MODELING OF THERMAL AND CHARGE/DISCHARGE CYCLE BEHAVIORS OF NICKEL METAL HYDRIDE (NI-MH) BATTERY SYSTEM

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MODELING OF THERMAL AND CHARGE/DISCHARGE CYCLE BEHAVIORS OF NICKEL METAL HYDRIDE (NI-MH) BATTERY SYSTEM

by

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Thesis submitted in fulfillment of the requirements for the degree of Master of Science

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APPROVAL AND DECLARATION

I hereby declare that I am the sole author of this dissertation. I have conducted, completed the research work and written the dissertation entitled “Modeling of Thermal and Charge/Discharge Cycle Behaviors of Nickel Metal Hydride (Ni-MH) Battery System”. I also declare it has not previously submitted for the basis of the award of any degree or diploma or other similar title of this for any other diploma/examining body or university. I understand that my dissertation may be made electronically available to the public.

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Date :
ACKNOWLEDGEMENT

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Surface Area of Nickel Substrate

$a_{MH}$  
Surface Area of MH Electrode
PEMODELAN TERMA DAN KITARAN CAS/DISCAS SISTEM BATERI NIKEL LOGAM HIDRIDA (NI-MH)

ABSTRAK

Berdasarkan kesan pencemaran persekitaran yang rendah, bateri Nikel Logam Hidrida dianggap sebagai salah satu bateri yang paling sesuai untuk kenderaan elektrik pada masa kini. Tenaga yang dihantar oleh bateri Nikel Logam Hidrida bergantung kepada profil discas. Secara amnya, tenaga keupayaan yang disimpan di dalam bateri tidak dapat dikeluarkan secara keseluruhannya. Dua model yang berbeza dan tidak bersandar, iaitu cas/discas dan terma telah dibina. Model persamaan pembezaan separa matematik yang diperolehi telah diselesaikan dengan menggunakan kaedah Explicit, penghampiran beza terhingga. Model penyelesaian dan simulasi ini telah dilakukan dengan menggunakan bantuan perisian MATLAB R2011a. Model cas/discas ini mampu untuk meramalkan jumlah masa untuk discas bateri di bawah pelbagai kadar discas. Model ini juga menunjukkan bahawa sel dengan elektrod tebal akan mempunyai potensi sel yang lebih rendah kerana rintangan dalaman yang tinggi. Jumlah ketebalan bagi sel 1 adalah 0.101 cm, sel 2 adalah 1.90 cm dan sel 3 adalah 0.12 cm, di mana sel 1 mempunyai potensi sekitar 1.35V, sel 2 1.29V, dan sel 3 1.34V. Selain itu, model terma yang telah dibina dalam 1-dimensi dan 2-dimensi mampu meramal taburan suhu di dalam sel. Kesahihan keputusan simulasi ini telah ditentu sahkan dengan data eksperimen daripada sumber-sumber rujukan dan juga dengan bantuan perisian MINITAB. Berdasarkan keputusan yang diperolehi daripada simulasi, ia boleh disimpulkan bahawa model 1-dimensi dibentangkan di dalam kerja-kerja ini boleh meramal kelakuhan terma di bawah olakan tabii manakala model 2-dimensi digunakan apabila pengecasan di bawah olakan paksa. Proses pengecasan ini adalah eksotermik dan akan mencapai suhu yang sangat tinggi kira-kira 44ºC sehingga 57ºC di bawah kadar pengecasan yang tinggi dan pengecasan terlampau.
MODELING OF THERMAL AND CHARGE/DISCHARGE CYCLE BEHAVIORS OF NICKEL METAL HYDRIDE (NI-MH) BATTERY SYSTEM

