
<th>( \log a_{\text{H}_2\text{O}} )</th>
<th>( \ln \gamma_{\text{H}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.925503</td>
<td>-0.167384</td>
<td>0.000576</td>
</tr>
</tbody>
</table>

Fig. 4.10 shows the \( E-C-T \) curve of the LaNi\(_{4.7}\)Al\(_{0.3}\) metal hydride electrode at room temperature (298 K). The \( E-C-T \) curve in Fig. 4.10 was measured immediately after the
activation when the hydrogen concentration is relatively large. For the potential measurements given in Fig. 4.7, the hydrogen concentrations were relatively lower (H/M varies from 0 to 0.68 at 298 K) following the polarization measurements, for which large overpotentials (+20 V vs. Hg/HgO) were applied to the negative electrode, and thus oxide formation on the electrode alloy may have taken place. Fig. 4.11 compares the calculated \( P-C-T \) curve from the data of Fig. 4.10 and Eqs. 4.3.14-4.3.17, and Eq. 3.6.3 with the experimental \( P-C-T \) curve. The desorption \( P-C-T \) curve of the LaNi\(_{4.7}\)Al\(_{0.3}\) alloy was taken from the Data Book for HY-STOR Introductory Kit No.53 of Ergenics Division, MPD Technology Corporation, Wyckoff, NJ, U.S.A. This curve was obtained by the conventional Sievert's methods (solid point in Fig. 4.11). It was found that the hydrogen pressures calculated from the equilibrium potentials are in good agreement with the equilibrium hydrogen pressure. The good agreement of the calculated and measured \( P-C-T \) curves in Fig. 4.11 shows Eqs. 4.3.14-4.3.17 and 3.6.3 are valid, and provide a ready means for obtaining accurate electrochemical \( P-C-T \) curves using the equilibrium potentials of metal hydride/KOH cells. There are some discrepancies between the calculated and experimental values at low and high H/M values. The discrepancy at high H/M values may be due to the fact that the chemical energy can not be fully converted to electrical energy, i.e., the transfer efficiency is less than one, and the hydrogen concentration calculated from the discharge capacity of the electrochemical reaction will be lower than that from the measurement of the gas-solid reaction. The small discrepancy at low H/M values may be due to experimental error, and this discrepancy is not important for the practical use of the MH alloy.
For the LaNi$_{4.7}$Al$_{0.3}$ alloy, the potential of -0.915 V vs. Hg/HgO corresponds to a hydrogen pressure of 0.302 atm, and the potential of -0.898 V vs. Hg/HgO corresponds to a pressure of 0.081 atm. The 17 mV change in equilibrium potential corresponds to a 3.7 fold increase in the equilibrium pressure. Thus, the pressure calculated from the electrochemical data is more accurate than the pressure measured in a gaseous environment, especially at low depths of discharge (DOD).
Figure 4.10  Electrochemical $E$-$C$-$T$ curve for the LaNi$_{4.7}$Al$_{0.3}$ alloy at 298 K.
Figure 4.11 Comparison of the calculated $P$-$C$-$T$ curve from the electrochemical method and the experimental $P$-$C$-$T$ curve from the conventional Sievert's method for the LaNi$_{4.7}$Al$_{0.3}$ alloy.
4.4 DISCHARGE CAPACITY OF MH ELECTRODE

The discharge capacity of the metal hydride electrode is a measure of the energy density of the battery. When the metal hydride electrode is discharged at a constant discharge current density, the discharge capacity is known as the specific discharge capacity. The specific discharge capacity is generally used with units mAh g⁻¹. The specific discharge capacity depends on several factors, including alloy composition, discharge current density, temperature, and number of charge/discharge cycles. If not specified, the specific discharge capacity is the maximum value for the metal hydride electrode at a given discharge current density (usually less than 120 mAh g⁻¹) at room temperature. The influence of these factors will be discussed in the following sections.

4.4.1 Specific discharge capacity and cycles

Fig. 4.12 shows the specific discharge capacity of LaNi₄.7Al₀.3 and Mm₀.9₅Ti₀.0₅Ni₃.₈₅Co₀.₄₅Mn₀.₃₅Al₀.₃₅ alloy powders as a function of number of cycles. The specific discharge capacity of the cell made using the Mm₀.₉₅Ti₀.₀₅Ni₃.₈₅Co₀.₄₅Mn₀.₃₅Al₀.₃₅ alloy powder reaches 276 mAh g⁻¹ after 5 cycles and decreases slowly to 250 mAh g⁻¹ after 40 cycles. The specific discharge capacity of a cell made from LaNi₄.₇Al₀.₃ alloy reaches a maximum value of 290 mAh g⁻¹ after 6 cycles and then the capacity decreases to about 240 mA g⁻¹ after 40 cycles. The decay in capacity results from a deterioration of the negative electrodes, due to oxidation and polarization of the MH alloy powder with charge/discharge cycles. The Mm(Ni₀.₇₁Co₀.₁₄Al₀.₀₈Mn₀.₀₆)₅.₀₂ alloy electrode was charged/discharged over 200 cycles and the specific discharge capacity at a 100 mAg⁻¹ discharge current density remained at 250 mAh g⁻¹ at 298 K.
4.4.2 Specific discharge capacity and current density

Fig. 4.13 shows the specific discharge capacity of the Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.06})_{5.02} alloy electrode at different discharge current densities. The specific discharge capacity decreases from 290 mAh g^{-1} at a 100 mA g^{-1} discharge current density to 248 mAh g^{-1} at a 600 mA g^{-1} discharge current density.

Fig. 4.14 shows the specific discharge capacity vs. the discharge current plot after 50 charge/discharge cycles for the Mm_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.43}Mn_{0.35}Al_{0.35} alloy at temperatures ranging from 292 K to 313 K. The discharge capacity is shown to decrease more slowly with increasing discharge current at higher temperatures, i.e. the high-rate discharge capability increases with temperature. The electrochemical reaction is controlled by the charge transfer process at the MH electrode/electrolyte interface and the mass transfer process in the bulk MH alloy. The charge transfer process is the cause of the activation polarization overpotential, whereas the slow hydrogen diffusion in the MH electrode is the cause of the concentration polarization overpotential. The activation and concentration overpotentials decrease the discharge capacity at the higher discharge current, but higher temperatures reduce the overpotentials and increase the high-rate discharge capability of the MH electrode. It has been reported by previous researchers that an increase in the high-rate discharge capability is related to a decrease in the activation and concentration overpotentials [8,156] and the microcracking of the MH alloy powder [53]. Although the deterioration of the MH electrode decreases the specific discharge capacity, the MH electrode can be stabilized to obtain a near constant specific discharge capacity.
4.4.3 Variation of specific discharge capacity with cycles at different current densities

Fig. 4.15 shows the specific discharge capacity of the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrode at different discharge current densities as a function of number of cycles. The specific discharge capacity of the alloy powder at 100 mA g$^{-1}$ reaches a saturation value of 275 mAh g$^{-1}$ after 6 cycles, while at 200 mA g$^{-1}$ a saturation value of 253 mAh g$^{-1}$ is obtained after 12 cycles, which shows that for complete activation of the MH alloy electrode more charge/discharge cycles are required at larger discharge current densities.

