

**Development and characterization of nanostructured Ni(OH)₂ electrodes for energy
storage applications**

by

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Abstract

Nanostructured $\text{Ni}(\text{OH})_2$ electrodes grown on metalized, electro-spun nanofibers have been developed and characterized. On an active mass basis these electrodes, measured using an Ag/AgCl reference electrode, showed excellent specific capacitance of 2,123 F/g and specific capacity of 283 mA•h/g compared to the theoretical limits of 2190 F/g and 289 mA•h/g respectively. These electrodes were also able to achieve a maximum specific energy of 90 W•h/kg at a specific power of 727 W/kg and maintain a specific energy of 32 W•h/kg at a power density of 10 kW/kg. When optimized, the nanostructured electrodes had an internal surface area 5 orders of magnitude greater than an equivalent flat plate electrode and achieved a surface area to volume ratio of $2.5 \times 10^5 \text{ cm}^{-1}$. Electrical equivalent circuit models were developed to understand device performance and showed a reasonable accuracy when compared with experimental data. Ultimately, device power density was limited by a combination of ohmic resistance and kinetic polarization. Significant mass transport polarization was suppressed due to a combination of low $\text{Ni}(\text{OH})_2$ nanostructure thickness and high electrode porosity. This device architecture features an integrated current collector and the fabrication process does not require any high temperature or electrochemical processing, opening avenues for both cost reduction and manufacturing simplification. Possible applications of this technology are in advanced nickel metal hydride batteries or $\text{Ni}(\text{OH})_2$ asymmetric storage devices.

Lay Summary

The demand for cost effective energy storage technologies is expected to rise over the next several decades, driven primarily by the rapid commercialization of electric cars and increasing consumer demand for mobile electronic devices. The work published here is focused on developing an improved battery electrode which stores more energy in a given volume (energy density) and charges and discharges more quickly than a conventional electrode. To achieve these improvements, the electrode structure and geometry were fabricated on the nanoscale (1 billionth of a meter) which allows the designer to tune various electrode parameters and improve performance. The main contributions of this work were a methodology to characterize the performance of complex, nanostructured electrodes and an electrode design that achieves both high energy and power densities.

Preface

The motivation for this project was a desire to determine the suitability of metal coated nanowire technology developed by UBC's Advanced Fibrous Materials Group for energy storage applications. The original identification of the research opportunity was undertaken by Dr. John Madden, Dr. Hee Jae Yang and Dr. Frank Ko. The design of the research program was completed jointly by Dr. Jungsu Choi and Matt Dawson (the author). All fabrication and the majority of the materials characterization (SEM and XRD) of the metalized nanowires and nanostructured electrodes evaluated in the thesis was done by Jungsu Choi with some additional SEM analysis provided by Garriott Yip. Important guidance on experimental set-up was provided by Yuta Dobashi and Ali Mahmoudzadeh. All electrical and electrochemical testing, characterization, modeling, data analysis, and thesis writing was performed by the author. No published work has resulted from this research.

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Dedication

To my parents, Marnie and Jim, for their endless love and support.

Chapter 1: Introduction

This chapter will discuss the motivation for this project, outline the objectives of the research and provide some background on the material systems that were developed and characterized in this work. In addition, a brief review of relevant literature will be presented along with a technical introduction to several types of energy storage technologies which may provide useful applications for the nanostructured electrode presented in this thesis.

1.1 Motivation

The demand for cost effective energy storage technologies is expected to rise over the next several decades. This is due to several factors including the rapid commercialization of electric cars, the increasing percentage of renewable energy sources on electricity grids and increasing consumer demand for mobile electronic devices with an ever expanding array of functionalities [8][11]. All these technologies require some balance of energy density, or the amount of energy that can be stored in a given volume of material, and power density, a measure of how quickly energy stored in a volume can be extracted for practical use. Energy density is quoted in units of watt hours per liter ($\text{W}\cdot\text{h/L}$). When a comparison based on the mass is required, the specific energy of a storage system is typically quoted in watt hours per kilogram ($\text{W}\cdot\text{h/kg}$). Similarly, power densities for storage technologies are often quoted in watts per liter (W/L), or when considering the power per unit mass, the specific power is given in watts per kilogram (W/kg). Comparing different energy storage technologies in terms of their energy to power ratio is often done with a Ragone plot where the energy density or specific energy of a device is graphed against its power density or specific power. Figure 1.1 is an example of such a Ragone plot and clearly illustrates how devices such as fuel cells and batteries tend to have higher specific

energies and lower specific powers while supercapacitor devices tend to have lower specific energies but higher specific powers.

