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Electrochemical properties of metal hydride electrodes.

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ELECTROCHEMICAL PROPERTIES OF METAL HYDRIDE ELECTRODES

By

Jianwen Han

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

Windsor, Ontario, Canada
2000
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The electrochemical characteristics of metal hydride electrodes made from either LaNi$_{4.7}$Al$_{0.3}$ or Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloys (Mm, mischmetal of rare earth elements) are examined in detail. With increasing number of charge/discharge cycles, the metal hydride alloy powders undergo micro-cracking into smaller particles, and thus the specific surface area of the electrode increases, which then influences the kinetic properties of the electrode reactions. The specific surface area increases with increasing number of charge/discharge cycles before reaching a constant value after about 30 cycles. Other parameters, such as the diffusion coefficient of hydrogen, exchange current density, limiting current density, symmetry factor, over-potential and resistance were found to be related to the specific surface area, varying with cycling and also reaching stable values after about 30 cycles. These parameters are all related to the electrochemical properties of metal hydride electrodes. The influences of charge/discharge cycling, hydrogen concentration (or depth of discharge) and temperature on the electrochemical behavior of metal hydride electrodes are discussed in detail. Addition of copper powders to the metal hydride electrodes was found to greatly improve the kinetic properties. Pd-coating of the MmNi$_5$-based alloy powders in the electrodes lead to a significant improvement in resistance to capacity decay. The polarization processes of the electrode reaction included ohmic polarization, activation polarization and concentration polarization. By measuring both the resistances and the over-potentials related to the different polarization processes, the rate-determining steps (RDS) of the metal hydride electrode reactions were determined at different discharge current densities. The thermodynamic and kinetic measurements showed that the
LaNi$_{4.7}$Al$_{0.3}$-based alloy electrodes have much better kinetic properties (higher exchange current density, larger RDS change current density, larger electrode reaction rate constant, lower activation energy and better low temperature behavior), than the MmNi$_5$-based alloy electrodes. However, the MmNi$_5$-based alloy electrodes have higher thermodynamic stability, better electrode reaction reversibility, stronger resistance to capacity decay, more readily become stabilized and have a lower cost than the LaNi$_{4.7}$Al$_{0.3}$-based alloy electrodes.
To My Parents

and

My Lovely Wife
ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. Derek O. Northwood for his supervision, guidance and friendship throughout the course of this study. The author also acknowledges Drs. W. V. Youdelis, A. T. Alpas and R. Aroca for stimulating and informative discussion, Mr. J. W. Robinson for technical assistance and Ms. B. Denomey for assistance in many aspects.

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- A3: LaNi$_{4.7}$Al$_{0.3}$+Ni; A2: LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu
NOMENCLATURE

\(a\)  
spherical radius of electrode alloy particles

\(A\)  
surface area of a metal hydride electrode.

\(C\) or \(C_{th}\)  
specific capacity

\(C_0\)  
initial specific capacity

\(C^b\)  
bulk concentration of the reactant

\(C^s\)  
surface concentration of the reactant

\(C_d\)  
double layer capacitance

\(C_H\)  
hydrogen content

\(C_{\text{max}}\)  
maximum discharge capacity

\(C_N\)  
double layer capacitance of pure mercury in a noble electrolyte  
\((C_N=20 \mu F/cm^2)\)

\(C^b_O\)  
bulk concentration of oxidative state reactant

\(C^s_O\)  
surface concentration of oxidative state reactant

\(C^b_R\)  
bulk concentration of reductive state reactant

\(C^s_R\)  
surface concentration of reductive state reactant

\(d\)  
density of the MH alloy

\(D\)  
diffusion coefficient

\(D_0\)  
pre-exponent factor (or frequency factor) of diffusion coefficient

\(D_H\)  
diffusion coefficient of hydrogen

\(E\)  
electrode potential

\(E_{eq}\)  
equilibrium potential

\(E_{ref}\)  
potential of reference electrode

\(E_{work}\)  
potential of working electrode

\(E_a\)  
activation energy

\(E_{axi}\)  
activation energy for oxidation process of the electrode reaction

\(E_{axi}^o\)  
activation energy for oxidation process when the electrode potential equal to zero (i.e. non-electrode reaction)

\(E_{red}\)  
activation energy for reduction process of the electrode reaction

\(E_{red}^o\)  
activation energy for reduction process when the electrode potential equal to zero (i.e. non-electrode reaction)

\(E^0(H)\)  
standard potential of a hydrogen electrode

\(E^0(H_2O/H_2)\)  
standard potential of a \(H_2O/H_2\) reactant couple

\(E^0(\text{HgO/Hg})\)  
standard potential of a \(\text{HgO/Hg}\) reference electrode

\(F\)  
Faraday's constant

\(\Delta G\)  
change in Gibbs free energy

\(H(a)\)  
adsorbed hydrogen atom

\(H_{ad}\)  
hydrogen atoms on the surface of the MH alloy powder

\(H_{ob}\)  
hydrogen atoms in the bulk of MH alloy powder

\(\Delta H\)  
change in enthalpy

\(\Delta H_e\)  
change in enthalpy calculated from electrochemical method

\(\Delta H_p\)  
change in enthalpy calculated from gaseous hydrogen method

\(l\)  
reaction current (charging or discharging current)

\(l(t)\)  
reaction current as a function of time

\(i\)  
electrode current density
### NOMENCLATURE

\[ i_B \] instantaneous current density at the moment a potential step is applied  
\[ i_c \] charging current density  
\[ i_L \] limiting current density  
\[ i_o \] exchange current density  
\[ i_{o,m} \] mass exchange current density  
\[ i_{o,S} \] area exchange current density  
\[ i_{ox} \] oxidative current density (or oxidation reaction rate)  
\[ i_{rd} \] reduction current density (or reduction reaction rate)  
\[ i_r \] reaction current (or charge transfer current)  
\[ i_\infty \] steady state reaction current after a potential step is applied  
\[ k \] rate constant  
\[ k_0 \] pre-exponent factor for rate constant  
\[ m \] concentration of KOH  
\[ m_O \] transport coefficient of oxidative state reactant  
\[ m_R \] transport coefficient of reductive state reactant  
\[ P_{eq} \] equilibrium pressure  
\[ P_{(H2)} \] equilibrium pressure of hydrogen  
\[ Q \] quantity of electric charge  
\[ R \] gas constant  
\[ R_{ct} \] charge transfer resistance  
\[ R_{diff} \] diffusion resistance (or concentration resistance)  
\[ R_e \] electrode resistance  
\[ R_{ohm} \] ohmic resistance (or solution resistance)  
\[ R_p \] polarization resistance  
\[ S \] specific reaction surface area  
\[ S_{A_{electrode}} \] specific surface area of a electrode  
\[ S_{A_{active}} \] specific surface area of active material in a metal hydride electrode  
\[ S_{A_{oxdprod}} \] specific surface areas of oxidation products in a metal hydride electrode  
\[ S_{real} \] real specific surface area of a metal hydride electrode  
\[ \Delta S \] change in entropy  
\[ \Delta S_{cell} \] change in entropy for unit cell during hydriding reaction  
\[ \Delta S_{MDx} \] formation entropy for unit cell with \( x \) deuterium atoms distributed in different interstices of the cell  
\[ \Delta S_M \] formation entropy for unit cell without any deuterium atoms  
\[ \Delta S_{D2} \] formation entropy for a deuterium molecule.  
\[ \Delta S_e \] change in entropy calculated from electrochemical method  
\[ \Delta S_p \] change in entropy calculated from gaseous hydrogen method  
\[ T \] absolute temperature  
\[ t \] time  
\[ \Delta U \] change in internal energy  
\[ \Delta U_{cell} \] change in internal energy for unit cell during hydriding reaction  
\[ \Delta U_{MDx} \] formation internal energy for unit cell with \( x \) deuterium atoms distributed in different interstices of the cell  
\[ \Delta U_M \] formation internal energy for unit cell without any deuterium atoms  
\[ \Delta U_{D2} \] formation internal energy for a deuterium molecule  
\[ V \] volume of unit cell for a metal hydride electrode
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V$</td>
<td>volume expansion of unit cell for a metal hydride electrode</td>
</tr>
<tr>
<td>$W$</td>
<td>weight of metal hydride alloy</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>reduction symmetry factor</td>
</tr>
<tr>
<td>$\alpha(H_2)$</td>
<td>hydrogen activity</td>
</tr>
<tr>
<td>$a(H_2O)$</td>
<td>water activity</td>
</tr>
<tr>
<td>$\alpha(t)$</td>
<td>reacted fraction</td>
</tr>
<tr>
<td>$\beta$</td>
<td>oxidation symmetry factor</td>
</tr>
<tr>
<td>$\gamma(H_2)$</td>
<td>hydrogen fugacity</td>
</tr>
<tr>
<td>$\delta$</td>
<td>effective thickness of diffusion layer</td>
</tr>
<tr>
<td>$\eta$</td>
<td>over-potential</td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>over-potential of Volmer reaction involving a one-electron transfer</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>over-potential of Tafel reaction</td>
</tr>
<tr>
<td>$\eta_{act}$</td>
<td>activation polarization over-potential</td>
</tr>
<tr>
<td>$\eta_{conc}$ ($\eta_{diff}$, $\eta_m$)</td>
<td>concentration polarization over-potential</td>
</tr>
<tr>
<td>$\eta_{ohm}$</td>
<td>ohmic polarization over-potential</td>
</tr>
<tr>
<td>$\eta_{anode}$</td>
<td>over-potential of an anodic reaction</td>
</tr>
<tr>
<td>$\eta_{cathode}$</td>
<td>over-potential of a cathodic reaction</td>
</tr>
<tr>
<td>$\phi$</td>
<td>electrode potential</td>
</tr>
<tr>
<td>$\phi_{eq}$</td>
<td>equilibrium electrode potential</td>
</tr>
<tr>
<td>$\Delta \phi$</td>
<td>potential step</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 DEVELOPMENT OF NICKEL/METAL HYDRIDE (Ni/MH) BATTERIES

The need for high energy density storage batteries has been growing in recent years. The advent of electric vehicles (EVs), portable computers, cellular phones, and new cordless appliances and tools has made this need even more urgent. Although conventional storage batteries such as nickel-cadmium (Ni/Cd) and lead-acid batteries have been significantly improved in design and packaging in the past several years, there is still a need for improved performance and power density. The innate toxicity of cadmium and lead has also come under scrutiny. The development of EVs requires the development of an advanced battery pack with high energy density, high specific power and long cycle lifetime. In an EV battery pack, it is also necessary to develop a battery management system to monitor the overcharge and overdischarge of each battery module, especially for the lead-acid, Ni/Cd, and lithium-ion batteries.

The use of metal hydrides as active negative electrode materials in rechargeable alkaline batteries has been studied for a long time. Ni/MH batteries have superior specific energy than the other two major aqueous electrolyte systems (lead-acid and Ni/Cd batteries). Although the new rechargeable lithium (Li-ion) batteries have much more specific energy than Ni/MH batteries, their high cost and complexity of safety control limit their application in many areas [1]. Also the overcharge and overdischarge performance of a Ni/MH battery are better than for other battery types.

Extensive research has been done on the Ti-Ni-based (AB- and AB2-type) and LaNi5-based (AB3-type) alloys due to their ability to store large amounts of hydrogen.
Such compounds are used as electrode materials when they meet the requirements of good thermal and electrical conductivity, high electrocatalytic surface activity, and high hydrogen diffusion rate in the bulk of the materials. These properties have to be attained even after a large number of charge/discharge cycles [2]

Two types of metal hydride alloys have been used as negative electrode materials in this study, LaNi$_{4.7}$Al$_{0.3}$ (LaNi$_5$-based) and Mn$_{0.95}$Ti$_{0.05}$Ni$_{1.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ (MnNi$_5$-based). According to William [3], the discharge capacity of LaNi$_5$-based alloy electrode decreases drastically owing to the pulverization of the alloy powder, which takes place both because of expansion of lattice during hydriding and because of the inherent brittleness of the alloy. The capacity decay in the LaNi$_5$-based alloy electrode on cycling also results from segregation of nickel and lanthanum at the surface of MH alloy powder. Sakai et al. [4, 5, 6, 7] have investigated MnNi$_5$-based alloys (Mn, mischmetal) as a low cost negative battery electrode. The replacement of nickel by cobalt and the coating of nickel on the powder surface were also effective in improving the cycle life but caused a decrease in both capacity and high-rate dischargeability. The high-capacity sealed Ni/MH battery had 1.5 to 2 times higher energy density with a longer charge/discharge lifetime and better rate capacity than a high-capacity Ni/Cd battery.

1.2 DESIRED IMPROVEMENTS IN METAL HYDRIDE 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 behavior (related to its high-rate charge/discharge ability) and a lower cost. The performance of a Ni/MH battery is mainly determined by
the metal hydride electrode, i.e. the negative electrode in the battery. Thus, 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

This study was focused on some important parameters that are related to the behavior of the metal hydride electrodes, including fabrication of the electrodes, thermodynamic properties, kinetic properties and other parameters related to the performance of the metal hydride electrodes. The metal hydride electrode alloys studied were limited to two types: 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. LaNi$_{4.7}$Al$_{0.3}$ is a representative of LaNi$_5$-based alloys. It shows high capacity and good kinetic properties, which make it a excellent candidate for studying the relationship between electrochemical behavior and electrode parameters. MnNi$_5$-based alloys are developed as metal hydride electrodes with low cost, high capacity, long cycle lifetime and good stability. The addition of Co, Mn and Al in the alloy can increase the stability, decrease over-potential and decay rate.

1.3.1 Fabrication of metal hydride electrodes

The two metal hydride alloys used in this study are relatively low cost materials. Since the Mn (mischmetal, which is rich in La or Ce) is used for the metal hydride alloy, rather than the pure rare-earth elements, it greatly decreases the cost.

Micro-encapsulation of metal hydride alloy powder with metal Cu or Ni has been found to decrease capacity decay [8], increase thermal conductivity and lead to fast reaction kinetics [9, 10]. However, the micro-encapsulation process is usually complex and increases cost. In this study, rather than micro-encapsulation, a simple way of mixing
Cu powders with metal hydride alloy powders is developed. Pd-coating of MnNi$_3$-based alloy particles of electrode was also investigated.

1.3.2 Measurement of thermodynamic parameters

Thermodynamic properties determine the stability of a metal hydride electrode on hydriding/dehydriding cycling. Two methods were developed to calculate thermodynamic parameters such as enthalpy ($\Delta H$), entropy ($\Delta S$), Gibbs free energy ($\Delta G$) and equilibrium pressure ($P_{eq}$) of the charge/discharge reaction for the metal hydride electrodes.

Method one is a theoretical quantum chemistry calculation, using the program GameSS. It is usually used for calculation of organic compounds. In this study, this program is developed to accommodate intermetallic compounds (or metal crystals), and to calculate the thermodynamic parameters of metal hydride alloys. This method requires a knowledge of the composition of the alloy and the coordinates of all atoms in a unit cell. The parameters that can be calculated from this method includes enthalpy ($\Delta H$), entropy ($\Delta S$), Gibbs free energy ($\Delta G$), internal energy ($\Delta U$), valence state of any atom in the unit and bond energy. This provides a possibility to predict theoretically, rather than determine experimentally, whether an intermetallic compound can be used as a metal hydride electrode material based on its thermodynamic properties.

Method two, called E-C-T method, was initially developed a number of years ago [11, 12, 13, 14]. In this study it is used to calculate thermodynamic parameters of the metal hydride electrode and to analyze the stability and reversibility of the metal hydride electrodes, i.e. through measuring E-C-T (variation of equilibrium potential with
hydrogen concentration at different temperatures) curves, some thermodynamic parameters can be obtained.

1.3.3 Kinetic properties of metal hydride electrodes

The kinetic properties of a metal hydride electrode are the main factors that determine whether an electrode has practical application as a negative electrode in a metal hydride battery. Thus, one of the focuses of this study is the kinetic properties of the metal hydride electrode. In order to develop metal hydride electrodes with improved kinetic performance, e.g. higher reaction rate, lower activation energy, larger rate constant and better properties at low temperatures, the process of the electrode reactions need detailed study. Kinetic properties examined in this research include: the characteristics, such as reaction rates and rate constants, for the different reaction stages in the electrode reactions; activation energies of discharge processes for different reaction stages; and the factors that influence the kinetic properties of the electrodes.

1.3.4 Parameters related to the performance of metal hydride electrodes

There are many factors that influence the performance of a metal hydride electrode. In order to develop commercially viable metal hydride electrodes, all these factors must be investigated to determine whether, and how, they influence the behavior of the electrodes. The parameters examined in this study include: specific surface area; hydrogen diffusion coefficient; exchange current density; symmetry factor; over-potential and resistance.

1.3.4.1 Specific surface area

The specific surface area of a metal hydride electrode has an influence on almost all its properties. It has been suggested that [15] the real specific surface area of an
electrode is one of the two factors that determine the activity of the electrode. The specific surface area of a metal hydride electrode is directly related to the exchange current density, which is also regarded as surface catalytic activity [16], and also to other kinetic properties. The specific surface area is usually measured by the BET method [17]. In this study, an electrochemical method has been developed to measure the specific surface area. This electrochemical method was used to measure specific surface areas for LaNi\(_{4.7}\)Al\(_{0.3}\) and Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\) electrodes. Relationships between the specific surface area and other parameters such as diffusion coefficient, exchange current density, over-potential and resistance of the electrode were established, and then used to improve the performance of a metal hydride electrode.

1.3.4.2 Diffusion coefficient of hydrogen

Besides specific surface area, the diffusion coefficient of hydrogen is the other property that determines the activity of an electrode [15]. The kinetic properties of a metal hydride electrode are influenced significantly by the diffusion behavior of hydrogen. In order to improve the electrochemical performance of a metal hydride electrode, the characteristics of hydrogen diffusion were studied. The diffusion coefficient of hydrogen and the activation energy were calculated. The diffusion process, which usually becomes the rate-determining step in an electrode process, was analyzed. The factors that influence the diffusion behavior, such as particle size and depth of discharge, were examined.

1.3.4.3 Exchange current density

As one of the key kinetic properties, the exchange current density of a metal hydride electrode was examined in detail. The exchange current density can be
considered to be the electrode reaction rate, and is also representative of the reversibility
of the electrode reactions. Thus, increasing the exchange current density of a metal
hydride electrode is considered to be one of the best ways to improve the kinetic
properties. In this study, the factors that determine the exchange current density were
investigated..

1.3.4.4 Symmetry factor and over-potential

The symmetry factor is a parameter that relates activation energy to the over-
potential of a metal hydride electrode. It is also a measure of the symmetry of the
activation barrier. The symmetry factors and over-potentials of LaNi$_{4.7}$Al$_{0.3}$ and
Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrodes were investigated together with the factors
that control these two parameters.

1.3.4.5 Resistance

Decreasing the resistance of a metal hydride electrode system is obviously one of
the more effective ways of increasing the current density of the battery system. The
ohmic resistance, charge transfer resistance and the diffusion resistance were investigated
together with the factors that determine these resistances in a metal hydride electrode.

Overall, the metal hydride electrode with proper specific surface area, larger
hydrogen diffusion coefficient, larger exchange current density, lower over-potential,
proper symmetry factor (closer to 0.5) and smaller resistance has more practical
application as a negative electrode in a metal hydride battery. The main focus of this
study was to try to identify the factors that control the electrochemical performance of a
metal hydride electrode, and to improve the performance of the electrode by
understanding and controlling these factors.
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO HYDROGEN STORAGE MATERIALS AND METAL HYDRIDE BATTERIES

2.1.1 Hydrogen Storage Materials

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 (IMC) or alloy, to form 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 easily be reversed as shown in Eq.2.1.1.

\[ M + \frac{x}{2} H_2 = MH_x \quad (2.1.1) \]

The formation reaction for the metal hydride is an exothermic, and usually spontaneous, reaction, 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.

Based on the crystal structure, hydrogen storage materials can be classified into five groups: AB, AB₂, A₂B, AB₃ and AB₅ (including the multi-component alloys based
on them). Of these, the $\text{AB}_2$ (e.g. ZrV$_2$-based alloys) and $\text{AB}_5$ (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.

The properties of these hydrogen storage materials make them attractive for use in various applications, such as hydrogen fuel storage for vehicles [18, 19, 20], purification and compression of hydrogen [21-25], energy conversion for thermal transformers, heat pumps and refrigerators [24-32], and metal hydride batteries [3, 33]. The metal hydride batteries have been widely developed throughout the world in recent years, and they are the focus of this study.

2.1.2 Nickel/Metal Hydride Rechargeable Batteries

Nickel/metal hydride batteries are a new type of high capacity, rechargeable batteries, which have been developed in recent years. The positive electrodes in these batteries are the same as the nickel electrodes (Ni(OH)$_2$/NiOOH) in sealed nickel-cadmium batteries. Hydrogen storage alloys are used as active negative electrode materials. The electrolyte is a KOH aqueous solution. The application of metal hydride electrodes in electrochemical batteries involves the use of hydrogen as fuel, which is stored in the hydrogen-absorbing electrode. At the surface of such an electrode, hydrogen is either formed by the electrochemical reduction of water, or stored hydrogen is oxidized [3].

Since a metal hydride electrode with high capacity is used instead of a cadmium electrode, the nickel/metal hydride battery has a specific energy of 70-80Wh/kg, which is much higher than nickel-cadmium battery (40-50Wh/kg). Also nickel/metal hydride batteries have other advantages over Ni-Cd batteries such as high charge/discharge rate
capacity, long charge/discharge cycle life, good electrochemical performance for overcharge and over-discharge, absence of a memory effect, low temperature capability and environmental friendliness (non-polluting nature) [3].

2.1.2.1 History of Nickel/Metal Hydride Batteries

The application of hydrogen storage materials in rechargeable batteries began in the 1970's, with research and development of the nickel/hydrogen battery. The nickel/hydrogen battery was developed for energy storage in satellites. It had advantages over both fuel cells and sealed nickel-cadmium batteries. The positive electrode of the nickel/hydrogen battery is the same as the nickel electrode (Ni(OH)₂/NiOOH) used in a sealed nickel-cadmium battery. The negative electrode is Pt, which is the same as that in a fuel cell, and the electrolyte is also a KOH aqueous solution. In the process of charging, hydrogen is produced at the negative electrode, and then is stored in the battery. In the process of discharging, the hydrogen, which is stored in the battery, is oxidized with the aid of the Pt catalyst, which is the negative electrode. The nickel/hydrogen battery has a number of advantages including high specific energy (about 60wh/kg), long cycle lifetime and good performance in both over-charge and over-discharge. However, there are a number of significant disadvantages including: high hydrogen pressure in the battery after charging (about 3~5 MPa), and thus it is also called the high-pressure nickel/hydrogen battery, and a high cost due to the use of the expensive metal Pt. It was through research aimed at overcoming these disadvantages that the metal hydride electrodes found application in nickel/metal hydride batteries.

Since hydrogen storage materials have the characteristic of absorbing/desorbing hydrogen through gas-solid reactions, Earl and coworkers [34, 35] put a LaNi₅ alloy
directly in the case of nickel-hydrogen battery to absorb the hydrogen produced during charging, thus decreasing the hydrogen pressure in the battery to about 0.3–0.5 MPa. At the same time Justi and his coworkers’ research [36, 37] had shown that certain hydrogen storage materials, e.g. LaNi₅ and Ti-Ni, act as electrocatalyst for the anodic oxidation of hydrogen. This discovery promoted researchers to think that hydrogen storage materials might be directly used as the negative electrodes in batteries instead of the expensive metal Pt. Research into the electrochemical characteristics of hydrogen absorption/desorption was initiated and attempts were made to use hydrogen storage materials as negative electrodes [38].

Markin and other investigators [39, 40, 41] developed a new type low-pressure nickel/hydrogen battery, i.e. nickel/metal hydride battery (Ni/MH battery), in which the hydrogen storage material LaNi₅ was used as negative electrode instead of Pt electrode, and the hydrogen pressure was thereby decreased greatly. During charging of the Ni/MH battery, hydrogen atoms which are produced at the negative electrode (i.e. the LaNi₅ electrode) are absorbed instantly by the hydrogen storage electrode to form a metal hydride. Since both the hydrogen storage materials and their hydrides are good conductors, the hydrogen atoms released from the metal hydride upon discharge are anodically oxidized at the same electrode and the hydrogen pressure in the battery is therefore greatly reduced.

2.1.2.2 Characteristics of Metal Hydride Electrodes

(1) Electrode Reactions

In a Ni/MH battery the hydrogen storage material is used as the negative electrode, and during the process of charging, the KOH aqueous solution is electrolyzed
to produce hydrogen atoms at the surface of the negative electrode. The hydrogen atoms are instantly \textit{adsorbed} by the electrode, then diffuse into the bulk of the electrode as \textit{absorbed} state and react with the alloy to form a metal hydride (MH\textsubscript{x}). This is the process of hydrogen storage. Upon discharging, the reverse reaction takes place and the absorbed hydrogen atoms are released from the metal hydride electrode and oxidized to form water. Therefore the metal hydride can be used as an electrode which can perform both the charge and discharge processes through the absorption or desorption of hydrogen.

The charge/discharge process are described in the following reactions:

\begin{equation}
M + H_2O + e^- \xrightarrow{\text{charge}} M - H_{ad} + OH^- \tag{2.1.2}
\end{equation}

\begin{equation}
M - yH_{ad} \xrightarrow{\text{discharge}} M - yH_{ab} \tag{2.1.3}
\end{equation}

\begin{equation}
M - yH_{ab} \xrightarrow{\text{discharge}} MH_y \tag{2.1.4}
\end{equation}

\begin{equation}
(x-y)H + MH_y \xrightarrow{\text{charge}} MH_x \tag{2.1.5}
\end{equation}

The total electrode reactions are:

\begin{equation}
M + xH_2O + xe^- \xrightarrow{\text{charge}} MH_x + xOH^- \tag{2.1.6}
\end{equation}
where $H_{ad}$ and $H_{ab}$ denote the hydrogen atoms on the surface of the MH alloy powders (adsorbed) and in the bulk of MH alloy (absorbed), respectively. Eq.2.1.2 reflects the charge transfer process at the interface between the MH alloy powder and the electrolyte. Eq.2.1.3 relates to the diffusion of hydrogen from the powder surface to the bulk of the MH alloy electrode. Eq.2.1.4 is the chemical reaction to form a metal hydride. Eq.2.1.5 is related to the phase transition. The total electrode reaction is shown in Eq.2.1.6. The electrolyte in the battery is usually a 6M KOH aqueous solution. According to this reaction, the equilibrium potential of the metal hydride electrode is very close to the equilibrium potential of a hydrogen electrode in an alkaline aqueous solution with the same concentration.

Hydrogen storage materials, which can potentially be used as metal hydride electrodes, must have the following properties [42]:

1. Stability in an alkaline electrolyte solution, with or without cycling, i.e. good corrosion resistance and long cycle life;

2. High electrochemical capacity (in mAhg$^{-1}$);

3. Suitable equilibrium hydrogen pressure, generally $10^{-4}$ to $10^{-1}$ MPa within a working temperature range of -20°C to 60°C;

4. Good surface activity and kinetic properties (e.g. high rate capacity);

5. High charge retention (high percentage charge retained after 14 or 21 days);


2. Electrochemical capacity

The electrochemical capacity of a metal hydride electrode is dependent on the hydrogen content of the metal hydride. Eq.2.1.6 shows that each absorbed hydrogen atom
corresponds to the storage of one electron. This results in a simple relation, which allows us to calculate the theoretical capacity per unit weight \( C_{th} \) for a hydrogen storage material. An \( AB_n \) type material is given as an example in Eq.2.1.7 [3].

\[
C_{th} = \frac{xF}{3.6M_{AB_n}} \text{mAh}^{-1}
\]  

(2.1.7)

where \( F \) is the Faraday constant, \( M_{AB_n} \) is the molecular weight of the \( AB_n \) compound and \( x \) is the number of hydrogen atoms per \( AB_n \) unit. For LaNi\(_5\), where the maximum value of \( x \), as determined by hydrogen gas desorption measurements is 6 [43], the theoretical storage capacity is calculated to be 372 mAh\(^{-1}\). However, the discharge capacity (the real capacity) of a metal hydride electrode obtained in discharge testing is usually less than this theoretical value. The discharge capacity of a metal hydride electrode is dependent on the characteristics of the electrode material such as hydrogen storage reversibility, thermodynamic stability, temperature, pressure and discharge rate. At lower discharge rates, for electrode materials with excellent hydrogen storage reversibility, e.g. LaNi\(_5\) and LaNi\(_4\)Cu, the discharge capacities are close to the theoretical values. For electrode materials with poor reversibility, the discharge capacities are lower than the theoretical value. For example, the theoretical capacities of Ti\(_{0.8}\)Zr\(_{0.2}\)Ni\(_{1.0}\) and ZrNi electrodes are 312 mAh\(^{-1}\) and 492 mAh\(^{-1}\), but their measured discharge capacities are 240 mAh\(^{-1}\) and 26 mAh\(^{-1}\), respectively [44].

(3) **Cycle lifetime**

The cycle lifetime of a metal hydride electrode is one of the most important characteristics that determine whether or not it can be used in 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 when the discharge capacity of the electrode decreases to a certain value. The half-life is often used as an evaluation of the cycle lifetime [44]. When the discharge capacity of the electrode decreases to half of its maximum capacity (usually the first cycle capacity after activation), the number of cycles that electrode has undergone 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 times for different metal hydride systems [3, 44, 45, 46]. Although some metal hydride electrodes, such as LaNi$_5$ and LaNi$_4$Cu, have high initial discharge capacities which are very close to their theoretical ones (about 370 mAhg$^{-1}$), the capacities decline 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. Now many multi-component electrodes with excellent characteristics have been developed which have cycle lifetimes long enough for commercial battery application.

2.1.2.3 Electrode Alloys

There are several types of hydrogen storage materials. However, only some of them have the required characteristics to be practical metal hydride electrode alloys. Up to now, AB$_5$ type alloys are the most successful. Although their capacities are not the largest, a stable, porous and corrosion resistant RE(rare-earth)-oxide surface layer guarantees that the alloy electrodes have good and balanced overall properties. Since the
RE-oxide surface layer protects the alloy from further oxidation, this reduces the
activation of the materials for hydrogen absorption. AB₂ alloys have higher hydrogen
capacities than the AB₅ type alloys. Zr and Ti, which are typical constituents of AB₂-
based alloys, both produce a thick, dense, passive oxide surface. Addition of V or Mn
makes the oxide porous, but these oxides are soluble in the KOH electrolyte, making the
electrode unstable. AB and A₂B alloys do not have any particular advantages, yet have
the same draw-backs as the AB₂ alloys [42].

2.1.2.4 Reaction Characteristics of Nickel/Metal Hydride Batteries

In a nickel/metal hydride battery, the positive electrode is the same as the nickel
electrode (sintered or porous) in a nickel-cadmium battery, and the negative electrode is
the metal hydride. The electrode reactions for the positive and negative electrodes are as
follows:

Positive electrode reaction:

\[
_{\text{charge}} \quad \frac{\text{Ni(OH)}_2 + \text{OH}^-}{\text{discharge}} \quad \text{NiOOH} + \text{H}_2\text{O} + e^- 
\]

(2.1.8)

Negative electrode reaction:

\[
_{\text{charge}} \quad \frac{M + \text{H}_2\text{O} + xe^-}{\text{discharge}} \quad MH_x + x\text{OH}^- 
\]

(2.1.9)

Therefore the overall battery reaction is:

\[
_{\text{charge}} \quad \frac{M + x\text{Ni(OH)}_2}{\text{discharge}} \quad MH_x + x\text{NiOOH} 
\]

(2.1.10)
where M and MH$_2$ stand for the hydride forming compound and the metal hydride, respectively. For both electrodes, 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 OH$^-$ and H$_2$O. This permits a simple and compact construction. As illustrated in Eq.2.1.8 to 2.1.10, charging and discharging of a nickel/metal hydride battery can be viewed as a mere pumping 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 nickel-cadmium battery [3]. In a nickel/metal hydride battery, the storage capacity of the hydride electrode exceeds that of the nickel electrode [3]. Oxygen, evolved at the nickel electrode during discharging, will be reduced to form water at the metal hydride electrode. The hydrogen gas evolved at the nickel electrode during over-discharging, has no negative effect on the cell performance since it will be absorbed by, and oxidized at, the hydride 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 nickel/metal hydride batteries. Furthermore, nickel/metal hydride batteries do not contain the poisonous heavy metals cadmium and mercury. This is particularly important for the widespread use of small batteries.

2.1.3 Typical Hydrogen Storage Materials
The intermetallic compounds used as hydrogen storage materials are usually divided into two groups, namely binary compounds (includes pseudo-binary compounds), e.g. AB, A₂B, AB₂, AB₃, AB₅, and multi-component compounds. The pure binary compounds are rarely used as metal hydride electrodes, rather, the pseudo-binary, binary-based and multi-component compounds find application as metal hydride electrodes. A general comparison of the composition and structure of the binary intermetallic compounds and their hydrides has been made by Shenoy and a summary is given in Tables 2.1.1 to 2.1.5 [47].

The metal hydrides made from equiatomic binary (AB) intermetallic compounds are listed in Table 2.1.1. The most studied compound in this class of material is FeTi and its hydrides. It is one of the most important materials for practical application, because of its isotherm characteristics, chemical stability on cycling, and cost.

Of the A₂B type intermetallic compounds listed in Table 2.1.2, Mg₂Ni has been most frequently cited for its high hydrogen storage capacity.

Table 2.1.3 lists the intermetallic compounds of AB₂ type. All of the compounds of the form AB₂ that have been investigated have a Laves phase structure, either the cubic (MgCu₂-type, or C15 type) or the hexagonal (MgZn₂-type, or C14 type) [42, 47]. For AB₂ type compounds, ZrV₂-based and TiCr₂-based alloys (usually formed by partial substitution with other elements such as Fe, Mn, Co, V or Cr) are used more often as metal hydride electrodes than the pure binary alloys, ZrV₂ and TiCr₂.

All the AB₃ compounds listed in Table 2.1.4 have the PuNi₃ structure, in which the A atoms occupy two crystallographically inequivalent sites while the B atoms occupy five inequivalent sites [47]. However, AB₃ compounds are rarely used as metal hydride
electrodes in practical applications because of their electrochemical properties, isothermal characteristics, chemical stability on cycling, and cost.

Table 2.1.5 lists the AB₅ hydrogen storage alloys. All these alloys have the CaCu₅ structure. LaNi₅-based alloys, including MmNi₅-based alloys (Mm denotes Mischmetal), are very important hydrogen storage materials, and are most commonly used as metal hydride electrodes because of their good electrochemical behavior.