ABSTRACT

Due to low environmental impact, the Nickel Metal Hydride battery has been considered to be one of the most promising candidate battery for electrical vehicle nowadays. The energy delivered by the Nickel Metal Hydride battery depends heavily on its discharge profile and generally it is not possible to extract the whole energy that is stored in the battery. Two independent models for charge/discharge cycle and thermal behavior have been developed. The governing equations are solved by the explicit method, using finite difference approximation. Then, the partial differential numerical simulation was performed using MATLAB R2011a software. The charge/discharge model is capable to predict the total discharge time of a battery under various discharge rates. It also shows that cell with thicker electrode have lower potential due to higher internal resistance. Total thickness for cell 1 is 0.101 cm, cell 2 is 1.90 cm, and cell 3 is 0.12 cm which is cell 1 have a potential approximately 1.35V, cell 2 1.29V, and cell 3 1.34V. On the other hand, the thermal models are developed in 1-dimensional and 2-dimensional and capable of predicting the temperature distributions inside a cell. The simulation results are validated and verified with referred sources of experimental data and using MINITAB software. Based on the results obtained from simulations, it can be concluded that the 1-dimensional model presented in this work can predict thermal behavior well under natural convention while 2-dimensional model was used when charging under forced convention. The charging process is exothermic and will reach very high temperature approximately 44ºC to 57ºC under high charging rate and overcharge.
CHAPTER 1

INTRODUCTION

1.1 Overview

As electronic products have come to feature more sophisticated functions, more compact sizes and lighter weights, the sources of power that operate these products have been required to deliver increasingly higher levels of energy.

A battery is a device that can directly convert chemical energy into electricity. Thus, it is an efficient way to make electricity portable. This process is due to the reaction which is known as electrochemical oxidation-reduction reaction or also known as ‘redox’ reaction. The electrochemical oxidation-reduction reaction involves the transfer of electrons from one material to another through an electric circuit. In a nanoelectrochemical redox reaction,
such as rusting or burning, the transfer of electrons occurs directly and only heat is involved.

Basically, when term ‘battery’ is used, the basic electrochemical unit being referred to is the ‘cell’. Originally, the term ‘battery’ means several electrochemical ‘cells’ connected together either in series or in parallel to give a higher voltage or a much larger current. Single electrochemical cell is an electric cells that are composed of two electrodes which solid electrical conductors and at least one electrolyte that is aqueous electrical conductor. In current cells, the electrolyte is often a moist paste so that the ions can move. Sometimes one electrode is the cell container (Reddy, 2011).

A cell consists of three main components:

i. Positive electrode or cathode electrode which receives electrons from the external circuit during discharge period.

ii. Negative electrode or anode electrode which donates electrons to the external circuit during charge and recharge period.

iii. Electrolyte which provides the medium for the charge to flow between the positive and negative electrodes.

To meet this requirement, Nickel-Metal Hydride (Ni-MH) batteries have been developed and manufactured with nickel hydroxide for the positive electrode and hydrogen-absorbing alloys, capable of absorbing and releasing hydrogen at high-density levels, for the negative electrode. Because Ni-MH batteries have about twice the energy density of Nickel Cadmium (Ni-Cd) batteries and a similar operating voltage as that of Ni-
Cd batteries, they are expected to become a mainstay in the next generation of rechargeable batteries (Panasonic, 2003).

Large-scale applications demand low cost and environmentally friendly batteries. Non-aqueous lithium ion batteries (LIBs) exhibit high energy density and stable performance, but their use is limited due to their high cost, ecological and safety concerns. The use of aqueous electrolytes in rechargeable batteries offers great safety, ecological, and manufacturing advantages. Aqueous Li-ion batteries could combine advantages of aqueous batteries and high energy density of non-aqueous Li-ion batteries, and become suitable energy storage for large-scale applications (Yermukhambetova et al., 2012).

1.2 Modeling of Nickel-Metal Hydride Batteries

i. Charge/Discharge Model

Charge/discharge model were previously presented by Paxton and Newman (1997), a detailed analytical method for discharge characteristics of Ni-MH batteries at a constant temperature. To take these microscopic phenomena into account, a modified pseudo 2-dimensional model based on the macro homogeneous model of Paxton and Newman, (1997) was proposed by De Vidts et al., (1995). In this model, the "macroscopic" dimension was defined across the cell, whereas the "microscopic" dimension was defined across the active material layer. Fick's law of diffusion and Ohm's law of electronic conduction were applied along the microscopic coordinate to account for proton diffusion
and ohmic drop. The microscopic equations were then coupled to the macroscopic governing equations for species and charge transfer across the cell, and together they were numerically solved simultaneously. While such a pseudo two-dimensional approach is capable of incorporating microscopic phenomena into a macroscopic model, it is computationally demanding and appears difficult to apply to practical situations wherein complex discharge or charge modes are involved as in electric vehicle applications.