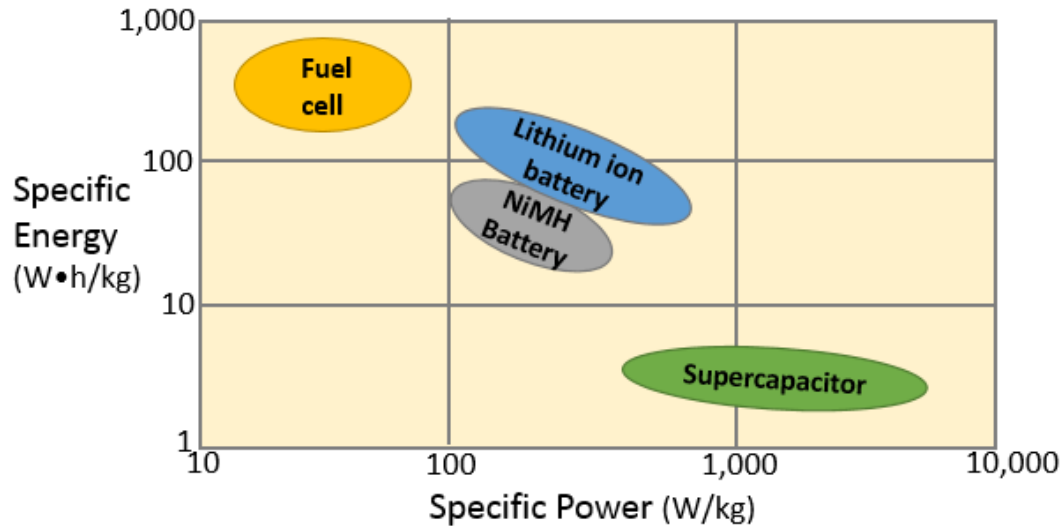


Figure 1.1: Ragone plot showing the specific energy and power of various energy storage devices. Adapted from [5].

At present, lithium ion batteries have emerged as one of the most widely adopted storage technologies due to their fundamental performance advantages of low weight, high operating voltage and low internal resistance. This results in both relatively high specific energy of ~ 300 W•h/kg and medium power densities of ~ 1500 W/L [11][8]. While the mass market adoption of lithium ion technology is expected to continue, primarily because of its suitability for EV applications, significant research into other types of energy storage technologies continues with the primary goals of improving overall performance and enriching the fundamental understanding of device operation. Nanostructured $\text{Ni}(\text{OH})_2$ electrodes, the devices explored in this work, have the potential to improve the performance and lower the cost of nickel metal hydride (NiMH) batteries and other storage devices that employ $\text{Ni}(\text{OH})_2$ as an active material. In addition, any insight gained here into tuning the nanostructure of an active material to improve

energy or power density may be applicable to other electrochemical storage technologies, including lithium ion.

1.2 Project Background: Metalized Nanowires

The core technology for the electrodes used in this research project was developed by Dr. Jungsu Choi, a post-doctoral researcher in UBC's Advanced Fibrous Material Laboratory. The AFM lab has long been active in electrospun polymer nanofiber research. However, in 2015 Dr. Choi developed a process to coat polymer nanowires with thin layers of various metals. To date, Dr. Choi has successfully demonstrated the deposition of platinum, palladium, manganese, cobalt and nickel on polymer nanofibers. SEM images of some of these metalized nanofibers are shown in Figure 1.2.

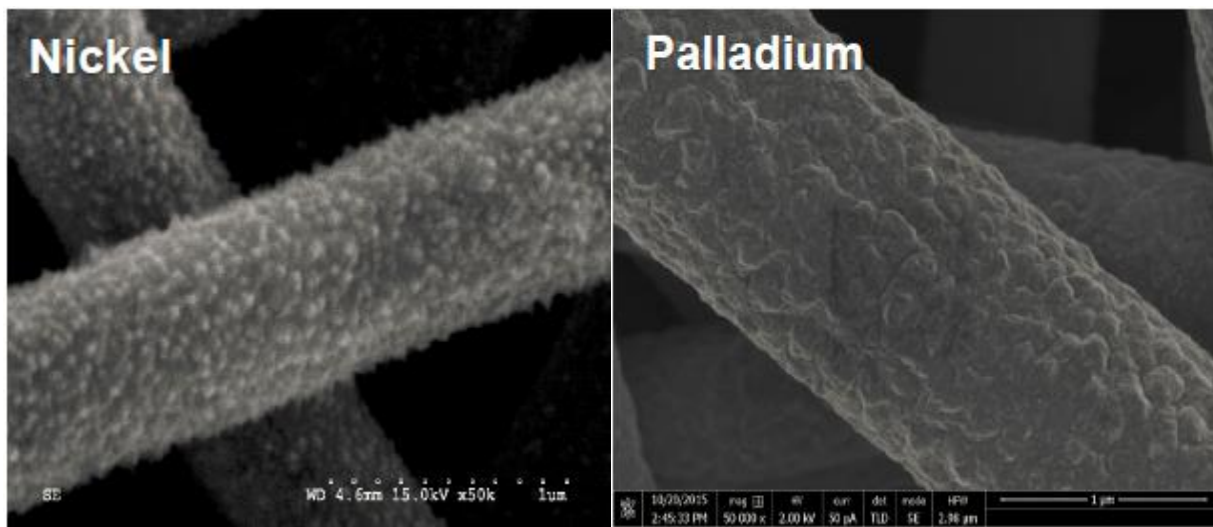


Figure 1.2: SEM images of nickel (left) and palladium (right) metalized nanofibers.

Typically, the “core” polymer nanowires are formed from polyacrylonitrile (PAN) which is doped with small amounts of a palladium salt enabling successful metal deposition and adhesion to the electrospun PAN core wires. The PAN core wires range between 400-800 nm in diameter while the deposited metal coatings are nominally 50-150 nm thick. Both the core wire and metal

coating thickness can be tuned by adjusting various process parameters. In this way, the process can create a flexible, highly porous (~60-70% free space) and electrically conductive structure that can be used for a variety of applications ranging from water filtration to advanced textiles. In terms of energy storage, this structure has the capacity to deposit or grow additional “active” materials, or materials capable of electrostatic or electrochemical energy storage, directly onto this porous, conductive scaffold. Such a structure was investigated here as it could enable the creation of a high-performance battery or supercapacitor electrode by leveraging the intimate contact between the active material and metal layer to reduce electronic resistance. In addition, this type of electrode configuration may offer cost and manufacturing advantages over conventional approaches. Most existing electrode designs are manufactured by combining active material, conductive additives and a binder with a solvent to form a slurry which is then deposited on a metal film acting as both a current collector and structural support for the electrode [7][8]. The electrospun, metalized nanowire electrodes investigated here offer the opportunity to eliminate the requirement for a current collector. This could reduce device weight and volume and thereby improve both energy and power density.