Table 2.1.1 Typical hydrides of AB compounds

<table>
<thead>
<tr>
<th>Intermetallic Compound</th>
<th>Metal Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTi</td>
<td>FeTiH₁₀,₁₁</td>
<td>CsCl</td>
</tr>
<tr>
<td>CuTi</td>
<td>CuTi₁₀,₉₇</td>
<td>CuTi</td>
</tr>
<tr>
<td>LaNi</td>
<td>LaNiH₂₆,₃₆</td>
<td>CrB</td>
</tr>
<tr>
<td>HfCo</td>
<td>HfCoH₃₂</td>
<td>CsCl</td>
</tr>
<tr>
<td>HfNi</td>
<td>HfNiH₁₀,₂₆</td>
<td>CrB</td>
</tr>
<tr>
<td>ThCo</td>
<td>ThCoH₁₂,₆−₁₂</td>
<td>CrB</td>
</tr>
<tr>
<td>ThNi</td>
<td>ThNiH₃₆</td>
<td>ThNi</td>
</tr>
<tr>
<td>ZrCo</td>
<td>ZrCoH₂₆,₅</td>
<td>CsCl</td>
</tr>
<tr>
<td>ZrNi</td>
<td>ZrNiH₂₆,₅</td>
<td>CrB</td>
</tr>
<tr>
<td>Ti(Fe₁₋ₓCoₓ)</td>
<td>Ti(Fe₁₋ₓCoₓ)H₁₀,₀</td>
<td>CsCl</td>
</tr>
<tr>
<td></td>
<td>Ti(Fe₁₋ₓCoₓ)H₂₀,₀</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2.1.2 Typical hydrides of A₂B compounds

<table>
<thead>
<tr>
<th>Intermetallic Compound</th>
<th>Metal Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg₂Ni</td>
<td>Mg₃NiH₄</td>
<td></td>
</tr>
<tr>
<td>Ti₂Cu</td>
<td>Ti₃CuH₂.58</td>
<td>Ti₃CuH₂.74</td>
</tr>
<tr>
<td>Hf₂Fe</td>
<td>Ti₂Ni</td>
<td>Hf₂FeH₃.0</td>
</tr>
<tr>
<td>Hf₂Mn</td>
<td>Ti₂Ni</td>
<td>Hf₃FeH₃.0</td>
</tr>
<tr>
<td>Hf₂Co</td>
<td>Ti₂Ni</td>
<td>Hf₂CoH₃.6</td>
</tr>
<tr>
<td>Hf₂Zn</td>
<td>Ti₂Ni</td>
<td>Hf₂ZnH₂.04</td>
</tr>
<tr>
<td>Hf₂Cu</td>
<td>MoSi₂</td>
<td>Hf₃CuH₂.9</td>
</tr>
<tr>
<td>Hf₂Ni</td>
<td>CuAl₂</td>
<td>Hf₂NiH₃.1</td>
</tr>
<tr>
<td>Zr₂Co</td>
<td>CuAl₂</td>
<td>Zr₂CoH₄.5</td>
</tr>
<tr>
<td>Zr₂Ni</td>
<td>CuAl₂</td>
<td>Zr₂NiH₄.5</td>
</tr>
</tbody>
</table>

### Table 2.1.3 Typical hydrides of AB₂ compounds

<table>
<thead>
<tr>
<th>Intermetallic Compound</th>
<th>Metal Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RFe₂ (R=Y,Dy,Er)</td>
<td>RFe₂H₂</td>
<td>Mg₂Cu</td>
</tr>
<tr>
<td></td>
<td>RFe₂H₃.5</td>
<td>Mg₂Cu</td>
</tr>
<tr>
<td></td>
<td>RFe₂H₄.1</td>
<td>o.r.</td>
</tr>
<tr>
<td>ErMn₂</td>
<td>ErMn₂H₄.0</td>
<td>MgZn₂</td>
</tr>
<tr>
<td></td>
<td>ErMn₂H₄.6</td>
<td>MgZn₂</td>
</tr>
<tr>
<td>DyT₂ (T=Co,Mn,Ni,Fe)</td>
<td>DyT₂H₂.0</td>
<td>MgZn₂</td>
</tr>
<tr>
<td></td>
<td>DyT₂H₃.4</td>
<td>MgZn₂</td>
</tr>
<tr>
<td></td>
<td>DyT₂H₄ (x&gt;4)</td>
<td>MgZn₂</td>
</tr>
<tr>
<td>LaNi₂</td>
<td>LaNi₂H₄.1-4.5</td>
<td></td>
</tr>
<tr>
<td>GdNi₂</td>
<td>GdNi₂H₄.35</td>
<td></td>
</tr>
<tr>
<td>EuRh₂</td>
<td>EuRh₂H₅.5</td>
<td>MgCu₂</td>
</tr>
<tr>
<td>ZrMn₂</td>
<td>ZrMn₂H₃.0</td>
<td>MgZn₂</td>
</tr>
<tr>
<td>ZrV₂</td>
<td>ZrV₂H₄.5</td>
<td>MgCu₂</td>
</tr>
<tr>
<td>TiCr₁.₈</td>
<td>TiCr₁.₈H₂.₄</td>
<td>o.r.</td>
</tr>
<tr>
<td></td>
<td>TiCr₁.₈H₃.₄</td>
<td>o.r.</td>
</tr>
<tr>
<td>CaNi₂</td>
<td>CaNi₂H₃.₄₄</td>
<td>MgCu₂</td>
</tr>
<tr>
<td>ScFe₂</td>
<td>ScFe₂H₂.₀</td>
<td>MgZn₂</td>
</tr>
<tr>
<td>RT₂ (R=Gd,La;T=Rh,Ru)</td>
<td>RT₂H₃.₂-4.₉</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2.1.4 Typical hydrides of AB$_3$ compounds

<table>
<thead>
<tr>
<th>Intermetallic Compound</th>
<th>Metal Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF$_{e3}$ (R=Gd,Dy,Ho,Tb,E)</td>
<td>PuNi$_3$</td>
<td>GdFe$<em>3$H$</em>{3.1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DyFe$<em>3$H$</em>{3.0}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HoFe$<em>3$H$</em>{3.6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TbFe$<em>3$H$</em>{4.2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ErFe$<em>3$H$</em>{2.7}$</td>
</tr>
<tr>
<td>RCo$_3$ (R=Nd,Gd)</td>
<td>PuNi$_3$</td>
<td>RCo$<em>3$H$</em>{2.4}$</td>
</tr>
<tr>
<td>DyCo$_3$</td>
<td>PuNi$_3$</td>
<td>DyCo$<em>3$H$</em>{1.0}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DyCo$<em>3$H$</em>{1.8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DyCo$_3$H$_x$ (x~3.5)</td>
</tr>
<tr>
<td>ErCo$_3$</td>
<td>PuNi$_3$</td>
<td>ErCo$<em>3$H$</em>{1.17}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ErCo$<em>3$H$</em>{1.67}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ErCo$<em>3$H$</em>{3.67}$</td>
</tr>
<tr>
<td>YNi$_3$</td>
<td>PuNi$_3$</td>
<td>YNi$<em>3$H$</em>{4.0}$</td>
</tr>
<tr>
<td>LaNi$_3$</td>
<td>PuNi$_3$</td>
<td>LaNi$<em>3$H$</em>{2.8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaNi$<em>3$H$</em>{5.0}$</td>
</tr>
<tr>
<td>CeNi$_3$</td>
<td>PuNi$_3$</td>
<td>CeNi$<em>3$H$</em>{4.1}$</td>
</tr>
<tr>
<td>CaNi$_3$</td>
<td>PuNi$_3$</td>
<td>CeNi$<em>3$H$</em>{4.1}$</td>
</tr>
</tbody>
</table>

### Table 2.1.5 Typical hydrides of AB$_5$ compounds

<table>
<thead>
<tr>
<th>Intermetallic Compound</th>
<th>Metal Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi$_5$</td>
<td>CaCu$_5$</td>
<td>LaNi$<em>5$H$</em>{6.0}$</td>
</tr>
<tr>
<td>LaCo$_5$</td>
<td>CaCu$_5$</td>
<td>LaCo$<em>5$H$</em>{3.35}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaCo$<em>5$H$</em>{4.2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaCo$<em>5$H$</em>{6.0}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaCo$<em>5$H$</em>{9.0}$</td>
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<tr>
<td>NdCo$_5$</td>
<td>CaCu$_5$</td>
<td>NdCo$<em>5$H$</em>{2.8}$</td>
</tr>
<tr>
<td>YCo$_5$</td>
<td>CaCu$_5$</td>
<td>YCo$<em>5$H$</em>{3.0}$</td>
</tr>
<tr>
<td>ThFe$_5$</td>
<td>CaCu$_5$</td>
<td>ThFe$_5$H$_x$ (x~1)</td>
</tr>
<tr>
<td>CaNi$_5$</td>
<td>CaCu$_5$</td>
<td>CaNi$_5$H$_x$ (x~1.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaNi$_5$H$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaNi$<em>5$H$</em>{4.5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaNi$<em>5$H$</em>{5.7}$</td>
</tr>
<tr>
<td>LaNi$_{5-x}$Al$_x$</td>
<td>CaCu$_5$</td>
<td>LaNi$_{5-x}$Al$<em>x$H$</em>{4.0}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaNi$_{5-x}$Al$<em>x$H$</em>{5.0}$</td>
</tr>
</tbody>
</table>
2.2 METAL HYDRIDE 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, MlNi₅-based alloys, MmNi₅-based alloys and MmBₓ-based alloys, where Ml donates 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 exhibited good electrochemical properties. Also Mg-based alloys are seen as promising metal hydride electrode alloys [48, 49], although they are only in the early experimental stage. They show excellent potential in terms of their high capacity and low cost. Table 2.2.1 summarizes the commercial alloys that have found application as metal hydride electrodes [42]:
The AB₅, AB₂ Laves phase alloys, Ti-Ni based alloys and A₂B (Mg-based) alloys are discussed in more detail in sections 2.2.1, 2.2.2, 2.2.3 and 2.2.4, respectively.

### 2.2.1 Development of AB₅ type alloys

#### 2.2.1.1 LaNi₅-based alloys

It was found that the volume expansion of the metal hydride electrode during hydriding is one of the main reasons for capacity decay [3]. Van Mal, Buschow and Kuijpers [50] found that even a partial substitution of Co for Ni in LaNi₅ results in a considerable reduction in the expansion of the unit cell for the metal hydride electrode ($\Delta V/V=24\%$ for LaNi₅ and $\Delta V/V=13\%$ for LaNi₂Co₃ [42]). The volume expansion of the corresponding electrode LaNi₅₋ₓCoₓ (x=0–3) decreases with increasing cobalt content, and the stability of the electrode is also improved. When a small amount of Al or Si is
also used to substitute for some of the nickel in the electrode, the volume expansion is further reduced. Also, if Nd or Ti is used to substitute for some of the La in the electrode alloy, a low expansion (12.8\%-14.6\%) and improved stability of the electrode can be obtained during hydriding. Willems reported that La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1} or La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1} were the optimum compositions for an electrode [3]. Such an electrode has an initial discharge capacity of 290 mA\text{h}^{-1}, which is slightly less than that for LaNi_{5} electrode, but the capacity only decays 30\% after 1000 charge/discharge cycles.

2.2.1.2 MnNi_{5}-based and MmNi_{5}-based alloys

Since pure lanthanum is expensive, new electrode materials have been developed in which mischmetal is used instead of pure lanthanum. The mischmetal used in the electrode is either rich in lanthanum (Ml) or rich in cerium (Mm). This type of electrode shows good electrochemical properties as the negative electrode in a nickel/metal hydride battery at a much lower cost than pure lanthanum.

A MnNi_{5} alloy, with a composition 43-51 wt.% La, 3-5 wt.% Ce, 9-11 wt.% Pr, 27-41 wt.% Nd, has the advantages such as quick activation, lower hysteresis, higher discharge capacity, good dynamic properties and lower cost (only 20\% of pure lanthanum) than LaNi_{5} [51]. When the Ni in the MnNi_{5}-based alloy is partially substituted for by Co, Mn, Ti or Al, the electrochemical properties of the electrode are further improved. A MmNi_{5}-based alloy electrode with the composition of Ml(NiCoMnTi)_{5} has a discharge capacity of 303 mA\text{h}^{-1}, and the capacity decreases only 23\% after 1000 charge/discharge cycles[52]. It was reported that the substitution of Ni by Mn, Al, Cu and Co all lead to a lowering of the hydrogen equilibrium pressure [42]. Mn is typically used as it lowers the equilibrium pressure without causing a significant reduction in storage
capacity. However, Mn diffuses faster than La within the alloy and forms a hydroxide on the surface which readily dissolves in the electrolyte. Also, a large Mn addition increases the internal strain of the alloy during hydriding and the alloy readily pulverizes on cycling. Co is effective in suppressing manganese hydroxide formation and is also very effective in prolonging the cycling life. However, it reduces the hydrogen storage capacity of the alloy. An electrode with a composition of Ml_{0.95}Ti_{0.03}Ni_{3.83}Co_{0.45}Mn_{0.35}Al_{0.35} has a discharge capacity of 281 mAgh^{-1}, exhibits a very slow capacity decay upon cycling, and shows excellent electrochemical behavior in nickel/metal hydride batteries [53, 54, 55].

When the Ni in an MmNi_{5} alloy (Mm consisting of 26-30 wt.% La, 50-52 wt.% Ce, 4.7-5 wt.% Pr and 13-15 wt.% Nd) is partially replaced with Co, Al or Mn, the electrochemical behavior is improved [4, 56, 57, 58]. Good electrochemical properties have been found for electrodes with the following compositions: MmNi_{3.5}Co_{0.7}Al_{0.8} (discharge capacity of 250 mAgh^{-1} and 10% capacity decay after 2000 cycles) [4, 57], MmNi_{3.5}Co_{0.75}Mn_{0.4}Al_{0.3} (220 mAgh^{-1}) and MmNi_{3.8}Mn_{0.4}Al_{0.3}Co_{0.5} (250 mAgh^{-1}) [59].

2.2.1.3 MmB_{x} alloys

Non-stoichiometric MmB_{x} alloys have been developed by the Sanyo Battery Co.[60]. In these MmB_{x} alloys, B=(Ni-Mn-Co-Al), the Ni:Mn:Co:Al ratio = 0.64 : 0.2 : 0.04 : 0.12, and 3.85 \leq x \leq 5. When x< 3.85 the stable phases (Ce_{2}Ni_{7} and CeNi_{3}) are formed with a corresponding capacity decay. Where x=4.17~5, the capacity increases with decreasing value of x. An alloy MmB_{4.75} has a good capacity and long cycle life, with a capacity decay after 500 cycles of only 3% [42].

2.2.2 Development of AB_{2}-based alloys
The main AB₂ Laves phase hydrogen storage alloys are the ZrM₂-based alloys (M=V, Cr, Mn, Fe, Co, Mo, Al) [61]. Of these, the ZrV₂-based, ZrCr₂-based and ZrMn₂-based alloys have been found to have large hydrogen absorption/desorption capacities (H/M=5). There are three kinds of possible crystal structures for the Laves phase alloys, namely the cubic MgCu₂ structure (C15 type), the hexagonal MgZn₂ structure (C14 type) and the MgNi₂ structure (C36 type). Although the binary Laves phase alloys ZrV₂, ZrCr₂ and ZrMn₂ have large hydrogen storage capacities, their hydrides are too stable for practical usage [42]. It has been found [62, 63] that elemental substitution leads to more desirable thermodynamic properties and large hydrogen capacities for these alloys. These substitutions can be carried out in a number of ways [42]:

1. Zr is partially substituted by Ti or Ho. e.g. Zr₀.₇Ti₀.₁Mn₂, Zr₀.₂Ho₀.₈Co₂.
2. V, Cr or Mn are substituted by the transitional elements Ni, Fe, Co, Mo, Al, V or Mn. e.g. ZrMn₁.₂Fe₀.₈.
3. Elements A and B are substituted simultaneously. e.g. Zr₀.₉Ti₀.₁Cr₀.₆Fe₁.₄.
4. Use excess B to form a non-stoichiometric alloy. e.g. ZrCrFe₀.₈, ZrCrFeNi₀.₈.

Various Zr-based alloys have been developed such as Zr-Cr-Ni, Zr-Mn-Cr-Ni, Zr-Mn-V-Ni, Zr-Co-V-Ni, Zr-Ti-Mn-V-Fe and Zr-Ti-Mn-V-Co [62, 63, 64]. Specific examples are as follows [42]:

(a) Ti₁₇Zr₁₆V₂₂Ni₃₉Cr₇, which was developed by the Ovonic Battery Co., U.S.A, has a discharge capacity of 350–400 mA·h·g⁻¹, and a cycle life at 1C, 100% DOD (depth of discharge), i.e. discharge to end point within 1 hour, up to 450 cycles. However, there are some disadvantages to this alloy, including difficult activation, large self-discharge and high internal pressure when used in a sealed battery [65].
(b) ZrCr$_{0.3}$Ni$_{1.2}$ and ZrMn$_{0.3}$Cr$_{0.2}$V$_{0.3}$Ni$_{1.2}$ alloys have discharge capacities of about 350 mAhg$^{-1}$ (Electrolyte, s.g. 1.30 KOH; alloy, 1 g; charge, 0.1A, 5.5h; discharge, 0.05A, 0.8V cut-off) [63].

(c) A Zr$_{0.5}$Ti$_{0.5}$(V$_{0.375}$Ni$_{0.625}$)$_2$ alloy has a discharge capacity of 370 mAhg$^{-1}$, and substitution of Ni by Fe and Cr increases the cycle life [66].

Overall, the AB$_2$-type electrode alloys have the following advantages and disadvantages [42].

Advantages.

(a) High discharge capacity. The discharge capacity of AB$_2$-type electrode alloys is as high as 350–400 mAhg$^{-1}$, which is much higher than for AB$_5$ type alloys where the average discharge capacity is 250 mAhg$^{-1}$.

(b) High gaseous state oxidation resistance. As a thick imperious oxide film is usually formed on the surface of AB$_2$ particles, sintering in a protective atmosphere is employed in the fabrication of electrodes. As there is no organic binder present in the sintered electrodes, the electrode is better suited to high current rate operation.

(c) Wide range of compositions. Many elements are suitable for the A and B components, and many elemental substitutions can be made for both A and B components. This makes it much easier to design alloys with the desired performance characteristics.

Disadvantages.

(a) The P-C-Isotherms of AB$_2$-type alloys are usually quite steep with no distinct pressure plateau. The sloping isotherms lead to large pressure changes in a sealed cell on charging and discharging.
(b) Both Zr and Ti form a dense, imperious oxide film. This makes the alloy hard to activate. Even when V or Mn is added to render the surface oxide porous, the film is unstable, as the V and Mn oxides are easily dissolved on cycling.

(c) As many phases are present in the alloy, micro-cells may be formed on the surface leading to high self-discharge or capacity decay.

2.2.3 Development of Ti-Ni-based alloys

According to the phase diagram for Ti-Ni, there are three different compounds formed between Ti and Ni, namely Ti$_2$Ni, TiNi and TiNi$_3$. Gutjahr's [67] research showed that only Ti$_2$Ni and TiNi can absorb hydrogen. Ti$_2$Ni can form four different hydrides, Ti$_2$NiH$_{0.5}$, Ti$_2$NiH, Ti$_2$NiH$_2$ and Ti$_2$NiH$_{2.5}$. However TiNi can only form one hydride, TiNiH. The maximum volume expansion for the Ti-Ni intermetallic compounds on hydriding is about 17%. It was also found that if Ti$_2$Ni and TiNi are mixed in a certain ratio, then hot pressed and sintered to form an electrode, the electrochemical properties are greatly improved. The discharge capacity of such a sintered electrode is about 300–320 mAh$^{-1}$. The life time can be more than 450 cycles even at a 80% depth of discharge (DOD). The average discharge capacity during cycling is about 200–250 mAh$^{-1}$.

Wakao's research [68] on TiNi$_x$ ($x=0.5$–1.0) and Ti$_{1-y}$Zr$_y$Ni$_x$ ($x=0.5$–1.0, $y=0.05$–1.0) showed that the Zr-substituted alloy electrodes generally have better corrosion resistance than the TiNi$_x$ electrodes. It was also found [44] that for Ti-Zr-Ni alloys, since there is a "new" phase, Zr$_7$Ni$_{10}$H$_{17}$, formed during hydriding, the capacity of the electrode is greatly increased (200 mAh$^{-1}$) compared to the Ti-Ni binary alloy. Since zirconium forms a passive film on the electrode surface, the electrode stability is
improved. The zirconium-rich alloys, Ti$_{0.5}$Zr$_{0.5}$Ni$_{1.0}$, Ti$_{0.2}$Zr$_{0.8}$Ni$_{1.35}$ and Ti$_{0.2}$Zr$_{0.8}$Ni$_{1.25}$, have quite large capacities and good durability. Nickel or copper plating the hydride powder is very effective in further improving the durability.

Other multi-component alloy electrodes, such as (Ti, Zr)-(Ni, V, X)$_{2-n}$ (x=Al, Fe, Cr, Mn) [58] and its vanadium-based alloys V$_3$TiNi$_x$ (0.75≤x≤0) [69, 70], have also been shown to have fairly large capacities and long cycle lives.

2.2.4 Research and development of Mg-based alloys

In this group, the Mg$_2$Ni and Mg$_2$Ni-based alloys are the most promising metal hydride electrode materials. Mg$_2$Ni is superior to the rare-earth alloys (AB$_5$) or the Laves-phase alloys (AB$_7$) in terms of material cost and theoretical hydrogen absorption capacity [71]. The theoretical discharge capacity of a Mg$_2$Ni metal hydride electrode (∼1000 mA·h·g$^{-1}$) is approximately 2.7 times higher than that of LaNi$_5$ (∼372 mA·h·g$^{-1}$). However, the hydrogen absorption/desorption reactions for this alloy occur only when the temperature is raised to about 200 to 300 °C [71], and the rate of reaction is very slow even at these high temperatures. To improve the characteristics of Mg$_2$Ni as the negative electrode in metal hydride battery, a mechanical grinding (MG) method has been applied [48, 49], which results in a marked improvement in the activation and hydrogen storage properties, and hydrogen can be readily absorbed to an acceptable level by the Mg$_2$Ni alloy. The gas-phase hydrogen absorption and desorption reactions of the mechanically treated Mg$_2$Ni alloy (MG-Mg$_2$Ni) occur even at a relatively low temperature of 80°C. The charge/discharge reactions of the MG-Mg$_2$Ni alloy electrode occur at room temperature with an initial capacity of 750 mA·h·g$^{-1}$. It has been demonstrated that the MG-Mg$_2$Ni alloy is transformed from a crystalline to an amorphous-like state. It has also
been found [49] that as a result of substitution of Mg with a more electronegative element (Al or Mn), absorption of hydrogen easily occurs readily at lower temperatures, and the hydrogen reversibility of the Mg-Mg$_{1.9}$Al$_{0.1}$Ni alloy electrode is significantly increased.

2.2.5 Composition and Pre-treatment of Metal Hydride Electrodes

2.2.5.1 Composition of the metal hydride electrodes

Because of various "defects" including corrosion of the hydrogen storage alloy in the electrolyte, short cycle life and poor charge retention, hydrogen storage alloy electrodes were not accepted by the battery industry until a break-through was made by Willems in 1984 in extending the cycle life of a LaNi$_5$ alloy electrode by partial substitution of Ni by Co and a small amount of Si. Since that time, La-Ni-Co-Si (or Al), Mm-Ni-Co-Si (or Al), MI-Ni-Co-Si (or Al) and AB$_5$ type alloys have been systematically studied and have seen rapid development. Also by 1985, AB$_2$ type V-Ti-Zr-Ni electrode alloys had been developed and were claimed by the Ovonic Battery Co. in the U.S.A to possess satisfactory properties [42]. Substitution of other elements in the AB$_5$, AB$_2$, and even A$_2$B (Mg$_2$Ni) type alloy electrodes have found wide application. It has been reported that substitution of Ce, Co and Sn in the LaNi$_5$-based alloy electrodes leads to a decreased plateau pressure, increased capacity and decreased capacity decay rate [72, 73]. Dou's group in Wollongong found that for some Zr-based AB$_2$ type alloy electrodes, the addition of Mn and Si has a significant effect on the reaction resistance of the alloys [74]. They also reported that the discharge capacity can be markedly improved via partial substitution of titanium for magnesium, and iron for nickel, in the Mg$_2$Ni alloy. A composite of Mg$_2$Ni and Ti$_2$Ni has a greatly increased discharge capacity compared to the magnesium-based alloy electrode [75].
Other methods that have been reported to improve the characteristic of the metal hydride electrodes include adding active materials, binding materials or compacting materials. It has been found that [76] mixing $\text{Y}_2\text{O}_3$ powder with a MmNi$_3$-based alloy powder, in which Ni is partially substituted by Al, Mn and Co, greatly improves the corrosion resistance of the electrode. It was suggested that a small amount of the $\text{Y}_2\text{O}_3$ powder dissolves in the alkaline electrolyte, is then adsorbed on the surface of the alloy and thereby suppresses the formation of the hydroxides of of Al, Mn and Co as well as the conversion of the rare earth metals to their hydroxides. Schlapbach's research [77] showed that the use of certain materials as compacting agents in the production of Zr(V,Ni)$_2$ metal hydride electrodes influences the electrode performance, e.g. cycle life and high rate dischargeability. Using nickel as a compacting powder gave the best activation results, while copper compacted electrodes showed the best cyclic stability. The differences in electrode performance can be explained by changes in the oxidation stability, hardness of the alloy powder and electrical conductivity of the compacting materials. Several additives, including Teflonized carbons, acetylene black and copper, have been evaluated as binding materials for AB$_2$- and AB$_5$-type electrodes [78]. The metal hydride electrodes with the Teflonized carbon additions show better stability and cycle life than the electrodes with copper additions. The probable reasons for the longer lifetime of the electrodes with the carbon additions are (i) the higher chemical stability of the electrodes with the carbon additives; and (ii) the flexible three-dimensional network with an intimate and a stable contact between the active alloy particles that is formed with the carbon additives.

2.2.5.2 Surface modification
Surface modification of the metal hydride electrodes is very important for improving their electrochemical performance, such as discharge capacity, high-rate discharge capacity, cycle lifetime, over-potential, activation, etc. Surface modification methods include grain size control (surface area control), micro-encapsulation, solution pretreatment and ultrasound treatment. These are discussed in more detail in the following sections.

1. Control of grain size

The grain size of the electrode alloy has a influence on the electrochemical performance, especially on the cycle lifetime, of the electrode. Therefore the cycle lifetime depends greatly on the casting conditions which controls the grain size. The results of Sakai [5] on the effects of mode of solidification and heat treatment of MnNi₃.₅Co₀.₇Al₀.₈ alloy electrodes show that a slow cooling or annealing treatment, which causes an increase in grain size, produces a decrease in the cycle lifetime. An as-cast sample with a columnar grain structure (smaller grain size), produced by an the induction melting-rapid quenching process, exhibited a longer cycle lifetime.

2. Micro-encapsulation

The performance of a nickel/metal hydride battery is limited by the metal hydride electrode. The efficiency and life of the metal hydride is reduced by several factors: (i) The formation of the metal hydride results in an expansion of the metal lattice, and repeated cycling results in degradation of the alloy. (ii) The reaction of the alloy with the hydrogen to form a hydride is an exothermic reaction, whereas the dehydriding is an endothermic reaction; thus, thermal management of the alloy is essential to the repeated use of the alloy. (iii) The corrosion of the reactive elements of the alloy in the aggressive
basic solution, and oxidation of the surface during overcharge, pose a problem of
degradation of the hydrogen storage ability of the alloy. (iv) Alloy degradation and
surface oxidation will reduce electrical conduction to the surface of the alloy. All of the
above-mentioned factors will adversely affect the use of the metal hydride as an electrode
in a metal hydride battery [79].

One of the most significant improvements in performance was realized by micro-
encapsulation of the hydrogen storage alloy powder with metals such as Cu or Ni, or with
Ni-P or Ni-B by electroless plating. Micro-encapsulation provides complete coverage of
the intermetallic alloy to prevent corrosion or oxidation. Metals such as Cu and Ni are
softer and less brittle than the intermetallics, and thus provide both the necessary binding,
and good electrical and thermal conduction [8].

Cu-encapsulated LaNi₅ and MmNi₄.₅Mn₀.₅ show a higher hydrogen storage
capacity and longer cycle lifetime than non-encapsulated materials. They also have high
thermal conductivity, leading to fast reaction kinetics [8, 9, 10]. Sakai and other
researchers also showed that micro-encapsulation of the intermetallic with Cu and Ni
results in improved cycle lifetime, higher rate capacity, improved performance at lower
temperatures, and lower pressures during overcharging for the nickel/metal hydride
batteries [8, 79, 80, 81, 82, 83]. Two methods, conventional electroless plating and
“novel” plating, are often used for micro-encapsulation of metal hydride electrode alloys.

(a) Conventional electroless plating of Cu, Ni and Pd

Conventional electroless plating methods have been developed by many
researchers over a long period of time [9, 10, 80, 81, 83, 84, 85, 86, 87]. For copper
plating, the alloy powders are first sensitized in an acidic SnCl₂ solution and then
activated in an acidic PdCl₂ solution. Finally, the activated powders are immersed in a solution containing copper ions and formaldehyde is added as a reducing agent [8, 9, 10, 80, 81, 83]. Because of the active material losses during the plating, the complexity of the electroless plating process, and the relative high cost of the plating process, these conventional plating methods have not been accepted in practical battery applications [8]. Nickel can be plated from a solution of nickel sulfate, citric acid, sodium hypophosphite, and ammonia [80, 79, 83, 84]. The Ni-P electroless plating method is a widely used commercial process [88]. The intermetallic compound is treated by using an alkaline solution containing hypophosphite as a reducing agent [88, 89, 90, 91]. It has been found [89] that treatment with a reducing agent gives rise to high electrocatalytic activity of the negative electrodes which, in turn, leads to a significant reduction in over-potential in charging and discharging.

A simple method of electroless copper plating for the preparation of metal hydride electrodes has been reported by Park and Kirchheim [92]. Copper is plated on (RE)Ni₅ or Mg₂Ni when the alloy was immersed in an acidic bath containing only copper sulfate (CuSO₄) and sulfuric acid (H₂SO₄). 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 Cu²⁺ ions and the alloy constituents. This method can be applied to rare earth-nickel-based hydrogen storage alloys only, but not to other alloys such as TiFe and the Laves phase alloys because of their inability to dissolve and reduce copper ions in solution [92].
It has been found [93] that a Pd-coated metal hydride alloy electrode exhibited a higher discharge capacity and better performance than uncoated alloy electrodes in an alkaline solution. The Pd coating was also very effective in decreasing the galvanostatic cycling time for activating the electrodes. The improved performance of the Pd-coated alloy electrodes is attributed to the catalytic effect of Pd on the charge-transfer step at the electrode surface.

(b) Novel plating of Cu

A novel plating method resulting in micro-encapsulation has been developed by Kammlott et al. [8]. By using the hydrogen already stored in the metal hydride as the reducing agent, a simpler electroless plating method is developed. Since the reducing agent is stored in the hydride alloy and not in the solution, the plating solution is extremely stable. No extraneous plating occurs and conventional stabilizers and inhibitors are not needed. There are no sensitizing and activating steps, and a closed-loop process can be developed to minimize any waste generation. With novel plating, micron-thick copper was plated successfully on LaNi$_5$, Ti$_2$Ni, ZrCrNi and Ti$_2$Ni$_{0.8}$Mn$_{0.2}$. Nickel has also been plated on LaNi$_5$ [8].

3. Solution treatment

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

(a) Alkaline solution treatment

In this type of treatment, the metal hydride alloy in immersed in an alkaline solution for a set period of time. Suitable alkaline solutions include aqueous solutions of potassium hydroxide (KOH) and sodium borohydride (NaBH$_4$) [94], or a solution of
KOH containing fluoride [95]. Treatment of a MnNi₅-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, which would cause the degradation of the activity of the alloy [94].

ZrNi₂-based alloys have poor activation behavior. A Zr(V₀₂₅Ni₀₇₅)₂ alloy electrode treated with a KOH solution containing fluoride (HF) showed a much larger initial capacity than the untreated one, and the activation time was greatly reduced [95].

(b) 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 [42, 96, 97]. The electrochemical performance of HF-treated Zr(V₀₄Ni₀₆)₂ and Zr(V₀₂Mn₀₂Ni₀₆)₂ alloy electrodes was 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 [96].

4. Ultrasound pretreatment

It has been found that surface modification with an ultrasound pretreatment can improve the electrochemical performance of metal hydride electrodes. Dou's group [98] reported that the surface modification of a Mg₁.₅Y₀.₁Ni₀.₉Al₀.₁ 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 life.

2.2.5.3 Mechanical alloying and ball milling

Ball milling method is often used for producing nano-crystalline or amorphous material, or for mechanical alloying. Ball milling has found application in the improvement of the electrochemical performance of metal hydride alloy electrodes [48, 99, 100]. In the preparation of the metal hydride electrodes, ball milling is either used for mechanical alloying the metal hydride alloys directly from the constituent pure elements, or for changing the surface properties or the crystal state to nano-crystalline or amorphous.

In metal hydride systems, the surface area and particle size of the material are important parameters in enhancing the hydrogen uptake, reducing in the activation time, temperature and pressure, and improving the kinetics. Mg$_2$Ni, for instance, is a low cost metal hydride alloy with a very high hydrogen storage capacity (Mg$_2$NiH$_4$, about 3.4 wt.%). However, its major disadvantage is a high activation and desorption temperature (about 300°C) [100]. A Mg$_2$Ni alloy formed by mechanical alloying from pure Mg and Ni (using high energy ball milling), which is in the form of nano-particles (about 4 nm), shows an improved activation behavior. It undergoes easy hydrogen activation and can be hydrogenated in the first cycle. The specific surface area (SSA, m$^2$g$^{-1}$) of mechanically alloyed Mg$_2$Ni powders, even though particles are larger than nano-particles, is still much larger than that of the “normal” metallurgical powders [101], and it is possible that this increased SSA is a reason for the easy activation of the mechanical alloyed Mg$_2$Ni.
The metal hydride alloys can also be ball-milled to improve the hydriding/dehydriding properties. The effect of ball milling on hydrogen absorption properties has been studied for FeTi, Mg₂Ni and LaNi₅ [102]. It was demonstrated that, although there is no change in crystal structure, ball milling of these alloy powders, which leads to the reduction in the particle size and to the creation of new clean surface, is effective in improving the initial hydrogen absorption rate.

Under certain conditions, such as the use of a high-energy mill, proper ball-to-powder weight ratio ($r$) and milling time, an amorphous structure can be formed through ball milling, e.g. ball milling of LaNi₅ with a high-energy planetary mill ($r=20:1$, $t=2$ h) produced an amorphous structure [103]. The exchange current density ($i_0=830$ mA/g) of the ball milled LaNi₅ is about 4 times higher than that of the initial conventional LaNi₅, and the corresponding SSA is greatly increased. It seems likely that the increase in $i_0$ can be attributed to the increase in SSA and the possible influence of active nickel clusters formed by oxidation during milling. Kanda's group obtained some interesting properties from an amorphous Mg₂Ni alloy obtained by ball milling (mechanical grinding, or MG) [48, 49]. An electrode fabricated from this alloy had a large discharge capacity (750 mAh g⁻¹ at 25°C) which is 2.5 times than that of a typical AB₅-type alloy. This significant improvement in the hydrogen storage properties seems to be achieved by an increase in the grain boundary area and the heterogeneous strain produced in the alloy. It is believed that the nano-crystalline grain boundary energy is responsible for driving the crystalline-to-amorphous phase transformation [104].

2.3 ELECTROCHEMICAL PERFORMANCE CHARACTERISTICS OF METAL HYDRIDE ELECTRODES
The metal hydride electrodes used in practical batteries must have excellent
electrochemical performance characteristics, including high discharge capacity, long
cycle lifetime, low self-discharge, good hydriding/dehydriding reversibility, reliable
performance at high rate charge/discharge and over-charge/over-discharge. The
electrochemical performance of the metal hydride electrode, and therefore of the battery,
is usually determined by the kinetics of the processes occurring at the metal-electrolyte
interface and the rate of hydrogen diffusion within the bulk of the alloy [105, 106]. Thus,
the electrochemical kinetic properties of an electrode such as exchange current density,
polarization resistance, over-potential, surface area of the electrode and hydrogen
diffusion rate are important parameters which can be used to characterize the
performance of a metal hydride electrode [15, 105, 107, 108, 109]. Through the study of
these parameters, the electrochemical performance of an electrode could be determined
and, hopefully improved.

2.3.1 Polarization Behavior

The polarization behavior is one of the most important characteristics of the
electrochemical performance of the electrode. The polarization curve, i.e. electrode
potential versus current curve ($E$~$i$) or over-potential versus current curve ($\eta$~$i$), can
provide information on such parameters as exchange current density ($i_0$, mA/cm$^2$),
polarization resistance ($R_p$, $\Omega$), over-potential (mV), limiting current ($i_L$, mA) and other
kinetic and thermodynamic properties.

2.3.1.1 Fundamentals of polarization

For a working electrode, when there is no current passing through the electrode,
the electrode potential $E_{eq}$ (vs. Reference electrode) is called the null potential, or open-
circuit potential. For the electrochemical process in a metal hydride electrode, it is the equilibrium potential \(E_{eq}\). However, when there is current passing through the electrode, the electrode potential shifts from the equilibrium position. The phenomenon of the electrode potential shift caused by the passage of current is called polarization. The difference between the potential with current and the equilibrium potential is called the over-potential at that particular current, and usually expressed as \(\eta\) (mV). The over-potential varies with the current density for the electrode. Polarization has three distinct components, namely ohmic polarization, activation polarization and concentration polarization, and their effects are more or less additive. The potential shift caused by each type of polarization is termed an over-potential, i.e. ohmic polarization over-potential \(\eta_{ohm}\), activation polarization over-potential \(\eta_{act}\) and concentration polarization over-potential \(\eta_{conc}\). The total over-potential \(\eta\) of an electrode is the sum of these three terms:

\[
\eta = \eta_{ohm} + \eta_{act} + \eta_{conc}
\]  

(2.3.1)

Each over-potential has the same sign as the current that causes it. Depending on the circumstances, two (or all three) over-potentials may have similar magnitudes; or any one of the polarization types may be dominant.