4.4.4 Specific discharge capacity and temperature

Fig. 4.16 is a specific discharge capacity vs. temperature plot for Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy electrode, each point estimated at 1% accuracy. The discharge capacity was measured for a 100 mA g$^{-1}$ discharge current. The specific discharge capacity has a maximum value of 290 mAh g$^{-1}$ at 298K, decreasing to 252 mAh g$^{-1}$ at 273 K and 246.4 mAh g$^{-1}$ at 335K. A lower temperature leads to a decrease in the hydrogen activity at the electrolyte/MH electrode interface, and a corresponding reaction rate decreases with the MH alloy, to give the lower hydrogen storage capacity. On the other hand a higher temperature makes the hydrogen atoms unstable in the alloy and thus also leads to a decrease in the hydrogen storage capacity. Thus there is a maximum in specific capacity vs. temperature, which for this alloy occurs at 298K.
Figure 4.12 Variation of the discharge capacity of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ alloys with number of charge/discharge cycles at 298 K.
Figure 4.13  Variation of specific discharge capacity of Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy electrode with discharge current density.
Figure 4.14 Specific discharge capacity of Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy as a function of discharge current density at temperatures ranging from 292 to 313 K.
Figure 4.15 Specific discharge capacity of Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy as a function of number of cycles at discharge currents of 50, 100 and 200 mA g$^{-1}$ at room temperature.
Figure 4.16 Variation of specific discharge capacity of Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_5$ alloy electrode with temperature.
4.5 **EXCHANGE CURRENT DENSITY**

Exchange current density represents the oxidation or reduction reaction rate on the electrode under equilibrium potential. The value of exchange current density depends on the characteristics of the electrode reactions such as: temperature, hydrogen concentration, Cu-coating and cycles. These factors are related to the nature of the interface of electrolyte/alloy particle.

4.5.1 **Determination of exchange current density**

In an alkaline aqueous solution, the hydrogen atoms produced at the surface of the MH alloy powder during the charge process are instantly adsorbed and then diffuse into the bulk of the MH alloy. The electrochemical reactions are therefore expressed as steps 3, 2 and 1 in section 4.2.1. Reaction (4.2.1) is the charge transfer process at the interface between the MH alloy powder and the electrolyte. The electrochemical kinetics of the charge transfer process is determined by DC polarization methods and the slope of the linear polarization curve represents the electrode resistance, composed of the ohmic and polarization resistances. The diffusion resistance is usually negligible in polarization tests at scan rates of 1 mV s\(^{-1}\). The charge transfer process can be determined by using the exchange current density. At a small overpotential (<20mV), the conventional Butler-Volmer equation can be rewritten as [60]

\[
    j = I_o \frac{F \eta}{RT} \tag{4.5.1}
\]

Therefore the exchange current density can be obtained from the slope of the \(j\) vs. \(\eta\) plot.
Typical linear polarization curves obtained for the LaNi$_{4.7}$Al$_{0.3}$ electrode alloy at different hydrogen concentrations and temperatures are shown in Fig. 4.17. Selected linear polarization curves obtained for the MH electrodes with and without Cu-coating at 298 K are shown in Fig. 4.18. It can be seen from Figs. 4.17 and 4.18 that there is a good linear relationship between overpotential and current density for current densities less than 400 mA g$^{-1}$, which is much larger than the practical discharge current density of about 60 mA g$^{-1}$ for an AB$_5$-type MH electrode.

The polarization curves for LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrodes at different cycles are shown in Figs. 4.19 and 4.20. The polarization measurements of the electrode were conducted after fully charging and a 1 hour wait period, at which time the MH electrode essentially reaches its equilibrium potential. The 1 hour wait period leads to a small decrease in the state of charge (SOC) of the MH alloy electrode due to self-discharge, which results from the gassing and a small current through the testing equipment and the recording computer.

The linear polarization process involves the hydrogen reduction and oxidation reactions at the surface layer of the alloy powder, and not the hydrogen diffusion process in the alloy powder. Thus the linear polarization is reversible for the hydrogen redox reactions. A high exchange current density indicates not only the high reaction rate for the electrode, i.e., high rate charge/discharge capability, but also a low degradation rate of electrode performance.

4.5.2 Effect of temperature on exchange current density
Fig. 4.21 shows that the exchange current densities increase with increasing temperature for the MH electrode. From a practical standpoint this indicates that, aside from other contributing factors, the charge/discharge performance of the MH electrode improves with increasing temperature. High exchange current density leads to the high dischargeability rate of MH electrodes. Liu et al [157] have found that high dischargeability rates can be considerably improved by hot-charging the electrode, e.g. pre-charging in a KOH solution at a temperature of 80-100 °C for 4-10 hours and then discharging at room temperature. The increase in the exchange current density with increasing temperature is attributed to the increase in electrolyte conductivity with temperature [158], and to the formation at higher temperatures of more active nickel clusters [159].

4.5.3 Effect of hydrogen concentration on exchange current density

The exchange current density decreases with increasing hydrogen concentration as shown in Fig. 4.21. This is attributed to the decrease of hydrogen adsorption capability of the MH alloy powder, and to the formation of more active nickel clusters during deeper dehydriding [159].

4.5.4 Effect of charge/discharge cycles on exchange current density

The exchange current density vs. number of charge/discharge cycles for both the LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrodes are shown in Fig. 4.22. An increase in the exchange current density with the number of cycles reflects the fast hydrogen adsorption process at the MH alloy/electrolyte interface. The exchange
current density of the LaNi$_{4.7}$Al$_{0.3}$ alloy electrode reaches 450 mA g$^{-1}$ after 30 cycles and then it slowly increases to a value of about 500 mA g$^{-1}$ after 40 cycles. Similarly, the exchange current density of the MmNi$_5$-based alloy electrode reaches 206 mA g$^{-1}$ after 30 cycles and then slowly increases to a value of about 235 mA g$^{-1}$ after 40 cycles. The exchange current densities of the MmNi$_5$-based alloy electrodes remain essentially constant after 20 cycles, indicating that the charge transfer process at the interface between the MH alloy powder and electrolyte is stabilized.

4.5.5 Effect of copper coating on exchange current density

The exchange current densities of the Cu-coated electrode are higher compared to the uncoated electrode at temperatures ranging from 298 to 318 K (Fig. 4.23), and indicates lower polarization, which can be attributed to: (i) corrosion or oxidation protection of alloy powders, and (ii) decrease in contact resistance (less ohmic polarization).

Microencapsulation by copper provides complete coverage of the intermetallic alloy powder surface and prevents corrosion or oxidation of both the active material (LaNi$_{4.7}$Al$_{0.3}$ alloy) and the catalyst (Ni cluster). The presence of copper grains also enhances the current collection processes to increase the exchange current density. Scanning electron microscopy (SEM) analysis shows that the surface of the uncoated alloy particles are typically relatively smooth cleavage planes, whereas the surface of the 9 wt. % Cu-coated alloy particles has an "orange-peel" appearance (see Fig. 4.24 (a) and (b)) characteristic copper film. The small particles on the smooth cleavage plane in Fig. 4.24 (a) are the LaNi$_{4.7}$Al$_{0.3}$ alloy debris.
Figure 4.17 Typical linear polarization curves for the LaNi$_{4.7}$Al$_{0.3}$ electrode at different hydrogen concentrations in the hydride alloy at different temperatures.
Figure 4.18 Steady-state polarization curves for both LaNi$_{17}$Al$_{0.3}$ electrodes with and without Cu-coating at different hydrogen concentrations at 298 K.
Figure 4.19  Polarization curves of the LaNi$_{4.7}$Al$_{0.3}$ electrode at different number of cycles at 298 K.
Figure 4.20 Polarization curves of the Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35} alloy electrode at different number of cycles at 25 °C.
Figure 4.21 Variation of exchange current density ($I_0$) of the LaNi$_{4.7}$Al$_{0.3}$ electrode with temperature at different hydrogen concentrations.
Figure 4.22. Exchange current densities of LaNi$_{4.7}$Al$_{0.3}$ and Mm$_{0.95}$Tl$_{0.65}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloys as a function of number of charge/discharge cycles.
Figure 4.23 Variation of exchange current density ($I_0$) of both LaNi$_{4.7}$Al$_{0.3}$ electrodes with and without 9 wt.% Cu-coating vs. temperature and hydrogen concentration in the hydride alloys.
Figure 4.24  Scanning electron micrograph of the LaNi$_{4.7}$Al$_{0.3}$ alloy particle surface without Cu-coating (a) and with 9.0 wt. % Cu-coating (b). In (a), the surface state of alloy particles is smooth cleavage and the small particles on the smooth cleavage plane are the LaNi$_{4.7}$Al$_{0.3}$ alloy debris. In (b), the surface state of alloy particles is changed and has an "orange-peel" appearance after Cu-coating.
4.6 HIGH-RATE DISCHARGEABILITY

High-rate dischargeability is determined from the ratio of high (200 mA g\(^{-1}\)) to low (20 mA g\(^{-1}\)) rate discharge capacity. Fig. 4.25 shows both high and low rate discharge curves for both the LaNi\(_{4.7}\)Al\(_{0.3}\) electrode and Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode, respectively. The high-rate dischargeabilities are 88.4% for the LaNi\(_{4.7}\)Al\(_{0.3}\) electrode and 99.4% for Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode (Table 4.4). The factors that improve high-rate dischargeability are the same that improve the exchange current density (section 4.5.5).