1.2.1 Electrospinning

As mentioned above, electrospinning is an enabling technology for the material system investigated in this research. First employed in the 1930’s, this technique is the most common approach for fabricating assemblies of nanofibers due to its relative low complexity and therefore low cost of equipment and processing [12]. In addition, process parameters can be adjusted to produce nanofibers with typical diameters ranging from 500-5000 nm having specific surface areas of up to $10^3 \text{ m}^2/\text{g}$ [12]. An SEM image of a typical nanofiber mesh along with a standard electrospinning equipment set up is shown in Figure 1.3.

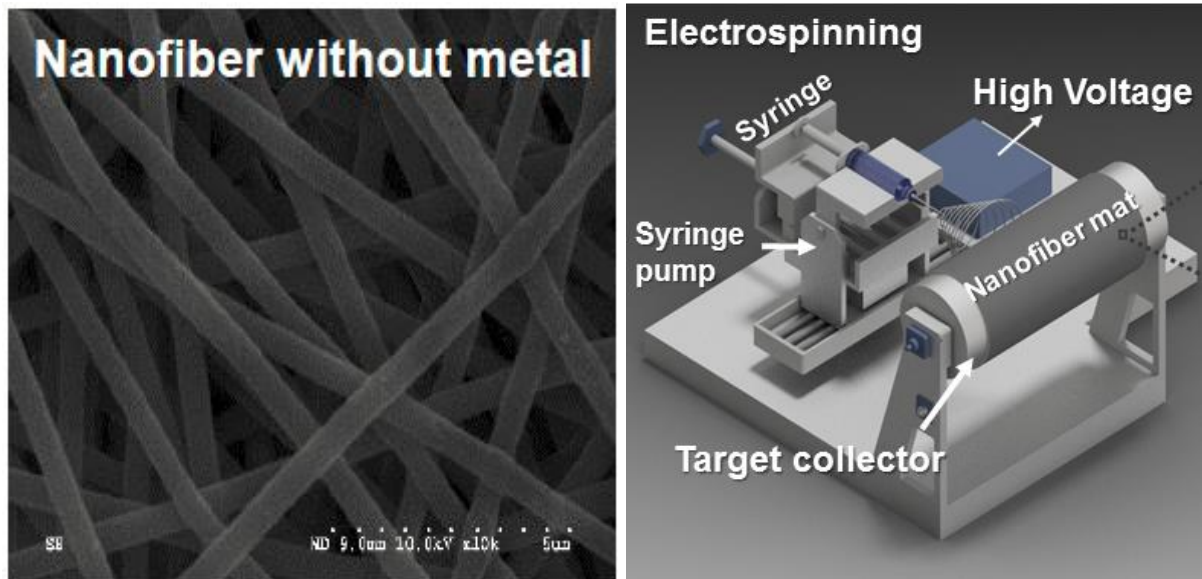


Figure 1.3: Polymer nanofibers mesh (left) and schematic of a typical electrospinning set up. (right) Courtesy Dr. J. Choi.

During operation, a syringe filled with a polymer dissolved in a solvent is mounted at one end of the electrospinning chamber and a nanofiber deposition target is mounted at the other end, approximately 50 cm from the syringe. A potential difference on the order of 10 kV is applied between the syringe tip and the deposition target and fluid is drawn out of the syringe as the electrostatic force on the polymer overcomes its surface tension [12]. As the material moves from the syringe to the target, the solvent evaporates and dries, contiguous nanofibers are deposited in either random or aligned orientations depending on the equipment set up. Multiple process parameters are significant in controlling fiber diameter and overall spin-ability of a given polymer. Electric field strength, polymer viscosity and syringe to target distance are considered to be some of the most important of these [12]. While there are significant benefits to the electrospinning process, there are limitations including a relatively low material deposition rate, a practical lower limit on fiber diameter of approximately 100 nm and the requirement to use toxic solvents [12].

1.3 Device overview

As indicated in the sections above, the device investigated in this research is an electrospun, nano-structured electrode. Nickel coated PAN nanofibers form a conductive scaffold upon which an active material layer of $\text{Ni}(\text{OH})_2$ nanoflakes is grown. When in operation, this electrode will store energy primarily through the electrochemical conversion of the $\text{Ni}(\text{OH})_2$ active material. This will be discussed in more detail in section 1.3.1. The fabrication process for this structure involves four main steps which are outlined in Figure 1.4.