2.3.1.2 Ohmic polarization

In order for current to flow, ions must move through the ionic conductor. This requires an electric field to maintain the motion of the ions, and this field is provided by the existence of a potential gradient across the cell. The magnitude of the ohmic polarization over-potential can be found by integration of Ohm's law across the cell:
\[ \eta_{\text{ohm}} = E_{\text{work}} - E_{\text{ref}} = \int_{\text{ref}}^{\text{we}} dE \]  \tag{2.3.2}

where \( E_{\text{work}} \) and \( E_{\text{ref}} \) are the potentials of the working electrode and the reference electrode, respectively. The difference \( E_{\text{work}} - E_{\text{ref}} \) is the potential difference between a point in the solution adjacent to the working electrode and a point in the solution adjacent to the reference electrode. It can be expressed in a simple way as follows:

\[ \eta_{\text{ohm}} = IR_{\text{sdn}} \]  \tag{2.3.3}

where \( R_{\text{sdn}} \) (or \( R_{\text{ohm}} \)) is the resistance of the solution between the two electrodes. This explains why the ohmic over-potential is often called "the IR drop". In most electrochemical studies, ohmic polarization is a nuisance and the experimental conditions are designed to minimize \( \eta_{\text{ohm}} \). The solution conductivity is increased, and hence \( \eta_{\text{ohm}} \) is reduced, by adding extra electrolyte, which provides ions that do not participate in, or interfere with, the electrode reaction, to the cell solution. The use of a three-electrode cell also serves to minimize ohmic polarization.

2.3.1.3 Activation polarization and the Butler-Volmer equation

Some electrode reactions, like certain ordinary chemical reactions, are inherently slow, and it is this slowness that gives rise to activation polarization. As with chemical reactions, slow kinetics are associated with high activation energy. This can be overcome, for chemical reactions, by increasing the temperature. The same is true for electrode reactions but, for these reactions, applying an extra voltage provides a second method of
overcoming the activation energy. This extra voltage, which is needed to counteract the slow kinetics is known as the activation over-potential, \( \eta_{\text{act}} \). Taking the cathode as an example, when a current passes through the cathode, a certain number of electrons are provided to the electrode within unit time. If the electrochemical reaction is fast enough to consume these electrons instantly, the equilibrium potential of the electrode remains unchanged. However, the reaction occurring at the electrode also needs an activation energy, in another words, the reaction can not proceed as quickly as required. Therefore, extra electrons are accumulated on the electrode, resulting in the charging of the double layer, and hence there is a shift in the electrode potential towards a more negative value. This activation polarization of the cathode is called cathodic polarization.

For a typical electrode reaction such as shown in Eq.2.3.4, there are two reactions taking place at the same time, namely the oxidation and reduction reactions:

\[
O(\text{soln}) + ne^- \rightleftharpoons R(\text{soln}) \tag{2.3.4}
\]

where \( O \) and \( R \) denote the oxidation and reduction state reactants, respectively. The reduction reaction rate \( (i_{\text{rd}}) \) and oxidation reaction rate \( (i_{\text{ox}}) \) for Eq.2.3.4 (they both have units of current density, mA cm\(^{-2}\) or mA g\(^{-1}\)) can be expressed as in Eqs.2.3.5 and 2.3.6:

\[
i_{\text{rd}} = -i_0 \exp\left(-\frac{\alpha nF}{RT} \eta_{\text{act}}\right) \tag{2.3.5}
\]

\[
i_{\text{ox}} = i_0 \exp\left(\frac{\beta n F}{RT} \eta_{\text{act}}\right) = i_0 \exp\left(\frac{(1-\alpha)nF}{RT} \eta_{\text{act}}\right) \tag{2.3.6}
\]
where \(i_o\) is the exchange current density, \(\eta_{act}\) is the activation over-potential, \(R\) is the gas constant, \(T\) is the temperature (K), \(F\) is the Faraday constant, \(\alpha\) is the reduction symmetry factor and \(\beta\) is the oxidation symmetry factor. The two symmetry factors represent the extent of influence on the activation energy by the over-potential, and \(\alpha+\beta=1\). The net rate, \(i\), could be thought of as being composed of two components: an oxidative current density \((i_{ox}\), positive) and a reductive density \((i_{rd}\), negative). The reaction will then obey Eq.2.3.7, which is known as the Butler-Volmer equation:

\[
i = i_{ox} + i_{rd} = i_0 \left\{ \exp \left[ \frac{(1-\alpha)nF}{RT} \eta_{act} \right] - \exp \left[ \frac{\alpha nF}{RT} \eta_{act} \right] \right\} \tag{2.3.7}
\]

According to the accepted convention, for an oxidation process \(i\) and \(\eta_{act}\) are positive, and for a reduction process \(i\) and \(\eta_{act}\) are negative. Therefore, for the above reaction, if the process of the working electrode under consideration is oxidation, \(\eta_{act}\) is positive, hence the current, \(i\), is positive. If the studied process is reduction, \(\eta_{act}\) and current, \(i\), are negative. From Eqs.2.3.5 and 2.3.6, we notice that, at null potential both \(i_{rd}\) and \(i_{ox}\) are equal to \(i_o\), a quantity known as the exchange current density, which is shown in Eq.2.3.8. \(i_o\) is defined as a positive value:

\[
(i_{ox})_{E_m} = -(i_{rd})_{E_m} = i_0 \tag{2.3.8}
\]

The exchange current density, \(i_o\), represents the oxidation or reduction reaction rate on the electrode when the electrode is under equilibrium potential. The magnitude of \(i_o\) depends on the solution concentration and the characteristics of the electrode reactions. It
can describe quantitatively the reversibility of the electrode reactions. According to Eq.2.3.5 and Eq.2.3.6, in order to reach a certain reaction rate, \( i_{rd} \) (or \( i_{ax} \)), the electrode reaction with a larger \( i_o \) needs a smaller over-potential (magnitude), and the reaction is more reversible, i.e. the electrode equilibrium is more stable than the electrode reaction with a smaller \( i_o \).

( i ) Linear-polarization:

At a low activation over-potential, i.e. when \( |\eta_{act}| << RT/nF \) (usually a few millivolts), Eq.2.3.7 may be approximated by expanding the exponential functions and discarding all but linear items. This leads to Eq.2.3.9:

\[
i \approx i_o \frac{nF}{RT} \eta_{act}
\]

(2.3.9)

Eq.2.3.9 illustrates that a simple method of measuring \( i_o \) is to determine the interdependence of the current density and the potential in the neighborhood of the null potential. The method is known as the linear-polarization method. When activation polarization is dominant, the slope of the \( \eta_{act} \sim i \) curve, as shown in Fig.2.3.1, at the null potential is equal to \( RT/nF \eta_o \), which has the dimensions of a resistance and is named the charge-transfer resistance, \( R_{ct} \), of the electrode. If an electrode is free from concentration polarization but suffers from the other two types of polarization (ohmic polarization and activation polarization), the slope at the null potential is the sum of \( R_{soln} \) and \( R_{cr} \).

( ii ) Tafel-polarization:

When the activation over-potential is large, or when \( >> i_o \), i.e. the polarization current is large, but not large enough to cause concentration polarization, then the electrochemical equilibrium on the electrode is destroyed, the electrode potential is far
away from the equilibrium potential, i.e. \( |\eta_{act}| \gg RT/nF \), usually about \( \eta_{act} > 100/n \) (mV). In this case, the difference between \( i_{rd} \) and \( i_{as} \) become large enough that one of them can be neglected.

For anodic polarization, \( i_{as} \gg |i_{rd}| \), \( \eta_{act} \) is large and positive, and accordingly \( i \approx i_{an} \), as shown in Eq.2.3.10:

\[
i \approx i_{as} = i_0 \exp \left\{ \frac{(1-\alpha)nF}{RT} \eta_{act} \right\}
\]

(2.3.10)

So that

\[
\eta_{act\ (anodic)} = - \frac{RT}{(1-\alpha)nF} \ln i_0 + \frac{RT}{(1-\alpha)nF} \ln i
\]

(2.3.11)

For cathodic polarization, \( \eta_{act} \) is large and negative, i.e. \( -\eta_{act} \gg RT/nF \), the current density, also negative, approximates \( i_{rd} \) and therefore

\[
\eta_{act\ (cathode)} = \frac{RT}{anF} \ln i_0 - \frac{RT}{anF} \ln |i|
\]

(2.3.12)

Eqs.2.3.11 and 2.3.12 are known as the Tafel Equations. A typical curve of \( \eta_{act} \sim \ln i \) is shown in Fig.2.3.2.

Of course, Eqs.2.3.9 to 2.3.12 assume that other types of polarization are absent.

In fact, ohmic polarization is more likely to interfere with the linear potential method, whereas concentration polarization often distorts the Tafel lines.
Fig. 2.3.1. Linear polarization curve of a LaNi$_{4.7}$Al$_{0.3}$ electrode
Fig. 2.3.2. Tafel polarization curve of a LaNi$_{4.7}$Al$_{0.3}$ electrode
2.3.1.4 Concentration polarization

Under steady-state diffusion, the rate of diffusion can be considered as equivalent to the rate for the electrode process. According to Fick's law and the characteristics of steady-state diffusion, the electrode current can be expressed as follows:

\[ i = nFD \frac{C^b - C^e}{\delta} \]  \hspace{1cm} (2.3.13)

where \( D \) is the diffusion coefficient, \( \delta \) is the effective thickness of the diffusion layer, and \( C^b \) and \( C^e \) are the bulk concentration and the electrode surface concentration of the reactant, respectively. When the rate of diffusion reaches a maximum with an increase in current, the concentration at the electrode surface reaches zero, \( C^e = 0 \), and the electrode current reaches a maximum, expressed as \( i_L \), called the limiting current. Limiting currents arise from concentration polarization and, importantly, they are unaffected by activation or ohmic polarization:

\[ i_L = \frac{nFDC^b}{\delta} \]  \hspace{1cm} (2.3.14)

Therefore,

\[ \frac{C^e}{C^b} = \frac{i_L - i}{i_L} \]  \hspace{1cm} (2.3.15)

From the Nernst Equation and Eq.2.3.15, the concentration polarization over-potential can be calculated from Eq.2.3.16 (for the anode) and Eq.2.3.17 (for the cathode):

\[ \eta_{\text{conc (anode)}} = \frac{RT}{(1-\alpha)nF} \ln \frac{i_L}{i_L - i} \]  \hspace{1cm} (2.3.16)
\[ \eta_{\text{conc (cathode)}} = \frac{RT}{\alpha n F} \ln \frac{i_L - i}{i_L} \] (2.3.17)

2.3.1.5 Coexistence of activation polarization and concentration polarization

The activation polarization, which is controlled by the electrochemical process, and the concentration polarization, which is controlled by the diffusion process, have been discussed separately, depending on whichever may be dominant. For a small current density, the activation polarization process is dominant, and at a large current density, the concentration polarization is dominant. However, for many electrochemical processes, the activation polarization and concentration polarization coexist. Thus, the rate of the “whole” electrode process is jointly controlled. Since the rate of charge transfer is usually similar to the rate of reactant ion diffusion, they both participate in the control of the rate of the electrode process under electrode polarization conditions. If we consider both activation and concentration polarization, then Eq.2.3.7 should be re-written as follows:

\[ i = i_{\text{cat}} + i_{\text{rd}} = i_0 \left[ \frac{C_R}{C_R^0} \exp \left( \frac{(1-\alpha)nF}{RT} \eta \right) - \frac{C_O}{C_O^0} \exp \left( -\frac{\alpha nF}{RT} \eta \right) \right] \] (2.3.18)

where the subscripts “O” and “R” for the concentration C denote the oxidative and reductive state reactants, and the superscript “s” and “b” represent the surface concentration and bulk concentration, respectively. As before, the anodic process and cathodic process are treated separately by neglecting either \( i_{\text{rd}} \) or \( i_{\text{cat}} \).
For the anodic process, \( i = i_{\text{act}} \), and Eq. 2.3.18 becomes Eq. 2.3.19, and the total over-potential \( \eta \) can be obtained from Eq. 2.3.20:

\[
i \approx i_{\text{act}} = i_0 \left[ \frac{C_{\text{R}}^\prime}{C_{\text{R}}^b} \exp \left\{ \frac{(1-\alpha)nF}{RT} \eta \right\} \right]
\]

(2.3.19)

\[
\eta_{(\text{anode})} = -\frac{RT}{(1-\alpha)nF} \ln i_0 + \frac{RT}{(1-\alpha)nF} \ln i + \frac{RT}{(1-\alpha)nF} \ln \frac{C_{\text{R}}^b}{C_{\text{R}}^\prime}
\]

(2.3.20)

Combining Eq. 2.3.20 and Eq. 2.3.15, Eq. 2.3.21 can be obtained:

\[
\eta_{(\text{anode})} = -\frac{RT}{(1-\alpha)nF} \ln i_0 + \frac{RT}{(1-\alpha)nF} \ln i + \frac{RT}{(1-\alpha)nF} \ln \frac{i_L}{i_L-i}
\]

(2.3.21)

Comparing Eq. 2.3.21 with Eq. 2.3.11 and Eq. 2.3.16, it can be seen that the first two terms of Eq. 2.3.21 are equal to \( \eta_{\text{act}} \), and the third term is equal to \( \eta_{\text{conc}} \). Therefore

\[
\eta = \eta_{\text{act}} + \eta_{\text{conc}}
\]

(2.3.22)

For the cathodic process, the total over-potential can be expressed as follows:

\[
\eta_{(\text{cathode})} = \frac{RT}{anF} \ln i_0 - \frac{RT}{anF} \ln (-i) + \frac{RT}{anF} \ln \frac{i_L-i}{i_L}
\]

(2.3.23)

Also, the first two terms are equal to \( \eta_{\text{act}} \), and the third term is equal to \( \eta_{\text{conc}} \). Again, the total over-potential is equal to the sum of the activation over-potential and the concentration over-potential.

2.3.1.6 Polarization of metal hydride electrodes
The electrochemical properties of metal hydride electrodes can be evaluated to a large extent by their polarization behavior, such as exchange current density, overpotential, limiting current and the resistance caused by polarization.

(i) Exchange current density:

The exchange current density of an electrode reaction can be expressed as either mAg\(^{-1}\) or mAcm\(^{-2}\). Some metal hydride electrodes are porous, hence the real surface area of the electrode is different from the apparent surface area, and in this case the exchange current density is usually expressed as mAg\(^{-1}\). In order to emphasize the surface area contribution for some electrode reactions, the exchange current density is expressed in units of mAcm\(^{-2}\). Since most metal hydride electrodes have good electrode reaction reversibility, the corresponding exchange current density is often larger than for other electrodes. Typically, the exchange current density is dependent on the characteristics of the electrode (such as composition), the solution concentration and the hydrogen content in the electrode.

According to Lee’s research [16] the area exchange current density, \(i_{0.5}\) (mAcm\(^{-2}\)), can be treated as the surface catalytic activity, and the mass exchange current density, \(i_{0.\text{m}}\) (mAg\(^{-1}\)), as the surface reaction kinetics. These two terms are connected to the specific reaction surface area, \(S\) (cm\(^2\)g\(^{-1}\)), i.e. \(i_{0.5} \text{ (mAcm}^{-2}\text{)} = i_{0.\text{m}} \text{ (mAg}^{-1}\text{)} \times \frac{1}{S} \text{ (cm}^{2}\text{g}^{-1}\text{)}\). For an electrode with a different composition, the exchange current density could be different and will have a different role in controlling the properties of the electrode. Lee reported that in the case of ZrMn\(_{0.3}V\_{0.5}Ni_{1.4+y}\) (\(y=0.0, 0.2, 0.4,\) and 0.6) alloys, the discharge efficiency and the rate capability decreased as the amount of Ni increased, while these values increased with Ni content for ZrMn\(_{0.3}V\_{0.7}Ni_{1.4+y}\) (\(y=0.0, 0.2, 0.4,\) and 0.6) alloys.
Measuring the specific reaction surface area and exchange current density confirmed that for the ZrMn$_{0.5}$V$_{0.5}$Ni$_{1.4+y}$ alloys the major factor controlling the electrode properties was the specific reaction surface area, not the exchange current density, while, for the ZrMn$_{0.3}$V$_{0.7}$Ni$_{1.4+y}$ alloys, the electrode properties were mainly controlled by the exchange current density, not the specific reaction surface.

Yayama’s research [109] showed that the logarithm of the exchange current density of metal hydride electrode is a linear function of the logarithm of the hydrogen content ($C_H$) at lower hydrogen concentrations, that is $lni_0$ increases almost linearly with increasing $lnC_H$. However, if the state of charge (SOC, %), instead of $C_H$, is used to represent hydrogen concentration, the relationship between exchange current density and SOC shows that [110, 111] $i_0$ increases with decreasing hydrogen content in the alloy and reaches a maximum value at approximately 15% state of charge. Then $i_0$ starts to decrease with decreasing hydrogen content in the $\alpha$ phase region of the alloy.

(ii) Over-potential:

Like exchange current density, the over-potential of the metal hydride electrode is also dependent on the characteristics of the electrode, especially the properties of electrode reactions and hydrogen diffusion in the electrode, the circuit current and solution concentration. The over-potentials of metal hydride electrodes have been widely studied by many researchers. Both the steady-state method [110, 111] and transient method [107, 108, 112, 113, 114] have been used for characterizing the over-potential.

For the steady-state method, the over-potential can be obtained from the polarization curves for the electrode. As shown in Eq.2.3.1, the total over-potential is the sum of ohmic, activation and concentration over-potentials. If the ohmic resistance is
neglected, or compensated for, which is typically the case in research studies, the over-potential then consists of the activation and concentration over-potentials, i.e.

\[ \eta = \eta_{act} + \eta_{conc} \]

According to Eq.2.3.21 or Eq.2.3.23, using the steady-state polarization curves for the metal hydride electrode, \( \eta_{act} \) and \( \eta_{conc} \) can be separated out from the total over-potential.

The over-potential is directly related to the hydrogen evolution reactions [107, 114, 115]. The Volmer-Tafel mechanism is well known for describing the hydrogen evolution reaction, which includes two elementary steps, discharge of water (Volmer step) and the recombination of the adsorbed hydrogen atoms \( H(a) \) (Tafel step). Also the adsorbed \( H(a) \) atoms combine with the alloy to form a metal hydride. These three reactions are shown in Eqs.2.3.24, 2.3.25 and 2.3.26:

Volmer reaction,

\[ H_2O + e^- \rightleftharpoons H(a) + OH^- \quad (2.3.24) \]

Tafel reaction,

\[ 2H(a) \rightleftharpoons H_2 \quad (2.3.25) \]

Metal hydride formation reaction,

\[ H(a) + M \rightleftharpoons MH \quad (2.3.26) \]

For the transient technique with a constant current [107], shown in the decay curve depicted in Fig.2.3.3, there is a clear break, which divides the total over-potential
into two components, $\eta_1$ and $\eta_2$. The over-potential $\eta_1$ decays rapidly and is followed by the slow decay of the over-potential $\eta_2$. Typical Tafel plots with respect to $\eta$, $\eta_1$ and $\eta_2$ for a metal hydride electrode are shown in Fig.2.3.4. The over-potential $\eta_1$ corresponds to Volmer reaction involving a one-electron transfer. The over-potential $\eta_2$ corresponds to the Tafel reaction. In this manner, the over-potential due to the Volmer reaction and Tafel reaction can be separated from the total over-potential.

From either the steady-state or transient method, the respective over-potentials can be obtained, and thus the corresponding mechanism for the electrode reactions and the kinetic properties such as the rate-determining step can be determined [107, 108].

(iii) Resistance:

Just as with the over-potential, the total resistance of a metal hydride electrode system (or battery) consists of three components: $R_{ohm}$, the ohmic resistance related to the electrode itself and the solution (sometimes neglected, or compensated for), $R_{ct}$, the resistance due to the charge transfer process, and $R_{diff}$, the resistance due to the diffusion of hydrogen in the electrode. The ohmic resistance $R_{ohm}$ can be determined through an ac impedance method or transient technique [116, 117]. The charge transfer resistance $R_{ct}$ can be calculated from the linear polarization curve as shown in Eq.2.3.9 (the slope of $\eta-i$ curve is the charge-transfer resistance, $R_{ct} = RT/nF_i$), if the ohmic and concentration polarization terms are neglected [118]. The resistance due to hydrogen diffusion varies with the current and the over-potential, and can be measured in constant-current electrolysis tests. It has been reported that the diffusion of hydrogen in the electrode is the dominant cause of the electrode resistance [15].
Fig. 2.3.3. Typical galvanostatic overpotential transient of electrode A3 (LaNi$_{4.7}$Al$_{0.3}$ + Ni) at 25°C
Fig. 2.3.4. Typical cathodic polarization curves of a LaNi$_{4.7}$Al$_{0.3}$ electrode
Further studies of the resistance for the metal hydride electrode reaction have shown that the ohmic resistance for the metal hydride electrode includes not only the solution resistance, like most other kinds of metal electrodes, but also the electrode resistance, which is related to the make-up and characteristics of the electrode itself [74, 119]. In the charging/discharging process for the electrode, the solution resistance, the electrode resistance, the contact resistance between the current collector and the alloy, and the contact resistance between alloy particles usually do not change. However, the reaction resistance on the alloy surface, given by the surface composition of the alloy and the real surface area of the alloy grains, increases because of degradation of the alloy surface [74, 119]. The reaction resistance arising from surface is an obstacle to increasing the rate capacity. Several measures to reduce the surface resistance have been used to improve the rate capacity [42]. These include: (a) Micro-encapsulation, which works as a micro-current collector in the electrode, and hence reduces the ohmic loss and thereby improves the rate capacity. (b) Control of additions. For the purpose of reducing cycling capacity, small amounts of Al, Si, Ti or Zr are added to passivate the surface. However, if too much is used, the oxide film formed from these elements at the surface will increase the surface resistance, and hence reduce the rate capacity. Research has also shown that small amount additions of Mn or Si have a significant effect on reducing the reaction resistance of ZrV₂-based alloy electrodes [74].

2.3.2 Thermodynamic Properties of Metal Hydride Electrodes

The thermodynamic parameters of metal hydride electrode materials such as $\Delta H$ (the change of enthalpy), $\Delta S$ (the change of entropy) and $P_m$ (equilibrium plateau pressure) have been widely studied. They are important properties for metal hydride
electrodes. The formation entropy of a metal hydride $\Delta S$ is usually small, so the
formation enthalpy of a metal hydride, $\Delta H$, represents the stability of the hydride. If $\Delta H$
is more negative, i.e. the metal hydride is more stable, the resistance to anodic oxidation
increases, and hence the ability for high rate discharge decreases [13]. $P_{eq}$ is the pressure
which is in equilibrium with the hydrogen in the metal hydride. The higher the value of
$P_{eq}$, the easier it is for the hydrogen to be released from the metal hydride. In the
nickel/metal hydride battery, the hydrogen that is released may reduce the high valence
nickel, thus resulting in the self-discharge of the battery.

Usually three methods are used to obtained these thermodynamic parameters,
namely (i) Pressure-composition isotherms ($P$-$C$-$T$ curve) for the gaseous hydrogen
absorption/desorption process [3, 120]. Through measuring plateau pressure at different
temperature, some thermodynamic parameters can be obtained. (ii) Theoretical
calculations from the analysis of the electronic structure, electron density,
electronegativity, bond number and hydrogen site occupancy of the metal hydrides [121,
122, 123, 124, 125, 126]. (iii) Calculations using the Nernst equation and the equilibrium
potential-composition isotherms ($E$-$C$-$T$ curve) for the charge/discharge processes of the
metal hydride electrode, i.e. converting an equilibrium potential to an equilibrium
pressure of hydrogen [11, 12, 13, 14].

Westlake [127, 128] has obtained the crystal structures for LaNi$_5$, LaNi$_4$Al ,
LaNi$_5$Mn and some other LaNi$_5$-based alloys, and analyzed the structures of the
deuterides and determined the preferred interstitial sites for deuterium atoms in the
alloys. However, he determined the hydrogen sites only from the geometry of the
structures and dimensions of the atoms, rather than from the stability of the configuration,
i.e. the values of energy are related to the atomic configuration. This forms one part of
the present study (section 4.1).

The conventional electrochemical method of calculating the $\Delta H$ and $\Delta S$ from an
$E-C-T$ curve has problems with low accuracy. Sakai [11, 12] determined equilibrium
pressures by the electrochemical method, and reported that the pressures were about 10%
higher than those obtained by the gaseous hydrogen method. Zhou et.al [13] found much
larger differences between the values for $\Delta H$, $\Delta S$ and $P_\text{eq}$ determined by the
electrochemical method and gaseous hydrogen method. Zhou suggested that at low
temperatures the difference are small, but at high temperatures the differences become
larger, due to the escape of hydrogen in form of gas bubbles in the electrochemical
method. However, Wang [14] reported that the errors incurred from calculations directly
from the Nernst equation in its common form are much larger, i.e. for this specific
hydrogen charge/discharge reactions, when using Nernst equation, some other items must
be taken into account. The enthalpy and entropy obtained directly from Nernst equation
are not the actual ones for the reactions. A new approach was suggested by Wang to
improve greatly the accuracy. According Wang's results, $\Delta H_e$ and $\Delta S_e$, calculated from
the electrochemical method using Nernst equation are related to $\Delta H_p$ and $\Delta S_p$, calculated
from the gaseous hydrogen method, which are considered as the actual values of the
reactions, as shown in Eqs.2.3.27 and 2.3.28:

\[
\Delta H_p = -195.28724 - \Delta H_e \ (kJ/mol) \quad (2.3.27)
\]

\[
\Delta S_p = -53.45 + \Delta S_e \ (J/mol \cdot K) \quad (2.3.28)
\]
By applying these corrections, the values of $\Delta H$ and $\Delta S$ calculated from the electrochemical method have errors of less than 6%.

2.3.3 Kinetic Properties of Metal Hydride Electrodes

2.3.3.1 Specific surface area of the electrodes

The specific surface area of the electrode is one of more important parameters that determine the properties of the electrode. Yayama [15] suggested that the surface area of the electrode is one of the two factors that determine the activity of the electrode, the other being the diffusion coefficient of hydrogen. Lee [16] regarded the exchange current density (mA cm$^{-2}$) as the surface catalytic activity, and suggested that for some metal hydride electrodes, the major factor controlling the electrode properties was the specific surface area.

Willems from Philips Research Laboratory has discussed the specific surface area and its measurement in detail [3]. The specific surface areas of different metal hydride alloys and their electrodes were studied using the BET method [17]. It was found that for the hydrogen gas absorption/desorption cycles in a LaNi$_5$ alloy, the specific surface area increases greatly in the first fifty cycles, and after that the specific surface area increases quite slowly even up to 1000 cycles. This suggests that the cracking mainly occurred during the first fifty cycles. However, for the charging/discharging cycles of an electrode, the specific surface area increases monotonically with cycling, and attains a very large value compared to the gas-cycled powder. Both the active material and the oxidation products contribute to the specific surface area, as shown in Eq.2.3.29:

$$SA_{\text{electrode}} = SA_{\text{active}} \cdot \frac{C}{C_0} + SA_{\text{oxidised}} \cdot (1 - \frac{C}{C_0}) \quad (2.3.29)$$
where $S_{A_{\text{electrode}}}$, $S_{A_{\text{active}}}$ and $S_{A_{\text{oxidprod}}}$ represent the specific surface areas of the electrode, active material and oxidation products, respectively. $C$ and $C_0$ represent the actual and the initial storage capacity. The quantities $C/C_0$ and $(1-C/C_0)$ express the fractions of the remaining active material and that of the oxidation products, respectively. Lee [16] found that for ZrV$_2$-based alloy electrodes, a ZrMn$_{0.5}$V$_{0.5}$Ni$_{1.4}$ alloy electrode has a much larger specific surface area than a ZrMn$_{0.5}$V$_{0.5}$Ni$_{2.0}$ alloy electrode. This was explained by the fact that there are more micro cracks in the alloy powder surface for the ZrMn$_{0.5}$V$_{0.5}$Ni$_{1.4}$ electrode, whereas the ZrMn$_{0.5}$V$_{0.5}$Ni$_{2.0}$ electrode had relatively few cracks.

2.3.3.2 Hydrogen diffusion

As previously noted, both the kinetics of the process occurring at the metal/electrolyte interface and the rate of hydrogen diffusion within the bulk of the hydrogen-absorbing alloy, are factors affecting the performance of metal hydride electrodes [129, 130]. To improve the electrochemical properties of metal hydride electrodes, the characteristics of hydrogen diffusion in the bulk material have been studied extensively. Many methods have been used to measure the diffusion coefficient of hydrogen ($D_H$) in hydrogen storage alloys. These have included nuclear magnetic resonance (NMR) [131, 132], quasielastic neutron scattering (QNS) [133] and electrochemical methods. The electrochemical methods of measuring hydrogen diffusion coefficient include constant potential discharge [106, 129, 134], constant current discharge [15, 110, 111], potential-step [135, 136], current pulse [137, 138], electrochemical impedance spectroscopy (EIS) [134] and electrochemical stripping techniques [139].
The hydrogen diffusion coefficient in a metal hydride electrode is determined by many factors including the composition of the electrode, the hydrogen content of the electrode, the electrode potential, the diffusion activation energy and the temperature.

The values of the hydrogen diffusion coefficient were found to decline significantly with an increase in the depth of discharge (DOD), i.e. with decreasing hydrogen concentration in the electrode [97, 134, 136]. Some metal hydride alloys can absorb a large amount of hydrogen, but the discharge capacity of electrodes made from these alloys are much less than expected, and research has suggested that the rechargeable capacity is limited by a small hydrogen diffusion coefficient [140]. The electrochemical discharge of the hydride electrode was strongly retarded in the low hydrogen concentration range, which corresponds to the higher potential region. This retardation is caused by the small hydrogen diffusion coefficient in the hydride, resulting in its lower discharge capacity [136].

It has been found that substitution for some elements in an alloy electrode increases the hydrogen diffusion coefficient. Liu [129] reported that for MnMn-based alloy electrodes (MnMn, MnMnMn, MnMnCo, MnMnAl), and Zr-based alloy electrodes (ZrV, ZrV, ZrV, ZrV, ZrV), the higher the content of Mn in the alloy, the larger the value of the hydrogen diffusion coefficient. Luo [134] also reported that the substitution of V and Al for Mg and Ni in MgNi could significantly reduce the diffusion resistance and thus increase the hydrogen diffusion coefficient in this alloy. This is believed to be beneficial for increasing the hydriding/dehydriding kinetics of the electrode, thus leading to a substantial increase in discharge capacity.
The hydrogen diffusion coefficient decreases with increasing electrode potential (to a more positive value). The large discharge over-potential in the higher potential region was attributed to the small diffusion coefficient, which consequently caused the poor discharge capacity [136].

The hydrogen diffusion process in a metal hydride electrode follows an Arrhenius behavior [131, 138, 139]. The hydrogen diffusion coefficient is connected with temperature by an activation energy through the Arrhenius expression as follows:

$$D_H = D_0 \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (2.3.30)

where $D_H$ is the hydrogen diffusion coefficient, $D_0$ is the pre-exponent factor for the diffusion coefficient, $E_a$ is the activation energy of the diffusion coefficient, $R$ is gas constant and $T$ is the temperature (K). Knowing that $\ln D_H$ is linear with $1/T$, the activation energy $E_a$, which is the energy required for diffusion to proceed, can be obtained through measuring $D_H$. Obviously, $D_H$ increases with increasing temperature.

The hydrogen diffusion coefficient was also found to be related to the high-rate discharge properties: the better the high-rate discharge, the larger the value of the hydrogen diffusion coefficient [129].

2.3.3.3 Rate-determining step

In a KOH aqueous solution, the main reactions of a metal hydride electrode are as follows [15]:

$$M + H_2O + e^- \xrightarrow{\text{charge}} MH_4^+ + OH^- \xrightarrow{\text{discharge}} M + H_2O + e^-$$  \hspace{1cm} (2.3.31)
\[ MH, \quad \frac{\text{charge}}{\text{discharge}} \quad MH \]

(2.3.32)

where M is the hydrogen storage alloy, and MH\(_4\) and MH\(_5\) denote the hydrogen in the surface and the bulk of the metal hydride electrode, respectively. Eq.2.3.31 represents the charge transfer process and Eq.2.3.32 represents the diffusion of hydrogen. In a KOH aqueous solution, the hydrogen produced on the electrode surface by electro-reduction of water is simultaneously absorbed, and then diffuses into the interior of the electrode. Usually, if the temperature is not too high, there is no tendency for hydrogen to be evolved as bubbles from the surface of the electrode.

The rate-determining step (RDS) of the electrochemical process for a metal hydride electrode has been studied by many researchers [3, 105, 107]. It is believed that the rate-determining step is either the charge transfer process or hydrogen diffusion or a mixed process, depending on the different states of the electrode, such as the depth of discharge (DOD), discharge current and temperature.

Dou [141] and Liu [74] reported that the DOD of the electrode influences the discharge kinetics of the electrode. For a fully charged electrode, hydrogen diffusion is relatively fast and the electrochemical process, i.e. the charge transfer process, is the RDS. At a medium depth of discharge, the process may be controlled by a combination of hydrogen diffusion and the charge transfer process. At the end of discharge, since the supply of hydrogen from the interior of the electrode is inadequate, the hydrogen diffusion process becomes the RDS and controls the discharge process of the electrode. It has also been reported [97] that the RDS could be a mixed process of charge transfer and
hydrogen diffusion up until the end of discharge for some electrodes. This result is explained by the fact that a decrease in hydrogen concentration will inevitably increase the transport resistance. Thus the diffusion process becomes more difficult as the hydrogen concentration decreases, and hydrogen diffusion gradually becomes the RDS gradually with the decrease in hydrogen content in the electrode.

The discharge current also has an influence on the RDS for the electrode reactions [15]. At a low discharge current density, the charge transfer process is the dominant reaction. At a high discharge current density, hydrogen diffusion within the electrode becomes the RDS. This is because at a low discharge current density the over-potential of the electrode is due to the charge transfer process, while at a high discharge current density the diffusion process can not “follow” the fast electrode reaction, and thus becomes the RDS of the electrode reactions.

A temperature increase is beneficial to hydrogen diffusion, as can be seen directly from the Arrhenius expression (Eq.2.3.30). Therefore, with increasing discharge temperature, the RDS of the discharge process is changed from hydrogen diffusion to charge transfer [141].

Zheng [105], however, reported a different result. Since the hydrogen charging efficiency of the metal hydride electrode under normal charging conditions (unless it is overcharged) is close to 100% (up to 95%), even at high rates (0.5C) of discharging, this high charging efficiency precludes the possibility that the hydrogen diffusion in the bulk of electrode is the RDS in the overall process. If it were the RDS, the result would be a lower charging efficiency.

2.4 NICKEL/METAL HYDRIDE BATTERIES
2.4.1. Design and Testing of Metal Hydride Batteries

The design of a sealed metal hydride battery is different from that of a test cell. In a test cell, in order to determine the characteristics of the metal hydride 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 nickel/metal hydride battery, in order to allow overcharging of the battery, the storage capacity of the metal hydride electrode must exceed that of the positive electrode. Willems [3] 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 hydride electrode will decrease during cycling owing to the corrosion of the metal hydride 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 hydride electrode. A schematic diagram of a sealed cylindrical battery (AA size, 1Ah) is shown in Fig.2.4.1.

Although the capacity of a metal hydride battery is usually tested at a low discharge rate, such as 0.125C, 0.2C or 0.25C, the high rate discharge capacity, which is the important parameter for the battery, also needs to be tested at high discharge rates
such as 0.5C, 1C or 1.25C. Usually the high rate capacity is smaller than the low rate capacity because of kinetic reasons.