Table 4.4 High-rate dischargeability parameters of both LaNi\(_{4.7}\)Al\(_{0.3}\) and 9.0 wt.% Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) alloy electrodes.

<table>
<thead>
<tr>
<th>Alloy electrode</th>
<th>Discharge current density (mA g(^{-1}))</th>
<th>Discharge time (h)</th>
<th>High-rate dischargeability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi(<em>{4.7})Al(</em>{0.3})</td>
<td>20</td>
<td>15.5</td>
<td>88.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>9.0 wt% Cu-coated LaNi(<em>{4.7})Al(</em>{0.3})</td>
<td>20</td>
<td>16.1</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4.25 shows that the discharge potential for the Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode is lower (i.e. more negative) than that for the LaNi\(_{4.7}\)Al\(_{0.3}\) electrode, especially at a large discharge current density (i.e. 200 mA g\(^{-1}\)). The discharge potential of the uncoated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode is -0.914 V vs. Hg/HgO at 20 mA g\(^{-1}\) discharge current density and -0.833 V vs. Hg/HgO at 200 mA g\(^{-1}\) discharge current density. The discharge potentials of the Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode are approximately the same value (i.e. -0.930 V
vs. Hg/HgO) at both 20 mA g$^{-1}$ and 200 mA g$^{-1}$ discharge current densities. Thus Cu-coating ensures both stable discharge performance and large specific discharge capacity of a Ni/MH battery at a relatively large discharge current density, which is attributed to the lower resistance of the electrode after Cu-coating the particles [19].
Figure 4.25 High-rate dischargeability of both LaNi$_{4.7}$Al$_{0.3}$ alloys electrodes with and without 9.0 wt. % Cu-coating.
4.7 APPARENT ACTIVATION ENERGY

The apparent activation energy is interpreted as the energy that the reactants must surmount in order for the reaction to occur. The exchange current density is related to the apparent surface area, the hydrogen content, and temperature, while the apparent activation energy is dependent only on the hydrogen content. Therefore to fully characterize the catalytic activity of a metal hydride electrode, the apparent activation energy must be given, as well as the electrode exchange current density behaviour. A high value of exchange current density and a low value of apparent activation energy are the factors required for high performance of MH electrodes.

The apparent activation energy is calculated from the plot of \( \ln I_0 \) vs. \( 1/T \) according Eq. 3.6.6 (p.62). The plots of \( \ln I_0 \) vs. \( 1/T \) for selected hydrogen concentrations are shown in Fig. 4.26. Fig. 4.27 shows that the apparent activation energy \( (E_a) \) for dehydriding decreases with increasing hydrogen concentration in the MH electrode. \( E_a \) for the \( \text{LaNi}_{4.7}\text{Al}_{0.3} \) metal hydride electrode reaction is in the range 15.5 to 22.5 kJ (molH\(^{-1}\)) for hydrogen concentration H/M=0.6 to 0.1 and temperatures ranging from 273-318 K. A higher \( E_a \) of 27.05 kJ (molH\(^{-1}\)) is reported for the dehydriding reaction in the \( \text{LaNi}_{4.7}\text{Al}_{0.3} \)-H\(_2\) system [160], which suggests a higher potential energy of the adsorbed state (\( \text{MH}_{y0,\text{ads}} \)) without a decrease in the activation energy \( (e_2) \) for desorption (see Fig 4.4, p.83). The decrease in the apparent activation energy at higher hydrogen concentration is the result of higher potential energy of hydrogen due to increased lattice strain energy (Fig. 4.4) and distortion, allowing easier egress of the hydrogen atoms from the electrode alloy.
Figure 4.26 Arrhenius plots [\(\ln(j_0)\) vs. \(1/T\)] for different hydrogen concentrations (DOD) of the LaNi\(_{4.7}\)Al\(_{0.3}\) alloy electrode.
Figure 4.27  Activation energy ($E_a$) vs. hydrogen concentration (H/M) in the LaNi$_{4.7}$Al$_{0.3}$ hydride electrode.
4.8 SYMMETRY FACTOR OF ELECTRODE REACTION

The symmetry factor ($\zeta$) is a measure of the symmetry of the activation barrier, and so an indicator of the reversibility of the electrode reactions. Because the discharge process is more important and more stable than the charge process of a metal hydride electrode, the present study is concentrated on the discharge process, which is an oxidation process.

Using Eq. 3.6.7 (cf. p.62), the plot of $\eta$ vs. $\ln/j/[\exp(F\eta/RT)-1]$ is linear with slope $RT/\zeta F$, from which the symmetry factor ($\zeta$) is obtained. Eq. 3.6.7 is valid only in the linear polarization region, and typical plots to evaluate the symmetry factor are shown in Fig. 4.28.

Fig. 4.29 shows that the values of $\zeta$ decrease with increasing hydrogen content in the hydride alloy for various temperatures. In the low hydrogen concentration region, which is the $\alpha$-phase region, the symmetry factor $\zeta$ decreases sharply with increasing hydrogen concentration. In the high concentration region, which is the $\beta$-phase region, the symmetry factor $\zeta$ decreases slowly with increasing hydrogen concentration, and at low temperatures (e.g. 0 °C and 25 °C) it changes slightly, which implies the electrode has better reaction reversibility at higher hydrogen concentrations. Fig. 4.29 also shows that symmetry factor ($\zeta$) increases with temperature, and temperature has less influence on $\zeta$ at high hydrogen concentrations.
Figure 4.28 Polarization curves. $\eta$ vs. $\ln[j/(\exp(\eta F/RT)-1)]/\text{Ag}^{-1}$, for the LaNi$_{4.7}$Al$_{0.3}$ hydride electrode at 308 K.
Figure 4.29  The symmetry factor ($\zeta$) of the LaNi$_{4.7}$Al$_{0.3}$ electrode at different temperatures as a function of hydrogen concentration in the hydride alloy.
4.9 HYDROGEN DIFFUSION COEFFICIENT

The electrochemical properties of metal hydride electrodes are determined largely by the metal hydride/electrolyte interface kinetics and the rate of hydrogen diffusion in the bulk of the electrode. A key parameter examined in this research is the diffusion coefficient for hydrogen.

Using the Potential Step Chrono-Amperometry (PSCA) method developed in this study, the hydrogen diffusion coefficients can be determined without prior hydrogen concentration and surface area data. The mechanism(s) of the rate-controlling step for the discharge process is investigated. The validation analysis of the PSCA method is performed and the method is compared with the conventional potential step technique.

4.9.1 Study of hydrogen diffusion using the PSCA method

The diffusion process in the electrode alloy is investigated by solving Fick's second law subject to the initial and boundary hydrogen concentrations.