Besides that, Gu et al., (1999) also reported an analytical method for charge/discharge characteristics at a constant temperature as well as comparisons between the predicted and measured voltage and current characteristics. The simulated cell potential curves agree well with the experimental data, especially with respect to the discharge capacity and midpoint cell potential. The overall results shows good agreements with the general shape of the experimental charge curves were successfully captured by the model.

ii. Thermal Behavior Model

2-dimensional and non-isothermal model for a Ni-MH cell that was constructed on the planar electrode approximation were developed by Wu et al., (2001) due to the charge/discharge characteristics strongly depend on the cell temperature. For simplicity, they are using a quasi-one dimensional model to describe the battery behavior and performance characteristics. Araki et al., (2005) reported examine numerically and experimentally the thermal behavior of the Ni-MH cell during rapid charge and discharge cycles by a one dimensional model.
1.3 Problem statement

The energy delivered by the Ni-MH battery depends heavily on its charge/discharge profile and it is generally not possible to extract the whole energy that is stored in the battery. It is necessary for the process scheduler of a battery operated system to take the discharge profile and battery non-linearity into account, which is not consistent, in order to guarantee longer battery life.

Consequently, it is also needed to know the thermal behavior of the battery at higher heat generated due to high charging/discharging rate that will cause safety problems and affect the lifespan of the battery.

1.4 Objective

The objectives for this works can be divided to:

i. Construct a model of charge/discharge and thermal behaviors of Nickel Metal Hydride (Ni-MH) into differential mathematical equation.

ii. Solve the differential mathematical equations of the constructed model using explicit finite difference numerical method with the support of MATLAB R2011a software.

iii. Predict the cell potential results and temperature distribution inside the battery system.
1.5 Chapter Arrangement and Scope of Study (Limitation)

Chapter 1 and chapter 2 discuss the overview of the study and research of the modeling of thermal and charge/discharge cycle behaviors of Ni-MH. Constructed a model of a battery system started by construct a model based on theory like Fick’s law and Fourier’s law. The cell-specific parameters and mathematical equation were extracted from work in literature, with the experimental results to substitute inside the model.

Chapter 3 discusses about constructed a model and to estimate the battery performance of nickel metal hydride (Ni-MH) battery. This project was divided into two parts; first part is the charge/discharge model and the second part is thermal model. Both models were developed based on its own theory but are solved by the same method, which is explicit finite difference method, and then simulated by using MATLAB R2011a software and Minitab software.

In the chapter 4, the simulated results from this project were validated by the experimental results from the chosen published work. In the chapter 5, the conclusions and future works have been made for charge/discharge model and thermal behaviors.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A battery is an electrochemical cell that is a chemical reactor containing reactive and electrically conductive materials which react in a controlled manner to produce direct current electricity.

Ideal electrodes for energy storage in batteries would be made from elements that come from two separate columns of the periodic table that produce good reversible electrochemical reactions of oxidation and reduction. For example negative electrodes such as lithium (Li), or sodium (Na) and positive electrodes such as oxygen (O₂) and sulphur (S) respectively. Most battery technologies use an electrochemical couple consisting metal
electrode and a metal oxide electrode. Electrodes such as air are created by using a conductive structure with a catalyst for promoting the reaction (Kopera, 2004).

2.1.1 Primary Battery and Secondary Battery

Primary batteries, or primary cells, can produce current immediately on assembly. These are most commonly used in portable devices that have low current drain, are used only intermittently, or are used well away from an alternative power source, such as in alarm and communication circuits where other electric power is only intermittently available. Disposable primary cells cannot be reliably recharged, since the chemical reactions are not easily reversible and active materials may not return to their original forms. Battery manufacturers recommend against attempting recharging primary cells (Manufacturing, 2010).