2.4.2. Overcharging of Metal Hydride Batteries

Sakai [142] has provided a detailed description of the overcharging of a metal hydride battery, which is now briefly summarized. During overcharging of the metal hydride battery, the oxygen evolved at the nickel electrode (as per Eq.2.4.1), is rapidly consumed at the metal hydride electrode (as per Eq.2.4.2 and Eq.2.4.3 or the reverse reaction of Eq.2.4.1).

Positive electrode reaction:

\[ \text{OH}^- \rightarrow \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} + e^- \quad (E^0 = +0.401 \text{ V}) \]  \hspace{1cm} (2.4.1)

Negative electrode reactions:

\[ M + x\text{H}_2\text{O} + xe^- \rightarrow MH_x + x\text{OH}^- \quad (E^0 = -0.828 \text{ V}) \]  \hspace{1cm} (2.4.2)

\[ \frac{x}{4} \text{O}_2 + MH_x \rightarrow M + \frac{x}{2} \text{H}_2\text{O} \]  \hspace{1cm} (2.4.3)

Hydrogen evolution is a side reaction at the metal hydride electrode, as shown in Eq.2.4.4, which leads to a lower charging efficiency. The consumption rate of hydrogen, as per Eq.2.4.5 is not high enough such that a significant increase in cell pressure is brought about. It is very important for the sealed battery to prevent the side reaction for hydrogen evolution.

Negative electrode reaction:

\[ \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \quad (E^0 = -0.828 \text{ V}) \]  \hspace{1cm} (2.4.4)
Positive electrode reaction:

\[ \frac{1}{2}H_2 + NiOOH \rightarrow Ni(OH)_2 \]  (2.4.5)

It was also 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.

2.4.3. Self-discharge of Metal Hydride Batteries

Self-discharge of a metal hydride battery leads to a capacity loss during storage in the open-circuit condition. The capacity loss is divided into two parts [143], namely the reversible and irreversible losses.

The reversible capacity loss has been attributed to the desorption of hydrogen from the metal hydride 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:

\[ NiOOH + \frac{1}{2}H_2 = Ni(OH)_2 \]  (2.4.6)

Other researchers believe that this reaction is the self-decomposition of the positive electrode as shown in Eq.2.4.7 [144]:
\[ \text{NiOOH} + \frac{1}{2} \text{H}_2\text{O} = \text{Ni(OH)}_2 + \frac{1}{4}\text{O}_2 \]  

(2.4.7)

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 hydride electrode.

There are many factors that influence the self-discharge rate, such as the gaseous environment, the electrolyte composition, storage time, temperature and nitrogen impurities [144, 145].

Usually the micro-encapsulation of the alloy with copper or a more effective separator, can 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 metal hydride batteries [143, 144, 145].

2.4.4 Comparison with Other Battery Types

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 [146,147]. The typical characteristics of rechargeable batteries, including cell voltage, specific energy and cycle lifetime are given in Table 2.4.1 [146].
### Table 2.4.1 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>Lead-Acid</td>
<td>PbO₂</td>
<td>2.1</td>
<td>175</td>
<td>30-40</td>
</tr>
<tr>
<td>Nickel-Cadmium</td>
<td>NiOOH</td>
<td>1.2</td>
<td>210</td>
<td>40-50</td>
</tr>
<tr>
<td>Nickel/Metal Hydride</td>
<td>NiOOH</td>
<td>1.2</td>
<td>220 (AB₃)</td>
<td>230 (AB₂)</td>
</tr>
<tr>
<td>Lithium Ion</td>
<td>CoO₂ NiO₂</td>
<td>4.0</td>
<td>455</td>
<td>90-110</td>
</tr>
<tr>
<td></td>
<td>Mn₃O₄ Li₄C₆</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium-Nickel Chloride</td>
<td>NiCl₂</td>
<td>2.5</td>
<td>788</td>
<td>80-100</td>
</tr>
<tr>
<td>(ZEBRA)</td>
<td>Na</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium-Sulfur</td>
<td>S</td>
<td>2.1</td>
<td>635~760</td>
<td>110</td>
</tr>
<tr>
<td>Zinc-Air</td>
<td>O₂</td>
<td>1.4</td>
<td>1085</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 environment, high energy density, long cycle life, high rate capacity, lower temperature capability and absence of memory effect [3, 38, 53]. Nickel/metal hydride batteries have been developed to replace the traditional batteries, such as Cd-Ni and Lead-Acid batteries.
Fig. 2.4.1. The schematic diagram of a sealed cylindrical battery (AA size, 1 Ah)
CHAPTER 3

EXPERIMENTAL DETAILS

3.1 SAMPLE PREPARATION

Three different hydrogen storage alloys were used for the electrochemical studies, namely:

1. LaNi$_{4.7}$Al$_{0.3}$, obtained from Ergenics Division, MPD Technology Corporation, Wyckoff, NJ, U.S.A. This is known as Hy-Stor Alloy 207.

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, 3.5 wt.% Ce, 13.3 wt.% Pr and 38.9 wt.% Nd) which was prepared by induction melting and rapid cooling. The cast alloy was annealed at 900 °C for 10 hours in vacuum. The sample was obtained from the Central Iron & Steel Research Institute, Beijing, China.

3. A Pd-coated Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy which was prepared using alloy 2 with an electroless coating deposit using the method developed by Buxbaum and Hsu [148]. The Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy was first mechanically pulverized to a particle size of around 40–60 μm before plating.

3.2 ELECTRODE PREPARATION

The hydrogen storage alloy ingot of Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ or LaNi$_{4.7}$Al$_{0.3}$ was mechanically pulverized by milling machine with nitrogen protection for 20 minutes to obtain a sifted particle size of around 45–53 μm using the Testing Sieves of 325 mesh and 270 mesh (W.S.Tyler, Inc., U.S.A). The pulverized and Pd-coated Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy powders were directly sieved to obtain a sifted particle size of around 45–53 μm.
3.2.1 Preparation of negative electrodes

The hydrogen storage alloy powders were mixed with nickel powder in a weight ratio of 1:1, or for some electrodes, with nickel and copper powder in a weight ratio of 1:1:1, together with a small amount (3wt.%) of polytetrafluoroethylene (PTFE) aqueous solution as a binder. Then a certain amount of mixed powders, which contains about 0.1 g hydrogen storage alloy powder, was covered by two pieces of porous nickel nets and then pressed in a cylindrical press at a pressure of 500 Mpa for 2 minutes. A pellet, which contains about 0.1 g hydrogen storage alloy, with a diameter of 1.0 cm and thickness of 0.8 mm, was formed at room temperature. This was used as the negative electrode in the experimental cells. The cylindrical press and a negative electrode are shown in Fig.3.2.1.

The negative electrodes used in this study are as follows:

Electrode A1 & A2: \( \text{LaNi}_{4.7}\text{Al}_{0.3} \) (45~53μm) mixed with Ni powder and Cu powder (1:1:1 weight ratio)

Electrode A3 & A4: \( \text{LaNi}_{4.7}\text{Al}_{0.3} \) (45~53μm) mixed with Ni powder (1:1 weight ratio)

Electrode B1 & B2: \( \text{Mm}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \) (where Mm denotes Mischmetal, comprising 43.1 wt.% La, 3.5 wt.% Ce, 13.3 wt.% Pr and 38.9 wt.% Nd) mixed with nickel powder (1:1 weight ratio)

Electrode B3 & B4: Pd-coated \( \text{Mm}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \) (where Mm denotes Mischmetal as electrode B1 and B2) mixed with Ni powder (1:1 weight ratio)

3.2.2 Preparation of positive electrodes
The positive electrode in the cell, a sintered Ni(OH)$_2$/NiOOH plate, was obtained from Central Iron & Steel Research Institute, Beijing, China. It was 1.5cm×4cm×0.07cm in dimensions. A positive electrode is shown in Fig.3.2.2

3.3 EXPERIMENTAL CELL SETUP

The set-up of the experimental cells was in a sintered glass apparatus with three compartments. The negative electrode (working electrode) was placed in the central compartment and the two Ni(OH)$_2$/NiOOH electrodes were placed on either side. The capacity of the positive electrode plates was designed to be higher than that of the negative electrode. The electrolyte in the cell was a 6 M KOH aqueous solution. A Hg/HgO electrode was used as the reference electrode in the experimental cell. The reference electrode was connected to the cell via a Luggin probe, the tip of which is placed as close as possible to the surface of the working electrode. The experimental cell and the set up of testing device for the electrochemical measurements are shown in Figs.3.3.1 and 3.3.2.

3.4 APPARATUS FOR ELECTROCHEMICAL MEASUREMENTS

The tests of the experimental cell and sealed battery were carried out using a Solartron 1285 Potentiostat with CorrWare software for Windows. The tests were conducted in a thermostated water bath, which allows the temperature to be controlled within ±0.1K. A schematic diagram of the experimental cell set up and practical measurement system are shown in Figs.3.4.1 and 3.4.2

3.5 METHODS OF ELECTROCHEMICAL MEASUREMENTS

The electrochemical measurements in this study include constant-current charge/discharge, constant-potential discharge, polarization curves and potential step.
Through these measurements, the characteristics of metal hydride electrode can be
calculated from the electrochemical measurements. Based on the setup of the Solartron
1285 Potentiostat, the anodic polarization current and over-potential are defined 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
(usually the end-of-charge-potential is about \(-0.90\)V to \(-0.92\)V), and discharged at a
current of 120 mA g\(^{-1}\) to an end-of-discharge-potential of \(-0.5\) V. The curves of negative
electrode potential versus time were recorded, which can then be used to calculate the
specific discharge capacity and cycle lifetime.

3.5.2 Constant potential discharge measurements

The constant-potential discharge curves were measured at different temperatures
and potentials. After fully charging of the electrode at a constant current of 120 mA g\(^{-1}\),
the electrode was discharged at constant-potential. The constant-potential was chosen as
\(-0.90\), \(-0.85\), \(-0.80\), \(-0.75\), \(-0.70\), \(-0.65\), \(-0.60\), \(-0.55\) and \(-0.50\) V. The testing
temperatures were chosen as 0, 25, 35, 45 and 55 °C. The corresponding current versus
time curves were obtained from these measurements. The kinetic parameters of the
electrode reactions can be calculated from the current versus time curves at different
potentials and temperatures.

3.5.3 Polarization curve measurements

The measurement of the polarization curves were made 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. The polarization curve was measured after the open-circuit potential was stabilized, i.e. the variation in the potential was less than 1 mV for 1 hour. The measurements were carried out at different temperatures of 0, 25, 35, 45 and 55 °C, and at different depths of discharge (DOD). Two scan ranges were set as -20 mV to +20 mV and -20 mV to +40 mV versus equilibrium potential for two different measurements, respectively. Each single measurement was carried out two times, one with ohmic resistance compensation, and the other without compensation. The exchange current density, over-potential, electrode resistance (ohmic resistance and polarization resistance), characteristics of the electrode reaction process, some thermodynamic and kinetic properties are obtained from the polarization curves.

3.5.4 Potential step measurements

A potential step technique (or transient voltammetry) was used to measure the hydrogen diffusion coefficients, electrode resistance, specific surface area of MH electrode and double layer capacitance. It is one of the most effective voltammetry methods for studying the electrode behavior for a transient process, especially for a porous electrode with a rough surface.

For a porous electrode, which is controlled by an electrochemical process involving simple oxidation-reduction reactions, the equivalent circuit is shown in Fig.3.5.1. The capacitor and the polarization resistance are in parallel, and these are then placed in series with a solution resistance.

When activation polarization is the rate-determining step in the electrochemical process, the potential step method can be used to measure the charge-transfer resistance ($R_d$), ohmic resistance ($R_{ohm}$), double layer capacitance ($C_d$) and real surface area of
electrode \((S_{\text{real}})\). When a small over-potential \((\eta < 10\text{mV})\) is applied to the electrode for a short time, concentration polarization can be neglected. In this case, activation polarization (electrochemical process) can be treated as the rate-determining step. At the moment when a potential step \((\Delta \varphi)\) is applied to the electrode, the voltage applied to the electrode is changed instantly \((\Delta \varphi)\), as shown in Fig. 3.5.2a. The transient wave curve \((i-t)\) can then be obtained as shown in Figs. 3.5.2b or 3.5.2c. However, because of the ohmic resistances and the limitation of the output current of the potentiostat, the charging current is not large enough to instantly complete the double layer charging. That is, although the voltage applied to the electrode changes instantly, the real electrode potential (i.e. potential difference of double layer), which is the key factor in determining the reaction rate, can not change as quickly as the electrode voltage. The instant potential step obtained is not the potential difference of double layer, instead, it is the voltage drop due to the ohmic resistance. At the moment a potential step is applied, the instantaneous current, \(i_B\), is equal to \(\Delta \varphi/R_{\text{ohm}}\), at which the double layer begins to be charged. With continuous charging, the potential difference of the double layer increases, i.e. the electrode potential increases, and thus the electrode reaction rate increases. Meanwhile, both the charging current and the voltage drop due to the decrease in ohmic resistance. By the end of the charging of the double layer, the charging current decreases to zero, and the corresponding reaction current reaches its steady state, \(i_\infty\). This is shown in Eqs. 3.5.1 and 3.5.2.

\[
\Delta \varphi = i_\infty (R_{\text{ohm}} + R_c)
\]  \hspace{1cm} (3.5.1)

\[
i_B = \Delta \varphi / R_{\text{ohm}}
\]  \hspace{1cm} (3.5.2)
The ohmic resistance ($R_{ohm}$) and reaction resistance (charge transfer resistance, $R_{ct}$) can be obtained from Eq.3.5.1 and Eq.3.5.2 through use of the potential step technique.

The double layer capacitance ($C_d$) of the electrode can be obtained by calculating the quantity of electric charge ($Q$, Coulomb) to the electrode using Eqs.3.5.3 and 3.5.4. When the ohmic resistance is small enough to be neglected or is compensated for (in this experiment, the ohmic resistance was compensated for by the current interruption $IR$ correction method), the potential step applied to the electrode is equal to the potential difference of the double layer at the end of charging of the double layer. From the current vs. time ($i$ vs. $t$) relationship obtained by the potential step method with $IR$ compensation, the quantity of electric charge ($Q$, Coulomb) can be calculated by integration of the $i$ vs. $t$ curve, i.e. the area ABC in Figs.3.5.2b or 3.5.2c:

\[
C_d = \frac{Q}{\Delta \varphi} \quad (3.5.3)
\]

\[
Q = \int_0^t i \cdot dt \quad (3.5.4)
\]

Since in the transient process for the potential step method, the electrode current is the sum of charging current ($i_c$) and the reaction current ($i_r$), i.e. $C_d$ and $R_{ct}$ are in parallel in the equivalent circuit, the measurement accuracy for $C_d$ will be influenced by $R_{ct}$. If the electrochemical reaction can be neglected, i.e. $R_{ct}$ ($R_1$, $R_2$, ..., $R_n$ in Fig.3.5.1) is large enough that the current through it is close to zero, $i_r \sim 0$, as shown in Fig.3.5.2c, the area $ABC$ should be the quantity of electric charge, $Q$. However, most of the time, the charge transfer current, $i_{ct}$ (or reaction current $i_r$) can not be neglected, as shown in Fig.3.5.2b. In this case, the area $ABDCA$ should be calculated to obtain $Q$, thus there
might be errors in the calculation of the integral area, since it is somewhat difficult to determine the $i_\alpha$ curve accurately. Fig.3.5.2d shows the variation of electric charge with time.

The double layer capacitance, $C_d$, is proportional to the real surface area of electrode. Most metal hydride electrodes are porous, i.e. the real surface area of metal hydride electrode is much larger than the apparent surface area. Given that $C_d$ is proportional to the real surface area of electrode, the real surface area of the electrode can be obtained by measuring $C_d$. Pure mercury has a very smooth surface, and the apparent surface area of pure mercury can be treated as the real surface area. The double layer capacitance of pure mercury in a noble electrolyte was measured as $C_N=20 \, \mu F/cm^2$ \cite{149}, which represents the capacitance of unit real surface area. The real surface area of electrode, $S_{real}$, can be obtained by measuring the double layer capacitance, $C_d$, and comparing it with $C_N$, the capacitance of unit real surface area, see Eq.3.5.5.

$$S_{real} = C_d / C_N$$  \hspace{1cm} (3.5.5)

For the metal hydride electrodes in the present study, $i_\alpha$ can not be neglected, and a typical $i\sim t$ curve for the potential step transient process of a metal hydride electrode is as shown in Fig.3.5.3, where the ohmic resistance is compensated for by the current interruption method. The integral area of the $i\sim t$ curve (Eq.3.5.4), ADBCA in Fig.3.5.3, is the electric quantity ($Q$) and the double layer capacitance ($C_d$) can be calculated using Eq.3.5.3.

The measurements were carried out at a $\pm 10 \, mV$ potential step with reference to the open-circuit potential. As for the measurements of the polarization curves, the
potential step measurements were also made at the state of full charge/discharge and at
different depths of discharge (DOD) after the open-circuit potential was stabilized, i.e.
the variation in potential was less than 1 mV for 1 hour. The DOD was usually chosen as
every 30 mAh/g during the discharge process, i.e. the potential step measurement was
carried out after every 30 mAh/g was discharged by constant current discharge method
until an end-of-discharge-potential of −0.5 V was reached.

The measurement process was as follows: After the open-circuit potential was
stabilized, the potential was set to be increased or decreased to +10 or −10mV with
reference to the open-circuit potential. 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 curves of current versus time during potential stepping were recorded and
were then used for the calculation of the electrode parameters.

Each single measurement carried out two times, one with ohmic resistance
compensation, and the other without compensation. The measurements were made at
temperatures of 0, 25, 35, 45 and 55°C.

3.5.5 Calculations of thermodynamic parameters for metal hydride electrodes

The quantum chemistry calculation program "Gamess" was used to calculate the
thermodynamic parameters of the hydriding/dehydriding process. The calculation was
performed on the SGI system at the Computer Center, University of Windsor. The CPU
time needed was up to 3 hours for each unit cell structure with different hydrogen sites.
In order to do the calculation, the element name and coordinates of the atoms in a unit
cell must be put into the "input" file in the program according the format provided by the
software. The thermodynamic parameters of $P_{eq}$, $\Delta G$, $\Delta H$ and $\Delta S$ were calculated by the
"Gamess", and were sent to the file named "output".

3.6 MEASUREMENT OF ELECTROCHEMICAL PARAMETERS FOR METAL HYDRIDE ELECTRODES

Through measuring the electrochemical parameters, the characteristics of a metal hydride electrode, such as specific capacity, cycle lifetime, equilibrium potential, specific surface area, diffusion behavior, exchange current density, symmetry factors, over-potential and electrode resistance, can be obtained. The thermodynamic properties and kinetic properties of the MH electrode can also be calculated from these measurements.

3.6.1 Specific discharge capacity and cycle lifetime

Using the constant current charge and discharge method, the specific discharge capacity for any cycle, $C_{dh}$, can be calculated from the product of the current density and the discharge time, as shown in Eq.3.6.1:

$$C_{ah} = \frac{I \cdot t}{W} \text{ (mAh/g)}$$  \hspace{1cm} (3.6.1)

where $I$ (mA/g) is current density, $t$ (hr) is discharge time and $W$ (g) is the weight of metal hydride alloy. By repeating the charge and discharge process, the decay in discharge capacity can be found and the cycle lifetime with respect to a certain percent capacity decay can be obtained, e.g. a cycle lifetime of 1000 cycles with 20% capacity decay.

3.6.2 Equilibrium potential and thermodynamic parameters

The equilibrium potential of a metal hydride electrode can be considered as the open-circuit potential. It can be measured as follows. After the open-circuit potential of a metal hydride electrode, which was fully charged or discharged or at a certain depth of
discharge, was stabilized, then the open-circuit potential that is 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 potential needs to be measured at
different depths of discharge. In this study, a $30\text{mAh/g}$ discharge was chosen. i.e. the
equilibrium potential was measured after every $30\text{ mAh/g}$ was discharged by constant
current discharge method until an end-of-discharge-potential of $-0.5\text{ V}$ was reached.
Thus, from the equilibrium potentials and the corresponding hydrogen concentrations, an
$E$-$C$-$T$ curve was obtained. Thus, the equilibrium pressures, $P_{eq}$, and the thermodynamic
parameters, $\Delta G$, $\Delta H$ and $\Delta S$, can be obtained.

3.6.3 Specific surface area

The potential step method was used to measure the specific surface area of a
metal hydride electrode. A potential step of $\pm 10\text{ mV}$, with reference to the open-circuit
potential, was applied to an open-circuit potential stabilized electrode, which is in a state
of full charge or discharge or a certain depth of discharge. The curves of current versus
time were recorded and then used to calculate the specific surface area by using Eq.3.5.3
to 3.5.5.

3.6.4 Diffusion coefficient

The potential step method was used to determine the diffusion coefficient of
hydrogen in a metal hydride electrode. A potential step of $10\text{ mV}$, with reference to the
open-circuit potential, was applied to the metal hydride electrode, which was in a state of
full charge and was stabilized (the variation in open-circuit potential was less than $1\text{ mV}$
over 1 hour). The reaction current as a function of time was recorded in order to determine the diffusion coefficient and other diffusion related parameters.

3.6.5 Exchange current density, symmetry factor and over potential

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.2.3.9, and the symmetry factor can be calculated by Eq.2.3.11 or 2.3.12. The over-potential is the difference between the equilibrium potential and the polarization potential. Since the polarization curves, in the study, were all with reference to the open-circuit potential (equilibrium potential), the over-potential can be obtained directly from the polarization curve.

3.6.6 Electrode resistance

Electrode resistance can be classified as three components namely ohmic resistance, charge transfer resistance and diffusion resistance. The ohmic resistance can be obtained by the potential step method, and the charge transfer resistance and diffusion resistance can be calculated from polarization curves.

3.6.7 Kinetic properties

The constant potential discharge method was used to study the kinetic properties of a metal hydride electrode. From the curves of current versus time at different temperatures, the kinetic properties such as reaction order, rate constant and activation energy can be obtained.
Fig. 3.2.1 Cylindrical presses and a negative electrode (LaNi$_{4.7}$Al$_{0.3}$)
Fig. 3.2.2 A Ni(OH)$_2$/NiOOH positive electrode
Fig. 3.3.1 Potentiostat and a test cell of three-electrode and two-circuit system
Fig. 3.3.2  A test cell
Working electrode (negative electrode): Metal hydride electrode
Counter electrode (positive electrode): Ni(OH)$_2$/NiOOH electrode
Reference electrode: Hg/HgO electrode
Fig. 3.4.1. Schematic diagram of the experimental battery and testing apparatus
Fig. 3.4.2  The electrochemical measurement system (Solartron 1285) used in the present study
Fig. 3.5.1  The equivalent circuit of a rough, porous electrode

$C_1, C_2, \ldots, C_n$: double layer capacitance

$R_1, R_2, \ldots, R_n$: polarization resistance

$R_1', R_2', \ldots, R_n'$: solution resistance in the micro-holes on the electrode surface.
Fig. 3.5.2 Curves of potential step measurements (a) Electrode potential vs time
(b) Transient wave curve of current vs. time with reaction current (c) Transient wave curve of current vs. time without reaction current (d) Electric charge vs. time
Fig. 3.5.3 A typical current vs. time \((i - \tau)\) curve for potential step measurements of a metal hydride electrode with IR compensation after full charging.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 THERMODYNAMIC PROPERTIES OF METAL HYDRIDE ELECTRODES

The thermodynamic properties of metal hydrides such as enthalpy of formation ($\Delta H$), entropy of formation ($\Delta S$), Gibbs free energy ($\Delta G$) and plateau pressure ($P_{eq}$) are very important parameters that determine most of the characteristics of metal hydrides, and hence, the electrochemical properties of metal hydride electrodes. As was discussed in Chapter 2, three methods can be used to measure the thermodynamic parameters, namely; $P$-$C$-$T$ curves, theoretical calculations and $E$-$C$-$T$ curves. In the present work, we used a method involving quantum chemistry calculations, to obtain the thermodynamic parameters of metal hydrides. Also, the electrochemical method ($E$-$C$-$T$) was used to analyze the thermodynamic properties of the metal hydride electrodes.

4.1.1 Quantum Chemistry Calculations of the Thermodynamic Parameters for LaNi$_5$, LaNi$_4$Al, LaNi$_4$Mn Metal Hydrides

Based on the crystal structures and lattice parameters of LaNi$_5$, LaNi$_4$Al, LaNi$_4$Mn and their hydrides, quantum chemistry calculations were performed using the program Gamess [150] to calculate the thermodynamic parameters for the metal hydrides above, namely enthalpy ($\Delta H$), entropy ($\Delta S$), free energy ($\Delta G$) and equilibrium pressure ($P_{eq}$). Gamess was originally developed by the National Resource for Computation in Chemistry Software Catalog, University of California, Berkeley, CA. The version of Gamess used in present research was edited by M.W.Schmidt [150] in 1993. This program can perform a wide range of quantum chemical computations. It is more
accurate for calculations of systems which include heavy atoms, such as the rare earth elements in the present study.

In order to calculate these thermodynamic parameters, we need to know the composition of the IMC and the coordinates of every atom in the metal hydride. For experimental convenience in structure determination, deuterium (D) rather than hydrogen (H) is often used to locate the atom positions in the hydride by neutron diffraction techniques.

4.1.1.1 Crystal structures of LaNi₅, LaNi₄Al, LaNi₄Mn and their hydrides

LaNi₅, LaNi₄Al, LaNi₄Mn and their hydrides all have a hexagonal structure. A schematic diagram of the hexagonal structure of one LaNi₅ crystal cell is shown in Fig.4.1.1. LaNi₄Al and LaNi₄Mn have the same structure as shown in Fig.4.1.1, except that one of the Ni atoms (Ni-7) is replaced by either a Al or a Mn atom. In one unit cell of the crystal, there are four types of tetrahedral interstices (6m, 12n, 12o and 4h) and one type of octahedral interstice (3f), as shown in Fig.4.1.2. The total number of interstices in one cell is 37 (6m+12n+12o+4h+3f = 37 interstices). When hydrogen (deuterium) reacts with a IMC, the hydrogen (deuterium) atoms will occupy (diffuse into) some of these interstices to form a metal hydride (deuteride). The lattice parameters of these three IMCs and their hydrides (deuteride) are given in Table 4.1.1 [151].

<table>
<thead>
<tr>
<th>IMC &amp; Deuteride</th>
<th>Lattice parameters (Å)</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi₅</td>
<td>a=b=5.014</td>
<td>c=3.892</td>
</tr>
<tr>
<td>LaNi₅D₅.5</td>
<td>a=b=5.399</td>
<td>c=4.290</td>
</tr>
<tr>
<td>LaNi₄Al</td>
<td>a=b=5.066</td>
<td>c=4.070</td>
</tr>
<tr>
<td>LaNi₄AlD₅.8</td>
<td>a=b=5.310</td>
<td>c=4.242</td>
</tr>
<tr>
<td>LaNi₄Mn</td>
<td>a=b=5.045</td>
<td>c=4.022</td>
</tr>
<tr>
<td>LaNi₄MnD₅.9</td>
<td>a=b=5.451</td>
<td>c=4.344</td>
</tr>
</tbody>
</table>
In the calculations, we take the position of Ni-7 as the origin and the horizontal plane passing through point Ni-7 as the x,y-plane. The coordinates of the atoms in the three IMCs and their deuterides are listed in Table 4.1.2. These atom positions can be visualized by reference to Figs.4.1.1, 4.1.3a and 4.1.3b.

**Table 4.1.2** Coordinates of atoms in the three intermetallic compounds and their deuterides

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinate (Å)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (La)</td>
<td>a*cos30</td>
<td>0</td>
<td>a/2</td>
<td>C/2</td>
</tr>
<tr>
<td>B (La)</td>
<td>0</td>
<td>0</td>
<td>-a/2</td>
<td>c/2</td>
</tr>
<tr>
<td>C (La)</td>
<td>-a*cos30</td>
<td>0</td>
<td>0</td>
<td>c/2</td>
</tr>
<tr>
<td>D (La)</td>
<td>0</td>
<td>a/2</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>a (La)</td>
<td>a*cos30</td>
<td>0</td>
<td>-a/2</td>
<td>-c/2</td>
</tr>
<tr>
<td>b (La)</td>
<td>0</td>
<td>a/2</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>c (La)</td>
<td>-a*cos30</td>
<td>0</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>d (La)</td>
<td>0</td>
<td>-a/2</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>1 (Ni)</td>
<td>-a*cos30/3</td>
<td>0</td>
<td>0</td>
<td>c/2</td>
</tr>
<tr>
<td>2 (Ni)</td>
<td>a*cos30/3</td>
<td>0</td>
<td>0</td>
<td>c/2</td>
</tr>
<tr>
<td>I (Ni)</td>
<td>-a*cos30/3</td>
<td>0</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>II (Ni)</td>
<td>a*cos30/3</td>
<td>0</td>
<td>0</td>
<td>-c/2</td>
</tr>
<tr>
<td>3 (Ni)</td>
<td>a*cos30/2</td>
<td>-a/4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 (Ni)</td>
<td>-a*cos30/2</td>
<td>-a/4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5 (Ni)</td>
<td>a*cos30/2</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6 (Ni)</td>
<td>a*cos30/2</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7 (Ni)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**4.1.1.2 Calculations of enthalpy, entropy, free energy and plateau pressure**

The formation reaction of metal hydride (MDₓ) from an intermetallic compound (M) and deuterium (D) is given in Eq.4.1.1:

\[
M + \frac{x}{2}D_2 \rightarrow MD_x
\]  

(4.1.1)
We assume that deuterium behaves as an ideal gas, hence the formation enthalpy of the metal hydride ($\Delta H$) can be expressed as shown in Eq.4.1.2:

$$\Delta H = \Delta U + P \Delta V = \Delta U - \frac{x}{2}RT$$  \hspace{1cm} (4.1.2)

where $\Delta U$ is the internal energy, $R$ is gas constant and $T$ is temperature ($K$). According to the equilibrium relationship for a chemical reaction, the free energy of the reaction ($\Delta G$) can be expressed as shown in Eq.4.1.3:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K = \frac{x}{2}RT \ln P_{eq}$$  \hspace{1cm} (4.1.3)

where $\Delta S$ is the formation entropy of the metal hydride, $K$ is equilibrium constant of the reaction and $P_{eq}$ is the equilibrium pressure of hydrogen (deuterium). Thus, the equilibrium pressure is given by Eq.4.1.4:

$$P_{eq} = \exp \left[ \frac{2(\Delta U - \frac{xRT}{2} - T\Delta S)}{xRT} \right]$$  \hspace{1cm} (4.1.4)

With the quantum chemistry calculation program "Gamess", we can calculate the internal energy ($\Delta U$) and entropy ($\Delta S$) directly from the crystal lattice parameters, and hence the enthalpy ($\Delta H$), free energy ($\Delta G$) and equilibrium pressure ($P_{eq}$) can be obtained. The internal energy change ($\Delta U$) of the reaction system, according to Eq.4.1.1, can be calculated from Eq.4.1.5:
\[ \Delta U = \Delta U_{M_D} - \Delta U_M - \frac{x}{2} \Delta U_{D_2} = \Delta U_{cell} - \frac{x}{2} \Delta U_{D_2} \]  
(4.1.5)

where \( \Delta U_{cell} = \Delta U_{M_D} - \Delta U_M \), \( \Delta U_{M_D} \) is the internal energy of one crystal cell with \( x \) deuterium atoms distributed in different interstices of the cell, \( \Delta U_M \) is the internal energy of one crystal cell without any deuterium atoms, and \( \Delta U_{D_2} \) is the internal energy of a deuterium molecule. The values of \( \Delta U_{cell} \) and \( \Delta U_{D_2} \) can be obtained directly from the quantum chemistry calculations using the program "Gauss", and thus \( \Delta U \) can be obtained. Similarly, \( \Delta S \) can be obtained by using Eq. 4.1.6:

\[ \Delta S = \Delta S_{M_D} - \Delta S_M - \frac{x}{2} \Delta S_{D_2} = \Delta S_{cell} - \frac{x}{2} \Delta S_{D_2} \]  
(4.1.6)

where \( \Delta S_{cell} = \Delta S_{M_D} - \Delta S_M \), \( \Delta S_{M_D} \) is the formation entropy of one crystal cell with \( x \) deuterium atoms distributed in different interstices of the cell, \( \Delta S_M \) is the formation entropy of one crystal cell without any deuterium atoms, and \( \Delta S_{D_2} \) is the formation entropy of a deuterium molecule. The values of \( \Delta S_{cell} \) and \( \Delta S_{D_2} \) can be obtained directly from the calculations, and thus \( \Delta S \) can also be calculated. Therefore \( \Delta H \), \( \Delta G \) and \( P_{eq} \) can all be obtained by using these theoretical calculations.

When hydrogen reacts with the intermetallic compounds (IMC) to form metal hydrides, the hydrogen atoms occupy preferred interstitial sites in the hydrides. It is reasonable to assume that the hydrogen atoms occupy the centers of spheres tangent to the surfaces of the metal atoms coordinating the interstices in the metal hydrides: in fact, this assumption is very close to the experimental results [127]. Westlake [127, 128] has
analyzed the electronic structures of the deuterides and determined the preferred interstitial sites for deuterium atoms. These are listed in Table 4.1.3.

Table 4.1.3 Preferred interstitial sites for deuterium atoms in three deuterides

<table>
<thead>
<tr>
<th>Deuterides</th>
<th>Site and number of deuterium atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi₃D₆.₅</td>
<td>6m = 2; 12n + 3f = 3; 12o = 1; 4h = 0.5.</td>
</tr>
<tr>
<td>LaNi₄AlD₄.₈</td>
<td>6m = 2; 12n = 3.</td>
</tr>
<tr>
<td>LaNi₄MnD₅.₉</td>
<td>6m = 2; 12n + 3f = 3; 12o + 4h = 1.</td>
</tr>
</tbody>
</table>

The numbers of deuterium atoms in the interstitial sites given in Table 4.1.3 are the maximum values. In fact, the stable compositions of the deuterides are LaNi₃D₃.₅, LaNi₄AlD₂.₄ and LaNi₄MnD₃.₅. The thermodynamic parameters were calculated using the stable deuterides rather than the deuterides with maximum number of deuterium atoms, as is commonly done in the determination of thermodynamic parameters for solid-gas reactions. In the solid-gas reaction process, experimental results for these parameters are obtained at equilibrium for the reactions, i.e. when the deuteride is in a stable state. This then creates a problem, namely the distributions of deuterium atoms in the stable deuterides will be different from those in the deuterides with the maximum number of deuterium atoms given in Table 4.1.3. In order to perform the calculations, the deuterium atom distributions must be known. Fortunately, the *Gamess* calculations can overcome this “problem” fairly readily. According to the structure analysis method of Westlake [127, 128], there are relatively few possible combinations of deuterium atom distributions in the deuterides. For every combination, the corresponding energy change (ΔU or ΔG)
for the IMC-deuterium reaction can be calculated with *Gamess*. According to the energy change of the reaction, the distribution with lowest energy (most stable) should be the most reasonable one. We assumed LaNi₅D₅, LaNi₄AlD₄ and LaNi₄MnD₅ to be the stable deuterides for the purpose of calculation. The deuterium atom distributions and corresponding energy changes are listed in Tables 4.1.4a, 4.1.4b and 4.1.4c. It is obvious that the type A distributions for the three deuterides are the most stable ones. The $\Delta H$, $\Delta S$, $\Delta G$ and $P_{eq}$ values for the three deuterides were all calculated with these stable distributions as shown in Table 4.1.5.

Table 4.1.4a Possible distributions of deuterium atoms in the deuterides and associated energy changes in the LaNi₅D₅ crystal cell.

<table>
<thead>
<tr>
<th></th>
<th>6m</th>
<th>3f</th>
<th>12n</th>
<th>12o</th>
<th>4h</th>
<th>$\Delta U$ (kJ/mol·LaNi₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-79.088</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>192.579</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>464.246</td>
</tr>
</tbody>
</table>

Table 4.1.4b Possible distributions of deuterium atoms in the deuterides and associated energy changes in the LaNi₄AlD₄ crystal cell.