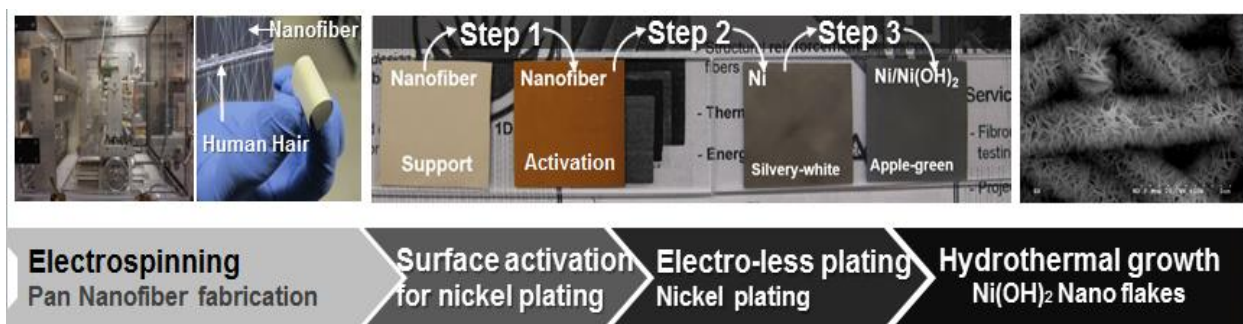


Figure 1.4: Process flow for nanostructured $\text{Ni}(\text{OH})_2$ electrodes. Four sequential process steps of electrospinning, thermal surface activation, electroless nickel plating and hydrothermal $\text{Ni}(\text{OH})_2$ growth are required for electrode fabrication.

First, palladium doped PAN nanofibers with a nominal diameter of 600 nm are electrospun to form a fiber mesh approximately 50 μm thick. After spinning, the fiber mesh is subjected to a low temperature heat treatment at 200°C for 2 hours to activate the fiber surface for the subsequent process steps. Next, an electroless plating step is performed to deposit approximately 100 nm of nickel onto the nanofibers, yielding metalized nanowires with a nominal diameter of 700 nm. In the final step, $\text{Ni}(\text{OH})_2$ nanoflakes are grown directly on the nickel metal layer using a hydrothermal process. Individual $\text{Ni}(\text{OH})_2$ flakes can be grown on the order of 10 nm thick and 1000 nm long depending on process conditions. SEM images of the resulting nanostructured electrode and a schematic cross section of an individual, textured micro-wire are shown in Figure 1.5.

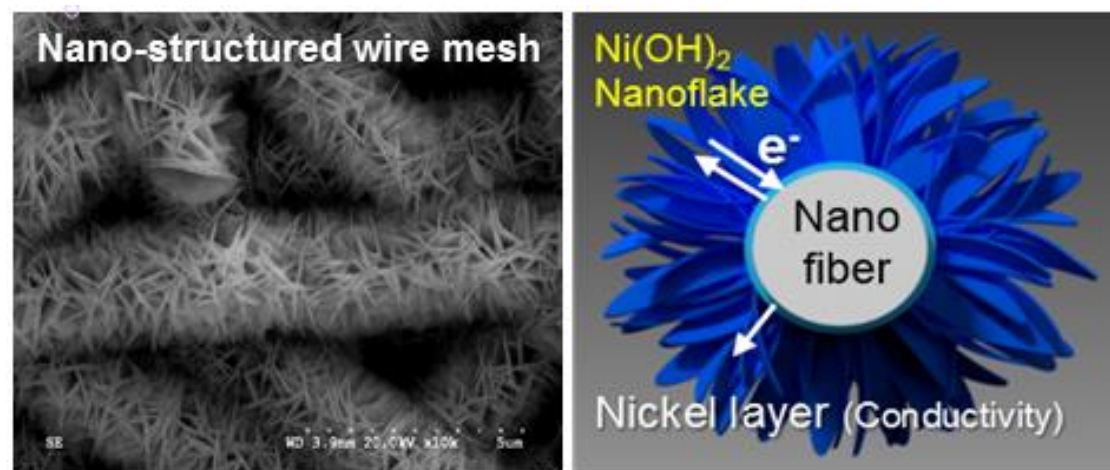


Figure 1.5: SEM image (left) and schematic cross section (right) of nanostructured fiber mesh electrode.

Courtesy Dr. J. Choi.

As can be seen from the above SEM image on the left, the resulting assembly is a nanostructured wire mesh where individual wires on the order of $2\ \mu\text{m}$ in diameter are interwoven with each other. While these microwires touch each other at multiple points, significant free space or porosity on the order of microns exists around the wires in all directions. This micro level porosity is expected to allow an electrolyte solution to completely flood the internal volume of the electrode while helping to minimize resistance to ion transport inside the mesh. In terms of an individual microwire, the cross-section view in Figure 1.5 depicts the roughly homogeneous arrangement of nanoflakes around each metalized fiber. While the magnitude and geometry of the spacing between nanoflakes is variable and process dependent, it is roughly on the order of 10 nanometers in an optimized electrode. This creates a dense structure of $\text{Ni}(\text{OH})_2$ flakes on the surface of each micro-wire. It is expected that this $\text{Ni}(\text{OH})_2$ nanostructure, in conjunction with the mesh electrode micro structure, will maximize the internal surface area of the electrode and in turn maximize the amount of active material in direct contact with the electrolyte solution. Given that the storage mechanism at work in this device is the electrochemical conversion of the

Ni(OH)₂ nanoflakes, it is expected that this large surface contact area between active material and electrolyte should minimize both the kinetic resistance associated with the chemical reaction and any mass transport resistance associated with the diffusion of reacting species either to the surface of the electrode or inside the bulk of the nanoflakes [9][13].

1.3.1 Nickel Hydroxide

Nickel hydroxide Ni(OH)₂ is an electroactive compound that is widely used as the cathode in nickel cadmium (NiCd) and nickel metal hydride (NiMH) batteries as well as in asymmetric storage devices [7]. Asymmetric devices, also known as hybrid storage devices, combine elements of batteries and supercapacitors into a single device with the goal of improving both energy and power density. This will be discussed in more detail in section 1.5.3. Ni(OH)₂ stores energy by forming a redox couple with nickel oxy-hydroxide according to equation # 1,



and has a maximum specific capacity of 289 mA*h/g [8][14]. It is generally accepted that this chemical reaction is the product of two individual steps which are represented in equations 2 and 3 [6][7]. During discharge, Ni⁺³ is reduced to Ni⁺² and NiOOH is converted to Ni(OH)₂, a process that is shown schematically in Figure 1.6 [4] and involves the reactions:



The second reaction requires that an electron be supplied by the external circuit and a proton (H⁺) be supplied from the electrolyte solution.