A secondary cell or battery contains chemical substances that allow a reaction in reverse of discharge to occur when charging current is supplied to the cell. Therefore, after a discharge, the cell can be restored to nearly its original amount of energy by application of the charge current in a specified manner. This charge/discharge activity may occur for several cycles to many thousands of cycles depending on the specific battery technology. In a secondary cell also, when on charge the negative electrode becomes the cathode and the positive electrode becomes the anode. Because of the reversal of roles in a secondary cell, the electrodes will be referred to as either positive or negative (which never changes) and the direction of current flow (charge or discharge) will be specified (Kopera, 2004).
2.2 Nickel Metal Hydride Battery

The Nickel-Metal Hydride (Ni-MH) battery uses an alkaline solution as the electrolyte. The Ni-MH battery is composed of nickel hydroxide on the positive electrode, and the negative electrode consists of an engineered alloy of vanadium, titanium, nickel, and other metals. The energy density of the Ni-MH battery is twice that of the lead–acid battery. The components of Ni-MH are harmless to the environment; moreover, the batteries can be recycled. The Ni-MH battery is safe to operate at high voltage and has distinct advantages, such as storing volumetric energy and power, long cycle life, wide operation temperature ranges, and a resistance to over charge and discharge (Khaligh and Li, 2010).
The Ni-MH battery is termed an alkaline storage battery due to the use of potassium hydroxide (KOH) as the electrolyte. Electrically, Ni-MH batteries are very similar to nickel cadmium batteries. The active materials in Ni-MH battery are composed of metal compounds or metallic oxide. The nickel oxide which is hydroxide electrode only exchanges proton in the charge/discharge reaction and the electron transfer is very rapid contributing to high power capacity (Kopera, 2005). A Ni-MH battery is composed of positive electrode, negative electrode, separator and electrolyte and each component have their own function and specific parameters.

2.2.1 Positive Electrode

The positive electrode of the Ni-MH battery is a nickel substrate in the form of nickel foam, felt, perforated sheet or other constructions with the active material nickel hydroxide paste or sintered onto the substrate. This is a well developed electrode material with almost 100 years of history and development since it is the same composition as it is for Nickel-Cadmium (Ni-Cd) batteries. Nickel based alkaline batteries are attractive since the nickel electrode can be fabricated with very large surface areas which lead to high capacities and high current densities. The electrolyte does not enter into the electrode reaction so that conductivity stays at a high level throughout the usable capacity of the battery. In addition the nickel active material is insoluble in the KOH electrolyte which leads to longer life and better abuse tolerance. Only a proton is involved in the charge/discharge reaction leading to very small density changes and improved mechanical stability of the electrode during cycling. Also the gravimetric and volumetric energy densities are very good for the nickel
electrode. The electrode potential for the nickel electrode is about +0.44V that is relatively to Hg/HgO reference electrode. The simplified nickel electrode reaction in the cell is (Kopera, 2005):

\[
\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \beta - \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (2.1)
\]

→: Discharging, ←: Charging

The actual reaction is more complicated because of several factors:

i. The nickel electrode is nonstoichiometric.

ii. The reaction involves proton diffusion in the solid state.

iii. Additives to the electrode affect charge transfer and crystal structure of the electrode, for example NiOOH is a low conductivity p-type semiconductor when nickel valence is less than 2.25.

iv. Transformations of the NiOOH occur in the KOH solution.

2.2.2 Negative Electrode

The active material for the negative electrode in the Ni-MH battery is actually hydrogen, the same as it is in a nickel hydrogen battery, except that the hydrogen ions (protons) are stored in the metal hydride structure which also serves as the electrode. The metal hydride can, depending on its composition, hold between 1% and 7% hydrogen by weight. As a hydrogen storage material, the metal hydride is very efficient, achieving better
volumetric efficiency than liquid hydrogen. Today’s practical materials for Ni-MH batteries hold between 1% and 2% hydrogen by weight (Kopera, 2004).

Using a hydrogen-absorbing alloy can reduce the volume of the hydrogen supplier to about one-sixtieth of that of a high-pressure gas cylinder. Other advantages of the supplier using a hydrogen-system absorbing alloy are relatively low operating pressure and moderate hydrogen discharging rate, which can contribute to the safety of the system (Nakamura et al., 1995).

Intermetallic compounds are alloys of two or more metallic elements with narrow bands of integer stoichiometries. The compounds are divided into groups classified by $A_xB_y$ based on their composition and crystal structure. The A and B components can each consist of a number of different elements in varying ranges of stoichiometry. The variation of the components of the metal hydride allows the design of materials with the desired characteristics for use in battery applications such as low equilibrium pressure, resistance to corrosion, mechanical stability, reversibility, hydrogen storage ability and others (Kopera, 2004).