<table>
<thead>
<tr>
<th></th>
<th>6m</th>
<th>3f</th>
<th>12n</th>
<th>12o</th>
<th>4h</th>
<th>$\Delta U$ (kJ/mol·LaNi₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-115.084</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>-74.857</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-34.634</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>1.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>5.592</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>45.821</td>
</tr>
</tbody>
</table>
Table 4.1.4c Possible distributions of deuterium atoms in the deuterides and associated energy changes in the LaNi₄MnD₅ crystal cell.

<table>
<thead>
<tr>
<th></th>
<th>6m</th>
<th>3f</th>
<th>12n</th>
<th>12o</th>
<th>4h</th>
<th>ΔU (kJ/mol·LaNi₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-120.517</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>367.940</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>856.398</td>
</tr>
</tbody>
</table>

Table 4.1.5a Calculated values of the thermodynamic parameters for a unit cell of the three different Deuterides

<table>
<thead>
<tr>
<th></th>
<th>LaNi₃D₆.5</th>
<th>LaNi₄AlD₄.₈</th>
<th>LaNi₄MnD₅.₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔU&lt;sub&gt;cell&lt;/sub&gt; (kJ/mol·M)</td>
<td>-7256.201</td>
<td>-5856.789</td>
<td>-7297.685</td>
</tr>
<tr>
<td>U&lt;sub&gt;D₂&lt;/sub&gt; (kJ/mol·D₂)</td>
<td>-2870.867</td>
<td>-2870.867</td>
<td>-2870.867</td>
</tr>
<tr>
<td>ΔU (kJ/mol·M)</td>
<td>-79.033</td>
<td>-115.054</td>
<td>-120.516</td>
</tr>
<tr>
<td>ΔS&lt;sub&gt;cell&lt;/sub&gt; (J/K·mol·M)</td>
<td>61.088</td>
<td>36.774</td>
<td>65.642</td>
</tr>
<tr>
<td>S&lt;sub&gt;D₂&lt;/sub&gt; (J/k·mol·D₂)</td>
<td>144.585</td>
<td>144.585</td>
<td>144.585</td>
</tr>
<tr>
<td>ΔS (J/K·mol·M)</td>
<td>-300.374</td>
<td>-252.396</td>
<td>-295.821</td>
</tr>
</tbody>
</table>
Table 4.1.5b Comparison of the calculated and experimental values of the thermodynamic parameters for the three different deuterides

<table>
<thead>
<tr>
<th></th>
<th>LaNi₅D₆.5</th>
<th>LaNi₄AI₄D₄.8</th>
<th>LaNi₄MnD₅.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔS ( (J/K\cdot mol\cdot D₂) )</td>
<td>Cal. -120.2</td>
<td>-126.2</td>
<td>-118.3</td>
</tr>
<tr>
<td></td>
<td>Exp. -118.8 [152]</td>
<td>-124.7 [152]</td>
<td>-115.5 [153]</td>
</tr>
<tr>
<td></td>
<td>Exp. -112.4 [143]</td>
<td>-123.7 [143]</td>
<td>-121.6 [143]</td>
</tr>
<tr>
<td>ΔH ( (kJ/mol\cdot D₂) )</td>
<td>Cal. -34.1</td>
<td>-60.0</td>
<td>-50.7</td>
</tr>
<tr>
<td></td>
<td>Exp. -34.3 [152]</td>
<td>-58.6 [152]</td>
<td>-48.5 [153]</td>
</tr>
<tr>
<td></td>
<td>Exp. -32.2 [143]</td>
<td>-52.3 [143]</td>
<td>-48.1 [143]</td>
</tr>
<tr>
<td>ΔG ( (kJ/mol\cdot D₂) )</td>
<td>Cal. 1.73</td>
<td>-22.4</td>
<td>-15.4</td>
</tr>
<tr>
<td></td>
<td>Exp. 2.26 [155, 156]</td>
<td>-21.5 [152]</td>
<td>-12.1 [154]</td>
</tr>
<tr>
<td>P_{eq} (atm)</td>
<td>Cal. 2.01</td>
<td>1.2×10⁻⁴</td>
<td>2.0×10⁻³</td>
</tr>
<tr>
<td></td>
<td>Exp. 1.56 [152]</td>
<td>1.7×10⁻⁴ [152]</td>
<td>7.5×10⁻³ [154]</td>
</tr>
</tbody>
</table>

As can be seen from the calculated results, the agreement between calculated and experimentally measured values of the ΔH, ΔS, ΔG and \( P_{eq} \) by P-C-T method, as discussed in section 2.3.2, is quite good. The calculation method, i.e. quantum chemistry calculation with program Gamess, can thus be used for the determination of the thermodynamic parameters of hydrogen storage materials.

### 4.1.2 Electrochemical Analysis of the Thermodynamic Parameters

In present work, the thermodynamic parameters ΔH, ΔS, ΔG and \( P_{eq} \) for the metal hydride electrodes were measured using an electrochemical method, i.e. \( E-C-T \) curves. Three metal hydride electrodes (B2, A4 and A1) were used for these measurements.

The \( E-C-T \) curves (equilibrium potential vs. hydrogen content) of the three electrodes were measured at temperatures of 0°C, 25°C, 35°C, 45°C and 55°C, and are shown in Figs.4.1.4, 4.1.5 and 4.1.6. The value of the equilibrium potential was chosen as
the potential at the middle of the E-C-T curve (plateau potential value of the curve). The relationship between the equilibrium potential and temperature for the three electrodes is shown in Fig. 4.1.7. The relationship between equilibrium potential \( E_{eq} \) and temperature for electrodes B2, A4 and A1 can be obtained from Fig. 4.1.7, and is shown in Eqs. 4.1.7, 4.1.8 and 4.1.9, respectively:

\[
E_{eq} = - 0.8842 - 2.649 \times 10^{-4} \ (T-273.15) \quad (4.1.7)
\]

\[
E_{eq} = - 0.9122 - 1.927 \times 10^{-4} \ (T-273.15) \quad (4.1.8)
\]

\[
E_{eq} = - 0.9172 - 2.110 \times 10^{-4} \ (T-273.15) \quad (4.1.9)
\]

According to electrochemical principles, the entropy \( \Delta S_e \) and enthalpy \( \Delta H_e \) of the electrochemical reaction can be calculated using Eqs. 4.1.10 and 4.1.11, respectively:

\[
\Delta S_e = n F \left( \frac{\partial E}{\partial T} \right)_p \quad (4.1.10)
\]

\[
\Delta H_e = \Delta G_e + T \Delta S_e = nFE - nFT \left( \frac{\partial E}{\partial T} \right)_p \quad (4.1.11)
\]

According to Wang's results [14], the relationships between \( \Delta H_e, \Delta S_e \) obtained by Nernst equation and \( \Delta H_p, \Delta S_p \) for the gaseous reaction can be described as in Eqs. 2.3.27 and 2.3.28, which are discussed in section 2.3.2 and shown below again:

\[
\Delta H_p = -195.28724 - \Delta H_e (kJ/K\cdot mol) \quad (2.3.27)
\]

\[
\Delta S_p = -53.45 + \Delta S_e (J/K\cdot mol) \quad (2.3.28)
\]
Thus the corresponding equilibrium pressure for the gaseous reaction can be calculated from the parameters obtained from the electrochemical measurements using Eq. 4.1.12 or Eq. 4.1.13:

\[
\ln P_{eq} = \frac{\Delta H_p - \Delta S_p}{RT} = \frac{-195287.24 + 53.45T - nFE_{eq}}{RT}
\]  

(4.1.12)  

(4.1.13)

where \( F \) is Faraday’s constant, \( (F = 96485.3 \text{ C/mol}) \). The calculated enthalpy, entropy and equilibrium pressure obtained from electrochemical measurement for the three electrodes are listed in Table 4.1.6. The \( P-T-C \) curves for the three electrodes determined from the \( E-C-T \) curves at temperatures of 0°C, 25°C, 35°C, 45°C and 55°C are shown in Figs. 4.1.8, 4.1.9 and 4.1.10.

Table 4.1.6 Comparison of the enthalpy, entropy and equilibrium pressure determined by the electrochemical and gaseous methods.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Method</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/K·mol)</th>
<th>( P_{eq} ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delta</td>
<td>( \Delta H_a )</td>
<td>( \Delta H_p )</td>
<td>( \Delta S_a )</td>
</tr>
<tr>
<td>B2</td>
<td>Electrochemical</td>
<td>-156.75</td>
<td>-38.53</td>
<td>-51.12</td>
</tr>
<tr>
<td>Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35} (mixed with Ni)</td>
<td>Gaseous</td>
<td>-32.02</td>
<td>-92.37</td>
<td>0.06 [157]</td>
</tr>
<tr>
<td>A4</td>
<td>Electrochemical</td>
<td>-165.91</td>
<td>-29.38</td>
<td>-37.19</td>
</tr>
<tr>
<td>LaNi_{4.7}Al_{0.3} (mixed with Ni)</td>
<td>Gaseous</td>
<td>-34.10</td>
<td>-113.19</td>
<td>0.4–0.6 [158]</td>
</tr>
<tr>
<td>A1</td>
<td>Electrochemical</td>
<td>-165.89</td>
<td>-29.39</td>
<td>-40.72</td>
</tr>
<tr>
<td>LaNi_{4.7}Al_{0.3} (mixed with Ni and Cu)</td>
<td>Gaseous</td>
<td>-34.10</td>
<td>-113.19</td>
<td>0.4–0.6 [158]</td>
</tr>
</tbody>
</table>
The thermodynamic parameters such as enthalpy, entropy and equilibrium pressure obtained by electrochemical method (E-C-T) are very close to the values obtained by the gaseous method (conventional P-C-T method). Also the electrochemical E-C-T curves for the discharging process can be used to calculate the P-C-T curves, which are related to the hydrogen desorption process for the gaseous reaction. Since the determination of the P-C-T curves for the gaseous reaction is usually conducted in a Sieverts' type apparatus with a well-sealed reactor and sensitive pressure measurement systems, the accuracy of the pressure measurement is limited, especially at low pressures. However, for the electrochemical method, the potential can be measured very accurately and conveniently, and thus the thermodynamic parameters can be determined more accurately than for the conventional P-C-T method.
Fig. 4.1.1 Schematic diagram of the hexagonal structure of LaNi$_5$. 
Fig.4.1.2 Schematic diagram of the hexagonal structure of LaNi$_5$ showing the four types of tetrahedral interstices and one type of octahedral interstice.
Fig. 4.1.3 Projection of the LaNi₅ (LaNi₄Al, LaNi₄Mn) structure on the plane of (a) z = ± c/2 (b) z = 0. For LaNi₄Al and LaNi₄Mn, position Ni-7 will become an Al or Mn atom, respectively.
Fig. 4.1.4 E-C-T curves for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$ mixed with Ni) at different temperatures.
Fig. 4.1.5 E-C-T curves for electrode A1 (LaNi₄₋₇Al₀₃ mixed with Ni and Cu) at different temperatures.
Fig. 4.1.6 E-C-T curves for electrode B2
\(\text{Mm}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \text{mixed with Ni}\) at different temperatures.
Fig. 4.1.7 The relationship between the equilibrium potential and temperature for electrodes \( B2 (\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \text{mixed with Ni}), \)
\( A4 (\text{LaNi}_{4.7}\text{Al}_{0.3} \text{mixed with Ni}) \) and \( A1 (\text{LaNi}_{4.7}\text{Al}_{0.3} \text{mixed with Ni and Cu}). \)
Fig. 4.1.8 P-C-T curves for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$ mixed with Ni) determined from E-C-T curves at different temperatures.
Fig. 4.1.9 P-C-T curves for electrode A1 (LaNi$_4$,Al$_{0.3}$ mixed with Ni and Cu) determined from E-C-T curves at different temperatures.
Fig. 4.1.10 P-C-T curves for electrode B2 
(Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ mixed with Ni) determined from E-C-T curves at different temperatures.
4.2 SPECIFIC SURFACE AREA OF METAL HYDRIDE ELECTRODE

Being a porous electrode, the metal hydride electrode has much larger specific surface area than the apparent area. The specific surface area determines many electrode properties, such as the hydrogen absorption/desorption processes, polarization and other kinetic properties. A transient measurement method, the potential step measurement, was used to analyze the double layer capacitance \( C_d \) and hence, the real surface area \( S_{\text{real}} \) of the metal hydride electrode.

4.2.1 Double layer capacitance

Four \( i-t \) curves, for the 0, 1, 5 and 15th cycles of the potential step transient process for electrode B3 (Pd-coated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \)) are shown in Fig.4.2.1. It is obvious that only before activation of the electrode (i.e. 0 cycle), can the reaction current, \( i_r \), be neglected, and the integral area of electric quantity calculated accurately. After activation or partial activation of the electrode, the reaction current cannot be neglected. Rather, it must be considered in the calculation of integral area, as shown in Figs.3.5.2b and 3.5.3. For the un-coated and Pd-coated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \) electrodes in present study, cycles 1 to 5 are part of the activation process. The variation in capacity with number of cycles for these two particular electrodes is shown in Fig.4.2.2.

It has been reported [159] that the absorbed species on the surface of electrode influence the measured value of the double layer capacitance. Even if the absorbed species do not participate in the electrochemical reactions, they still influence the measurement of the double layer capacitance, since they change the double layer structure of the electrode.
4.2.2 Specific surface area

The specific surface area of metal hydride is one of the most important parameters related to the kinetic properties of the electrode. All kinetic properties of the electrode, such as exchange current density, limiting current density, over-potential, high rate charge/discharge ability and electrocatalytic activity, are related to the real specific surface area. Through the measurement of the real specific surface area of a metal hydride electrode, the electrode properties can be determined.

4.2.2.1 Variation of the real specific surface area with number of cycles

The real specific surface areas of un-coated (B1) and Pd-coated (B3) Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35} electrodes were measured by the potential step method after different number of cycles for both charging and discharging. The variation of the specific surface area with number of cycles for these two electrodes is shown in Figs. 4.2.3 and 4.2.4 for the un-coated and Pd-coated electrodes, respectively. The general features are as follows:

(a) The specific surface area of the metal hydride electrode increases with increasing number of cycles. The increase in specific surface area results from the micro-cracking of the alloy powders in the electrode. Since the hydriding/dehydriding processes lead to crystal lattice expansion, this produces strain and hence stresses. Since, the intermetallic compounds are brittle, the hydriding/dehydriding process results in the micro-cracking of the alloy powders and produces new, smaller particles. The reduction in particle size leads to an increase in specific surface area.

(b) For the first 30 cycles, the specific surface area increases significantly. However, after 30 cycles, the rate of increase in specific surface area is small. Also for the first
cycle, the rate of surface area increase is much greater than for subsequent cycles. Thus, the degree of micro-cracking in the first cycle is greater than in any subsequent cycle. The specific surface area after the first cycle is 4 times (electrode B1) to 10 times (electrode B3) larger than that of the original electrode before activation.

(e) In the curves of specific surface area vs. number of cycles shown in Figs. 4.2.3 and 4.2.4, obvious differences develop after 5–10 cycles between the specific surface areas after charging and after discharging. We developed a model of hydrogen absorption on an electrode surface to explain this difference as shown in Fig. 4.2.6. After activation (5–10 cycles), because of the characteristics (rough surface and porous) and the micro-cracks in the electrode, there are more cracks produced in both the bulk and on the surface of the electrode with cycling. The cracks are also filled with electrolyte. Since the double layers exist at the interface of electrode and electrolyte, they also must exist at the interface between the crack surfaces and electrolyte. During charging of the double layers in the potential step process, all the double layers between the crack surfaces and electrolyte are assumed to be charged. However, as mentioned in section 4.2.1, the absorbed species can influence the measurement of the double layer capacitance. For a metal hydride electrode, when the potential step measurement is conducted after discharging of the electrode, there is no hydrogen absorbed on the crack surface and the electrode surface. In this case, all the double layers at the interface between the crack surface and electrolyte can be fully charged. Thus, in this case, the double layer capacitance, and the specific surface area, can be measured accurately. However, after charging of the electrode, the surface of the electrode is partially covered by absorbed hydrogen and also the crack surfaces in the bulk of the electrode are partially covered by the absorbed hydrogen atoms diffused in
from the surface of the electrode. When the potential step measurement is conducted after charging, the paths from the surface of the electrode to the crack surface in the bulk are mainly blocked by the absorbed hydrogen atoms at the surface of the electrode, as shown in Fig.4.2.6. As a consequence, the charging process of the double layers between the crack surfaces and the electrolyte in bulk will be at least partially blocked. Thus the double layer capacitance, and therefore the specific surface area values, measured after charging are smaller than those measured after discharging. Thus there is a difference in specific surface area measured after charging and after discharging; see Figs.4.2.3 and 4.2.4.

However, for the first 5 cycles the two curves after charging or discharging are very similar. This implies that during the first 5 cycles, most of the micro-cracking occurs on the surface rather than in the bulk of the electrode, i.e. there are few crack surfaces in the bulk and most of the double layers are on the surface of the electrode. The specific surface areas, both after charging and after discharging, reflect the rough surface of the electrode. After 10 cycles, micro-cracking occurs not only on the surface but also in the bulk of the electrode. The specific surface area after charging increases slowly with cycling, but the specific surface area after discharging increases much more rapidly with cycling. This means that, after 10 cycles, the micro-cracking in the bulk of the electrode is the dominant factor, i.e. micro-cracking occurs much more readily in the bulk than on the surface of the electrode. Up to 5 cycles, micro-cracking on the surface of the electrode is dominant, i.e. micro-cracking occurs mainly on the surface of the electrode rather than in the bulk of the electrode. Since there are no absorbed species on the surface or in the bulk of the electrode after discharging, the specific surface area measured after
discharging is little influenced by absorbed species, and is closer to the real specific
surface area. Thus, the specific surface area of the electrode measured after discharging is
considered to be the real specific surface area of the electrode. It can be seen in Fig. 4.2.5
(which is a comparison of Figs. 4.2.3 and 4.2.4) that the specific surface areas of the two
electrodes (B1 and B3) measured after charging are approximately the same for all
numbers of cycles. The real specific surface area (measured after discharging) of the Pd-
coated electrode is essentially the same as that for un-coated electrode up to the 20th
cycle. However, it becomes larger than that of un-coated electrode after the 25th cycle.
This implies that the Pd-coated Ml0.95Ti0.05Ni3.85Co0.45Mn0.35Al0.35 electrode undergoes
greater micro-cracking than an un-coated electrode after 25 cycles and thus more “fresh”
surface area is produced. This should affect the kinetic properties such as the exchange
current density and limiting current density for the electrode reactions. This behavior is
discussed in more detail in section 4.4.

(d) A comparison of the specific surface area (after discharge) of electrodes B1 (un-
coated Ml0.95Ti0.05Ni3.85Co0.45Mn0.35Al0.35), B3 (Pd-coated
Ml0.95Ti0.05Ni3.85Co0.45Mn0.35Al0.35), A3 (LaNi4.7Al0.3+Ni) and A2 (LaNi4.7Al0.3+Ni+Cu) is
shown in Fig. 4.2.7. The magnitude of the specific surface areas of electrodes B1, B3, A3
and A2 are in the order of S(B1) < S(B3) < S(A3) < S(A2), and the specific surface areas of
electrodes A3 and A2 (LaNi4.7Al0.3) are much larger than that of electrodes B1 and B3
(Ml0.95Ti0.05Ni3.85Co0.45Mn0.35Al0.35). This means that electrodes A2 and A3 pulverize
more readily than electrodes B1 and B3. This is one of the more important reasons that
Mm-based metal hydride alloy electrodes have a much longer cycle life than LaNi4.7A0.3
electrodes. As for electrodes B1 and B2, the specific surface area of electrodes A2 and
A3 increases significantly in the first 5 cycles (which is the activation process for the electrodes), and after about 30 cycles, any further changes in specific surface area are quite small. Comparing the specific surface areas of electrodes A3 and A2, it seems that the Cu addition in the LaNi$_{4.7}$Al$_{0.3}$ electrode significantly increases the specific surface area of the electrode.

4.2.2.2 Variation of specific surface area with hydrogen concentration in the electrode

Fig.4.2.8 shows the variation of the specific surface area with hydrogen concentration for the Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrode (B1). As with the P-C-T curves for metal hydrides, the curve shown in Fig.4.2.8 can be divided into three phase regions, namely the $\alpha$-phase, the $\alpha+\beta$ phases and the-$\beta$ phase region. In the $\alpha+\beta$ region, a phase transformation occurs from the $\alpha$-phase to the-$\beta$ phase at hydrogen concentrations (H/M) in the range of about 1~3. There is a single phase, the $\alpha$ phase, for hydrogen concentrations (H/M) less than 1, and only the $\beta$-phase for H/M greater than about 3. In the $\alpha+\beta$ phase region, the measured specific surface area remains almost constant. However, in the $\alpha$ or $\beta$-phase regions, the measured specific surface area increases with the depth of discharge. In particular, the specific surface area increases greatly at the end of discharge in the $\alpha$-phase region. The increase in area results from two factors. The first is the hydrogen concentration. Since the absorbed hydrogen atoms influence the measurement of double layer capacitance and surface area, the measured specific surface area increases with decreasing hydrogen concentration. The other factor is micro-cracking of the alloy powders of the electrode. We assume that the micro-cracking occurs in the $\alpha+\beta$ phase region at the same rate as in the single phase regions ($\alpha$ or $\beta$). However,
the real specific surface area in the $\alpha+\beta$ or $\beta$-phase regions cannot be measured accurately because of the influence of the absorbed hydrogen. If the above assumption is true, the measured specific surface area in the $\beta$-phase region should be the same as that in the of $\alpha+\beta$ phase region. Since the surface of the electrode was mainly covered by the absorbed hydrogen because of the high hydrogen concentration in $\alpha+\beta$ and $\beta$-phase regions, thus the measured specific surface area merely reflects the electrode’s apparent surface, not including the bulk of the electrode. Therefore, the specific surface area measured in the $\alpha+\beta$ and $\beta$-phase regions should be the same, i.e. the apparent surface area of the electrode. However, the measured specific surface area in the $\beta$-phase region increases with depth of discharge, rather than in the case of the $\alpha+\beta$ phase region, where the specific surface area does not change with depth of discharge. This implies that there is higher micro-cracking rate in the $\beta$-phase region than in the $\alpha+\beta$ region, which indicates that the above assumption, i.e. assuming that the micro-cracking occurs in the $\alpha+\beta$ phase region at the same rate as in the single phase regions ($\alpha$ or $\beta$), is not reasonable. Also in the $\alpha$-phase region, the measured specific surface area increases greatly at the end of discharge. This behavior also results from two factors as in $\alpha+\beta$ phase region (i.e. hydrogen concentration and micro-cracking of the alloy powders of the electrode). However, as in the $\beta$-phase region, the micro-cracking in the $\alpha$-phase region should also be greater than in the $\alpha+\beta$ phase region. When going from the $\alpha+\beta$ phase region to the $\alpha$-phase region, the decrease in hydrogen concentration is not large enough to significantly increase the measured specific surface area (from 10 to 13 m$^2$/g). It is thus reasonable to conclude that the micro-cracking rate in the $\alpha$ phase region is greater than
that in the $\alpha+\beta$ phase region. From the above analysis, it can be seen that micro-cracking does not occur evenly over the range of discharge, rather, it occurs to a much greater degree in the single phase regions, namely the $\beta$ phase region (beginning of discharge) and the $\alpha$ phase region (end of discharge) than in the two-phase ($\alpha+\beta$) region.

4.2.3 Kinetic parameters related to specific surface area

As discussed in section 4.4.2.2-1, the specific surface areas measured after charging and after discharging both increase with cycling. However, after 30 cycles, the real specific surface area (the area measured after discharging) increases very slowly with further cycling, and remains at a nearly constant value. This implies that the kinetic behavior of the electrode remains stable after about 30 cycles. Kinetic parameters such as the diffusion coefficient (diffusion rate), exchange current density, limiting current and over-potential should be also tend to become stable after about 30 cycles. The relationship between the kinetic parameters and the specific surface area is discussed further in sections 4.3, 4.4 and 4.6.
Fig. 4.2.1 Variation of current with time at a 10mV potential step for electrode B3 (Pd-coated Mm_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.43}Mn_{0.35}Al_{0.35}) at 25°C after full charging.
Fig. 4.2.2 Variation of the discharge capacity of uncoated (B1) and Pd-coated (B3) $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ electrodes with number of cycles at 25°C.
Fig. 4.2.3 Variation of specific surface area with number of cycles for an uncoated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ electrode (B1) at $25^\circ\text{C}$.
Fig. 4.2.4 Variation of specific surface area with number of cycles for a Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35} electrode (B3) at 25°C.
Fig. 4.2.5 Variation of specific surface area with number of cycles for uncoated (B1) and Pd-coated (B3) $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ electrodes at $25^\circ\text{C}$.
Fig. 4.2.6 Schematic illustration of hydrogen absorption on the rough surface of a metal hydride electrode.
Fig. 4.2.7 Variation of specific surface area (after discharge) with number of cycles at 25°C for electrodes:
A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni), A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu)
B1 and B3 (uncasted and Pd-coated-Mn$_{0.9}$Ti$_{0.05}$Ni$_{1.65}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.2.8 Variation of specific surface area with hydrogen concentration for electrode B1 (Mm_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at 25 °C. Data are for the 25th cycle.
4.3 DIFFUSION OF HYDROGEN IN A METAL HYDRIDE ELECTRODE

The electrochemical behavior of metal hydride electrodes are mainly controlled by the kinetic processes at the metal/electrolyte interface and the rate of hydrogen diffusion in the bulk of the electrode. One of the key parameters, examined in this research, was the diffusion coefficient for hydrogen ($D_H$). The diffusion coefficients for different metal hydride electrodes were determined by a potential step method (potentiostatic discharge). The factors which influence the diffusion behavior of hydrogen, such as the number of cycles, the specific surface area, the hydrogen concentration, temperature, discharge potential and diffusion activation energy are discussed in sections 4.3.1 to 4.3.4.

4.3.1 Determination of the Diffusion Coefficient of Hydrogen

The reaction current as a function of time in a potential step measurement was recorded to study the diffusion process. The sharp increase in reaction current at $t=0$ is believed to result from the ohmic resistance (as discussed in section 4.2.1). The charge transfer process occurs at short times for discharging the double layer, or for desorbing hydrogen on the surface of the MH particles. The hydrogen diffusion process occurs in a time which is much longer than that for the charge transfer process. The hydrogen diffusion will result in a decrease in the reaction current with an increase in time.

Assuming that the hydride powders are spherical, the variation of diffusion current with time follows Eq.4.3.1 [106]:

$$\log i = \log \left[ \pm \frac{6FD}{da^2}(C_0-C_t) \right] - \frac{\pi^2}{2.303} \left( \frac{D}{a^2} \right) t$$  \hspace{1cm} (4.3.1)
where $D$ is the diffusion coefficient of hydrogen (cm$^2$·s$^{-1}$), $C_0$ is the initial hydrogen concentration in the bulk of alloy (mol·cm$^{-3}$), $C_s$ is a constant concentration of hydrogen at the spherical surface (mol·cm$^{-3}$), $a$ is the sphere radius (cm), $d$ is the density of the MH alloy (g·cm$^{-3}$), $t$ is the charge or discharge time (s) and $i$ is the diffusion current (A·g$^{-1}$).

The ± sign indicates either the charge (-) or discharge (+) process.

By curve fitting the $\log(i)$ vs. $t$ plots to Eq.4.3.1, the $D/a^2$ ratio can be calculated. $\log(i)$ decreases linearly with time at sufficiently large times, and thus the $D/a^2$ ratio can be determined by the slope of the straight line plot for large values of $t$. If the sphere radius $a$ is known, the diffusion coefficient $D$ can be obtained.

4.3.2 Diffusion Coefficient and Particle Size

Plots of the reaction current as a function of time for electrodes A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni), A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni +Cu), B1 and B3 (un-coated and Pd-coated Ml$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) for different number of cycles are shown in Figs.4.3.1 to 4.3.4. At longer time (usually after 500 seconds for the systems studied in this research), there is a linear relationship between $\log(i)$ and time (s). The corresponding $D/a^2$ ratios calculated for the different electrodes are given in Fig.4.3.5. With increasing number of cycles, the $D/a^2$ ratio increases greatly in the first 30 cycles, and then remains almost constant on further cycling. This means after about 30 cycles, the electrochemical properties become stabilized. The $D/a^2$ ratios for electrodes A2 and A3 (LaNi$_{4.7}$Al$_{0.3}$) are much larger than for electrodes B1 and B3 (Ml$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).

Upon charge/discharge cycling, the particle size gradually decreases, i.e. the sphere radius decreases. However, the hydrogen diffusion coefficient $D_H$ does not change
very much with changing particle size [135], and thus the \( D/a^2 \) ratio increases with increasing number of cycles. The metal hydride electrode alloys used in the present work were mechanically pulverized to obtain sifted particle sizes of around 45\( \mu \)m to 53\( \mu \)m, and this value can then be used to estimate the hydrogen diffusion coefficient \( D_H \). Taking electrode B1 (Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\)) as an example, and assuming that the sphere radius of the electrode alloy is 45\( \mu \)m at the beginning of cycling, if we took the experimental result for the \( D/a^2 \) ratio of the un-cycled electrode B1, i.e. 1.9\times 10^{-5} \text{ (s}^{-1}), we calculate a hydrogen diffusion coefficient, \( D_H \), of 3.9\times 10^{-10} \text{ (cm}^2/\text{s}). Similarly for electrode B3, the calculated diffusion coefficient is 4.1\times 10^{-10} \text{ (cm}^2/\text{s}); for electrode A3, it is 3.2\times 10^{-10} \text{ (cm}^2/\text{s}); and for electrode A2, it is 4.1\times 10^{-10} \text{ (cm}^2/\text{s}). However, the above calculation has some inaccuracies, since the particle size was not experimentally measured, but rather was estimated from the sieve size.

Experimental values for the hydrogen diffusion coefficient quoted by different researchers vary quite widely, ranging from 10\(^{-9}\) to 10\(^{-11}\) \text{ cm}^2/\text{s} [106, 131, 135, 138]. In the present study, the diffusion coefficient measurement for each cycle was conducted after fully charging, and thus the hydrogen concentration can be considered to be the same for each measurement. Thus the hydrogen diffusion coefficient measured after fully charging for each cycle can be regarded as a constant. In order to determine the particle size variation with cycling, it is assumed that the hydrogen diffusion coefficients for the four electrodes are the values determined as above. Hence the particle radius of the electrode alloy powder can be calculated from the \( D/a^2 \) ratio and the diffusion coefficient. Results for the sphere radius as a function of number of cycles are shown in Fig.4.3.6. According to Fig.4.3.6, during the first 10 cycles, the particle size of electrodes A3
(LaNi$_{4.7}$Al$_{0.3}$+Ni) and A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni +Cu) decrease much faster than that of electrodes B1 and B3 (un-coated and Pd-coated Ml$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$). In another words, electrodes A3 and A2 pulverize more easily than electrodes B1 and B3, which is the same conclusion drawn in section 4.2.2.1. Electrodes A2 and A3 have nearly the same pulverization rate, which means that mixing Cu powder with the electrode alloy does not improve the pulverization behavior of the LaNi$_{4.7}$Al$_{0.3}$ electrode. Electrodes B1 and B3 have better resistance to pulverization than electrodes A2 and A3. Pd-coating (B3) greatly improves the resistance to pulverization. Since the pulverization of the electrode alloy powder is one of the main factors limiting the cycle lifetime of the electrode, Pd-coating is a promising method for improving electrode performance.

As already discussed, it can be seen from Fig.4.3.5 that the $D/a^2$ ratio increases with cycling and reaches a stable value after about 30 cycles. If the hydrogen diffusion coefficient $D_H$ is considered to be a constant, the sphere radius ($a$) must decrease in the manner shown in Fig.4.3.6. The sphere radius decreases rapidly for the first 10 cycles, and then becomes constant after about 30 cycles. Comparing this result with the specific surface area vs. cycling results given in Figs.4.2.8 and 4.2.10, there is good agreement. As the specific surface area ($S$) increases, the sphere radius ($a$) decreases. This demonstrates that the diffusion behavior is related to the specific surface area through the sphere radius ($a$).

4.3.3 Diffusion Coefficient and Depth of Discharge (DOD)

The $D/a^2$ ratio was also measured at different depths of discharge. After the electrode was fully charged and rested at equilibrium potential until it was stabilized (variation in potential was less than 1 mV over 1 hour), the potential step measurement
was conducted to record the current variation with time. Then the electrode was
discharged for 30mAh/g each time and rested until stabilized before making another
measurement. The process was repeated until the total capacity was discharged (the
discharge potential reached -0.60V). The diffusion current as a function of time for
electrode B2 (Ml_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at different depths of discharge at 25°C
is shown in Fig.4.3.7. The log(t) vs. t curves show a linear relationship at longer times.
The slope of the linear section (D/α^2) increases with increasing the depth of discharge, i.e.
the D/α^2 ratio increases with decreasing hydrogen concentration in the electrode. The
D/α^2 ratios for electrode B2 as a function of DOD at the temperatures of 0°C, 25°C,
35°C, 45°C and 55°C are shown in Fig.4.3.8. The D/α^2 ratios increase significantly with
increasing temperature.