4.9.1.1 Theory of hydrogen transport in electrode alloy particles

The model for the MH electrode used in this theoretical analysis is a small, flat, disc-like electrode composed of spherical metal alloy particles, i.e., similar to that used in the present experiments (Fig. 4.30). Since the specimens are good electronic conductors, the potential gradient across the pellet is negligible. A potential step, applied to the specimen relative to the reference electrode by use of a potentiostat, is thus equivalent to a step in the hydrogen activity at the particle-electrolyte interface, under the conditions where the charge-transfer reaction at the particle-electrolyte interface is fast, and where ionic
transport through the electrolyte is not rate limiting. As a response to this abrupt change in the interfacial hydrogen activity, the concentration of hydrogen in the particles will decrease through chemical diffusion of hydrogen to a new equilibrium distribution which is fixed by the applied potential. The resulting time-dependent flux of hydrogen across the electrolyte-particle interface manifests itself as a diffusion current which is monitored as a function of time. For the diffusion of hydrogen inside the particle, we have Fick's second law

\[
\frac{\partial C(r,t)}{\partial t} = D \left[ \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right]
\]

(4.9.1)

with the initial condition

\[
C(r,0) = C_o \quad 0 \leq r \leq a \quad t=0
\]

(4.9.2)

and the boundary conditions

\[
C(a,t) = C_s \quad r=a \quad t>0
\]

(4.9.3)

\[
C(0,t) = C_o \quad r=0 \quad 0<t<\tau
\]

(4.9.4)

\[
D \left[ \frac{\partial C(r,t)}{\partial r} \right]_{r=a} = \pm \frac{j(t)}{nFA}
\]

(4.9.5)
where \( C(r,t) \) denotes the hydrogen concentration in the alloy with respect to radius and time, \( D \) is average (or integral) diffusion coefficient of hydrogen, \( r \) is the radial distance from the center of the sphere [161], \( a \) is the radius of the particle sphere, \( t \) is the time (s), \( C_0 \) is the initial hydrogen concentration in the bulk of the alloy throughout the sample, \( C_s \) is the hydrogen concentration at the particle surface, \( \tau \) is the time (s) at which the boundary condition shown in Eq. 4.9.4 becomes non-valid, \( n \) denotes the number of Faradays (or electrons) involved in the reaction \((n=1 \text{ for this electrochemical system})\), \( A^* \) is the specific surface area of the particles.

The initial and boundary conditions (Eqs. 4.9.2 and 4.9.3) imply that the sphere is initially at a uniform concentration \( C_0 \), and the surface concentration is kept constant at \( C_s \) during the experiment. The \( \pm \) sign in Eq. 4.9.5 indicates the charge (+) and discharge (-) process when the current density is always considered to be a positive value. Application of the Laplace transformation method to Eq. 4.9.1 together with the initial and boundary conditions Eqs. 4.9.2-4.9.4, gives for small times [161]

\[
\frac{C-C_0}{C_s-C_0} = \frac{a}{r} \sum_{m=0}^{\infty} \left[ \text{erfc} \left( \frac{2m+1)a-r}{2\sqrt(Dt)} \right) - \text{erfc} \left( \frac{2m+1)a+r}{2\sqrt(Dt)} \right) \right] \tag{4.9.6}
\]

where \( m \) is an integer \((1, 2, 3 \ldots \infty)\). The expression for Eq. 4.9.6 for \( m=0 \) and \( m=1 \) produces four erfc terms. Typical values for \( D, a, \) and \( t \) for the experimental conditions in this study, i.e., \( a=6\times10^{-6} \text{ m}, 0\leq r\leq a, D=10^{-13}\sim10^{-14} \text{ m}^2 \text{ s}^{-1} \) and \( t<\tau=7\sim500 \text{ s} \) (\( \tau \) is critical time and is changed with the value of \( D \)), when used in the erfc terms give the following relationships
\[
\text{erfc} \frac{a + r}{2\sqrt{D t}} \gg \text{erfc} \frac{3a + r}{2\sqrt{D t}}
\]

(4.9.7)

\[
\text{erfc} \frac{a - r}{2\sqrt{D t}} \gg \text{erfc} \frac{3a - r}{2\sqrt{D t}}
\]

(4.9.8)

The higher order terms, \(m \geq 1\), give erfc values that can be neglected in the series and Eq. 4.9.6 is reduced to

\[
\frac{C - C_0}{C_s - C_0} = \frac{a}{r} \left[ \text{erfc} \frac{a - r}{2\sqrt{(D t)}} - \text{erfc} \frac{a + r}{2\sqrt{(D t)}} \right]
\]

(4.9.9)

The diffusion current density \(j(t)\), which is related to the concentration gradient at the particle surface \(\frac{\partial C}{\partial r}|_{r=a}\) is given by

\[
j(t) = \pm FA^* D \left[ \frac{\partial C(r, t)}{\partial r} \right]_{r=a}
\]

\[
= \pm FA^* D (C_s - C_0) \left\{ \frac{1}{\sqrt{\pi D}} \cdot \frac{1}{\sqrt{t}} \left[ \exp \left( -\frac{a^2}{D t} \right) + 1 \right] - \frac{1}{a} \text{erf} \left( \frac{a}{\sqrt{D t}} \right) \right\}
\]

(4.9.10)

For large \(a/\sqrt{D t}\), \(\text{erf}(a/\sqrt{D t})\) approaches unity and \(\exp(-a^2/D t)\) approaches zero, which substituted into Eq. 4.9.10 gives
\[ j(t) = \pm FA^* D \left( C_s - C_0 \right) \left( \frac{1}{\sqrt{\pi D}} \cdot \frac{1}{\sqrt{t}} - \frac{1}{a} \right) \] (4.9.11)

Eqs. 4.9.1-4.9.11 apply where the only species reacting at the electrode are supplied by hydrogen diffusion. Additional current densities due to reaction of adsorbed hydrogen, double layer charging/discharging, or oxide film formation or removal may also contribute to the measured current densities; however, these additional current densities in the simplest cases will be independent of the current densities resulting from hydrogen diffusion and are assumed to be negligible.

Thus, a plot of \( j(t) \) (i.e. \( j(t)_{\text{total}} \)) against \( t^{-1/2} \) gives a straight line (cf. Fig. 4.31) with the intercept, \( I \), and slope, \( S \) given by

\[ I = FA^* \left| C_s - C_0 \right| \frac{D}{a} \] (4.9.12)

\[ S = FA^* \left| C_s - C_0 \right| \frac{\sqrt{D}}{\sqrt{\pi}} \] (4.9.13)

to give for \( D \)

\[ D = \left( \frac{I}{S} \right)^2 \cdot \frac{a^2}{\pi} \] (4.9.14)
Eq. 4.9.14 is valid for only small time periods (less than about 500 s), a consequence of using only the first term in the series solution of Eq. 4.9.6, and gives the "instantaneous" value of the hydrogen diffusion coefficient. The initial assumption that $a/\sqrt{Dt}$ is large is easily satisfied in actual experiments. This method does not require prior knowledge of either the hydrogen concentration or the surface area ($A^*$) of alloy particles for solution of the diffusion equation.

It should be noted that present method is different from one based on the Cottrell equation [162]. According to Cottrell, when stepping the potential of the working electrode from a value at which no Faradic reaction occurs to a potential at which the surface concentration of the electroactive species becomes zero for a spherical electrode, the current decays with the time as follows:

$$j(t) = FA^*DC_0 \left( \frac{1}{\sqrt{\pi D}} \cdot \frac{1}{\sqrt{t}} + \frac{1}{a} \right)$$  \hspace{1cm} (4.9.15)

Eq. 4.9.15 is different from Eq. 4.9.11 although they have quite similar form. Eq. 4.9.15 treats the diffusion of ions in a liquid solution, i.e., the area outside spherical particles, and boundary conditions of unlimited diffusion space. In Eq. 4.9.11, the diffusion phenomena is that inside the spherical particles and there is limited diffusion space.
4.9.1.2 Determination of hydrogen diffusion coefficient

A large step potential is applied to overcome both the resistance at the counter electrode/solution interface and the solution ohmic drop in the experiment, and to ensure that the overpotential across the working electrode/solution interface is sufficient to reduce free hydrogen atoms pairs. Fig. 4.32 shows the potential step chronoamperograms obtained at room temperature for various potential steps from the saturation state of the MH electrode. Figs. 4.33 (a)-(d) show the corresponding \( j(t) \) vs. \( t^{1/2} \) plots. It is evident that the plots of current density \( j(t) \) against \( t^{1/2} \) yield straight lines for short time periods (between 40 and 500 s), i.e. the diffusion current density obeys Eq. 4.9.11. For the \( D \) calculation in this study, it is assumed that the powder consists of spherical particles, with an average diameter of 6 \( \mu \)m (obtained from SEM analysis, cf. Fig. 4.34). The values of \( I \), \( S \) and \( D \) for the saturated state at different potential steps at 298 K are summarized in Table 4.5.