Many elemental metal hydride materials exist but were not practical for battery application due to the high equilibrium pressure exhibited by these materials at room temperature. This changed when intermetallic compounds were developed that combined strong and weak hydride forming materials. Tailoring the metal hydrides for the desired equilibrium pressure and other chemical properties is achieved by adjusting the ratio between these two types of material components (Kopera, 2005).
The reactions for the negative electrode can be written as follow:

\[ M + H_2O + e^- \leftrightarrow MH + OH^- \]  \hspace{2cm} (2.2)

\[ \rightarrow: \text{Discharging,} \hspace{0.5cm} \leftarrow: \text{Charging} \]

Where, M represent the Metal Hydride material.

\textbf{Figure 2.2:} A completed schematic representation of Ni-MH cell (Kopa, 2005)
2.2.3 Electrolyte

The electrolyte, which is an aqueous solution of potassium hydroxide, has a very high conductivity and usually does not enter into the cell reaction to any significant extent. The electrolyte concentration (and therefore a major component of cell resistance) remains fairly constant over the entire range of state of charge or discharge. These factors lead to a battery with high power performance and long cycle life (Kopera, 2004).

In Ni-MH battery, the electrolyte is 30 weight percent KOH in water. The electrolyte serves as the path for completing the electrical circuit inside of the cell via the transport of ions from one electrode to the other.

2.2.4 Separator

Nonwoven separators used in rechargeable alkaline batteries commonly consist of either polyamide, polyolefine, or a mixture of both. Since a permanently hydrophilic surface is a key item for separator materials (the separator must not “dry out” during cycling), from this point of view, polyamide with its polar groups should be the favoured material choice. Consequently, polyamide separators are mostly used in nickel–cadmium (NiCd) cells. Polyolefine-based materials have to be post-treated to obtain a hydrophilic surface. Additionally, homogeneity of the material has to be as good as possible to avoid electrical shorts inside the battery, especially after high numbers of storage/discharge cycles (Kritzer, 2004).
The separator of Ni-MH battery is usually made of felt or a porous nylon material. A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes. A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and micro porous flat sheet membranes made from polymeric materials (Arora and Zhang, 2004).

2.2.5 Why is Nickel-Metal Hydride Chosen?

There are many types of battery nowadays. Batteries can be divided into primary and secondary batteries. Primary batteries are batteries that can be used only once and cannot be recharged while secondary batteries can be recharged and reused again.

Ni-MH is one of the secondary battery types. Therefore, it can be recharged and be reused. Generally, research of Ni-MH system started in the seventies as a means for hydrogen storage for a Nickel Hydrogen battery. In other words, the Ni/H₂ cell was an adaptation of the Ni-Cd which used the NiO₂H electrode coupled to a H₂ fuel cell electrode in a pressurized and sealed battery. Compared to Ni-Cd battery, a Ni-MH battery has higher density energy at the expense of reduced cycle life. Besides, the Ni-MH battery has a longer cycle life and does not suffer from the memory effect which Ni-Cd do. Most importantly, the Ni-MH battery contains no toxic and poisonous heavy metals. In addition,
the recognized environmental problem associated with the Ni-Cd batteries has shifted the market in favor of Ni-MH (Mantell, 1983).

Today, the Ni-MH cells are becoming common for most portable equipment such as camcorders, cellular phones, laptop computers and other domestic appliances. Fortunately, with the developments of new Ni-MH battery system, improvements in electronics have now been matched by significant improvements in the batteries that power them. Ni-MH battery cells provide more power (in equivalently size packages) than the Ni-Cd cells while also eliminating some of the concerns over use of heavy metals in the cells. In today’s world of technology, the Ni-MH battery holds promises for application in electric and hybrid-electric vehicle. Due to its advantages and performances, the Ni-MH batteries are being marketed by several companies worldwide. More and extensive efforts are being made and continued to develop advanced Ni-MH batteries to meet the stringent requirements of electric vehicle batteries (Kleperis et al., 2001).
2.2.6 Advantages of Nickel-Metal Hydride battery