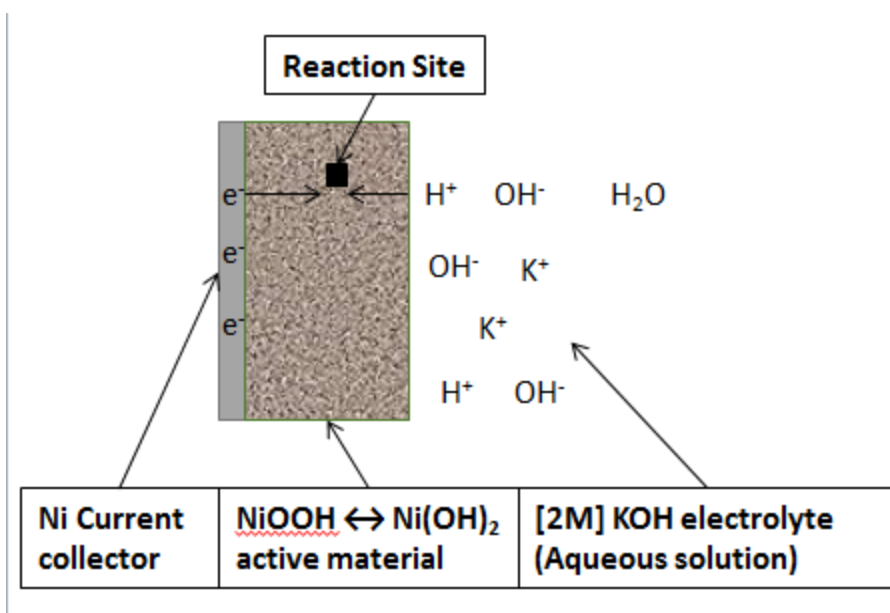


Figure 1.6: Conversion of NiOOH to Ni(OH)₂ during electrode charging requires electrons from the external circuit and protons from the electrolyte to diffuse inside the electrode material to reaction sites. Adapted from [6].

While the chemical species required for the reaction to proceed are readily available at the solid electrolyte interface, in order for the reaction to occur in the bulk of the electrode, protons must diffuse to the reaction site inside the Ni(OH)₂ / NiOOH solid solution [4]. Given the relatively low diffusion coefficient for protons in Ni(OH)₂ and thicknesses on the order of 10's of microns for conventional flat plate electrode designs, the rate of proton diffusion has been suggested as one of the limitations for fast discharge and thus power density of traditional Ni(OH)₂ electrodes [6][13]. The Ni(OH)₂ / Ni(OOH) redox couple has a standard reduction potential of 490 mV with respect to a normal hydrogen electrode (NHE). This translates to a reduction potential of approximately 293 mV with respect to a saturated Ag/AgCl reference electrode [8]. While this storage mechanism is clearly electrochemical, many research groups developing Ni(OH)₂ electrodes for asymmetric storage devices refer to their designs as pseudo capacitors and therefore quote their performance in terms of F/g or F/cm² [15]. To the best of our knowledge,

there is no objective standard for converting nickel hydroxide specific capacity into specific capacitance. However, there is a reasonable way to determine an approximate value and this will be discussed in section 3.1. There are two polymorphs of Ni(OH)_2 , α and β , where alpha has a higher capacity than β [8]. In typical battery applications, Ni(OH)_2 is deposited on high surface area nickel mesh or sintered nickel current collectors and used in conjunction with a 6M KOH electrolyte [8]. While Ni(OH)_2 has several advantages as an electrode active material, one significant drawback is its low electrical conductivity, ranging from 10^{-4} to 10^{-7} S/m depending on its oxidation state [16]. As a result, modern battery electrodes typically combine Ni(OH)_2 with certain amounts of cobalt and or zinc to improve electrical conductivity and therefore power density [8]. Similarly, Ni(OH)_2 electrodes developed for asymmetric storage device applications often include electrically conductive additives such as graphene to reduce electrical resistance [17]. Several important physical characteristics are listed in Table 1.1.

Visual Appearance	Green crystals – Ni(OH)_2 (Black Solid – NiOOH)
Molar Mass	92.724 g/mol
Density	4.10 g/cm ³

Table 1.1: Selected physical properties of Ni(OH)_2 [1].

1.4 Thesis Objectives and Structure

This research project had three objectives:

- To determine if electrospun, metalized nanowires have potential applications in energy storage devices. Specifically, can this structure be integrated with an electrochemically active material and operate reliably as a component of an energy storage device?

- To characterize the performance of nanostructured Ni(OH)_2 electrodes grown on metalized nanowires and compare their performance to conventional Ni(OH)_2 electrodes and to similar electrospun technologies being developed by other research groups.
- To determine if the morphology of the nanostructured Ni(OH)_2 electrodes investigated here can be controlled and optimized during the fabrication process to improve device performance and specifically be designed to maximize energy and power density.