4.3.4 Diffusion Activation Energy and Temperature

Temperature is one of the key factors influencing the behavior of metal hydride
electrodes. The hydrogen diffusion coefficient D_H varies with temperature according to
Arrhenius expression as shown in Eq.4.3.2:

\[ D_H = D_0 \exp(-\frac{E_a}{RT}) \]  \hspace{1cm} (4.3.2)

where D_0 is frequency factor, E_a is the activation energy, T is the absolute temperature, R
is the gas constant. From the values of D_H at different temperatures, an activation energy
can be obtained. After the electrode was stabilized (after 30 cycles), the diffusion current
was measured at different temperatures for the two electrodes. The diffusion current as a
function of time for electrodes A4 (LaNi_{4.7}Al_{0.3}) and B2
(Ml_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at the temperatures of 0°C, 25°C, 35°C, 45°C and
55°C is shown in Figs.4.3.9 and 4.3.10. According to Fig.4.3.6, after stabilization of the electrode, the sphere radius of the electrode alloy for electrodes A3 (A4) and B1 (B2) are about 18μm and 27μm, respectively. Since the measurements were conducted after the electrodes were stabilized (i.e. the particle size of the electrode alloy decreases very slowly with cycling), thus from the $D/d^2$ ratio and the stabilized sphere radius as previously determined, the hydrogen diffusion coefficient $D_H$ for the two electrodes at different temperatures was obtained. The results for hydrogen diffusion coefficient as a function of temperature are shown in Fig.4.3.11. According to Fig.4.3.11, the hydrogen diffusion coefficient increases with increasing temperature, which is consistent with the Arrhenius expression as shown in Eq.4.3.2. From Eq.4.3.2 one can obtain the relationship between $D_H$ and $T$ as shown in Eq.4.3.3:

$$\ln D_H = \ln D_0 - \frac{E_a}{R} \left( \frac{1}{T} \right)$$  \hspace{1cm} (4.3.3)

A plot of $\ln D_H$ vs. $1/T$ should produce a straight line with a slope of $(-E_a/R)$, from which the activation energy ($E_a$) for hydrogen diffusion can be calculated. The Arrhenius plots of the hydrogen diffusion coefficient $D_H$ (i.e. $\ln D_H$ v.s. $1/T$) for electrodes A4 and B2 are shown in Fig.4.3.12. The fit to a linear relationship was good enough ($R^2 \geq 0.999$) to give confidence in the calculated values for the activation energy ($E_a$). The calculated diffusion activation energy ($E_a$), stable sphere radius ($a$) and hydrogen diffusion coefficient at 25°C for electrodes A4 and B2 are given in Table 4.3.1:
Table 4.3.1 Diffusion activation energy, stable sphere radius and hydrogen diffusion coefficient for electrodes A4 and B2

<table>
<thead>
<tr>
<th>Electrode</th>
<th>A4</th>
<th>B2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LaNi$<em>{4.7}$Al$</em>{0.3}$</td>
<td>Mn$<em>{0.95}$Ti$</em>{0.05}$Ni$<em>{3.85}$Co$</em>{0.45}$Mn$<em>{0.35}$Al$</em>{0.35}$</td>
</tr>
<tr>
<td>$C_{\text{max}}$ (mAh/g)</td>
<td>300</td>
<td>275</td>
</tr>
<tr>
<td>$a$ (μm)</td>
<td>18</td>
<td>27</td>
</tr>
<tr>
<td>$D_H$ (cm$^2$/s)</td>
<td>$1.1 \times 10^{-10}$</td>
<td>$1.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol·H)</td>
<td>22.6</td>
<td>25.5</td>
</tr>
</tbody>
</table>

It can be seen that the diffusion coefficients for electrodes A4 and B2 are almost the same, and the activation energies for the two electrodes are not significantly different. Although the maximum discharge capacity of electrode A4 is slightly higher than that of electrode B2, the decay rate of discharge capacity of electrode A4 is larger than that of electrode B2 (see Fig.4.9.1 for electrodes A3 and B1, the maximum discharge capacity of electrode A3 is slightly higher than that of electrode B1, the decay rate of discharge capacity of electrode A3 is larger than that of electrode B1, which is the same as for electrodes A4 and B2). This behavior can be explained by the fact that electrode B2 has a larger stable sphere radius for the electrode alloy particles than electrode A4, thus indicating that electrode B2 has a greater resistance to pulverization resulting from cycling, and thus has a longer cycle life. The reported activation energies for metal hydrides vary in a large range, from 14 kJ/mol to 50 kJ/mol [131, 138]. The activation energies obtained in present study are relative smaller comparing with the reported values. This may be resulted from the Ni addition in the electrode alloy, which acts as a catalyst for hydrogen reaction with the alloy, and also for hydrogen absorption and desorption, thus the activation energy was decreased.
Fig. 4.3.1 Logarithm of current vs. time for electrode A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) at 25°C.
Fig. 4.3.2 Logarithm of current vs. time for electrode A2
(\text{LaNi}_{4.7}\text{Al}_{0.3}\text{+Ni+Cu}) \text{ at } 25 \degree \text{C.}
Fig. 4.3.3 Logarithm of current vs. time for electrode B1
\((\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35})\) at 25 °C.
Fig. 4.3.4 Logarithm of current vs. time for electrode B3 (Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at 25 °C.
Fig. 4.3.5 D/a² ratio vs. number of cycles for electrodes:
A3: LaNi₄.7Al₀.3 +Ni; A2: LaNi₄.7Al₀.3 +Ni+Cu
B1: uncoated Mn₀.95Ti₀.05Ni₃.85Co₀.45Mn₀.35Al₀.35;
B3: Pd-coated Mn₀.95Ti₀.05Ni₃.85Co₀.45Mn₀.35Al₀.35.
Fig. 4.3.6 Sphere radius of electrode alloy particles vs. number of cycles for electrodes:

A3: LaNi$_{4.7}$Al$_{0.3}$ +Ni; A2: LaNi$_{4.7}$Al$_{0.3}$ +Ni+Cu
B1: uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.43}$Mn$_{0.35}$Al$_{0.35}$;
B3: Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.43}$Mn$_{0.35}$Al$_{0.35}$. 
Fig. 4.3.7 Logarithm of current vs. time at different DOD for electrode B2 (Mn_{0.95}Ti_{0.025}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at 25 °C.
Fig. 4.3.8 $D/a^2$ ratio vs. DOD at different temperatures for electrode B2 ($Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}$).
Fig. 4.3.9 Logarithm of current vs. time for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$) at different temperatures.
Fig. 4.3.10 Logarithm of current vs. time for electrode B2 (Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) at different temperatures.
Fig. 4.3.11 $D_H$ vs. temperature for electrodes A4 (LaNi$_{4.7}$Al$_{0.3}$) and B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.15}$Mn$_{0.35}$Al$_{0.35}$) measured after fully charging.
Fig. 4.3.12 Arrhenius plot of the diffusion coefficient for electrodes A4 (LaNi_{4.7}Al_{0.3}) and B2 (Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) measured after fully charging.
4.4 CURRENT DENSITY

The exchange current density and the limiting current density are two important parameters related to the kinetic properties of a metal hydride electrode. In the following sections, the two parameters are discussed in some detail.

4.4.1 Exchange Current Density

Exchange current density \(i_0\) is one of the kinetic parameters of the electrode reactions. It represents the oxidation or reduction reaction rate on the electrode under equilibrium potential, and the reversibility of the electrode reactions. The value of exchange current density depends on the characteristics of the electrode reactions and also on electrolyte concentration. Exchange current density can be measured by a linear polarization curve (as Eq.2.3.9), a Tafel polarization curve (as Eq.2.3.11) or by a polarization curve which includes the effect of any mass transfer process (as Eq.2.3.21a).

For linear polarization, Eq.2.3.9 indicates that when the polarization over-potential is small, there is a linear relationship between the activation over-potential \(\eta_{act}\) and the polarization current. Thus, \(i_0\) can be obtained from the slope of the \(\eta_{act} \sim i\) curve, \((RT/nF)i_0\). For polarization which includes the effect of a mass transfer process, Eq.2.3.21a shows that a plot of \(\eta\) vs \(\ln(\frac{i}{i_L-i})\) should produce a straight line in the middle range of the polarization curve, with its slope being \(RT/\beta F\) and intercept being \(RT/\beta nF\ln(\frac{i_L}{i_0})\). Therefore \(\beta\) (which will be discussed in section 4.5) and \(i_0\) can be calculated from the data for \(i_L\) and \(T\).

4.4.1.1 Exchange current density variation with number of cycles

The exchange current densities of electrodes B1, B2, A3 and A2 were measured
by both linear polarization and polarization including the effect of mass transfer method. The results showed that the exchange current densities obtained by the two methods both increase with increasing number of cycles as shown in Figs.4.4.1 and 4.4.2.

As one of the parameters related to the kinetic properties of electrode, the exchange current density would be expected to be related to the specific surface area of the electrode. The variation of exchange current density with the number of cycles for electrodes B1 (un-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}), B3 (Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}), A3 (LaNi_{4.7}Al_{0.3}+Ni), and A2 (LaNi_{4.7}Al_{0.3}+Ni+Cu) are shown in Figs.4.4.1 and 4.4.2. The exchange current density shows a similar variation with number of cycles as the specific surface area. The exchange current density increases with number of cycles for the first 30 cycles, and thereafter it increases very slowly and can be considered to be stable. When the rate of micro-cracking is greatly decreased after 30 cycles, the specific surface area of the electrode, and the particle size of the alloy powders, attain near-constant values, and thus the exchange current density also reaches a “steady-state” value.

According to Figs.4.4.1 and 4.4.2, the relative order of the exchange current densities is \( I_0(A2) > I_0(A3) > I_0(B3) > I_0(B1) \), which is the same relative order as for the real specific surface areas of the four electrodes. The differences in real specific surface area are likely to be the main cause for the differences in exchange current density between the four electrodes. Also, up to the 20th cycle, the exchange current density of electrode B3 (Pd-coated MnNi_{5-based alloy}) is almost the same as that of electrode B1 (un-coated MnNi_{5-based alloy}). However, after the 25th cycle, it becomes larger than that of un-coated one. This obviously results from differences in the real specific surface areas of
the two electrodes. Up to the 20th cycle, the specific surface areas of the two electrodes are very similar, but after the 25th cycle the specific surface area of electrode B3 is higher than that of electrode B1 (compare Fig. 4.2.6 with Fig. 4.2.7). For electrodes A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) and A2 ((LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu), there are large differences in exchange current density, just as there were significant differences in specific surface area. The addition of Cu seems to have an important effect in increasing both the specific surface area and the exchange current density. It is believed that the addition of metals such as Cu or Ni can act as micro current collectors, facilitating electron transfer during charging/discharging [42], thus increasing the exchange current density.

From Figs. 4.4.1 and 4.4.2, it can be seen that for all four electrodes the exchange current density for linear polarization is greater than that incorporating the effects of mass transfer. The differences for electrodes A2 and A3 are much larger than the differences for electrodes B1 and B3.

1. Linear polarization

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 can therefore be expressed as in Eqs. 4.4.1 and 4.4.2:

$$H_2O + e^- \rightarrow H_{ad} + OH^- \quad (4.4.1)$$

$$H_{ad} \rightarrow H_{ab} \quad (4.4.2)$$

where $H_{ad}$ and $H_{ab}$ denote the hydrogen atoms on the surface of the MH alloy powder and in the bulk of MH alloy, respectively. Reaction 4.4.1 reflects the charge transfer
process at the interface between the MH alloy powder and the electrolyte, and reaction 4.4.2 relates to the diffusion of hydrogen from the powder surface to the bulk of the MH alloy.

The electrochemical kinetics of the charge transfer process was determined by DC polarization methods. The slope of the linear polarization curve represents the polarization resistance \( R_p \), which is composed of the ohmic resistance \( R_{\text{ohm}} \) and the charge transfer resistance \( R_{\text{ct}} \). The polarization resistance is mainly determined by the charge transfer process at the interface between the MH electrode and the electrolyte, i.e. the polarization resistance \( R_p \) can be considered as the charge transfer resistance \( R_{\text{ct}} \). 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 in Eq.4.4.3:

\[
R_n = \frac{RT}{FJ_0}
\]  
(4.4.3)

where \( R \) is the gas constant, \( T \) the temperature, \( F \) the Faraday's constant and \( J_0 \) the exchange current density. When the magnitude of \( R_{\text{ohm}} \) is much smaller than \( R_{\text{ct}} \), the slope of the linear polarization curve can generally be used to estimate the exchange current density. The exchange current densities vs. the number of charge/discharge cycles for the four electrodes are shown in Fig.4.4.1. An increase in the exchange current density with number of cycles reflects the fast hydrogen adsorption process at the interface between the MH alloy powder and the electrolyte. Taking electrodes B1 and B3 as examples, the exchange current density of electrode B1 (un-coated MnNi5-based alloy) reaches 164 mAg\(^{-1}\) after 20 cycles and then it slowly increases to a value of about 230mAg\(^{-1}\) after 50
cycles. Similarly, the exchange current density of electrode B3 (Pd-coated MmNi₃-based alloy) reaches to 172 mAg⁻¹ after 20 cycles and then increases to a value of about 267 mAg⁻¹ after 50 cycles. In contrast, the discharge capacity of the un-coated Mm₀.₉₅Ti₀.₀₅Ni₃₈₅Co₀.₄₅Mn₀.₃₅Al₀.₃₅ alloy powder decreases after 10 cycles, because of oxidation and pulverization of the alloy powder. The value of the polarization resistance is inversely proportional to that of the exchange current density. In other words, the capacity decay of the alloy powders will not result in an increase of the polarization resistance. The exchange current densities of both electrodes B1 and B3 (uncoated and Pd-coated MmNi₃-based alloy) remain almost constant after 30 cycles. This implies that the charge transfer process at the interface between the MH alloy powder and electrolyte is stabilized, i.e. the electrochemical reaction for hydrogen adsorption at the interface is stabilized.

2. **Effect of mass transfer on polarization**

When the electrochemical reactions are controlled by charge transfer processes, the electrode potential of the MH alloy electrode is far removed from the equilibrium potential, typically being at an over-potential (η) of about 100mV. The over-potential of the MH electrode (η) is composed of the charge transfer over-potential (ηₜ₉) and the mass transfer over-potential or concentration over-potential (ηₐ or ηconc). The charge transfer over-potential is proportional to ln(i) and the mass-transfer over-potential is proportional to the logarithm of the reactant concentration. For anodic polarization, polarization leads to a decrease in the activation energy of the oxidation reaction. An increase in the oxidation reaction rate, meanwhile leads to an increase in the activation energy of the reduction reaction, and a decrease in the rate of the reduction reaction. Therefore the
reduction reaction in the anodic polarization process can be neglected in comparison with the rate of oxidation reaction. Based on the concept of free energy curves and Fick's law, the anodic overpotential can be expressed as Eq. 4.4.4 (another form of Eq. 2.3.21):

\[
\eta = \frac{RT}{(1-\alpha)F} \ln \left( \frac{i_L}{i_0} \right) + \frac{RT}{(1-\alpha)F} \ln \frac{i}{i_L - i}
\]  

(4.4.4)

where \( \eta \) is the over-potential, \( \alpha \) is the transfer coefficient, \( i_L \) is the limiting current. From Eq. 4.4.4, a plot of \( \eta \) vs. \( \ln(i/i_L - i) \) should produce a straight line in the middle range of the polarization curve with its slope being \( RT/(1-\alpha)F \) and an intercept of \( RT/(1-\alpha)F \ln(i/i_0) \).

Therefore \( \alpha \) and \( i_0 \) can be calculated from data for \( i_L \) and \( T \).

Figs. 4.4.1 and 4.4.2 show that the exchange current densities evaluated from the polarization curves which include effects of the mass transfer process are lower than those calculated from linear polarization. For more than 20 charge/discharge cycles, there is a larger difference between \( i_0 \) for linear polarization and that for polarization which includes the effects of mass transfer. Generally, the magnitude of ohmic polarization increases with increasing polarization potential. Ohmic polarization at higher overpotential leads to a decrease in the polarization current, which also leads to a decrease in the limiting current. Thus the exchange current densities, obtained by the polarization curves which include the effects of mass transfer process in both alloy electrodes, are influenced by the ohmic polarization, which results in a decrease in the limiting current.

The difference in the exchange current densities between electrodes B1 and B3 (uncoated and Pd-coated MH alloy) may result from a larger exchange current density for hydrogen absorption at the surface of the Pd layer. The exchange current density of
hydrogen at the interface between Pd and the electrolyte is much larger than that at the interface between the MH alloy powder and the electrolyte. The exchange current density of electrode A2 is larger than that of electrode A3, and this also results from the Cu addition in electrode A2, which acts as a micro-current collector. The exchange current density at the interface between Cu and the electrolyte is larger than that at the interface between the MH powder and the electrolyte. On the other hand, the specific surface area of an electrode also contributes to the differences of the exchange current densities, as previously discussed in section 4.2.2. Fig.4.2.10 shows that electrode A2 has a larger specific surface area than electrode A3. This indicates that the alloy of electrode A2 (mixed with Cu) pulverizes easier than that of electrode A3, thus producing more fresh surface area, and then increasing the exchange current density. Therefore it is reasonable to conclude that an Cu addition in LaNi$_{4.7}$Al$_{0.3}$ alloy can not only act as a micro-current collector but also speed up the pulverization of the electrode alloy powder, and thus increase the exchange current density.

The fact that the exchange current densities of electrodes A2 and A3 are much larger than those of electrodes B1 and B3 also results from the differences in specific surface area. Electrodes A2 and A3 have much larger specific surface areas than electrodes B1 and B3, and this results in the increase of the exchange current density for electrodes A2 and A3.

4.4.1.2 Area exchange current density

The exchange current density is usually expressed as mA/g (mostly used in the present study for a metal hydride electrode) or mA/cm$^2$. When we express the real specific surface area in mA/cm$^2$ (area exchange current density) we found that the area
exchange current density is very small, around $1.0 \times 10^{-4}$ mA/cm$^2$ (or 1 mA/m$^2$). This can explain the good high rate charge/discharge performance and good reversibility of the metal hydride electrodes. When a large apparent current density (mass current density, mA/g) is applied to an electrode whose reversibility and capacity would be damaged by the large current, the area current density (mA/cm$^2$) is, in fact, quite small. It is this small area current density that maintains the good reversibility and high rate capacity of the metal hydride electrode. The variation with number of cycles of area exchange current densities (mA/cm$^2$) for both linear polarization and polarization with a mass transfer effect for electrodes B1, B3, A3 and A2 is shown in Figs. 4.4.3 and 4.4.4. After 30 cycles, the area exchange current density also becomes stabilized.

4.4.1.3 Variation of exchange current density with hydrogen concentration and temperature

The exchange current densities for electrodes A4, A1 and B2 were obtained from linear polarization curves at different hydrogen concentrations and temperatures (0°C, 25°C, 35°C, 45°C and 55°C). These are shown in Figs. 4.4.5, 4.4.6 and 4.4.7 for electrodes A4, A1 and B2, respectively. The current density increases with increasing temperature. Generally, the current density decreases with increasing hydrogen concentration and remains almost constant in the $\alpha+\beta$ phase region. When the hydrogen concentration is less than about 0.05 H/M, which is the $\alpha$-phase region, the exchange current density begins to decrease rapidly. A higher hydrogen concentration (in the $\beta$-phase region) in the MH alloy will result in a decrease in the activation on the interface of electrode/electrolyte, which limits the hydrogen adsorption at the surface of the MH alloy powders. This may also limit hydrogen diffusion in the bulk of the MH alloy. The
adsorption capability for hydrogen at the surface of the MH alloy powder is thus a main factor controlling the electrocatalytic activity of the MH electrode reaction. The fact that the exchange current density decreases with increasing hydrogen concentration (H/M) may result from a decrease in adsorption capability for hydrogen at the surface of MH alloy powders. When the hydrogen concentration is very low, which is in the α-phase region (H/M<0.05), there are few active sites, and thus the exchange current density ($I_0$) is much smaller than that at higher hydrogen concentrations. The fact that exchange current density ($I_0$) is relatively high at hydrogen concentrations (H/M) around 0.1, or at higher temperatures, can also be attributed to the more active nickel clusters formed either during deeper dehydriding or at higher temperatures [160]. The values of exchange current densities of the three electrodes are in the order: A1 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) > A4 (LaNi$_{4.7}$Al$_{0.3}$+Ni) > B2 (Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$). This should result from differences in the pulverization rates (or the specific surface areas) of the three electrodes.

### 4.4.2 Limiting Current Density

Limiting currents arise from concentration polarization, and they are unaffected by activation or ohmic polarization.Basically, for a typical electrode reaction as given in Eq.4.4.5, the concentration over-potential ($\eta_{conc}$) can be shown as in Eq.4.4.6 [161]:

$$ R \rightarrow ne^- + O $$

$$ \eta = \frac{RT}{nF} \ln \left( \frac{m_R C_R^b}{m_O C_O^b} \right) + \frac{RT}{nF} \ln \left( \frac{nFmA O C_O^b + I}{nFmA R C_R^b - I} \right) $$

(4.4.6)

where $m_O$ or $m_R$ are known as transport coefficient (unit: m/s), the subscripts “O” and “R” for the concentration (C) and transport coefficient (m) denote the oxidative and reductive
state reactants, and the superscript "b" represents the bulk concentration, and A is the surface area of electrode. This equation shows that the current (I) can not exceed 

\[ nF \Delta m_R C_R^b \] and approaches this value as a limit as \( \eta_{\text{conc}} \to +\infty \). Likewise, as \( \eta_{\text{conc}} \to -\infty \), the current (I) approaches the constant \(-nF \Delta m_Q C_Q^b\). The current limit is defined as the limiting current. The value obtained when the electrode potential (or over-potential) is sufficiently positive is the anodic limiting current. The value corresponding to a large negative electrode potential (or over-potential) is the cathodic limiting current. The polarization curve showing the limiting current for electrode B1 is given in Fig.4.4.8.

When the polarization approaches the limiting current, the reaction rate is controlled by the diffusion process, i.e. the mass transfer process is the rate determining step (RDS).

The limiting current densities for electrodes A3, A2, B1 and B3 were measured after a different number of cycles, and the results are shown in Fig.4.4.9. The limiting current density reaches a steady value after 30 cycles, in the same manner as the exchange current density and the specific area. The limiting current density, as for the exchange current density, increases with increasing specific surface area after activation, and after the specific surface area reaches a steady value (after about 30 cycles), the limiting current density is also stabilized. As with the exchange current density, Fig.4.4.9 shows the limiting current density for the four electrodes are in the same order as for the exchange current density, i.e. \( I_L(B1) > I_L(B3) > I_L(A3) > I_L(A2) \). This is also the same order as that for the specific surface area of the four electrodes as shown in Fig.4.2.9. The limiting current density of electrodes A3 and A2 (LaNi\(_{4.7}\)Al\(_{0.3}\)) is much larger than that of electrodes B1 and B3 (Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)CO\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\)). The electrode with a Cu addition (A2) has a larger limiting current density than that without a Cu addition (A3).
For electrodes B1 and B3, after the 25th cycle the limiting current density of the Pd-coated MnNi₅-based alloy electrode is larger than that of the un-coated electrode. This also results from the difference between the specific surface area of the two electrodes. After 30 cycles, the limiting current densities are stabilized, as was the case for the exchange current density, which means that the electrochemical properties of the electrodes are stabilized.

As with area exchange current density, the limiting current density can also be expressed in terms of mA/m², i.e. the area specific surface area. The variation of area limiting current density with number of cycles is shown in Fig. 4.4.10. As with the other kinetic parameters, the area limiting current density becomes stabilized after 30 cycles.
Fig. 4.4.1 Variation of exchange current density with cycling for linear polarization at 25°C for electrodes:
A3 (LaNi₄₋₇Al₀₋₃+Ni), A2 (LaNi₄₋₇Al₀₋₃+Ni+Cu),
B1 and B3 (uncoated and Pd-coated Mn₀₋₉₅Ti₀₋₀₅Ni₃₋₈₅Co₀₋₄₅Mn₀₋₃₅Al₀₋₃₅).
Fig. 4.4.2 Variation of exchange current density with cycling for mass transfer polarization at 25°C for electrodes:
A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni), A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu),
B1 and B3 (uncoated and Pd-coated
Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.4.3 Variation of area exchange current density (linear polarization) with cycling at 25°C for electrodes: A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni), A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu), B1 and B3 (uncoated and Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.4.4 Variation of area exchange current density (mass transfer effect) with cycling at 25°C for electrodes:
A3 (LaNi4.7Al0.3+Ni), A2 (LaNi4.7Al0.3+Ni+Cu),
B1 and B3 (uncoated and Pd-coated
Mn0.95Ti0.05Ni3.8S0.45Co0.45Mn0.35Al0.35).
Fig. 4.4.5 Exchange current density as a function of hydrogen concentration at different temperatures for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$+Ni).
Fig. 4.4.6 Exchange current density as a function of hydrogen concentration at different temperatures for electrode A1 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu).
Fig. 4.4.7 Exchange current density as a function of hydrogen concentration at different temperatures for electrode B2
(Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Anodic limiting current
\[ I = nF \Delta m_R C_R^b \]
Cathodic limiting current
\[ I = nF \Delta m_O C_O^b \]

Fig. 4.4.8 Polarization curves of \( \eta \) vs. \( i \) for electrode B1 (uncoated \( \text{Mm}_{0.95} \text{Ti}_{0.05} \text{Ni}_{3.85} \text{Co}_{0.45} \text{Mn}_{0.35} \text{Al}_{0.35} \) alloy mixed with Ni) determined at a scan rate of 1 mV/s at 25 °C.
Fig. 4.4.9 Variation of limiting current with number of cycles at 25°C for electrodes:

B1: Uncoated-Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}

B3: Pd-coated-Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}

A3: LaNi_{4.7}Al_{0.3}+Ni; A2: LaNi_{4.7}Al_{0.3}+Ni+Cu.
Fig. 4.4.10 Variation of area limiting current density with cycling at 25°C for electrodes:

B1: Uncoated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$
B3: Pd-coated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$
A3: $\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}$; A2: $\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}+\text{Cu}$. 
4.5 **SYMMETRY FACTOR OF ELECTRODE REACTIONS**

The symmetry factors, \( \alpha \) and \( \beta \), are two important parameters determining the electrochemical behavior of an electrode. These symmetry factors are also called transfer coefficients. \( \alpha \) is the reductive symmetry factor and \( \beta \) is the oxidative symmetry factor, and \( \alpha + \beta = 1 \). The symmetry factor is a measure of symmetry of the activation barrier, being close to 0.5 for a metallic electrode and a simple electron transfer process [161]. It also represents the extent of the influence on the activation energy of the electrode potential (or over-potential), as shown in Eqs. 4.5.1 and 4.5.2 \( (\eta = \phi - \phi_{eq}) \). Thus the symmetry factor is an indicator of the reversibility of the electrode reactions:

\[
E_{\text{red}} = E_{\text{red}}^0 + \alpha nF \phi = E_{\text{red}}^0 + \alpha nF (\phi_{eq} + \eta_{\text{cathode}}) \tag{4.5.1}
\]

\[
E_{\text{oxi}} = E_{\text{oxi}}^0 - \beta nF \phi = E_{\text{oxi}}^0 - \beta nF (\phi_{eq} + \eta_{\text{anode}}) \tag{4.5.2}
\]

where \( E_{\text{red}} \) and \( E_{\text{oxi}} \) are the activation energies for reduction process and oxidation process of the electrode reaction, respectively. \( E_{\text{red}}^0 \) and \( E_{\text{oxi}}^0 \) are the activation energies for reduction process and oxidation process when the electrode potential is equal to zero (i.e. non-electrode reaction), respectively. \( \eta_{\text{cathode}} \) and \( \eta_{\text{anode}} \) are the over-potentials of the cathodic and anodic reactions, respectively. \( F \) is Faraday's constant. \( \alpha \) and \( \beta \) are all less than 1 \( (\alpha + \beta = 1, \alpha > 0, \beta > 0) \).

For a metal hydride electrode undergoing charging, which is a reduction process (see Eq. 2.1.9), more electrons are accumulated on the electrode (cathode), resulting in the charging of a double layer, and hence a shift of the electrode potential \( (\phi) \) to a more negative value. From Eq. 4.5.1, when the electrode potential \( (\phi) \) becomes more
negative, the activation energy of the reaction ($E_{\text{red}}$) also becomes smaller too, making the reduction reaction occur more readily. For an electrode undergoing discharge, which is an oxidation process, the electrode potential ($\varphi$) becomes more positive, hence reducing the oxidation activation energy ($E_{\text{ox}}$) (Eq.4.5.2) and making the oxidation reaction occur more readily.

According to Eqs.4.5.1 and 4.5.2, $\alpha$ and $\beta$ are the multiplying factors for the electrode potentials for the reduction process and oxidation process, respectively. For the anodic process (discharging, oxidation), since the electrode potential ($\varphi$) is negative, the larger the value of $\beta$, the larger is the oxidation activation energy ($E_{\text{ox}}$), and the more difficult is the oxidation reaction. On the other hand, the larger the value of $\eta_{\text{anode}}$ (positive), the smaller is the oxidation activation energy ($E_{\text{ox}}$), and the easier it is for the oxidation reaction to occur.

4.5.1 Symmetry factor under coexistence of activation and concentration polarization

Generally for the electrode process, the current density is usually large enough to cause activation polarization as well as concentration polarization. When activation polarization and concentration polarization coexist, the relationship between the over-potential ($\eta$) and the current density ($i$) can be expressed as given in Eq.2.3.21. For the anodic process, we can rewrite Eq.2.3.21a as Eq.4.5.3:

$$\eta_{\text{anode}} = \frac{RT}{\beta nF} \ln \frac{i_L}{i_0} + \frac{RT}{\beta nF} \ln \frac{i}{i_L - i}$$ (4.5.3)
where \( i_L \) is limiting current and \( n=1 \). A typical polarization curve showing a limiting current is given in Fig. 4.5.1. According to Eq. 4.5.3, a plot of \( \eta \) vs. \( \ln[\dot{\mathcal{U}}/(i_L-i)] \) should produce a straight line with a slope of \( RT/\beta n F \). Hence \( \beta \) can be calculated from such a plot. The over-potential \( \eta \) vs. \( \ln[\dot{\mathcal{U}}/(i_L-i)] \) plots for electrodes A3 (LaNi\(_{4.7}\)Al\(_{0.3}\)+Ni), A2 (LaNi\(_{4.7}\)Al\(_{0.3}\)+Ni +Cu), B1 and B3 (un-coated and Pd-coated)

ML\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.8}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\) are shown in Figs. 4.5.2, 4.5.3, 4.5.4 and 4.5.5. All the measurements were conducted after fully charging the electrodes at 30mA/g for 12 hours at 25°C. Obviously, a linear relationship between \( \eta \) and \( \ln[\dot{\mathcal{U}}/(i_L-i)] \) exists in the middle range of polarization, and departure from linearity occurs in the low or high over-potential region. In the low over-potential region, activation polarization is dominant, the over-potential comes mainly from activation over-potential, and in this case, Eq. 4.5.3 is not applicable. In the high over-potential region, i.e. high polarization, the electrode current, \( i \), is close to the limiting current, \( i_L \), and thus, \( \ln[\dot{\mathcal{U}}/(i_L-i)] \) is close to infinity and there is a departure from the linear relationship between \( \eta \) and \( \ln[\dot{\mathcal{U}}/(i_L-i)] \). With a linear relationship in the middle range of polarization, the symmetry factor, \( \beta \), can be calculated from the slope of the straight line. The symmetry factor, \( \beta \), for electrodes A3, A2, B1 and B3, obtained using Eq. 4.5.3, as a function of number of cycles are shown in Fig. 4.5.6.

According to Fig. 4.5.6, the value of symmetry factor \( \beta \) for the four electrodes are in the order of \( \beta(A2)>\beta(A3)>\beta(B1)>\beta(B3) \). As we discussed before, \( \beta \) represents the symmetry of the reduction/oxidation reaction, or the reversibility of the reduction/oxidation reaction. Thus it can be seen that electrodes B1 and B3 have better reaction reversibility than electrodes A2 and A3.
As can be seen in Fig. 4.5.6, the \( \beta \) values for electrodes B1 and B3 (un-coated and Pd-coated MnNi\(_{5}\)-based alloy) quickly become stabilized (after only about 10 cycles). This means that the electrode reaction becomes stabilized after 10 cycles at \( \beta \) close to 0.5, showing a much better reaction reversibility of these electrodes than electrodes A2 and A3. It takes longer for electrodes A2 and A3 to be stabilized (around 25 to 30 cycles) than electrodes B1 and B3. With the larger \( \beta \) value and longer stabilization time, electrodes A2 and A3 seem to have a disadvantage with respect to reversibility and stabilization properties compared to electrodes B1 and B3. Also the addition of Cu (electrode A2) seems to increase the reaction rate of the anodic process, yet have a negative influence on the reversibility of the electrode.

Since the \( \beta \) values were obtained by taking into consideration the mass transfer effect (concentration polarization), it is reasonable to conclude that electrodes B1 and B3 (which have \( \beta \) close to 0.5) have much better characteristics of reaction reversibility and rapid stabilization at large current density.

### 4.5.2 Symmetry factor under activation polarization only

When the activation potential is low, there is no concentration polarization, i.e. only activation polarization exists. Thus the relationship between the over-potential (\( \eta \)) and the current density (\( i_i \)) can be expressed as Eq. 4.5.4 (n=1) [105] and the symmetry factor \( \beta \) can be determined from \( i_0 \) and \( \eta \):

\[
\frac{i}{\exp\left( \frac{F \eta}{RT} \right) - 1} = i_0 \exp(-\beta F \eta / RT) \quad (4.5.4)
\]
Taking the logarithm of Eq. 4.5.4, one obtains Eq. 4.5.5:

\[ \eta = \frac{RT}{\beta F} \ln i_o - \frac{RT}{\beta F} \ln \left[ \frac{i}{\exp\left( \frac{F}{\eta} \frac{\eta}{RT} \right) - 1} \right] \] (4.5.5)

A plot of \( \eta \) vs. \( \ln[\eta/\exp(F\eta/RT)-1] \) should give a straight line with a slope of \( RT/\beta F \).

Hence \( \beta \) can be readily calculated. Eq. 4.5.5 is only valid in the linear polarization region.

Typical linear polarization curves for electrode A2 are shown in Fig. 4.5.7, and the experimental results shown in Fig. 4.5.7 are then plotted in Fig. 4.5.8 in order to evaluate the symmetry factor \( \beta \). The symmetry factor \( \beta \) for electrodes A3, A2, B1 and B3 as a function of the number of cycles obtained by using Eq. 4.5.5 are given in Fig. 4.5.9.

Almost all \( \beta \) values fall in the region of 0.5–0.7. Although the \( \beta \) values are in the order of \( \beta(A2) > \beta(A3) > \beta(B3) > \beta(B1) \), which is the same order as for the exchange current density under linear polarization: \( I_d(A2) > I_d(A3) > I_d(B3) > I_d(B1) \) (Fig. 4.4.1), there is very little difference in the \( \beta \) values for the four electrodes. This means that all four electrodes show good reaction reversibility in the linear polarization region, which is controlled by the activation process. Also the \( \beta \) value quickly becomes stabilized, almost from the beginning of cycling.

### 4.5.3 Comparison of the symmetry factors obtained by the two polarization methods

A comparison of the symmetry factors, \( \beta \), determined both by a linear polarization curve and by polarization which considers the concentration effect for electrodes A3 and A2, B1 and B3 is shown in Figs. 4.5.10 and 4.5.11. For electrodes A2 and A3 shown in Fig. 4.5.10, the \( \beta \) values taking into account the mass transfer effect are larger than those
for linear polarization (activation polarization). The mass transfer process has a large influence on the reversibility of the electrode reaction. As for electrodes B1 and B3 shown in Fig.4.5.11, there is little difference in the β values for linear polarization and polarization with a mass transfer effect. This means that for electrodes B1 and B3 (un-coated and Pd-coated MnNi5-based alloy), the reversibility of the electrode reaction is not significantly influenced by concentration polarization. The above analysis suggests that for electrodes A2 and A3 at a low discharge current (linear polarization), the electrode process is controlled by the activation process, or the charge transfer process, but at a large discharge current density, the electrode process is controlled by a mass transfer, or the diffusion process. For electrodes B1 and B3 at a low discharge current density, the electrode process is controlled by an activation process as for electrodes A2 and A3, and at a large discharge current density the electrode process is not controlled by a mass transfer process in itself, but may be mainly under the control of an activation process and, to some degree, by a mass transfer process.

4.5.4 Symmetry factor variation with hydrogen concentration and temperature

The variation of symmetry factor with number of cycles has already been discussed. However, the experimental results show that the symmetry factor varies not only with number of cycles, but also with hydrogen concentration and temperature. The variation of symmetry factor β with hydrogen concentration at different temperatures for electrodes A4 (LaNi4.7Al0.3+Ni), A1 (LaNi4.7Al0.3+Ni+Cu) and B2 (Mn0.95Ti0.05Ni1.85Co0.45Mn0.35Al0.35) are shown in Figs.4.5.12, 4.5.13 and 4.5.14, respectively. The symmetry factor β increases with increasing temperature and decreases with increasing hydrogen concentration.
4.5.4.1 Variation of symmetry factor with hydrogen concentration

With increasing hydrogen concentration, the symmetry factor $\beta$ decreases. In the low hydrogen concentration region, which is the $\alpha$ phase region, the symmetry factor $\beta$ decreases sharply with increasing hydrogen concentration. In the high concentration region, which is the $\beta$ phase region, the symmetry factor $\beta$ decreases slowly with increasing hydrogen concentration, and at low temperatures (e.g. 0°C and 25°C), it remains unchanged. This means at high hydrogen concentrations, the electrode shows a much better reaction reversibility than at low hydrogen concentrations.