The Ni-MH batteries retain many of the advantages of the Ni-Cd batteries. Some of the advantages are (Picciano, 2007):

i. *Environmental Friendly*

The rechargeable Ni-MH battery is free of toxic or hazardous elements such as cadmium, lead, and mercury. Thus, it serves as a portable energy sources which do not harm the environment.

ii. *High Reliability*

The line of Ni-MH battery is manufactured with the raw materials of high quality control, which enable the batteries to perform with outstanding reliability.

iii. *Long Cycle Life*

The Ni-MH battery has an excellent cycle life. It has more than 500 charge and discharge cycles under normal use.

iv. *High Energy Density*

The demand for a highly diversified, smaller and lighter products have put much pressure on battery manufactures to increase the energy density, which is important parameter that determines the size and weight of a battery unit. This eventually results through the capacity performance of the Ni-MH battery which is 50% over a Ni-Cd battery of smaller size.
v. *Excellent Discharge Characteristic*

The discharge voltage is similar to that of Ni-Cd batteries. High rate discharge is also achievable.

vi. *No Memory/Voltage Depression*

In some applications where Ni-Cd cells are routinely partially discharged, a depression in the discharge voltage profile has been reported when the discharge extends from the routinely discharge to rarely discharged zones. While the severity of this problem in Ni-Cd cells is open to differing interpretations, the source of the effect is generally agreed to be in the structure of the nickel electrode. With the elimination of cadmium in the Ni-MH cell, memory is no longer a concern.

There has been an increasing interest in the potential use of Ni-MH battery power sources for many applications due to their advantageous characteristics, which include high energy density, high rate capability, tolerance to overcharge and over discharge, the lack of any poisonous heavy metals, and no electrolyte consumption during the charge/discharge cycle (Jahantigh and Afshari, 2008).

The use of metal hydrides as active negative electrode materials in rechargeable alkaline batteries has been studied for some considerable time. Although Ni-MH batteries have superior specific energy than other two aqueous electrolyte systems (lead-acid and Ni-Cd batteries), they remain largely inferior to the new rechargeable lithium batteries. However, lithium batteries are much more expensive to produce. It has been estimated that
the approximate cost (per watt hour) for Ni-Cd, Ni-MH, and lithium batteries are in the 2
ratios of 1: 1.35: 2-3, respectively. In addition, lithium batteries cannot be operated for
safety reasons without electronic control of each individual cell, because the lithium
batteries are very sensitive to overcharge and overdischarge. The overcharge and
overdischarge performance of a Ni-MH battery are better than that of other batteries (Geng
et al., 1999).

In addition, an exciting new battery market is emerging due to the demand for electric
vehicles. Because cars propelled by internal combustion engines are the primary source of
local air pollution in city centers, widespread use of emission-free electric vehicles can
significantly improve the quality of urban air. Only a few kinds of batteries can meet the
specific demand for electric vehicle applications. The nickel metal hydride battery has been
considered to be one of the most promising candidate batteries for electric vehicle by virtue
of its high energy density, high rate capability, long cycle life, and low environmental
impact (Wu et al., 1998).

2.3 The Battery Model (Charge/Discharge)

The Ni-MH battery system consists of a metal hydride negative electrode and a nickel
oxide positive electrode. The separator is usually made of felt or a porous nylon material,
and the electrolyte is 30 weight percent (w/o) KOH in water. Both of the electrodes are
porous electrodes, as shown in the Figure 2.3 below.
2.3.1 System Definition

The earlier idealized Ni-MH cell model which has been designed by Gu et al., (1998), has provided the following system definitions for charge/discharge model:

i. The nickel electrode consists of composite cylindrical needles with a substrate inside and its porosity remains constant.
ii. The MH electrode consists of spherical particles with uniform size and constant porosity.

iii. The solid phase is completely wetted by the electrolyte. In other words, there is no contact between solid active material and the gas phase.

iv. Convection effects in the electrolyte and gas are neglected, leaving the species transport to diffusion and/or migration.

v. Interfacial chemical equilibrium exists in the liquid phase for all species other than the dissolved oxygen, which has a relatively small value of mass diffusivity in the liquid electrolyte. Electrical equilibrium exists in the liquid phase due to the large value of ionic conductivity of the electrolyte.

vi. Thermal effects are ignored.