While trying to meet these objectives, my collaborator, Dr. Choi and I went through several cycles of learning on both the electrode fabrication process and the device characterization methodology. Chapter 1 introduces the motivation for the work along with brief overviews of the device concept, electrospinning technology and electrochemistry theory relevant to Ni(OH)_2 storage technology. Chapter 2 describes the fabrication process of the nanostructured electrodes and summaries the work done to characterize the material composition and nanoflake morphology. Chapter 3 presents the electrochemical measurements and analyses done to characterize electrode performance as well as additional modeling work aimed at understanding both the overall limitation of device performance and the impact of the Ni(OH)_2 nanostructure morphology. Finally, Chapter 4 summarizes the key learnings and contributions derived from this research and outlines some potential directions for future work.

1.5 Technical Background

The following four subsections will provide a basic introduction to several energy storage technologies and devices (supercapacitors, batteries and asymmetric storage devices) that could be useful applications for the electrospun, nanostructured electrodes investigated in this work.

The intent is not to provide a deep technical understanding of these devices, but rather to

introduce the physical concepts behind their operation, key equations used to describe their performance, and important figures of merit used to gauge energy and power density.

1.5.1 Super Capacitors

Supercapacitors, also known as ultra-capacitors, are energy storage devices characterized by a lower energy density when compared to batteries, but which possess significantly higher power density and operational life. These advantages are a consequence of the device storing energy electrostatically such that no chemical transformation of the active material is required during device charging and discharging [7]. Like traditional capacitors, supercapacitors store energy in an electric field sustained between two oppositely charged regions separated by a dielectric. However, instead of using an electric field established between two conductive plates, supercapacitors store energy in the so called electric double layer, or the electric field at the interface between an electrode and electrolyte solution [9]. A simplified model of an electrical double layer is shown in Figure 1.7 where a space charge region is established between a negative electric charge in the electrode and a net positive ionic charge in solution. While the electric charge is confined to the surface of the electrode, the ionic charge is distributed in a diffuse region known as a Helmholtz layer [9]. The effective thickness of the Helmholtz layer has some dependence on solution concentration and mean ion size but is typically assumed to extend approximately 10 nm out from the electrode surface [9].

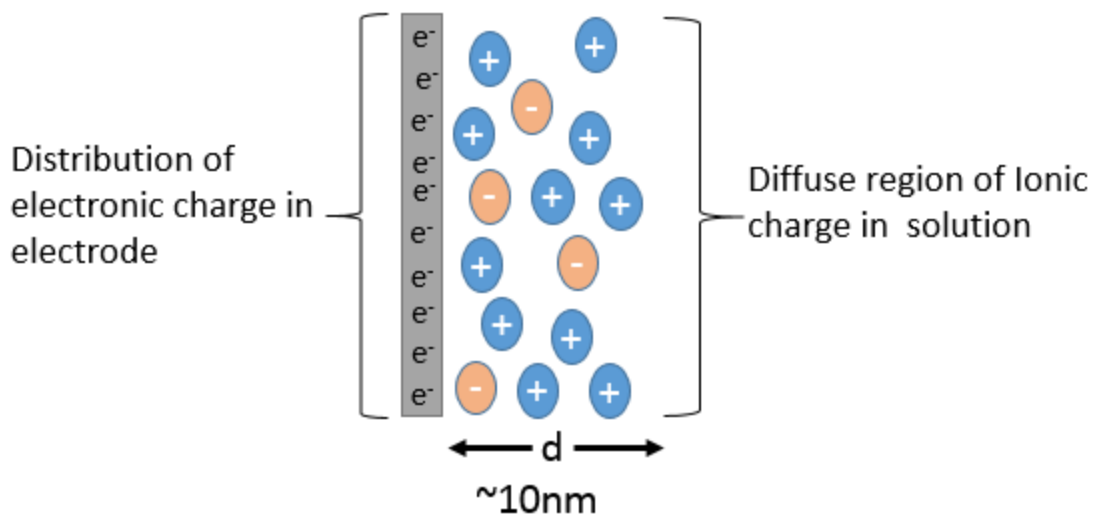


Figure 1.7: Simplified conceptual model of an electrode solution interface. A net positive region of positive ions in solution is attracted to a net negative charge in an electrode. While the electronic charge is tightly bound near the electrode surface, the ionic charge is contained in a diffuse region extending out approximately 10 nm from the surface of the electrode. Adapted from [9].

For typical electrode / electrolyte systems the double layer capacitance ranges between 10-40 $\mu\text{F}/\text{cm}^2$ [9] and thus determining the double layer capacitance of an electrode can provide a reasonable estimate its surface area. It should be noted that the polarity of a double layer can be switched by establishing a net positive charge on the electrode. This will establish a Helmholtz layer of negative ionic charge. In a typical supercapacitor device, two identical electrodes, each with its own double layer capacitor are connected electrically in series and insulated from each other by an ionic separator, as illustrated in Figure 1.8. During cycling, the electric charge on each electrode switches from positive to negative and in turn positive and negative ions shuttle back and forth between electrodes, charging and discharging both double layers.