<table>
<thead>
<tr>
<th>Potential step/ V vs. Hg/HgO</th>
<th>( I/l ) A g(^{-1})</th>
<th>( S/l ) A g(^{-1}) s(^{1/2})</th>
<th>( D/a^2/l ) ( 10^4 ) s(^{-1})</th>
<th>( D/l ) ( 10^{14} ) m(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.9323 ( \rightarrow ) -0.4323</td>
<td>4.27</td>
<td>71.76</td>
<td>11.3</td>
<td>4.06</td>
</tr>
<tr>
<td>-0.9322 ( \rightarrow ) -0.5322</td>
<td>3.75</td>
<td>69.27</td>
<td>9.33</td>
<td>3.36</td>
</tr>
<tr>
<td>-0.9310 ( \rightarrow ) -0.6310</td>
<td>2.83</td>
<td>63.40</td>
<td>6.33</td>
<td>2.28</td>
</tr>
<tr>
<td>-0.9330 ( \rightarrow ) -0.7330</td>
<td>3.12</td>
<td>62.69</td>
<td>7.89</td>
<td>2.84</td>
</tr>
</tbody>
</table>

Table 4.5 Diffusion parameters obtained for the LaNi\(_{4.7}\)Al\(_{0.3}\) alloy electrode in hydrogen saturation state for 298 K.
The average calculated value of $D$ in the saturated state is $3.1 \times 10^{-14}$ m$^2$ s$^{-1}$ which is in good agreement with the results ($3 \times 10^{-15}$ to $10^{-14}$ m$^2$ s$^{-1}$) reported for similar composition alloys [68,73]. Zheng et al. [68] used the constant potential and constant current discharge techniques to measure the hydrogen diffusion coefficients in an LaNi$_{4.25}$Al$_{0.75}$ powder electrode. They reported values of the diffusion coefficient of $2.97 \times 10^{-15}$ and $3.30 \times 10^{-15}$ m$^2$ s$^{-1}$ estimated from the potentiostatic and galvanostatic discharge experiments, respectively. Van Rijswick [73] using the transfer-limited portion of a potentiostatic discharge of curve estimated the hydrogen diffusion coefficient in an LaNi$_5$ electrode to be in the order of $10^{-14}$ m$^2$ s$^{-1}$.

4.9.1.3 Electrochemical analysis of rate-determining step

In general, mass transport can be achieved by electromigration, convection, or diffusion. In the case of a strong electrolyte and a stationary electrode, as in the present experiment, mass transport occurs by diffusion only. According to Eq. 4.9.11, if the current in the potential-step measurement is diffusion-controlled, the depletion of H near the MH electrode surface will be a $t^{1/2}$ function, and the current also proportional to $t^{1/2}$. During the first stage of the potential step (region a in Figs. 4.33 (a)-(d)), however, the current is almost constant. Thus, it is clear that discharge current depends on different mechanisms for region "a" and region "b". In region "a", the plots (Figs. 4.33 (a)-(d)) do not show linear dependence of $j(t)$ on $t^{1/2}$, which suggests current generation is not limited to hydrogen diffusion in the electrode. Also, the current variation in this region cannot be the result of capacitance build-up, as it occurs within milliseconds. When the positive potential step is applied to the MH electrode, the adsorbed hydrogen on the MH
electrode surface may be rapidly exhausted to a nil level. In the region "b", the plots of
\( j(t) \) vs. \( t^{1/2} \) are linear, indicating that the flow of hydrogen through the MH electrode is
governed solely by diffusion in the solid. The region "b" develops after about 40-70 s of
discharge time for the large applied potentials (larger than +0.2 V vs. Hg/HgO).

4.9.1.4 Variation of hydrogen diffusion coefficient with hydrogen concentration

The present method allows a comparison of the hydrogen diffusion coefficients at
different H concentrations, as the measurements extend over a short time period only,
which is in the validity range of Eq. 4.9.11. To investigate the effect of hydrogen
concentration in the alloy powder on its diffusion coefficient, the diffusion experiments
are carried out at successive discharge stages of the MH electrode under a constant
potential step. Since hydrogen diffusion becomes the rate-determining step after an initial
period, which becomes shorter at higher potentials, a large potential step (+0.6 V vs.
Hg/HgO) is employed.

The linear "b" parts of the \( j(t) \) vs. \( t^{1/2} \) plots at different initial hydrogen
concentrations are plotted in Fig. 4.35, and Fig. 4.36 shows the calculated diffusion
coefficient plotted against the hydrogen concentration for the LaNi\(_{4.7}\)Al\(_{0.3}\) alloy at 298 K.
The hydrogen diffusivity decreases about an order of magnitude as the hydrogen
concentration (H/M) increases to \( \sim 0.8 \). This decrease in diffusivity with increasing
hydrogen concentration has been reported by Völkl and Alefeld [163]. The chemical
diffusion coefficient is related to the mobility, \( M \), of the diffusing species according to the
Einstein formula
\[ D = M k T \] (4.9.16)

where \( k \) is the Boltzmann constant. One factor that restricts hydrogen mobility is its concentration. With increasing concentration, the mutual interaction of atomic hydrogen in a metal or an alloy will lower its mobility, thus lowering the hydrogen diffusivity \( D \). Another factor is that at higher concentrations, transitory trapping of hydrogen by the dislocation structure in the \( \beta \)-hydride takes place (when hydrogen concentration is high enough, \( \beta \)-hydride forms in the alloy, creating dislocations). The dislocations trap hydrogen atoms (to decrease their energy), which decreases overall mobility. The diffusivity in the low hydrogen concentration region, where dislocation densities are lower, gives a more accurate measure of the lattice diffusion coefficient. The attractive interaction between hydrogen and dislocations, and its effect on diffusivity, has been investigated in several papers [164-166].

### 4.9.1.5 Validation analysis of the present method

It was previously noted that Eqs. 4.9.1-4.9.14 apply for the case where the only species reacting at the electrode are supplied by hydrogen diffusion. Additional currents due to the reaction of adsorbed material, double layer charging, or oxide film formation or removal, may also contribute to the current measured upon application of a potential step to the electrode. However, these processes are not significant, except for the initial few seconds, which do not effect the hydrogen diffusion stage of the reaction. Regarding capacitance, a fixed number of coulombs are required to charge the double layers. For a \( 0.05 \times 10^{-4} \text{ m}^2 \) electrode and a capacitance of \( 20 \times 10^4 \mu \text{F m}^2 \), a 0.5 V step would require a
charge of 0.5 \( \mu \text{C} \), which is an extremely small fraction of the total coulombs passed to the electrode [167]. The currents corresponding to the first part of the discharge, i.e. region "a" in Fig. 4.33 ((a)-(d)) can be related to the hydrogen absorption/desorption and/or oxide film formation/removal on the particle surface, which is assumed to be near instantaneous. In the case where the absorption/desorption and/or oxide film formation/removal is still present after an extended period, the transport process is quite complex, and the intercepts on the \( j \) axis of the \( j(t) \) vs. \( t^{1/2} \) plots should produce positive values on the \( j \) axis because of the current contributions of absorption/desorption and/or oxide film formation/removal processes. The experimental results show that the intercepts on the \( j \) axis of the \( j(t) \) vs. \( t^{1/2} \) plots are always negative for the discharge reaction of a MH electrode and as essentially constant for different applied potentials (see typical plots in Fig. 4.37). The results of this investigation do not support assumptions that absorption/desorption and/or oxide film formation/removal still contribute to the discharge current density even after long time intervals.

4.9.2  **Study of hydrogen diffusion using the conventional method**

The charge transfer process occurs over a short time interval for charging/discharging the double layer or for hydrogen absorption/desorption on the surface of MH particles after application of the potential step. Because of the inadequate time resolution of the test, a sharp increase in reaction current at the beginning of an applied potential step is believed to result from the ohmic resistance and the charge transfer resistance. The hydrogen diffusion process occurs in a time that is much longer than that of the charge transfer process, and hydrogen diffusion results in a decrease in
the reaction current with time. The discharge current as a function of time plots for the LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloys are shown in Fig. 4.38 (a) and (b) respectively.