2.3.2 Porous Electrode Theory

In this theory, "the electrode is treated as the superposition of two continuing, one representing the solution and the other representing the matrix (solid phase)." These two phases are in intimate contact at an interface which has a specific surface area, a. A detailed characterization of the electrode's internal geometry is unnecessary, as the control volume is larger than the microstructure of the electrode but small in relation to its overall dimensions (Paxton and Newman, 1997).
There are some advantages and disadvantages of using porous electrode theory as following:

Advantages of porous electrodes theory:

i. In systems where the reaction kinetics is slow increasing the area allows for larger currents with less voltage drops. Some Li-ion batteries fall into this category.

ii. The large surface area means that a large area for double layer formation. Electrochemical capacitors take advantage of this concept.

iii. Reactants like sulfuric acid in a lead-acid cell can be stored very close to the reaction site allowing for high rates by decreasing transport losses.

Disadvantages of porous electrode theory:

i. Electrons and ions have to travel long distances (0.5 cm in the above case). If the conductivity of the electrolyte is low, this can lead to large ohmic potential drops in the solution phase. This is the reason why Li-ion batteries have a thickness of 50-100 μm as opposed to a lead acid cell that can be ~2-3 mms thick.

ii. In systems where the particles are not very conductive, electronic resistance can be large in the electrode. This is the reason why typical Li-ion batteries have conductive additives, like carbon.

iii. In systems where transport of ions is limiting, sustained discharge can lead to large concentration polarization due to the larger distances over which transport occurs.
There are several parameters that characterize porous electrodes:

i. Thickness of the electrode.

ii. Porosity of the electrodes (volume of voids/total volume of the electrode).

iii. Total surface area of the electrode. Represented as total surface area per unit volume. In this model, nickel hydride electrode is assumed to be consisting of composite cylindrical needles and the surface area per unit volume is:

\[
\frac{\alpha_{\text{Ni}}}{V_{\text{Ni}}} = \frac{\alpha_0}{\sqrt{1 - \varepsilon_{\text{Ni}}}} \frac{1 - \varepsilon_{\text{Ni}}}{1 - \varepsilon_{\text{b}}}
\]

(2.3)

where \(\varepsilon_{\text{Ni}}\) is the porosity of nickel electrode, \(\varepsilon_{\text{b}}\) is the porosity of nickel substrate, \(\alpha_0\) is area of nickel substrate, \(\alpha_{\text{Ni}}\) is surface area of nickel electrode, \(V_{\text{Ni}}\) is volume of the nickel electrode and can be written as (De Vidts et al., 1995):

\[
\alpha_0 = \frac{2(1 - \varepsilon_{\text{b}})}{r_{\text{Ni}}}
\]

(2.4)

where \(r_{\text{Ni}}\) is the radius of the nickel electrode.

The MH particles are assumed to consist of the metal hydride material only, without any deposited metal layer on their surface. The active surface area was estimated assuming that the spherical alloy particles are all of the same size and their entire surface is exposed to the electrolyte, leading to the following expression:
\[
\frac{\alpha_{\text{MH}}}{V_{\text{MH}}} = \frac{3 \varepsilon_{\text{MH}}}{r_{\text{MH}}}
\]  

(2.5)

where \( \alpha_{\text{MH}} \) is the surface area of nickel electrode, \( V_{\text{MH}} \) is the volume of metal hydride electrode, \( \varepsilon_{\text{MH}} \) is the porosity of the metal hydride electrode, and \( r_{\text{MH}} \) is the radius of the metal hydride electrode.

2.3.3 Concentrated Solution Theory

Transport in the solution phase is modeled using concentrated solution theory. Since it assumed that all the electrode materials are sparingly soluble in the alkaline solution, there are only three mobile species, K+, OH-, and H2O (Paxton and Newman, 1997).

The ion left after a certain period is depended on the total rate of ion transport from positive electrode to negative electrode during discharge and vice versa. Total rate of transport is depending on:

i. total number of ion

ii. rate of ion transport

The driving force to transport the ion through the electrolyte is depended on voltage gradient and concentration gradient. The concentration gradient causes a physical process called diffusion, which is the motion of all species in the presence of a concentration gradient. A potential gradient causes a physical process called migration, which is the motion of charged species in the presence of an electric field.