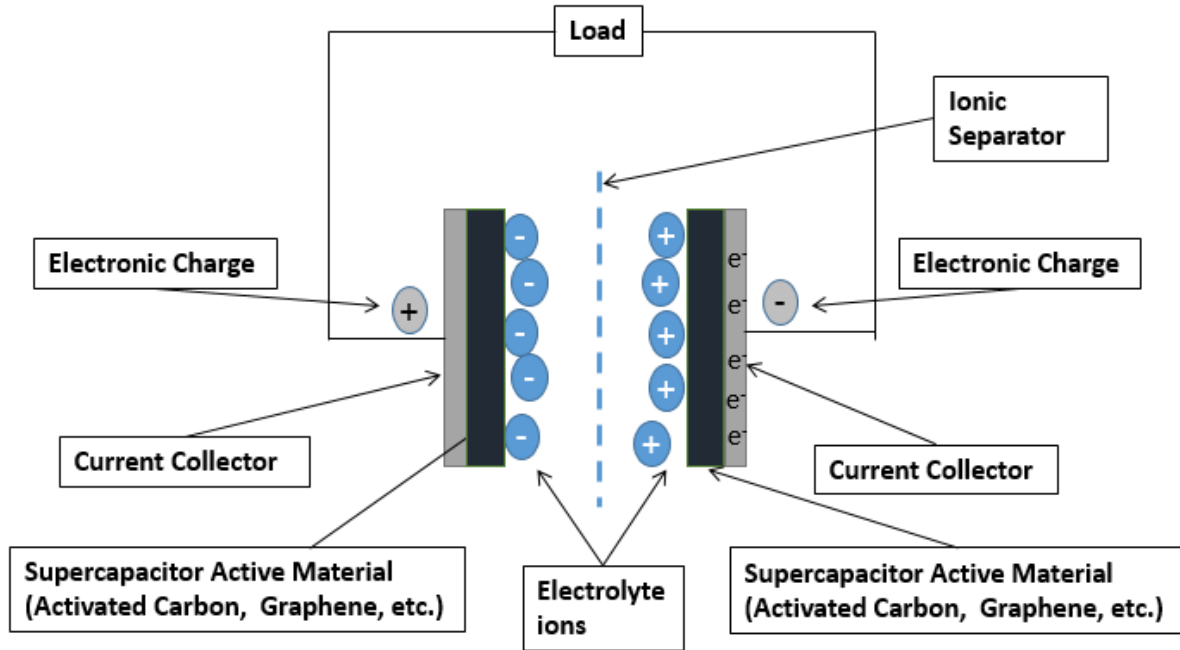


Figure 1.8: Layout of a symmetrical supercapacitor. The device has two identical electrodes connected in series and separated by an ionic separator. Energy is stored in double layers which form at each electrode in response to accumulations of positive or negative electronic charge. Adapted from [7].

While this traditional supercapacitor configuration, known as a symmetric design, has several advantages such as facile manufacturing and long service life, it does have one drawback in terms of specific energy. Since the two double layer capacitors have the same active mass and are connected in series, the net specific capacitance and thus the specific energy for the device is approximately 25% of that for a single electrode [7]. One of the methods of overcoming this design limitation is to develop asymmetric devices. This will be discussed in section 1.5.3. Despite storing energy in an electrical double layer, supercapacitors have the same governing equations as traditional capacitors and the most frequently used are shown below. The capacitance is defined by

$$\text{Capacitance } (C) = \frac{\text{Charge } (q)}{\text{Voltage } (V)} \quad (4)$$

In which q is the charge in the double layer and V is the voltage. Alternatively, capacitance is defined by

$$Capacitance = \frac{(\varepsilon) \cdot (A)}{(d)} \quad (5)$$

where ε is the material dielectric constant, A is the double layer area, and d is the Helmholtz layer thickness [7]. The unit of capacitance is the farad which is equivalent to a coulomb / volt and supercapacitor performance is typically quoted as farads / gram of active mass (F/g) or farads / cubic centimeter of active material (F/cm³). It can be shown that supercapacitor energy in joules is defined by

$$Energy = \frac{1}{2} \cdot C \cdot V^2 \quad (6)$$

where C and V are as previously defined and R_s is the equivalent series resistance in the device [7]. Supercapacitor power in watts is defined by

$$Power = \frac{1}{4} \cdot \frac{V^2}{R_s} \quad (7)$$

It is clear from equations 6 and 7 that capacitance and voltage must be increased to drive up device energy and power. In terms of capacitance, this typically results in supercapacitor electrodes being manufactured from porous and/or high surface area material such as activated carbon or graphene. Device voltage is typically limited by the electrochemical window of the electrolyte, which is approximately 1.6 volts for an aqueous solution but can be pushed as high as four volts with advanced ionic liquid electrolytes. While maximizing voltage improves supercapacitor power, reducing R_s is also critical. This requires efforts to minimize sources of both electronic and ionic resistance in the device. A useful figure of merit for overall

supercapacitor performance is the device time constant, tau (τ) which is a measure of how quickly a given device can be charged or discharged [2][9] and is defined by

$$\tau = R_s \cdot C \quad (8)$$

where R_s and C are as defined previously. One final concept relevant to this research is that of a pseudocapacitor, also known as an electro-chemical capacitor. In a pseudocapacitor, energy is stored through faradic charge transfer between the electrolyte and electrode as opposed to being stored in an electric field [7]. While this type of energy storage mechanism is typically associated with batteries, several groups of materials such as electro-active polymers and certain transition metal oxides act as pseudocapacitors because they exhibit a quasi linear charge to voltage relationship during operation. Since this quasi linear relationship allows the capacitance, and thus the energy density of these devices to be described by equation 6 and 7 above, they are classified by many researchers as a type of capacitor [7]. In the case of Ni(OH)_2 , while the material does fall into the category of a transition metal oxide, its storage mechanism and charge voltage characteristics are clearly those of a battery. However, because a wide variety of research describes Ni(OH)_2 as a pseudo capacitor, some performance characteristics of the electrodes developed here will be presented as such so that comparisons to other work in the field can be made [18][19].