Assuming that the hydride alloy powders are spherical, the diffusion current density $j(t)$ vs. $t$ is given by [68]

$$j(t) = \pm \frac{6FD}{\rho a^2} \cdot (c_0 - c_s) \sum_{m=1}^{\infty} \exp\left(-\frac{m^2\pi^2 D t}{a^2}\right)$$  \hspace{1cm} (4.9.17)

which for a sufficiently large $t$ becomes

$$\log j(t) = \log\left[\pm \frac{6FD}{\rho a^2} \cdot (c_0 - c_s)\right] - \frac{\pi^2}{2.303} \cdot \frac{D}{a^2} \cdot t$$  \hspace{1cm} (4.9.18)

where $\rho$ is the density of the MH alloy. The $\pm$ sign in Eqs. 4.9.17 and 4.9.18 indicates either charge (-) or discharge (+).

From the slopes of log($j$) vs. $t$ plots for sufficiently large $t$ according Eq. 4.9.18, the $D/a^2$ ratios are obtained. The calculated $D/a^2$ values for LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy powders, based on the slopes of the log($j$) vs. $t$ plots (cf. Fig. 4.38 (a) and (b)), are shown Fig. 4.39. The increase in the value of $D/a^2$ with increasing number of cycles results from the decrease in the particle size, which is a microcracking process accompanying the hydrogen absorption/desorption process. To ensure the same initial concentration of hydrogen at the particle surface for each cycle, the electrodes were charged and rested 1 h for each cycle.
The $D/a^2$ ratio increases from $1.7 \times 10^{-5}$ to $9.1 \times 10^{-5}$ s$^{-1}$ after 20 charge/discharge cycles for the LaNi$_{4.7}$Al$_{0.3}$ alloy and then continues to increase to $12.8 \times 10^{-5}$ s$^{-1}$ after 45 cycles. Similarly, the $D/a^2$ ratio increases from $1.9 \times 10^{-5}$ to $5.1 \times 10^{-5}$ s$^{-1}$ after 20 cycles and then slowly increases to $6.4 \times 10^{-5}$ s$^{-1}$ after 45 cycles for the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrode. Assuming that the hydrogen diffusivity is $1 \times 10^{-14}$ m$^2$ s$^{-1}$, and the average radius of the LaNi$_{4.7}$Al$_{0.3}$ alloy particle $\sim 18.0$ \(\mu\)m after the first charge/discharge cycle, the decrease to $\sim 10.5$ \(\mu\)m occurs after 20 charge/discharge cycles, and to $\sim 8.8$ \(\mu\)m after 45 charge/discharge cycles. The radius of the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy powder decreases from 22.9 \(\mu\)m after the first cycle to a $\sim 14.0$ \(\mu\)m after 20 cycles and then it slowly decreases to $\sim 12.5$ \(\mu\)m after 45 cycles. The faster increase in the $D/a^2$ ratio with increasing number of cycles for the LaNi$_{4.7}$Al$_{0.3}$ alloy electrode compared to the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrode indicates the LaNi$_{4.7}$Al$_{0.3}$ alloy powder is more easily pulverized on cycling.

### 4.9.3 Diffusion constants: conventional vs. PSCA method

Both the conventional and PSCA methods can be used to study the hydrogen diffusion coefficients in MH electrode alloys. In the conventional method, the value of $D/a^2$ obtained (Eq. 4.9.18) for the fully charged LaNi$_{4.7}$Al$_{0.3}$ alloy after 50 cycles is $1.3 \times 10^{-4}$ s$^{-1}$. It is comparable to the average $D/a^2$ value of $8.7 \times 10^{-4}$ s$^{-1}$ obtained using the PSCA method for the same alloy at the same state (cf. Table 4.5). However, the conventional method for $D/a^2$ determination requires long time discharge times (e.g. 700s), and the $D$ value obtained is an average value for the whole discharge process during which the hydrogen concentration changes. Thus the conventional method is
suitable for studying the variation of $D$ vs. number of cycles. The PSCA method gives $D/a^2$ values for specific hydrogen concentrations and is suitable for studying the variation of $D$ vs. hydrogen concentration.
Figure 4.30 A schematic diagram of (top) specimen geometry of the MH negative electrode and (bottom) the hydrogen concentration profile during discharge process in a spherical particle of the alloy.
Figure 4.31 Typical plot of $j(t)$ vs. $t^{1/2}$ gives a straight line. The absolute values of intercept, $I$ (A g$^{-1}$), and slope, $S$ (A g$^{-1}$ s$^{-1/2}$), for this line can be calculated.
Figure 4.32 Potential step chronoamperogram of LaNi$_{4.7}$Al$_{0.3}$ MH electrode at various applied potentials in the saturation state; $T=298$ K. Potential step and potential sequence are respectively:

(a) $+0.5$ V, -0.9323 $\rightarrow$ -0.4323 V; (b) $+0.4$ V, -0.9322 $\rightarrow$ -0.5322 V;
(c) $+0.3$ V, -0.9310 $\rightarrow$ -0.6310 V; (d) $+0.2$ V, -0.9330 $\rightarrow$ -0.7330 V.

The reference electrode is Hg/HgO.
Figure 4.33 (a) The current density data in Figure 4.32 is plotted vs. $t^{-1/2}$ at an applied potential in the saturation state of the LaNi$_{4.7}$Al$_{0.3}$ MH electrode; $T=298$ K. The straight line fits Eq. 4.9.11 in the range 40 to 500 s. Potential step and potential sequence: +0.5 V, -0.9323 → -0.4323 V; The reference electrode is Hg/HgO.
Figure 4.33 (b) The current density data in Figure 4.32 is plotted vs. $t^{-1/2}$ at an applied potential in the saturation state of the LaNi$_{4.7}$Al$_{0.3}$ MH electrode; $T=298$ K. The straight line fits Eq. 4.9.11 in the range 40 to 500 s. Potential step and potential sequence: +0.4 V, -0.9322 $\rightarrow$ -0.5322 V; The reference electrode is Hg/HgO.
Figure 4.33 (c) The current density data in Figure 4.32 is plotted vs. \( r^{-1/2} \) at an applied potential in the saturation state of the LaNi\(_{4.7}\)Al\(_{0.3}\) MH electrode; \( T=298 \) K. The straight line fits Eq. 4.9.11 in the range 40 to 500 s. Potential step and potential sequence: +0.3 V, -0.9310 → -0.6310 V. The reference electrode is Hg/HgO.
Figure 4.33 (d) The current density data in Figure 4.32 is plotted vs. $t^{1/2}$ at an applied potential in the saturation state of the LaNi$_{4.7}$Al$_{0.3}$ MH electrode; $T=298$ K. The straight line fits Eq. 4.9.11 in the range 40 to 500 s. Potential step and potential sequence: +0.2 V, -0.9330 → -0.7330 V. The reference electrode is Hg/HgO.
Figure 4.34 Scanning electron micrograph of the LaNi$_{4.7}$Al$_{0.3}$ alloy particle size after the electrode was completely activated. We assume that the powder consists of spherical particles and the particle size was measured as an average diameter of 6 μm.
Figure 4.35 \( j(t) \) as a linear function of \( t^{-1/2} \) for LaNi\(_{4.7}\)Al\(_{0.3}\) alloy at various initial hydrogen concentrations; \( T=298 \) K. The magnitude of the potential step for every sequence is +0.6 V vs. Hg/HgO reference electrode. The initial hydrogen concentration and the potential sequences are:

1: H/M=0.82, -0.9291 → -0.3291 V; 2: H/M=0.51, -0.9188 → -0.3188 V;
3: H/M=0.28, -0.9179 → -0.3179 V; 4: H/M=0.14, -0.9150 → -0.3150 V;
5: H/M=0.06, -0.8218 → -0.2218 V.
Figure 4.36 Diffusion coefficients ($D$) of hydrogen in LaNi$_{4.7}$Al$_{0.3}$ as a function of initial hydrogen concentration (H/M) at 298 K.
Figure 4.37 Typical plots show that the intercepts on the $j$ axis of the $j(t)$ vs. $t^{-1/2}$ plots are always negative for the discharge reaction of a LaNi$_{4.7}$Al$_{0.3}$ MH electrode and remain almost constant at different applied potentials.
Figure 4.38 (a) The diffusion current of LaNi$_{4.7}$Al$_{0.3}$ alloy as a function of time (solid lines: calculated data).
Figure 4.38 (b)  The diffusion current of Mn$\text{M}_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy as a function of time (solid lines: calculated data).
Figure 4.39  \( D/a^2 \) ratio for LaNi\(_{4.7}\)Al\(_{0.3}\) and Mm\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\) alloys as a function of number of charge/discharge cycles.
4.10 SUMMARY OF MH ELECTRODE PROPERTIES

In this section, the discharge capacity, cycle lifetime and high-rate dischargeability of the four hydride electrodes investigated, including other factors related to electrodes' performance, are reviewed based on the results presented in sections 4.2 to 4.9.

4.10.1 Specific discharge capacity and cycles of metal hydride electrodes

The specific discharge capacity of an MH electrode in a Ni/MH battery decreases with the cycle lifetime. In this study, the specific discharge capacities of the cell using the LaNi$_{4.7}$Al$_{0.3}$, Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$, and Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy electrodes maintain a level of 250 mA h g$^{-1}$ at 100-120 mA g$^{-1}$ discharge current density after 20, 40 and 200 cycles respectively. Thus with regard to cycle lifetime the Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ and Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloys are considerably superior to LaNi$_{4.7}$Al$_{0.3}$ alloy. It is evident that the multi-component electrode alloys are superior to unalloyed AB$_5$ electrode alloys in specific discharge capacity and cycle lifetime.

4.10.2 Factors related to the performance parameters of electrode

Factors such as hydrogen concentration, temperature, number of cycles, and Cu-coating affect the intrinsic performance parameters, which include exchange current density, apparent activation energy, symmetry factor, hydrogen diffusion coefficient, and equilibrium potential.

4.10.2.1 Hydrogen concentration/depth of discharge (DOD)
The above noted parameters are all related to the hydrogen concentration, i.e., depth of discharge (DOD). As the hydrogen concentration decreases, the exchange current density, apparent activation energy, hydrogen diffusion coefficient, and symmetry factor increase, while the equilibrium potential increases with decreasing hydrogen concentration. Thus, comparison of the parameters is valid only for equal hydrogen concentrations.

4.10.2.2 Temperature

The parameters discussed above are for the most part temperature related. As the temperature increases, the exchange current density and symmetry factor increase. The specific discharge capacity reaches a maximum at room temperature for the Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.06})_{5.02} alloy, and the equilibrium potential decreases with increasing temperature. Activation can be considerably improved at higher temperatures.

4.10.2.3 Number of cycles

With increasing number of cycles, the exchange current density, \( D/a^2 \), and the equilibrium potential, increase in the first 30 to 40 cycles, and then attain a stable value, which is the minimum cycles for stabilization.

4.10.2.4 Cu-coating

Cu-coating of the electrode alloys increases the exchange current density and the high-rate dischargeability of the metal hydride electrodes, and decreases the discharge potential, especially for higher discharge current densities. The discharge potentials for
the Cu-coated electrode showed little change with discharge current density differences, indicating the stabilizing effect of Cu-coating on the battery performance.

4.11 APPLICATIONS OF RESULTS OF PRESENT STUDY TO THE IMPROVEMENT OF MH ELECTRODE PERFORMANCE

In this section the results of this investigation are examined for potential applications to improving metal hydride electrode performance and developing new metal hydride electrodes.

4.11.1 Transformation between P-C-T and E-C-T curves

The P-C-T curve is related to the E-C-T curve, and both provide essential information for the selection of MH electrode materials in Ni/MH batteries. The E-C-T curves can be calculated from the P-C-T curves using Eq. 4.3.14, and properties such as theoretical specific discharge capacity and equilibrium potential can be determined. The higher the value of the specific discharge capacity and the lower the value of the equilibrium potential, the better the battery performance.

The electrochemical E-C-T curves for the discharge process can be used to calculate the P-C-T curves, which relate to the hydrogen desorption process for the gaseous reaction. The determination of the P-C-T curves for the gaseous reaction is usually conducted in a Sievert-type apparatus, with a well-sealed reactor and sensitive pressure measurement systems, which limits the accuracy of the pressure measurement. However, the potential can be measured very accurately, and thus the thermodynamic parameters
such as enthalpy and entropy can be determined more accurately than using the conventional $P-C-T$ method.

### 4.11.2 Prediction of the discharge performance of metal hydride electrodes

Eq. 4.2.4 can be used to predict the discharge curves at temperatures different from those at which measurements are made. Eq. 4.2.4 also gives the hydrogen concentration in the metal hydride alloy, i.e., remaining energy in the battery. This is of particular use in the practical application of Ni/MH batteries in electric vehicles, since the remaining energy in the battery (i.e. mileage range of the vehicle) can be obtained simply from a measurement of the discharge potential.

### 4.11.3 Strategies to improve metal hydride electrode performance

Various strategies are available to improve the performance of metal hydride electrodes. These strategies include: substitution of alloy components, modifying of the intrinsic parameters of alloys, and surface treatment.

#### 4.11.3.1 Substitution of alloy components

Substitution of the components of the alloy by other appropriate elements is the most effective method for optimizing electrode performance of Ni/MH batteries. Equilibrium potential, specific discharge capacity, cycle lifetime and exchange current density can be improved using Co and Mm as substitution elements or alloys, e.g., $\text{Mm}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ and $\text{Mm(}\text{Ni}_{0.71}\text{Co}_{0.14}\text{Al}_{0.08}\text{Mn}_{0.06})_{5.02}$ show high
durability compared to LaNi$_{4.7}$Al$_{0.3}$. Thus high-durability alloys can be fabricated at low cost using Mm instead of La, as the amount of Co used is small.

4.11.3.2 Modification of intrinsic parameters of alloys

For optimum performance of MH electrodes, the following suggestions are made to assist in designing compositions. An alloy with the highest exchange current density, the lowest apparent activation energy, the highest hydrogen diffusion coefficient, the smallest value of parameter $B$, and highest value of parameter $\lambda$ is desired. Changes in exchange current density and apparent activation energy can be produced by changes in the alloy composition and/or particle treatment (e.g. coating or ion treatment). Changes in hydrogen diffusion coefficient and the parameters, $B$ and $\lambda$, can be produced by changes in the alloy composition.

High values of exchange current density and hydrogen diffusion coefficient will lead to long cycle lifetimes and high-rate dischargeability. A low value of parameter $B$ will lead to a low value of discharge potential and produce a high value of specific discharge capacity. A high $\lambda$ parameter will produce flat discharge curves, and consequently stable electrochemical performance.

4.11.3.3 Microencapsulation

An effective method to maintain a specific discharge capacity and improve the high-rate dischargeability of Ni/MH batteries is Cu-coating of the MH electrode alloy. The metal coating acts in principally two ways: (1) protects the alloy surface against corrosion, and (2) acts as a micro-current conductor around the alloy particle and thus
speeds up the charge transfer process. In this study, microencapsulation by copper resulted in complete coverage of the intermetallic alloy powder surface, which retards or prevents corrosion or oxidation of both the active material (LaNi$_4$$_7$Al$_0$$_3$ alloy) and the catalyst (Ni). The net result is the higher high-rate dischargeability of the coated alloy electrode compared to that of the un-coated alloy electrode.
CHAPTER 5

CONCLUSIONS

The electrochemical characteristics of LaNi$_{4.7}$Al$_{0.3}$, LaNi$_{4.7}$Al$_{0.3}$ (with Cu-coating), Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$, and Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ alloy electrodes were determined at different hydrogen concentrations, number of cycles and temperatures. A discharge performance model and a new method to determine the hydrogen diffusion coefficient were developed. The main conclusions from this study are as follows:

1. By consideration of the hydrogen-metal reaction kinetics and the hydrogen-hydrogen interactions, a theoretical model is developed for the plateau region of the $P$-$C$ isotherms of hydrogen-absorbing alloys. The model is used to elucidate the hydrogen reaction mechanism in the alloy powders, determine the enthalpies for the hydride decomposition and formation, and give a parameter that accounts for plateau slope differences. The model has potential for selecting the most suitable alloys for application in Ni/MH batteries.