4.5.4.2 Variation of symmetry factor with temperature

As the temperature increases, the symmetry factor $\beta$ also increases. In the low hydrogen concentration region ($\alpha$-phase region), the symmetry factor $\beta$ increases much faster than in the high hydrogen concentration ($\beta$-phase region). In the $\alpha$-phase region, the symmetry factors ($\beta$) at the four temperatures vary to a significant degree, ranging from 0.57 to 0.88. However, in the $\beta$-phase region, the symmetry factors ($\beta$) are similar, ranging from 0.46 to 0.53. This means the temperature has little influence on the symmetry factor $\beta$ at high hydrogen concentrations, but has a greater influence on $\beta$ at low hydrogen concentrations.
Fig. 4.5.1 Polarization curves of $\eta$ vs. $i$ for electrode B3 (Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy mixed with Ni) at the 5th cycle determined at a scan rate of 1 mV/s at 25 °C.
Fig. 4.5.2 Overpotential, $\eta$, of electrode A3 (LaNi$_{4.7}$Al$_{0.3}$Ni) as a function of $\ln[i/(i_{L}-i)]$ at 25°C.
Fig. 4.5.3 Overpotential, $\eta$, of electrode A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) as a function of $\ln[i/(i_L-i)]$ at 25°C.
Fig. 4.5.4 Overpotential, $\eta$, of electrode B1 (uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) as a function of $\ln[i/(i_L-i)]$ at 25°C.
Fig. 4.5.5 Overpotential, $\eta$, of electrode B3 (Pd-coated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$) as a function of $\ln[i/(i_L-i)]$ at 25°C.
Fig. 4.5.6 Symmetry factor $\beta$ with concentration polarization vs. number of cycles at 25°C for electrodes:

- A3: LaNi$_4$Al$_{0.3}$ +Ni;
- A2: LaNi$_4$Al$_{0.3}$ +Ni+Cu
- B1: uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{1.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
- B3: Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{1.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
Fig. 4.5.7 Polarization curves, $\eta$ vs. $i$, for electrode A2 (LaNi$_{4.7}$Al$_{0.3}$ +Ni+Cu) at 25°C.
Fig. 4.5.8 Polarization curves, $\eta$ vs. $\ln\{i/[\exp(\eta F/RT)-1]\}$, for electrode A2

(LaNi$_{4.7}$Al$_{0.3}$ + Ni + Cu) at 25°C.
Fig. 4.5.9 Symmetry factor, $\beta$, as a function of number of cycles at 25°C for electrodes:

- A3: LaNi$_{4.7}$Al$_{0.3}$ + Ni; A2 LaNi$_{4.7}$Al$_{0.3}$ + Ni + Cu
- B1: uncoated Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
- B3: Pd-coated Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
Fig. 4.5.10 Symmetry factor, $\beta$, as a function of number of cycles at 25°C for electrodes:
A3: LaNi$_{4.7}$Al$_{0.3}$ + Ni; A2: LaNi$_{4.7}$Al$_{0.3}$ + Ni + Cu.
Fig. 4.5.11 Symmetry factor, \( \beta \), as a function of number of cycles at 25°C for electrodes:

B1: uncoated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \);

B3: Pd-coated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \)
Fig. 4.5.12 Symmetry factor, $\beta$, for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$ +Ni) as a function of hydrogen concentration at different temperatures.
Fig. 4.5.13 Symmetry factor, $\beta$, for electrode A1 (LaNi$_4$$_7$Al$_{0.3}$ +Ni+Cu) as a function of hydrogen concentration at different temperatures.
Fig. 4.5.14 Symmetry factor, $\beta$, for electrode B2 
($\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.33}\text{Al}_{0.35}$) as a function of hydrogen concentration at different temperatures.
4.6 OVER-POTENTIALS OF METAL HYDRIDE ELECTRODES

The over-potential of a metal hydride electrode has three components, namely the ohmic polarization over-potential ($\eta_{\text{ohm}}$), the activation polarization over-potential ($\eta_{\text{act}}$) and the concentration polarization over-potential ($\eta_{\text{conc}}$). When the ohmic resistance is small or is compensated for, then the total over-potential consists of two parts, the activation polarization over-potential and the concentration polarization over-potential. They can be calculated using polarization curves as shown in Fig.4.5.1 and Eq.2.3.21 or Eq.2.3.23. However, if the ohmic resistance is too large to be neglected, or is not compensated for, the ohmic polarization is more likely to affect the results of the linear potential test. In this case, the activation polarization over-potential measured from polarization curves and Eqs.2.3.21 or 2.3.23 will not be the “pure” activation over-potential, but will include the ohmic polarization over-potential.

4.6.1 Over-potential

4.6.1.1 Polarization regions

The polarization curve of a metal hydride electrode can be divided into three regions. A typical polarization curve for electrode A3 (LaNi$_4$-Al$_{0.3}$+Ni) is shown in Fig.4.6.1. In region I, where the current density is below 400mA/g, there is a linear relationship between the electrode potential (or over-potential) and the current density, i.e. $\eta=i(\frac{RT}{nF}i\eta)$ (Eq.2.3.9). Therefore the electrode reaction process is controlled by activation polarization. In the region II, where the current density is between 400 mA/g and 2000mA/g, there is a linear relationship between electrode potential (or over-potential) and $\log(i)$. This is Tafel polarization, as expressed in Eq.2.3.11. In the region III, where the current density is over 2000mA/g, the electrode potential increases sharply
with increasing current density. In this region, the electrode reaction process is controlled by diffusion polarization.

4.6.1.2 Variation of over-potential with cycling

The polarization curves for electrodes A3, A2, B1 and B3 for different discharge cycles are shown in Figs.4.6.2, 4.6.3, 4.6.4 and 4.6.5, respectively. At any current density value, the over-potential decreases with cycling. The variation of over-potential with number of cycles for the four electrodes at a current density of 500 mA/g cycles is shown in Fig.4.6.6. The over-potential decreases steeply on cycling for the first 10 cycles, but then the rate of decrease slows down on further cycling. After about 30 cycles the over-potential reaches a steady-state value. As for the exchange current density, the over-potential is stabilized when the specific surface area is stabilized after 30 cycles, and then remains at a constant value on further cycling.

Figs.4.6.2 and 4.6.3 show that electrode A2 (with Cu additions) has a lower over-potential than electrode A3 (without Cu additions). Thus a Cu addition to the LaNi$_4$Al$_{0.3}$ alloy electrode reduces the over-potential, or polarization effect, which is a desirable characteristic for a metal hydride electrode. According to Figs.4.6.4 and 4.6.5, electrodes B1 and B3 have very similar polarization curves at the same number of cycles. Fig.4.6.6 shows that the variation of over-potential with cycling of the two electrode is also very similar. Thus, it appears that Pd-coating (electrode B3) does not change the over-potential of the MnNi$_3$-based alloy electrode.

According to Fig.4.6.6, it can be seen that the over-potentials of electrodes A3 and A2 (LaNi$_{4.7}$Al$_{0.3}$) are much lower than that of electrodes B1 and B3 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$), i.e. the LaNi$_{4.7}$Al$_{0.3}$ alloy electrodes (A2 and A3).
have a greater resistance to polarization than the MmNi₅-based alloy electrodes (B1 and B3). The principle reason for this behavior is thought to be the fact that the LaNi₄.₇Al₀.₃ alloy electrodes (A2 and A3) pulverize more readily on cycling thus producing more “fresh” surface (see Fig.4.2.7). This leads to an increase in the exchange current density, the electrode reaction rate increases, and therefore, the over-potential of the electrode reaction decreases. The difference in over-potential between electrodes A3 and A2 also results from the differences in specific surface areas. Electrode A2 (with a Cu addition) has a larger specific surface area than electrode A3 (with no Cu addition). This results in a lower over-potential for electrode A2. Overall, a Cu addition to a LaNi₄.₇Al₀.₃ alloy electrode decreases the over-potential by increasing the specific surface area of the electrode. Also, we can see from Figs.4.4.1 and 4.4.2 that, in general, the larger exchange current density (Iₒ), then the smaller is the over-potential (η).

4.6.1.3 Over-potential under limiting current density

The over-potential of a metal hydride electrode is also related to the limiting current density. The over-potential at the point when the limiting current is reached for the electrodes A3, A2, B1 and B3 at different number of cycles is shown in Fig.4.6.7. As discussed in section 4.4.2, limiting currents arise from concentration polarization and they are unaffected by activation or ohmic polarization. When the rate of diffusion reaches a maximum on an increase in current, the reactant concentration at the electrode surface reaches zero, and the current of the electrode reaches a maximum, i.e. the limiting current (Iₒ). Thus the over-potential at the point where the current becomes the limiting current represents a critical point, beyond which the electrode process will be controlled by concentration polarization alone, i.e. the diffusion process will be the rate determining
step. In the region where the limiting current is reached, if the potential of the electrode is increased further, the over-potential will increase without an increase of current, since the current has the maximum value \((i_L)\).

### 4.6.1.4 Activation and concentration polarization

As discussed in section 2.3, the activation polarization and concentration polarization can be separated out from the total polarization using Eq.2.3.21 or Eq.2.3.23. For the anodic process, Eq.2.3.21 can be re-arranged as:

\[
\eta_{\text{anode}} = \eta_{\text{act}} + \eta_{\text{conc}} = \frac{RT}{\beta F} \ln \frac{i}{i_0} + \frac{RT}{\beta F} \ln \frac{i_L}{i_L - i} \tag{4.6.1}
\]

where the first term of the right-hand side of the equation is the over-potential due to activation polarization, \(\eta_{\text{act}}\), and the second term is the over-potential due to concentration polarization, \(\eta_{\text{conc}}\). Using the polarization curve showing the limiting current of the metal hydride electrode, \(\eta_{\text{act}} \) and \(\eta_{\text{conc}} \) were calculated separately from the total over-potential \((\eta_{\text{total}})\). \(\eta_{\text{act}} \) and \(\eta_{\text{conc}} \), as a function of the discharge current density for electrodes A2, A3, B1 and B3 after fully charging for a different number of cycles, are shown in Figs.4.6.8, 4.6.9, 4.6.10 and 4.6.11, respectively. In the low discharge current density region, the activation over-potential is much higher than the concentration over-potential, and the concentration polarization can be neglected. Thus in this low current region, activation polarization in dominant. However, with a further increase in discharge current density, the rate of increase of activation over-potential decreases, whereas, the rate of increase of concentration over-potential increases. When the discharge current density reaches the limiting current density, the concentration over-potential becomes
large enough compared to the activation over-potential that it can not be neglected, and in this region, the electrode process may be considered to be controlled by both activation polarization and concentration polarization. At a high discharge current density, which is around the limiting current density, the concentration over-potential increases greatly and becomes dominant. Thus as the discharge current density increases, the rate-determining step (RDS) changes from activation polarization to concentration polarization, i.e. from a charge transfer process to diffusion of hydrogen in the electrode. The current density at which the rate-determining step changes from a charge transfer process to diffusion of hydrogen is quite different for the two electrode types (A and B). Taking the 30\textsuperscript{th} cycle as an example (usually the electrode behavior tends to be stable after the 30\textsuperscript{th} cycle), the current densities for the RDS change are about 3500 mA/g and 4500 mA/g for electrodes A3 and A2, respectively. However, they are only about 1500 mA/g and 2000 mA/g for electrodes B1 and B3. This suggests that the diffusion of hydrogen has a greater influence on the electrochemical properties of the M\textsubscript{10.95}Ti\textsubscript{0.05}Ni\textsubscript{3.85}Co\textsubscript{0.45}Mn\textsubscript{0.35}Al\textsubscript{0.35} alloy electrodes (B1 and B3) than the LaNi\textsubscript{4.7}Al\textsubscript{0.3} alloy electrodes (A2 and A3).

A comparison of the activation over-potential and the concentration over-potential for electrodes B1, B3, A3 and A2 at a discharge current density of 1000mA/g are given in Figs.4.6.12 and 4.6.13. Both the activation over-potential and the concentration over-potential of the M\textsubscript{10.95}Ti\textsubscript{0.05}Ni\textsubscript{3.85}Co\textsubscript{0.45}Mn\textsubscript{0.35}Al\textsubscript{0.35} alloy electrodes (B1 and B3) are larger than for the LaNi\textsubscript{4.7}Al\textsubscript{0.3} alloy electrodes (A2 and A3), i.e. the same behavior as seen for the total over-potential in Fig.4.6.6.

4.6.1.5 The influence of temperature and hydrogen concentration on over-potential
The measurement of the polarization curves was conducted at different hydrogen concentrations (or different depths of discharge, DOD) and at temperatures of 0°C, 25°C, 35°C, 45°C and 55°C. Selected polarization curves at different hydrogen concentrations and temperatures for electrodes A4, A1 and B2 are shown in Fig.4.6.14, 4.6.15 and 4.6.16. It can be seen from these figures that with an increase in temperature, the current density, at the limit of the linear relationship, increases from about 20mA/g at 25°C to 450mA/g at 55°C. At the same current density, the over-potential decreases with increase in temperature. Thus at higher temperatures, the electrode reaction takes place more readily. Thus, in order to obtain the same reaction rate, the higher the temperature, the lower is the over-potential required for the reaction.

The over-potential at a set value of current density as a function of hydrogen concentration for electrodes B2, A4 and A1 at temperatures of 0°C, 25°C, 35°C, 45°C and 55°C are shown in Figs.4.6.17, 4.6.18, 4.6.19, 4.6.20 and 4.6.21.

When the hydrogen concentration is high, i.e. in the β-phase region, the over-potential increases. In the middle range of the hydrogen concentrations, i.e. the α+β phase region, the over-potential only changes slightly. This means that at higher hydrogen concentrations, the reaction requires a higher over-potential to occur than at relatively lower hydrogen concentrations. The related exchange current density should be smaller at the higher hydrogen concentrations. This is consistent with the experimental results for the exchange current density as shown in Figs.4.4.5 to 4.4.7.

The over-potential of electrode A1 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) is much lower than that of electrode A4 (LaNi$_{4.7}$Al$_{0.3}$+Ni) and electrode B2 (M$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$). This probably results from the Cu addition. The Cu addition acts as a micro-current
collector, and makes the electrode reaction easier, thus decreasing the over-potential required for the electrode reaction to occur.

4.6.2 Equilibrium potential

The equilibrium potential of the electrode is mainly determined by the electrode reactions during the charge/discharge processes. It is also related to certain characteristics of the electrode such as the composition and additives, electrolyte concentration, number of cycles, hydrogen concentration and temperature. The equilibrium potential \( E_{eq} \) of the metal hydride electrode can be expressed as shown in Eq.4.6.2 [12]:

\[
E_{eq} = [E^0(H) - E^0(HgO/Hg)] + \frac{RT}{2F} \ln \left( \frac{\alpha(H_2O)}{\gamma(H_2)P(H_2)} \right)
\]  \( (4.6.2) \)

where, \( E^0(H) - E^0(HgO/Hg) \) is a difference in potential between a standard hydrogen electrode and a HgO/Hg reference electrode. \( \gamma(H_2) \) is the hydrogen fugacity, which is about 1.00059 in the temperature range 273 K - 298 K. \( a(H_2O) \) is the water activity which varies with KOH concentration and temperature. \( P(H_2) \) is the equilibrium pressure of hydrogen, and is dependent on the hydrogen concentration in the MH alloy and the crystal structure of the MH alloy. Polarization measurements of the electrodes were conducted after fully charging and when the open-circuit potential was stabilized (the variation in potential was less than 1mV over 1 hour period). The potential of the metal hydride electrode, which was stabilized, essentially reaches an equilibrium state, which can be considered as the equilibrium potential for the electrode.

The equilibrium potential as a function of number of cycles for electrodes A3, A2, B1 and B3 is shown in Fig.4.6.22. The equilibrium potentials of electrodes B3, A3 and
A2 decrease, i.e. become more negative, upon cycling. However, the equilibrium potential of electrode B1 (un-coated MmNi$_5$-based alloy) increases, i.e. becomes more positive, upon cycling.

The equilibrium potential of the B1 (un-coated MmNi$_5$-based alloy electrode) increases by 7mV after 20 cycles and then remains almost constant with increasing number of cycles. However, the equilibrium potential of electrode B3 (Pd-coated MmNi$_5$-based alloy) decreases by 4mV after 5 cycles and then remains constant. The Pd layer at the surface of the MH alloy powders leads to a fast stabilization of the equilibrium potential of the MH electrode with cycling. For electrodes A3 and A2, the equilibrium potentials decrease greatly in the first 15 cycles, and then become almost constant.

With an increasing number of charge/discharge cycles, the MH alloy powder is pulverized into a micro-sized particles and the micro-sized particles show a micro-strain, or distortion in the crystal structure and fresh surface is generated, which makes hydrogen dissociation easier and results in a decrease in the hydrogen equilibrium pressure. Lundin and Lynch [162] postulated that the hydrogen atoms are occluded in the interstitial sites in the metal lattice and the resulting strain imposed on the lattice increased the interstitial hole size. The increase in the equilibrium potential of electrode B1 (uncoated MmNi$_5$-based alloy) may be attributed to the larger interstitial hole size in the lattice which, in turn, leads to a decrease in the free energy. The decrease of the equilibrium potential of a Pd-coated MH electrode is related to the fact that Pd-coating leads to an increase in the formation free energy of the metal hydride, $\Delta G$, and also to a positive increase in the formation enthalpy, $\Delta H$, of the metal hydride. Given the thermodynamic relationship,
\( \Delta G = \Delta H - T \Delta S \), and the fact that the entropy, \( \Delta S \), only changes a small amount for a metal hydride, \( \Delta H \) can be considered to be the main factor influencing the stability of a metal hydride [13]. The formation enthalpy of a metal hydride is defined as negative because it is an exothermic process. The more negative the formation enthalpy, the more stable the metal hydride, and the more resistant it is to anodic oxidation. With an increasing number of charge/discharge cycles, the Pd-coating at the surface of the MH alloy powder makes the formation enthalpy of the metal hydride more positive (smaller in absolute value). Hence it, i.e. Pd-coating, decreases the resistance to anodic oxidation, and increases the reaction rate for anodic oxidation and the exchange current density. The variation in the equilibrium pressure of hydrogen, \( \Delta ln[P(H_2)] \), is -0.54 at the fully charged state for the un-coated alloy electrode during the first 20 cycles. Even though the equilibrium potential changes with temperature, it only increases about 0.3 mV for a temperature increase of 1K. In this experiment, where there was an increase of 7 mV in the equilibrium potential with cycling at the fully charged state, the change in potential mainly results from a decrease in free energy or the hydrogen equilibrium pressure. Electrodes A3 and A2 (LaNi_{4.7}Al_{0.3}) have larger equilibrium pressures (0.4–0.6 atm. [158]) than electrode B1 (Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.15}) (~0.06 atm. [157]), and thus have much more negative equilibrium over-potentials (Eq.4.6.2).
Fig. 4.6.1 Polarization curve of electrode potential vs. current density after 5 cycles for electrode A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) after fully charging at 25°C.
Fig. 4.6.2 Polarization curves of $\eta$ vs. $i$ at 25 °C for electrode A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) determined at a scan rate of 1 mV/s.
Fig. 4.6.3 Polarization curves of $\eta$ vs. $i$ at 25°C for electrode A2 (LaNi$_4$Al$_{0.3}$Ni+Cu) determined at a scan rate of 1 mV/s.
Fig. 4.6.4 Polarization curves of $\eta$ vs. $i$ at 25 °C for electrode B1 (uncoated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$ alloy mixed with Ni) determined at a scan rate of 1 mV/s.
Fig. 4.6.5 Polarization curves of \( \eta \) vs. \( i \) at 25 °C for electrode B3 (Pd coated Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\) alloy mixed with Ni) determined at a scan rate of 1 mV/s.
Fig. 4.6.6 Overpotential vs. number of cycles \((i=500\, \text{mA/g, scan rate}=1\, \text{mV/s})\) at 25°C for electrodes:

- **B1**: uncoated \(\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}\)
- **B3**: Pd-coated \(\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}\)
- **A3**: \(\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}\); **A2**: \(\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni+Cu}\)
Fig. 4.6.7 Overpotential at limiting current vs. number of cycles at 25°C for electrodes:

B1: uncoated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \)

B3: Pd-coated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \)

A3: \( \text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni} \); A2: \( \text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}+\text{Cu} \)
Fig. 4.6.8 The relationship between overpotential (activation and concentration) and discharge current density at 25°C for electrode A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) after fully charging.
Fig. 4.6.9 The relationship between overpotential (activation and concentration) and discharge current density at 25°C for electrode A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) after fully charging.
Fig. 4.6.10 The relationship between overpotential (activation and concentration) and discharge current density at 25°C for electrode B1 ($\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$) after fully charging.
Fig. 4.6.11 The relationship between overpotential (activation and concentration) and discharge current density at 25°C for electrode B3 (Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) after fully charging.
Fig. 4.6.12 $\eta_{\text{act}}$ vs. number of cycles ($i=1000\text{mA/g, scan rate}=1\text{mV/s}$) at $25^\circ\text{C}$ for electrodes:

- B1: uncoated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$
- B3: Pd-coated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$
- A3: $\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}$; A2: $\text{LaNi}_{4.7}\text{Al}_{0.3}+\text{Ni}+\text{Cu}$
Fig. 4.6.13 η_{conc} vs. number of cycles (i=1000mA/g, scan rate=1mV/s) at 25°C for electrodes:
B1: uncoated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
B3: Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A3: LaNi_{4.7}Al_{0.3}+Ni; A2: LaNi_{4.7}Al_{0.3}+Ni+Cu
Fig. 4.6.14 Polarization curves of $\eta$ vs. $i$ for electrode A4 (LaNi$_4$Al$_{0.5}$+$\text{Ni}$) at different hydrogen concentrations and different temperatures determined at a scan rate of 1 mV/s.
Fig. 4.6.15 Polarization curves of $\eta$ vs. $i$ for electrode A1 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) at different hydrogen concentrations and different temperatures determined at a scan rate of 1 mV/s.
Fig. 4.6.16 Polarization curves of $\eta$ vs. $i$ for electrode B2
($\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$) at different hydrogen concentrations and different temperatures determined at a scan rate of 1 mV/s.
Fig. 4.6.17 Overpotential vs. hydrogen concentration (i=15mA/g, scan rate=1mV/s) at 0°C for electrodes:

B2: uncoated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A4: LaNi_{4.7}Al_{0.3}+Ni; A1: LaNi_{4.7}Al_{0.3}+Ni+Cu
Fig. 4.6.18 Overpotential vs. hydrogen concentration (i=60mA/g, scan rate=1 mV/s) at 25°C for electrodes:

B2: uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
A4: LaNi$_{4.7}$Al$_{0.3}$+Ni; A1: LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu
Fig. 4.6.19 Overpotential vs. hydrogen concentration (i=120mA/g, scan rate=1 mV/s) at 35°C for electrodes:

B2: uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$

A4: LaNi$_{4.7}$Al$_{0.3}$+Ni; A1: LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu
Fig. 4.6.20 Overpotential vs. hydrogen concentration (i=180mA/g, scan rate=1 mV/s) at 45°C for electrodes:
B2: uncoated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A4: LaNi_{4.7}Al_{0.3}+Ni; A1: LaNi_{4.7}Al_{0.3}+Ni+Cu
Fig. 4.6.21 Overpotential vs. hydrogen concentration (i=240mA/g, scan rate=1 mV/s) at 55°C for electrodes:
B2: uncoated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A4: LaNi_{4.7}Al_{0.3}+Ni; A1: LaNi_{4.7}Al_{0.3}+Ni+Cu
Fig. 4.6.22 Variation of equilibrium potential vs. number of cycles at 25°C for electrodes:

B1: uncoated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
B3: Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$
A3: LaNi$_{4.7}$Al$_{0.3}$+Ni; A2: LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu
4.7 RESISTANCE OF METAL HYDRIDE ELECTRODES

The resistance of a metal hydride electrode system consists of three components, namely the ohmic resistance \( R_{\text{ohm}} \), the charge transfer resistance \( R_{\text{ct}} \) and the diffusion resistance \( R_{\text{diff}} \). At a low current density, where the concentration polarization is too small to have a significant effect, the diffusion resistance can be neglected. In the linear region of activation polarization, the slope of the \( \eta-i \) curve is the polarization resistance \( R_p \), which includes ohmic resistance and charge transfer resistance \( R_p = R_{\text{ohm}} + R_{\text{ct}} \). If the ohmic resistance is small enough to be neglected, or is compensated for, the slope only represents the charge transfer resistance. At a large current density, where concentration polarization becomes quite large and dominant, the diffusion resistance should be considered.

4.7.1 Ohmic resistance and charge transfer resistance in linear region

The ohmic resistance \( R_{\text{ohm}} \) was measured by the method detailed in section 4.2.1 (Eq.4.2.2), i.e. the potential step method. The polarization resistance \( R_p \) was measured from the slope of the \( \eta-i \) curve in the linear polarization region. Thus the charge transfer resistance was obtained from the difference between the polarization resistance \( R_p \) and the ohmic resistance \( R_{\text{ohm}} \). The ohmic resistance \( R_{\text{ohm}} \) and charge transfer resistance \( R_{\text{ct}} \) for electrodes B1, B3, A3 and A2 are shown in Figs.4.7.1, 4.7.2, 4.7.3 and 4.7.4, respectively. The ohmic resistances are larger than the charge transfer resistances, which means that the activation over-potentials are mainly due to ohmic resistance rather than charge transfer resistance. The ohmic resistance and charge transfer resistance of electrodes A2 and A3 (LaNi\(_{4.7}\)Al\(_{0.3}\)) are much lower than that of electrodes B1 and B3 (M\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\)). Also the resistances of electrodes A3 and A2
become stabilized after 25 and 15 cycles, respectively, which is quicker than for electrodes B1 and B3, which become stabilized after 30 and 35 cycles, respectively. The fact that the resistances decrease with increasing of the number of cycles for all four electrodes can be explained by the micro-cracking of the electrode powders, which leads to further "fresh" surface area. It has been reported that the reaction resistance on the alloy surface, which is given by the surface composition of the alloy and the real surface area of the alloy grains, increases because of the degradation of the alloy surface [74, 119]. However, in the case of the ohmic resistance (which includes the reaction resistance as defined above) and the charge transfer resistance, this is not so. Although degradation of the alloy surface increases the resistance, the micro-cracking of the electrode alloy powders upon cycling produces more "fresh" surface area, which is more than enough to compensate for the degradation, and the resistance decrease with cycling.

A comparison of ohmic resistance and charge transfer resistance for the four electrodes is shown in Figs. 4.7.5 and 4.7.6. The values of both the ohmic resistance and the charge transfer resistance are in the order \( R(B1) > R(B3) > R(A3) > R(A2) \), which is consistent with the surface areas of the four electrodes, i.e. \( S(B1) < S(B3) < S(A3) < S(A2) \). As discussed above, a larger surface area results in a smaller resistance of the electrode system. Electrode B1 has smaller specific surface area due to less micro-cracking than the other electrodes, thus it has less "fresh" surface area, which leads a larger resistance. The above analysis shows that the ohmic resistance and charge transfer resistance are mainly dependent on the real specific surface area of the electrode. Also, electrode A2 (with Cu) has a smaller resistance than electrode A3 (without Cu), and electrode B3 (Pd-coated) has
a smaller resistance than electrode B1 (un-coated), since both Cu and Pd are good
electrical conductors.

4.7.2 Influence of hydrogen concentration and temperature on the resistance

The resistance of a electrode system depends on not only the characteristics of the
electrode system but also a hydrogen concentration and temperature. The variation of
polarization resistance (the sum of ohmic resistance and charge transfer resistance) with
hydrogen concentration and temperature for electrodes A4, A1 and B2 are shown in
Figs. 4.7.7, 4.7.8 and 4.7.9. The polarization resistance, ohmic resistance and charge
transfer resistance at different temperatures for electrodes B2 and A4 after fully charging
are shown in Figs. 4.7.10 and 4.7.11.

With increasing temperature, the polarization resistance decreases sharply for
both electrodes B2 and A4. This results from the fact that as the temperature increases,
the electrode reaction rate \(i_0\) increases, and thus the polarization resistance \(R_p\), which
is inversely proportional to \(i_0\) \(R_p = RT/nF i_0\), decreases, as was discussed in section
4.4.1.3.

The polarization resistance increases slowly with increase in hydrogen
concentration, except in the \(\beta\)-phase region (large hydrogen concentrations) where the
polarization resistance increases sharply as the hydrogen concentration increases. This
may result from a decrease in adsorption capability for hydrogen at the surface of the MH
alloy powder, which was discussed in detail in section 4.4.1.3 when analyzing the
variation of \(i_0\) with hydrogen concentration.

According to Figs. 4.7.10 and 4.7.11, the ohmic resistance and charge transfer
resistance both decrease with increasing temperature. The polarization resistance \(R_p\) of
electrode B2 is larger than that of electrode A4. Since the charge transfer resistances ($R_{ct}$) of the two electrodes are quite similar (compare Fig. 4.7.10 and Fig. 4.7.11), the difference results from the ohmic resistance. According to Figs. 4.7.5 and 4.7.6, the ohmic resistance of electrodes B (B1 and B3) is larger than that of electrodes A (A3 and A2). However, the charge transfer resistances of the two types of electrodes are quite similar, which is consistent with Figs. 4.7.10 and 4.7.11.

4.7.3 Polarization resistance and diffusion resistance at large current density

When the current density (or over-potential) is large enough that the concentration polarization can not be neglected, the diffusion resistance arising from the concentration polarization must be taken into account. In section 4.6.1.4, the activation polarization (related to the polarization resistance) and concentration polarization (related to the diffusion resistance) were discussed separately. As shown in Figs. 4.6.11 to 4.6.14, by using the curves of activation over-potential and concentration over-potential vs. discharge current density ($\eta_{act-i}$ and $\eta_{concr-i}$), the polarization resistance ($R_p$) and diffusion resistance ($R_{diff}$) at different discharge current densities can be obtained. The polarization resistance and diffusion resistance at different number of cycles as a function of discharge current density for electrodes A3, A2, B1 and B3 are shown in Figs. 4.7.12, 4.7.13, 4.7.14 and 4.7.15. With increasing discharge current density, the polarization resistance gradually decreases, and the diffusion resistance increases gradually at first but when the current comes close to the limiting current, the diffusion resistance greatly increases and actually exceeds the polarization resistance. Both the polarization resistance and the diffusion resistance decrease with increasing number of cycles, as was
the case for low current density (the linear polarization region), which also results from an increase in the real specific surface area.

For electrode A3 at the 10th cycle, the diffusion resistance exceeds the polarization resistance at a current density of about 2500 mA/g, which means that the rate-determining step for the electrode process changes from activation polarization to concentration polarization. At the 20th cycle, the current density at which the rate-determining step (RDS) changes, increases to about 3600 mA/g, and after that it increases slowly, and reaches about 4000 mA/g for the 40th cycle. For electrode A2, even for the 10th cycle, the current density at which the rate-determining step changes is about 4500 mA/g, and this increases slowly to about 5000 mA/g for the 40th cycle.

For electrode B1 at the 10th cycle, the RDS change current is only about 800 mA/g, and this increases gradually to 1300, 1400 and 1500 mA/g for the 20th, 30th and 40th cycles. For electrode B3 at the 10th cycle, the RDS change current density is about 1000 mA/g, and this increases to 1600 mA/g for the 20th cycle. After the 30th cycle, the current density becomes stabilized at about 2000 mA/g. Compared with electrode B1, electrode B3 shows a larger RDS current density and it is more readily stabilized. This may result from the Pd-coating of the electrode alloy powders.

The above analysis shows that for electrodes A3 and A2, the rate-determining step is usually activation polarization. Only at very large current densities, above 3500 to 4000 mA/g, does concentration polarization become the rate-determining step. Electrode A2 (with Cu) shows a larger RDS change current density than electrode A3 (without Cu), which means that the addition of Cu to the electrode increases the activation polarization region. Electrodes B1 and B3 show smaller RDS change current densities than electrodes
A3 and A2. This results in a smaller activation region, i.e. the diffusion process will become the rate-determining step at relatively lower current density (about 1000 to 2000 mA/g) compared to electrodes A3 and A2 (about 2500 to 5000 mA/g).
Fig. 4.7.1 Ohmic resistance and charge transfer resistance vs. number of cycles for electrode A3 (LaNi$_4$Al$_3$ +Ni) at 25 °C.
Fig. 4.7.2 Ohmic resistance and charge transfer resistance vs. number of cycles for electrode A2 (LaNi$_{4.7}$Al$_{0.3}$ +Ni+Cu) at 25 °C.
Fig. 4.7.3 Ohmic resistance and charge transfer resistance vs. number of cycles for electrode B1 (Un-coated \( \text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35} \)) at 25 °C.
Fig. 4.7.4 Ohmic resistance and charge transfer resistance vs. number of cycles for electrode B3 (Pd-coated $\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$) at $25^\circ\text{C}$. 
Fig. 4.7.5 Ohmic resistance vs. number of cycles at 25°C for electrodes:

B1: Un-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
B3: Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A3: LaNi_{4.7}Al_{0.3} + Ni; A2: LaNi_{4.7}Al_{0.3} + Ni + Cu
Fig. 4.7.6 Charge transfer resistance vs. number of cycles at 25°C for electrodes:

B1: Un-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$

B3: Pd-coated Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$

A3: LaNi$_{4.7}$Al$_{0.3}$ +Ni; A2:LaNi$_{4.7}$Al$_{0.3}$ +Ni+Cu
Fig. 4.7.7 Polarization resistance as a function of hydrogen concentration for electrode A4 (LaNi$_x$Al$_{0.5}$+Ni) at different temperatures.
Fig. 4.7.8 Polarization resistance as a function of hydrogen concentration for electrode A1 (LaNi₄₋₀·₃Al₀·₃+Ni+Cu) at different temperatures.
Fig. 4.7.9 Polarization resistance as a function of hydrogen concentration for electrode B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) at different temperatures.
Fig. 4.7.10 Polarization resistance, ohmic resistance and charge transfer resistance as a function of temperature after fully charging for electrode B2 ($\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$).
Fig. 4.7.11 Polarization resistance, ohmic resistance and charge transfer resistance as a function of temperature after fully charging for electrode A4 (LaNi$_4$Al$_{0.3}$+Ni).
Fig. 4.7.12 Polarization resistance and concentration resistance at different number of cycles as a function of discharge current density for electrode A3 (LaNi$_{4.7}$Al$_{0.3}$+Ni) after fully charging at 25°C.
Fig. 4.7.13 Polarization resistance and concentration resistance at different number of cycles as a function of discharge current density for electrode A2 (LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu) after fully charging at 25°C.
Fig. 4.7.14 Polarization resistance and concentration resistance at different number of cycles as a function of discharge current density for electrode B1 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{1.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) after fully charging at 25°C.
Fig. 4.7.15 Polarization resistance and concentration resistance at different number of cycles as a function of discharge current density for electrode B3 (Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}) after fully charging at 25°C.
4.8 KINETICS OF METAL/HYDRIDE ELECTRODE REACTIONS

The kinetic characteristics of metal hydride electrodes are key in determining whether the electrode has any practical application in a nickel/metal hydride battery. In this section, the reaction rate, rate constant, reaction order and activation energy are discussed in detail for electrodes A4 \((\text{LaNi}_{4.7}\text{Al}_{0.3})\) and B2 \((\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35})\).

4.8.1 Reacted fraction

For potentiostatic measurements the integrated value of the \(I(t)\) vs. time plot represents the total charge. Thus the reacted fraction, \(\alpha(t)\), for the discharge process of a MH electrode can be estimated as follows:

\[
\alpha(t) = \frac{\int_0^t I(t)\,dt}{\int_0^\infty I(t)\,dt} \tag{4.8.1}
\]

where \(\int_0^\infty I(t)\,dt\) represents the maximum charge, \(\int_0^t I(t)\,dt\) represents the charge that the electrode discharges at time \(t\). Thus from the plot of \(I(t)\) vs. \(t\), the variation of the reacted fraction, \(\alpha(t)\), with time can be obtained.

The experimentally determined values of \(\alpha(t)\) at different temperatures and discharge potentials for electrodes A4 \((\text{LaNi}_{4.7}\text{Al}_{0.3})\) and B2 \((\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35})\) are shown in Figs. 4.8.1 to 4.8.6. It is obvious that for the same reaction time, the reacted fraction (and thus the reaction rate) increases with increasing temperature, in a manner consistent with thermally activated processes.

From the experimental results shown in these figures, the applied discharge potential has an obvious influence on the reaction rate. For electrode A4 at 298K, the
reacted fraction is 80% after 300 seconds discharge at an applied discharge potential of –0.8 V (vs. Hg/HgO). However it only requires 175 seconds and 100 seconds to reach the same reacted fraction at applied discharge potentials of –0.7 V and –0.6 V, respectively.

Electrode B2 shows a similar behavior. The reaction rate increases with increasing applied discharge potential, and the electrochemical discharge of the metal hydride electrode is strongly retarded when the applied discharge potential is lower than –0.8 V.

The effect of the applied discharge potential on the reacted fraction can be rationalized as follows: The electrochemical reaction at the interface between the MH electrode and the electrolyte is given by Eq.4.8.2:

$$H_2O + e^{-} \xrightarrow{\text{charge}} \ x \xrightarrow{\text{discharge}} H + OH^-$$  \hspace{1cm} (4.8.2)

For computational convenience it can be also expressed as Eq.4.8.3:

$$H_2O + e^{-} \xrightarrow{\text{charge}} \ x \xrightarrow{\text{discharge}} \ 1/2 \ H_2 + OH^-$$ \hspace{1cm} (4.8.3)

Based on the Nernst equation and a Hg/HgO reference electrode, the relationship between the MH electrode potential \(E\) and the hydrogen activity, \(\alpha(H_2)\), can be expressed as Eq.4.8.4 [12]:

$$E = E^0(H_2O/H_2) + \frac{RT}{2F} \ln \frac{\alpha(H_2O)}{\alpha(H_2)}$$ \hspace{1cm} (4.8.4)
where $E^0(H_2O/H_2)$ is standard potential of the $H_2O/H_2$ reactant couple and is the only temperature related factor, and $\alpha(H_2O)$ is the activity of water, which can be calculated as follows [163]:

\[
\log\alpha(H_2O) = -0.0225m + 0.001434m^2 + (1.38m - 0.9254m^2)/T \tag{4.8.5}
\]

where $m$ is the concentration of $KOH$: $m=6$ for present study. Thus at a given temperature, the $MH$ electrode potential is only related to the hydrogen activity, $\alpha(H_2)$.