2. Based on electrochemical reaction kinetics, a theoretical model describing the relationship between equilibrium potential and hydrogen concentration is developed for the equilibrium discharge process of a MH electrode. There is agreement between the measured and calculated values. The results of equilibrium discharge measurements at four temperatures are used to derive the slope factor ($\lambda$) of the equilibrium discharge curve for the MH electrode, which is a useful parameter for selecting suitable materials used in the Ni/MH batteries. It can also be used to predict the hydrogen concentration (i.e. remaining energy) at a low discharge current density from the measured value of discharge potential.

3. The relationship between equilibrium potential of a metal hydride electrode reaction and hydrogen pressure in a gaseous hydrogen environment is derived. Using this equation, $E$-$C$-$T$
curves can be accurately transformed to $P$-$C$-$T$ curves and vice versa. This procedure was validated for a LaNi$_{4.7}$Al$_{0.3}$ alloy, where a $P$-$C$-$T$ curve was derived from the $E$-$C$-$T$ curve.

4. The exchange current density for the MH electrode reaction increases with decreasing hydrogen concentration, increasing temperature, and increasing number of charge/discharge cycles. The exchange current density also increases on Cu-coating the LaNi$_{4.7}$Al$_{0.3}$ alloy electrode. The exchange current density of the LaNi$_{4.7}$Al$_{0.3}$ alloy electrode reaches a stable value of 500 mA g$^{-1}$ after 40 cycles. The exchange current density of the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrode stabilizes at 206 mA g$^{-1}$ after 20 cycles. Micro-cracking increases the electrode surface area, resulting in an increase in the exchange current density.

5. The symmetry factor for the MH electrode reaction, obtained from polarization measurements, increases with decreasing hydrogen concentration and with increasing temperature.

6. The apparent activation energy is derived from the polarization measurements, and decreases with increasing hydrogen concentration in the MH electrode reaction. The apparent activation energy for the LaNi$_{4.7}$Al$_{0.3}$ electrode is in the range 15.5 to 22.5 kJ (molH)$^{-1}$, which is lower than that for the dehydriding reaction in the LaNi$_{4.7}$Al$_{0.3}$-H$_2$ system (27.05 kJ (molH)$^{-1}$). This suggests a higher energy ground state for the adsorbed hydrogen in the MH-H$_2$ (gas) system than for the MH-aqueous KOH system.

7. The specific discharge capacity of the cell made using the LaNi$_{4.7}$Al$_{0.3}$, Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ and Mm(Ni$_{0.71}$Co$_{0.14}$Al$_{0.08}$Mn$_{0.06}$)$_{5.02}$ electrodes are 250 mAh g$^{-1}$ at 100-120 mA g$^{-1}$ discharge current density after 20, 40 and 200 cycles.
respectively. Thus the multi-component compositions for electrodes are superior to unalloyed AB₅ alloys in specific discharge capacity and cycle lifetime.

8. The specific capacity of the \( \text{Mm(Ni}_{0.71}\text{Co}_{0.14}\text{Al}_{0.08}\text{Mn}_{0.06})_{5.02} \) alloy electrode reaches a maximum value at 298 K, decreasing to 252 mAh g\(^{-1}\) at 273 K and 246.4 mAh g\(^{-1}\) at 335 K.

9. The Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) alloy electrode shows a much-improved performance compared to the un-coated alloy, as evidenced by a decrease in discharge potential as well as a high-rate capability. The high-rate dischargeabilities are 88.4\% for LaNi\(_{4.7}\)Al\(_{0.3}\) electrode and 99.4\% for Cu-coated LaNi\(_{4.7}\)Al\(_{0.3}\) electrode, which indicates that Cu-coating ensures stable discharge performance and large specific discharge capacity for a relatively large discharge current density.

10. A novel and relatively simple electrochemical method, i.e., Potential Step Chrono-Amperometry (PSCA) method, is developed to determine the hydrogen diffusion coefficient of hydrogen-absorbing alloy particles. The technique is particularly useful in studying the diffusivity of hydrogen in alloy particles with no prior knowledge of hydrogen concentration or surface area. The diffusion coefficient of hydrogen in LaNi\(_{4.7}\)Al\(_{0.3}\) alloy particles is in the range of 3.1\(\times\)10\(^{-14}\) to 8.6\(\times\)10\(^{-13}\) m\(^2\) s\(^{-1}\). The diffusion coefficient decreases with increasing hydrogen concentration for a hydrogen concentration H/M>0.06.

11. At the initial saturation state, when a sufficiently high potential step (larger than +0.2 V vs. Hg/HgO) is applied, the discharge process of the MH electrode is governed solely by hydrogen diffusion in the alloy particles after a short time discharge. At the beginning of the discharge process, current generated is probably due to the existing hydrogen that is adsorbed at the surface of the electrode. At longer discharge times current generation is due to the hydrogen that has diffused from within the solid particles.
12. For optimum performance of MH electrodes the alloy having: highest exchange current density, lowest apparent activation energy, highest hydrogen diffusion coefficient, smallest value of parameter $B$, and highest value of parameter $\lambda$ ($B$ and $\lambda$ can be derived from Eq. 4.2.7) is desired. Changes in the parameters of the exchange current density and apparent activation energy are produced by changes in the alloy composition or particle treatment (e.g., surface coating). Changes in the hydrogen diffusion coefficient and the derived parameters ($B$ and $\lambda$) result from changes in the alloy composition.
CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

Based on the results of the present investigation, the following areas are suggested for future work:

1. The hydrogen diffusion behaviour and diffusion coefficient of different kinds of alloys should be investigated using the newly developed "PSCA" method. The effect of temperature on the hydrogen diffusion coefficient also needs to be investigated to obtain the apparent activation energy for the hydrogen diffusion process in the metal hydride alloys.

2. The effect of microencapsulation (Cu-coating or other kinds of coating) on the electrochemical characteristics of metal hydride electrodes should be investigated more extensively. The reaction mechanisms of metal hydride electrodes with and without microencapsulation should be studied using a cyclic voltammetry method.

3. The electrochemical properties of metal hydride electrodes are closely related to the alloy composition and reaction conditions. More research on alloy composition effects on electrochemical behaviour is required for developing the most efficient electrodes.

4. A mathematical model of the dynamic discharge process of metal hydride electrodes, i.e. the discharge process at large discharge current densities, is required for simulation studies to advance MH electrode development.
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The best fits for the P-C-T curves are obtained by selecting appropriate values for the parameters $A$, $A_0$, and $c_m$, and there is only one value of $A$, $A_0$, and $c_m$ respectively that gives the best fit curve for the experimental points. This is evident from the several examples given below. For a given temperature, $A$ determines the level of the P-C-T curve, $A_0$ the slope of the plateau region and curvature of the $\beta$-region, and $c_m$ the length of the curve and the slope of the plateau region. A change in $A$ affects only the level of the curve, and does not change the shape, whereas a change in $A_0$ or $c_m$ changes the level as well as the shape (curvature) of the curve (particularly in the $\beta$-region) and the slope of the plateau region. For the AB$_5$-type alloy, $c_m$ is taken as approximate 1 because the saturated hydrogen concentration is close to 1, and increasing the value of $c_m$ far above 1 (e.g. 2) tends to lose the $\beta$-region of the curve.
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PUBLICATIONS DERIVED FROM THIS DISSERTATION


PRESENTATIONS