According to Eq.4.8.4, when the $MH$ electrode potential ($E$) becomes lower (more negative), the corresponding hydrogen activity, $\alpha(H_2)$, must be increased. This means that more hydrogen ($H$ or $H_2$) must exist in the electrode process to keep the MH potential more negative. However, the discharge process needs to consume hydrogen to produce $H_2O$ (Eq.4.8.2 or 4.8.3). As a result, the discharge process will be retarded at lower (more negative) discharge potentials.

Comparing the reacted fractions, for electrodes A4 and B2, it is seen that the reaction rate of electrode A4 (LaNi$_{4.7}$Al$_{0.3}$) is much higher than that of electrode B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{1.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) (as shown in Figs.4.8.1 to 4.8.6). At an applied discharge potential of $-0.8$ V and 298 K, it takes about 300 seconds to reach a reacted fraction of 80% for electrode A4. Yet, under the same conditions, it takes about 1800 seconds for electrode B2 to reach the same reacted fraction. Similar results are seen for all other discharge potentials and temperatures. This is consistent with the results obtained for the specific surface area (section 4.2) and the exchange current density (section 4.4). As shown in Fig.4.2.9, the specific surface area of electrode A is much larger than that of electrode B, and thus electrode A has more activation sites and a higher
reaction rate than electrode $B$. Fig.4.4.2 shows that the exchange current density of electrode $A$ is much higher than that of electrode $B$. Although the exchange current density represents the equilibrium reaction rate, it determines the kinetic properties of the electrode reaction, and the higher exchange current density result in a higher reaction rate for electrode $A$.

4.8.2 Reaction order and rate constant

According to the nucleation and growth (NG) theory, as originally developed by Avrami [164] and Johnson and Mehl [165], the reacted fraction $\alpha(t)$ is given by the AJM equation.

$$\alpha(t)=1-\exp(-kt^*)$$  \hspace{1cm} (4.8.6)

where $k$ is the rate constant, $n$ is reaction order. Luo et al. [166] have shown that transformation kinetics can be described by another, equivalent form of the AJM equation (referred to as the modified AJM equation) for which an Arrhenius treatment of the rate data more directly yields the activation energy for a singular, rate controlling process, given by Eq.4.8.7.

$$\alpha(t)=1-\exp(-k^*t^*)$$  \hspace{1cm} (4.8.7)

The logarithmic form of Eq.4.8.7 gives

$$\log\ln\left(\frac{1}{1-\alpha}\right)=n\log t+n\log k$$  \hspace{1cm} (4.8.8)
which is a straight line function from which \( n \) (slope) and \( k \) (intercept) for the reaction are obtained. Plots of \( \log \ln[1/(1-\alpha)] \) versus \( \log (t) \) for the discharge process of electrodes A4 and B2 at different temperatures and discharge potentials are given in Figs. 4.8.7 to 4.8.12. For both electrodes A4 and B2, the discharge plots are not linear over the entire reaction range. However, they can be considered to consist of two stages, the first stage (stage I), which is in the range of \( \alpha = 0 \) to \( \alpha = 0.9 \), is linear, and the second stage (stage II) is in the range of \( \alpha = 0.9 \) to \( \alpha = 1 \). It is evident from the reacted fraction curves, and the logarithmic plots, that the reaction is up to 90% completed during the first stage of the discharge. Accordingly, the kinetic analysis of the discharge process is applied to the first stage only, as the points on the above plots for the second stage are limited, and the accuracy of the slope determination is poor. The reaction orders and rate constants for the first stages of electrodes A4 and B2, at different discharge potentials and temperatures, determined according to Eq. 4.8.8, are listed in Tables 4.8.1 to 4.8.2:

Table 4.8.1 Reaction orders for the first discharge stage at different discharge potentials and temperatures for electrodes A4 (LaNi\(_{4.7}\)Al\(_{0.3}\)) and B2 (Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\))

<table>
<thead>
<tr>
<th>Electrode</th>
<th>T(K)</th>
<th>Discharge Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-0.8</td>
</tr>
<tr>
<td>A4</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>298</td>
<td>1.07 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.8.2 Rate constants for the first discharge stage at different discharge potentials and temperatures for electrodes A4 (LaNi$_4.7$Al$_0.3$) and B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>T(K)</th>
<th>Discharge Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-0.8</td>
</tr>
<tr>
<td>A4</td>
<td>298</td>
<td>0.0046</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.0107</td>
</tr>
<tr>
<td>B2</td>
<td>298</td>
<td>0.0009</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.0029</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.0050</td>
</tr>
</tbody>
</table>

The initial reaction rate (stage I) is the fastest, i.e. when $\alpha$ is nucleating and $\alpha$-nuclei are rapidly growing. Later (stage II), the overall reaction rate is slower. The rate constant determined by the slope of the first stage is considered to be representative of the total discharge process for the electrode. In the second stage of discharge process, the conversion of the $\beta$-phase to the $\alpha$-phase is complete, and the rate for the process is determined by the desorption rate of low concentration hydrogen.

Consider the reaction order of electrode A4, as listed in Tables 4.8.1. The discharge reaction order in the first stage remains the same, 1.16± 0.01, at different temperatures and discharge potentials. However, for electrode B2, the discharge reaction order of the first stages is close to 1 (1.07 ± 0.01 and 0.96 ± 0.03) at different discharge potentials except at −0.6V, when it is about 0.54.

Comparing electrode B2 with A4, the differences in the rate constants and reaction orders, $k_{(A4)}>k_{(B2)}$ and $n_{(A4)}>n_{(B2)}$, results in faster reaction rates for electrode A4 than for electrode B2.
The rate constants increase with increasing temperature, as shown in Table 4.8.2. They also increase with increasing the discharge potential (more positive), which is consistent with the decrease in hydrogen activity, \( \alpha(\text{H}_2) \), as discussed in section 4.8.1.

### 4.8.3 Activation energy

The logarithmic form for the Arrhenius relation, \( k = k_0 \exp(-E_a/RT) \), is:

\[
\ln k = \ln k_0 - \left( \frac{E_a}{R} \right) \frac{1}{T}
\]  

(4.8.9)

where \( k \) is rate constant, \( k_0 \) is pre-exponential factor, \( E_a \) is activation energy, and \( R \) is gas constant. A plot of \( \ln k \) versus \( 1/T \) should be a straight line with a slope of \( -E_a/R \). The plots of \( \ln k \) versus \( 1/T \) for the first stage of discharge process at different discharge potentials are shown in Figs.4.8.13 and 4.8.14. The activation energies calculated for the different discharge potentials are listed in Tables 4.8.3:

Table 4.8.3 Activation energies for the first discharge stage at different discharge potentials for electrodes A4 (LaNi\(_{4.7}\)Al\(_{0.3}\)) and B2 (Mn\(_{0.95}\)Ti\(_{0.05}\)Ni\(_{3.85}\)Co\(_{0.45}\)Mn\(_{0.35}\)Al\(_{0.35}\))

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{\text{dis}} = -0.8 ) V</td>
</tr>
<tr>
<td>A4</td>
<td>33.24 ( \pm ) 5.50</td>
</tr>
<tr>
<td>B2</td>
<td>45.95 ( \pm ) 0.30</td>
</tr>
</tbody>
</table>

The activation energy for electrode B2 is larger than that of electrode A4. This is consistent with the experimental results shown in Figs.4.8.1 to 4.8.6, i.e. the reaction rate of electrode B2 is much slower than that of electrode A4.

For electrode A4, the discharge process in the first stage can be treated as diffusion controlled. Since hydrogen diffusion in the metal hydride electrodes is usually known to be a first-order process \([168]\), then electrode A4 has a reaction order close to 1.
(1.16±0.02). It was reported that diffusion of hydrogen in a crystal with dislocation is about 33 kJ/mol [167]. For metal hydride electrode process, the activation energy of a typical diffusion processes is from 22 kJ/mol to 45 kJ/mol [131, 168, 169]. The activation energies of electrodes A4 are in this range. Further more, from the results presented in section 4.6 (Fig.4.6.8), it was found that after 30 cycles (when the electrode becomes stable, and the discharge experiments were conducted), and at a current density higher than 3500 mA/g, the diffusion process, which results in concentration polarization, becomes the controlling process. For the discharge process of electrode A4, the discharge current density is not lower than 3500 mA/g until more than 55% (E=−0.8 V) to 75% (E=−0.6 V) of the reaction is completed. That means that the first 55% to 75% of the discharge process of electrode A4 should be diffusion control and the rest process should be charge transfer controlled.

For electrode B2, it is a little more complicated. The reaction order in the first stage is also close to 1, except for the −0.6 V potential, and the activation energy is close to the range of diffusion processes. However, this does not preclude charge transfer as a rate controlling mechanism (e.g. n=1). The results in section 4.6 (Fig.4.6.10) shows that after 30 cycles, at a current density lower than 1500 mA/g, the reaction is charge transfer controlled, otherwise, it is diffusion controlled. However, for the discharge process of electrode B2 at −0.8 V to −0.6 V, when the current density goes down to less than 1500 mA/g, only 1% of the reaction completed, which means all the reaction happens at a current density lower than 1500 mA/g. Thus, the discharge reaction of electrode B2 could be charge transfer controlled.
The activation energies of the two electrodes are different at different discharge potentials. However, it seems that no clear conclusions can be made regarding the effect of discharge potential on the activation energy.

The activation energies of electrode B2 are larger than those of electrode A4. It was reported that the lattice dimension could have some effect on activation energy, and that an increase in unit cell volume of metal hydride results in higher activation energy [169, 170]. The cell volume of electrode A4 is 87.35, and electrode B is 88.27, thus electrode B has larger activation energy than electrode A4.
Fig. 4.8.1 Constant potential (-0.8V) discharge curves at different temperatures for electrode A4 (LaNi$_4.7$Al$_{0.3}$).
Fig. 4.8.2 Constant potential (-0.7V) discharge curves at different temperatures for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$).
Fig. 4.8.3 Constant potential (-0.6V) discharge curves at different temperatures for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$).
Fig. 4.8.4 Constant potential (-0.8V) discharge curves at different temperatures for electrode B2 (Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.45}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.8.5 Constant potential (-0.7V) discharge curves at different temperatures for electrode B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.8.6 Constant potential (-0.6V) discharge curves at different temperatures for electrode B2 (Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$).
Fig. 4.8.7 $\log \ln[1/(1-\alpha)]$ vs. $\log (t)$ for constant potential discharge (-0.8V) at different temperatures for electrode A4 (LaNi$_4$7Al$_{0.3}$)
Fig. 4.8.8 Log \( \ln[1/(1-\alpha)] \) vs. \( \log(t) \) of constant potential discharge (-0.7V) at different temperatures for electrode A4 (LaNi\(_{4.7}\)Al\(_{0.3}\))
Fig. 4.8.9 Log ln[1/(1-\(\alpha\))] vs. log (t) of constant potential discharge (-0.6V) at different temperatures for electrode A4 (LaNi\(_{4.7}\)Al\(_{0.3}\))
Fig. 4.8.10 Log ln[1/(1-\(\alpha\))] vs. log (t) of constant potential discharge (-0.8V) at different temperatures for electrode B2
\((\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35})\)
Fig. 4.8.11 Log ln[1/(1-\(\alpha\))] vs. log (t) of constant potential discharge (-0.7V) at different temperatures for electrode B2 (Mm_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35})
Fig. 4.8.12 Log ln[1/(1-α)] vs. log (t) of constant potential discharge (-0.6V) at different temperatures for electrode B2 (Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35})
Fig. 4.8.13 Arrhenius plots [ln(k) vs. 1/T] at different discharge potentials for electrode A4 (LaNi$_{4.7}$Al$_{0.3}$)
Fig. 4.8.14 Arrhenius plots $[\ln(k) \text{ vs. } 1/T]$ at different discharge potentials for electrode B2 ($\text{Mn}_{0.95}\text{Ti}_{0.05}\text{Ni}_{3.85}\text{Co}_{0.45}\text{Mn}_{0.35}\text{Al}_{0.35}$)
4.9 SUMMARY OF METAL HYDRIDE ELECTRODE PROPERTIES

Discharge capacity and cycle life are two of the principle properties that determine whether the electrode can be used as a negative electrode in a nickel/metal hydride battery. Good kinetic properties (especially high electrode reaction rate) of an electrode are also very important for large current charging/discharging of the battery, which can lead to wide application. In this section, the discharge capacity, cycle life and other related parameters of four metal hydride electrodes (A3:LaNi$_{4.7}$Al$_{0.3}$+Ni; A2: LaNi$_{4.7}$Al$_{0.3}$+Ni+Cu; B1: un-coated M$_{1.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$; B3: Pd-coated M$_{1.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$) are reviewed based on the results presented in sections 4.1 to 4.8.

4.9.1 Capacity and cycle life

The discharge capacities of electrodes A3, A2, B1 and B3 are shown in Fig.4.9.1. For the LaNi$_{4.7}$Al$_{0.3}$ alloy electrodes, the electrode with a Cu addition (A2) has a higher discharge capacity than the one without a Cu addition (A3). Thus a Cu addition significantly increases the discharge capacity. The discharge capacities of the two LaNi$_{4.7}$Al$_{0.3}$ alloy electrodes (A3 and A2) decay more quickly than the M$_{1.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy electrodes (B1 and B3). For the first 25 cycles of electrodes B1 and B3 (M$_{1.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$), the Pd-coated electrode (B3) has a lower discharge capacity than the un-coated one (B1). However, after 25 cycles, the discharge capacity of Pd-coated electrode exceeds that of the un-coated one, and stabilizes after 35 cycles. Obviously, the Pd-coating significantly slows down the decay of discharge capacity.

4.9.2 Other parameters related to the behavior of the electrodes
Parameters such as specific surface area \((S)\), symmetry factor \((\beta)\), over-potential \((\eta)\), resistance \((R)\), exchange current density \((I_0)\), activation energy \((E_a)\) are all related to the behavior of the metal hydride electrodes. The relationship between these parameters and the properties of the electrode reactions are summarized in sections 4.9.2.1 to 4.9.2.3.

### 4.9.2.1 Number of cycles \((N)\)

With increasing number of cycles, the specific surface area, \(S\), increases in the first 30 cycles, and then attains a stable value (section 4.2). The ratio \(D/\alpha^2\) also increases with increasing number of cycles, and stabilizes after 30 cycles (section 4.3). On cycling, the specific surface area, \(S\), increases and the resistance, \(R\), decreases. Also the exchange current density, \(I_0\), increases and becomes nearly constant after 30 cycles (section 4.4).

The symmetry factor, \(\beta\), with concentration polarization (or mass transfer effect), increases with increasing number of cycles, and after 10 to 30 cycles (depending on the composition of electrode) also becomes stable. However, the symmetry factor, \(\beta\), with only linear polarization remains almost unchanged on cycling (section 4.5). With decreasing over-potential, \(\eta\), the activation energy \((E_a)\) increases (section 4.5). The over-potential, \(\eta\) (including activation over-potential, \(\eta_{\text{act}}\), and concentration over-potential, \(\eta_{\text{conc}}\)) decreases on cycling up to 30 cycles, and then remains almost constant (section 4.6). The polarization resistance, \(R_p\) (including ohmic resistance, \(R_{\text{ohm}}\), and charge resistance, \(R_{\text{ch}}\)) decreases on cycling, and after about 30 cycles it also becomes stable (section 4.7). The above observations can be summarised as follows:

\[
N \uparrow \Rightarrow S \uparrow, \quad R \downarrow \Rightarrow I_0 \uparrow \Rightarrow \beta \uparrow, \quad \eta \downarrow, \quad D/\alpha^2 \uparrow \Rightarrow E_a \uparrow
\]

### 4.9.2.2 Hydrogen concentration/depth of discharge \((\text{DOD})\)
For the same number of cycles, all the parameters listed in section 4.9.2.1 are related to the depth of discharge (DOD), or the hydrogen concentration. As the DOD increases (the hydrogen concentration decreases), the specific surface area, \( S \) (section 4.2), the ratio \( D/\alpha^2 \) (section 4.3), and the exchange current density, \( I_0 \) (section 4.4) increase. The symmetry factor, \( \beta \), increases with increasing DOD during the complete discharge process (section 4.5). The over-potential, \( \eta \), decreases with increasing DOD only in the \( \beta \)-phase region, and in other phase regions remains almost stable (section 4.6). The polarization resistance, \( R_p \), decreases slowly with increasing DOD, except in the \( \beta \)-phase region (section 4.7). This can be summarized as follows:

\[
DOD \uparrow \Rightarrow S \uparrow, R_p \downarrow \Rightarrow I_0 \uparrow \Rightarrow \beta \uparrow, \eta \downarrow, D/\alpha^2 \uparrow
\]

4.9.2.3 Temperature

Almost all the parameters discussed above are temperature related. As the temperature increases, the hydrogen diffusion coefficient (\( D_H \)), the ratio \( D/\alpha^2 \) (section 4.3), exchange current density (\( I_0 \)) (section 4.4) and symmetry factor (\( \beta \)) (section 4.5) all increase. The over-potential, \( \eta \) (including activation over-potential, \( \eta_{ac} \), and concentration over-potential, \( \eta_{conc} \)) (section 4.6) and the polarization resistance (\( R_p \)) (including ohmic resistance, \( R_{ohm} \), and charge resistance, \( R_c \)) (section 4.7) decrease with increasing temperature. The above observations can be summarized as follows:

\[
T \uparrow \Rightarrow I_0 \uparrow \Rightarrow \beta \uparrow, D/\alpha^2 \uparrow, D_H \uparrow, R_p \downarrow \Rightarrow \eta \downarrow
\]

4.9.3 Comparison of activation energies for hydrogen diffusion and electrode reactions

In present study, we have determined the apparent activation energies for both hydrogen diffusion and the electrode reactions. For electrodes A4 and B2, the activation
energies for hydrogen diffusion are 22.6 kJ/mol and 25.5 kJ/mol, respectively (section 4.3.4). The activation energies for the electrode reactions (-0.8V, stage I, which is almost the same conditions at which the diffusion activation energy was obtained) are 33.24 kJ/mol and 45.95 kJ/mol, respectively. The activation energy for the electrode reactions is obviously larger than that for diffusion in both electrodes.

As discussed in 4.8.3, the electrode process for electrode A4 is mainly diffusion controlled. However, it was also observed that after 55% (E=-0.8V) of the reaction is completed, the discharge current density decreases, and the process becomes charge transfer controlled. For electrode A4 in section 4.3.4, the electrode process is totally diffusion controlled. This is likely the reason that the activation energy for electrode A4 as discussed in section 4.8.3, is larger than that discussed in section 4.3.4.

For electrode B2, as discussed in section 4.8.3, the electrode process is totally charge transfer controlled. Thus, the activation energy is quite different from the value obtained in section 4.3.4, which is diffusion controlled.

4.9.4 Effect of copper addition

Copper addition in the LaNi_{4.7}Al_{0.3} electrode improves the electrode performance greatly. Basically, the function of Cu addition can be summarized as two aspects: one is that addition of Cu, which is a excellent conductor, acts as a micro-current collector during charging/discharging process. Thus the charge transfer process, or the exchange current density, can be increased. Another is that since the Cu powders were mixed with metal hydride alloy powders and then pressed with high pressure when preparing the negative electrode, in this case, Cu addition acts as a good connector among the metal hydride alloy powders. Thus the resistance of the electrode was decreased, and then the reaction
current was increased. As a result, the kinetic performance including reaction rate of the electrode process was improved by Cu addition. Also during charge/discharge process, a little blue color was found in the electrolyte, implied that there is Cu being oxidized, which should be further studied in the future work.
Fig. 4.9.1 Variation of the discharge capacity with number of cycles at 25 °C for electrodes:

B1: Un-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
B3: Pd-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35}
A3: LaNi_{4.7}Al_{0.3}+Ni;  A2: LaNi_{4.7}Al_{0.3}+Ni+Cu
CHAPTER 5

CONCLUSIONS

The electrochemical behavior and thermodynamic parameters of LaNi$_{4.7}$Al$_{0.3}$-based and Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$-based alloy electrodes (with or without Ni, Cu additions and Pd-coating) were determined at different number of cycles, hydrogen concentrations and temperatures. The main conclusions are:

1. A quantum chemistry method was used to calculate the thermodynamic parameters for the LaNi$_5$-based alloy. The calculated values of $\Delta S$, $\Delta H$, $\Delta G$ and $P_{eq}$ at 298K are -120.2 (J/K·mol), -34.1 (kJ/mol), 1.73 (kJ/mol) and 2.01 (atm), respectively for LaNi$_5$; -126.2 (J/K·mol), -60.0 (kJ/mol), -22.4 (kJ/mol) and 1.24×$10^{-4}$ (atm), respectively for LaNi$_4$Al; and -118.3 (J/K·mol), -50.7 (kJ/mol), -15.4 (kJ/mol) and 2.0×$10^{-3}$ (atm), respectively for LaNi$_4$Mn. All the results are consistent with published experimental values.

2. The thermodynamic parameters for Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$-based and LaNi$_{4.7}$Al$_{0.3}$-based alloy electrodes were measured using electrochemical methods. Measured values of $\Delta S$, $\Delta H$ and $P_{eq}$ were -104.57 (J/K·mol), -38.53 (kJ/mol) and 0.05 (atm), respectively for an electrode of the Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ alloy with a Cu addition; -90.64 (J/K·mol), -29.38 (kJ/mol) and 0.39 (atm), respectively for an electrode of the LaNi$_{4.7}$Al$_{0.3}$ alloy with a Ni addition; and -94.17 (J/K·mol), -29.39 (kJ/mol) and 0.59 (atm), respectively for an electrode of the LaNi$_{4.7}$Al$_{0.3}$ alloy with both Ni and Cu additions. The fact that a Mm$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$-based alloy electrode has more negative (larger in absolute value) $\Delta S$ and $\Delta H$ parameters than the LaNi$_{4.7}$Al$_{0.3}$-based alloy electrodes indicates that the metal hydride of the MmNi$_5$-based
alloy is more thermodynamically stable and has a stronger resistance to anodic oxidation reactions than the LaNi$_5$-type alloy. Thus it has poorer high-rate discharge properties than a LaNi$_{4.7}$Al$_{0.3}$-based alloy electrode.

3. The kinetic parameters of the Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrodes and LaNi$_{4.7}$Al$_{0.3}$ electrodes show that the discharge reaction rates (or the reaction rate constants) increase with increasing applied discharge potential, and that the electrochemical discharge is strongly retarded when the applied discharge potential is lower than $-0.8$ V. The discharge reaction order for LaNi$_{4.7}$Al$_{0.3}$ electrode is $1.16 \pm 0.01$ at discharge potential of $-0.8$ V to $-0.6$ V in the temperature range of 298 K to 318 K. For Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrode, in the temperature range of 298 K to 328 K, the reaction order is very close to 1 ($1.07 \pm 0.01$ and $0.96 \pm 0.03$) at discharge potential of $-0.8$ V and $-0.7$V, however, it is only $0.54 \pm 0.06$ at discharge potential of $-0.6$ V. The activation energies for the reactions corresponding to the $\alpha+\beta$ phase region, which is the main state for the discharge process of a metal hydride electrode, at applied discharge potentials of $-0.8$, $-0.7$ and $-0.6$V were measured as $33.24 \pm 5.50$, $30.26 \pm 5.32$ and $27.64 \pm 5.02$ (kJ/mol), respectively for the LaNi$_{4.7}$Al$_{0.3}$ electrode; and $45.95 \pm 0.30$, $52.59 \pm 1.80$ and $48.65 \pm 2.53$ (kJ/mol), respectively for the Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrode.

4. Measurements of the specific surface areas of metal hydride electrodes made from LaNi$_{4.7}$Al$_{0.3}$-based and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$-based alloys show that the specific surface area increases with increasing number of cycles, and after about 30 cycles, the specific surface area reaches a stable value and remains unchanged on further cycling. The specific surface area also increases with increasing depth of discharge.
(DOD). A model for the hydrogen absorption in the metal hydride electrode is proposed to explain the variation of specific surface area with hydrogen concentration. It was also found that almost all of the electrochemical properties are influenced by the specific surface area of the metal hydride electrodes.

5. The hydrogen diffusion coefficients ($D_h$) in the LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrodes at 25°C were determined to be $1.1 \times 10^{-10}$ and $1.0 \times 10^{-10}$ (cm$^2$/s), respectively. $D_h$ increased with increasing temperature. The activation energy for the hydrogen diffusion process in the two electrodes was determined to be 22.6 and 25.5 (kJ/mol), respectively. The ratio of hydrogen diffusion coefficient to the square of spherical radius of electrode alloy particles ($D/a^2$) increases with increasing depth of discharge, and increases with increasing temperature. $D/a^2$ increases with increasing number of cycles for both types of electrode. As was the case for the specific surface area, the $D/a^2$ ratio becomes stable after about 30 cycles, and remains unchanged upon further cycling. The same behavior was found for the particle size of the electrode alloy powders, i.e. the particle size decreases with increasing number of cycles, but after about 30 cycles it also becomes stable.

6. Both the exchange current density (linear polarization and the polarization with mass transfer effect) and limiting current density were found to increase with increasing number of cycles. Also, as is the case for the specific surface area, they all become stable after about 30 cycles. Micro-cracking activation, resulting from an increase in reaction surface area and an improvement in the electrode surface activation, increases the exchange current density. The exchange current density was also found to decrease slightly with increasing hydrogen concentration.
7. The symmetry factor for linear polarization remains almost unchanged upon cycling. However, the symmetry factor for concentration polarization increases with increasing number of cycles, but also becomes stable after about 30 cycles. The symmetry factor decreases with increasing hydrogen concentration.

8. Both the over-potential and the resistance of a metal hydride electrode decrease with increasing number of cycles, and become stable after about 30 cycles. They also increase slightly with increasing hydrogen concentration. The ohmic, polarization and charge transfer resistances all decrease with increasing temperature. Measurement of the resistances and over-potentials show that at lower current densities, activation polarization is the rate-determining step. However, at larger current densities, concentration polarization becomes the rate-determining step.

9. LaNi$_{4.7}$Al$_{0.3}$ electrodes with either a Ni addition or a Ni + Cu addition show different electrochemical behavior during charge/discharge cycling. The enthalpies ($\Delta H$) for the two electrodes are the same, which implies that the stability of the electrode is not affected by a Cu addition. However, the Cu addition makes the entropy ($\Delta S$) more negative (it changes from $-90.64$ to $-94.17$ J/K·mol) and also gives rise to an increase in the equilibrium pressure ($P_{eq}$ changes from 0.39 to 0.59 atm). The Cu addition greatly increases the specific surface area, making the stable specific surface area increase from about 25 m$^2$/g to 85 m$^2$/g. This increase in specific surface area is the main reason that the electrode with the Cu addition shows much better kinetic properties. The Cu addition increases the stable D/a$^2$ ratio from $1.3\times10^6$ to $1.6\times10^6$ (s$^{-1}$), but does not affect the particle size of the electrode alloy powders. It increases the exchange current density, making the stable linear exchange current density increase from 500 to 750 mA/g, and
stable exchange current density with mass transfer effect increase from 350 to 550 mA/g. These increases directly result in an improvement in the kinetic properties, especially low temperature kinetic properties. The exchange current density at 0°C of the electrode with a Cu addition is about 150 mA/g, but it is only about 30 mA/g for the electrode without a Cu addition. The Cu addition also increases the limiting current density, symmetry factor and discharge capacity. Measurements of over-potentials and resistances show that a Cu addition decreases both the over-potential and resistance, which also results in an improvement in kinetic properties.

10. A comparison of Pd-coated and un-coated Mn_{0.95}Ti_{0.05}Ni_{3.85}Co_{0.45}Mn_{0.35}Al_{0.35} electrodes shows that the Pd-coated electrode has better electrochemical properties. The discharge capacity of the un-coated electrode is 276 mAh/g and this decreases to 250 mAh/g after 40 charge/discharge cycles. The discharge capacity of the Pd-coated electrode is 225 mAh/g before cycling, and it increases to a maximum value of 275 mAh/g after 40 cycles, and then remains almost constant with increasing number of cycles. The Pd-coated electrode also shows a longer cycle lifetime. Pd-coating does not affect the specific surface area greatly, but it decreases the D/a^2 ratio, and increases the particle size of the electrode alloy powders. Pd-coating increases both the exchange current density and the limiting current density. It was found that Pd-coating makes the symmetry factor closer to 0.5, resulting in much better reversibility for the electrode reaction. Pd-coating does not influence the over-potential. However, it makes the equilibrium potential more negative. There is not much difference in resistance between the un-coated and Pd-coated electrodes, but the Pd-coated electrode shows a larger RDS change current density and it is more readily stabilized.
11. LaNi$_{4.7}$Al$_{0.3}$ and Mn$_{0.95}$Ti$_{0.05}$Ni$_{3.85}$Co$_{0.45}$Mn$_{0.35}$Al$_{0.35}$ electrodes show different electrochemical properties. For the first 30 cycles, the discharge capacities of the LaNi$_{4.7}$Al$_{0.3}$ electrodes are larger than for the MnNi$_5$-based alloy electrodes. However, after about 30 cycles, the discharge capacities of MnNi$_5$-based alloy electrodes become larger than for the LaNi$_{4.7}$Al$_{0.3}$ electrodes. Also MnNi$_5$-based alloy electrodes have a lower capacity decay rate and longer cycle lifetime. A MnNi$_5$-based alloy electrode has a more negative enthalpy and entropy, and a smaller equilibrium pressure ($\Delta H = -38.53$ kJ/mol, $\Delta S = -104.57$ J/K·mol, $P_{eq} = 0.05$ atm) than a LaNi$_{4.7}$Al$_{0.3}$ electrode ($\Delta H = -29.39$ kJ/mol, $\Delta S = -90.64 \sim 94.17$ J/K·mol, $P_{eq} = 0.39 \sim 0.59$ atm). The specific surface areas of the LaNi$_{4.7}$Al$_{0.3}$ electrodes are much larger than for the MnNi$_5$-based alloy electrodes, thus resulting in better kinetic properties for the LaNi$_{4.7}$Al$_{0.3}$ electrodes. There is not much difference in hydrogen diffusion coefficient for the two electrode types. However, the LaNi$_{4.7}$Al$_{0.3}$ electrode has a higher cracking rate than the MnNi$_5$-based alloy electrode, and it has a stable particle size of 18$\mu$m, which is much smaller than a MnNi$_5$-based alloy electrode with a stable particle size of 27$\sim$30$\mu$m. The LaNi$_{4.7}$Al$_{0.3}$ electrode has a smaller diffusion activation energy (22.6 kJ/mol) than the MnNi$_5$-based alloy electrode (25.5 kJ/mol). The LaNi$_{4.7}$Al$_{0.3}$ electrode has much larger exchange current density and limiting current density than the MnNi$_5$-based alloy electrode, which results in better kinetic properties of the LaNi$_{4.7}$Al$_{0.3}$ electrodes. MnNi$_5$-based alloy electrodes have symmetry factors much closer to 0.5 than the LaNi$_{4.7}$Al$_{0.3}$ electrodes, which means that MnNi$_5$-based alloy electrodes have much better electrode reaction reversibility. LaNi$_{4.7}$Al$_{0.3}$ electrodes have lower over-potentials and more negative equilibrium potentials, and also much smaller resistances than MnNi$_5$-based alloy electrodes. The
RDS change currents of the LaNi$_{4.7}$Al$_{0.3}$ electrodes are much larger than for the MnNi$_5$-based alloy electrodes. After the electrode is stabilized, the RDS change current density for a LaNi$_{4.7}$Al$_{0.3}$ electrode is about 4000–5000 mA/g, but it is only 1500–2000 mA/g for a MnNi$_5$-based alloy electrode. Overall, LaNi$_{4.7}$Al$_{0.3}$ electrodes have better kinetic properties, whereas MnNi$_5$-based alloy electrodes have better reversibility, lower capacity decay rates and longer cycle lifetimes.
CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

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

1. The behavior of each element, especially corrosion behavior, in the metal hydride alloy electrodes during charge/discharge cycling should be investigated in detail. In order to obtain information on the basic reactions related to elemental corrosion, each reaction process corresponding to different potentials should be investigated separately.

   Electrochemical measurements using a cyclic voltammogram is one of the powerful methods for analyzing the specific reaction under a certain applied potential.

2. The hydrogen behavior at the interface between the electrode alloy and electrolyte needs to be further investigated. The processes to be investigated include mechanisms and kinetics of hydrogen adsorption/desorption, and hydrogen interfacial transfer into the metallic host. The transport processes of hydrogen at the interface determines the high rate charging/discharging ability of the metal hydride electrodes.

3. The phase transformation processes of the electrode alloy on charge/discharge cycling is one of the most important factors that determine the cracking behavior of metal hydride electrode alloy powders, and thus, the capacity decay of the electrode.

   Experimental methods including cyclic voltammogram, X-Ray Diffraction and SEM can be used to investigate the process by analyzing the microstructure of the alloy, the surface characteristics of the alloy powders, and the phase compositions at different hydrogen concentrations (or DODs).
REFERENCES

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VITA AUCTORIS

Name: Jianwen Han

Education: M.Sc. in Chemistry
Nankai University
Tianjin, P.R.China
1990

B.Sc. in Chemistry
Nankai University
Tianjin, P.R.China
1987
PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS DISSERTATION

PUBLICATIONS

1. Mingming Geng, Jianwen Han, Feng Feng and Derek O. Northwood, Electrochemical measurements of a metal hydride electrode for the Ni/MH battery 

2. Jianwen Han, Feng Feng, Mingming Geng, Robert Buxbaum and Derek O. Northwood, Electrochemical characteristics of the interface between the metal hydride electrode and electrolyte for an advanced nickel/metal hydride battery 

3. Feng Feng, Jianwen Han, M. Shen, Mingming Geng, Ziqiang Zhou and Derek O. Northwood, Electrochemical properties of a LaNi$_{4.7}$Al$_{0.3}$ alloy used for the negative electrode in nickel/metal hydride batteries 

4. Mingming Geng, Jianwen Han, Feng Feng and Derek O. Northwood, Charging/discharging stability of a metal hydride battery electrode 

5. Mingming Geng, Jianwen Han, Feng Feng and Derek O. Northwood, Characteristics of the high-rate discharge capability of a nickel/metal hydride battery electrode

6. Feng Feng, Xinyi Ping, Ziqiang Zhou, Mingming Geng, Jianwen Han and Derek O. Northwood, The relationship between equilibrium potential during discharge and hydrogen concentration in a metal hydride electrode


7. Mingming Geng, Jianwen Han, Feng Feng and Derek O. Northwood, Hydrogen absorbing alloys for the nickel-metal hydride battery


8. Mingming Geng, Jianwen Han and Derek O. Northwood, Decay in the hydrogen storage capacity of a LaNi$_4$$\gamma$Al$_{0.3}$ alloy powder with exposure to air with hydriding-dehydriding cycles


PRESENTATIONS:

1. Feng Feng, Jianwen Han, Mingming Geng and Derek O. Northwood, Hydrogen desorption kinetics of a LaNi$_4$$\gamma$Al$_{0.3}$ metal hydride electrode using potentiostatic measurements, IUMRS-ICAM’99, Beijing, China, June, 1999

2. Mingming Geng, Jianwen Han, Feng Feng and Derek O. Northwood, Charge/discharge performance of the experimental nickel/metal hydride battery


3. Mingming Geng, Jianwen Han and Derek O. Northwood, The discharge characteristics of the negative electrode alloys for the nickel-metal hydride batteries

4. Jianwen Han and Derek O. Northwood, Quantum chemistry calculations of the structure and thermodynamic properties of the deuterides of LaNi₅, LaNi₄Al and LaNi₄Mn.