1.5.2 Batteries

In contrast to supercapacitors, batteries store energy in the electrochemical conversion of various types of active materials, of which Ni(OH)_2 is one example. This chemical conversion results in a thermodynamically reversible change in oxidation state of the storage material, often referred to as a redox process [8][9]. Materials undergoing this type of process are known as redox couples and are said to be oxidized when releasing an electronic charge which increases their

oxidation state. Conversely, a redox couple is reduced when it incorporates electrons during a chemical conversion resulting in a drop in oxidation state [8]. Oxidation and reduction processes are driven by faradic currents, or electric charge flowing between the battery electrode, comprised of the redox material, and an electrolyte solution comprised of mobile ions [8]. A typical battery design is shown below in Figure 1.9 with two redox couples (one at each electrode) immersed in an electrolyte solution and isolated electrically by an ionic separator.

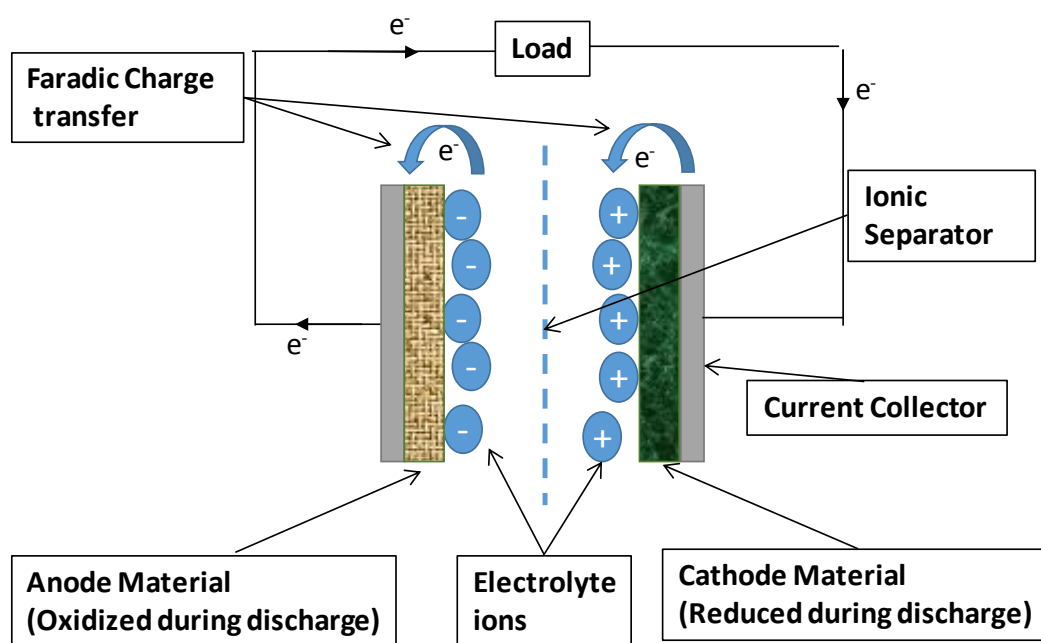


Figure 1.9: Layout of a Battery. Energy is stored in the chemical conversion of redox couples. During discharge, an oxidation reaction takes place at the anode, which releases electrons which are transferred through an external circuit to perform work and then returned to the cathode where they participate in a reduction reaction. Adapted from [8].

When the battery is discharged, electrons are released from the electrode undergoing oxidation, known as the anode, and are driven through an external load and supplied to the electrode being reduced, known as the cathode [8]. In parallel, negative and positive ions, known as anions and

cations, flow to the respective electrodes to maintain charge balance in the system and participate in the redox processes [8]. When the battery has discharged its available energy, and needs to be recharged, an external voltage is connected to the cell. This drives the electronic and ionic currents in the reverse direction and resets the redox couples at the anode and cathode to their original state. The total energy in a battery electrode is defined as

$$Energy (E) = \int Charge (Q) \cdot Voltage (V) \quad (9)$$

where Q is the net charge in the active material and V is the voltage of the redox couple [8]:

Active material charge is often quoted as specific capacity in units of mA*h/g and can be calculated using the molar mass of the material and Faraday's constant. To a first approximation, the reversible electrode potential (E) under equilibrium conditions is described by the Nernst equation [9]:

$$E = E^{0''} + \frac{RT}{nF} \ln \frac{Co(x=0)}{Cr(x=0)} \quad (10)$$

where E^0 is the standard reduction potential of the electrode's redox couple, R is the universal gas constant (8.31 J/mol•K), T is the system temperature in degrees kelvin, n is the number of electrons involved in the redox couple conversion, F is Faraday's constant (96485 C/Mol) and the (ln) term describes the relative concentrations of oxidized and reduced species at the surface of the electrode. In the context of the $Ni(OH)_2$ electrodes studied here equation 10 could be rewritten as

$$E = 0.293 + \frac{R \cdot T}{F} \cdot \ln \frac{[NiOOH](x=0)}{[Ni(OH)_2](x=0)} \quad (11)$$

given that the standard reduction potential of the $Ni(OH)_2 / NiOOH$ redox couple is 293 mV vs. Silver/Silver Chloride, and n is 1 for this reaction [8][6]. It is clear from looking at equation 11

that the $\ln$ term will maintain a relatively steady voltage plateau if the relative concentrations of the two redox couple species are of the same order of magnitude. However, as the concentration of one species or the other at the surface of the electrode begins to approach zero, the electrode voltage will begin to change rapidly [9]. This “Nernstian” behavior of the $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ redox couple is illustrated in Figure 1.10 where the couple voltage is plotted as a function of state of charge (% SoC), or the relative concentration of the two species.

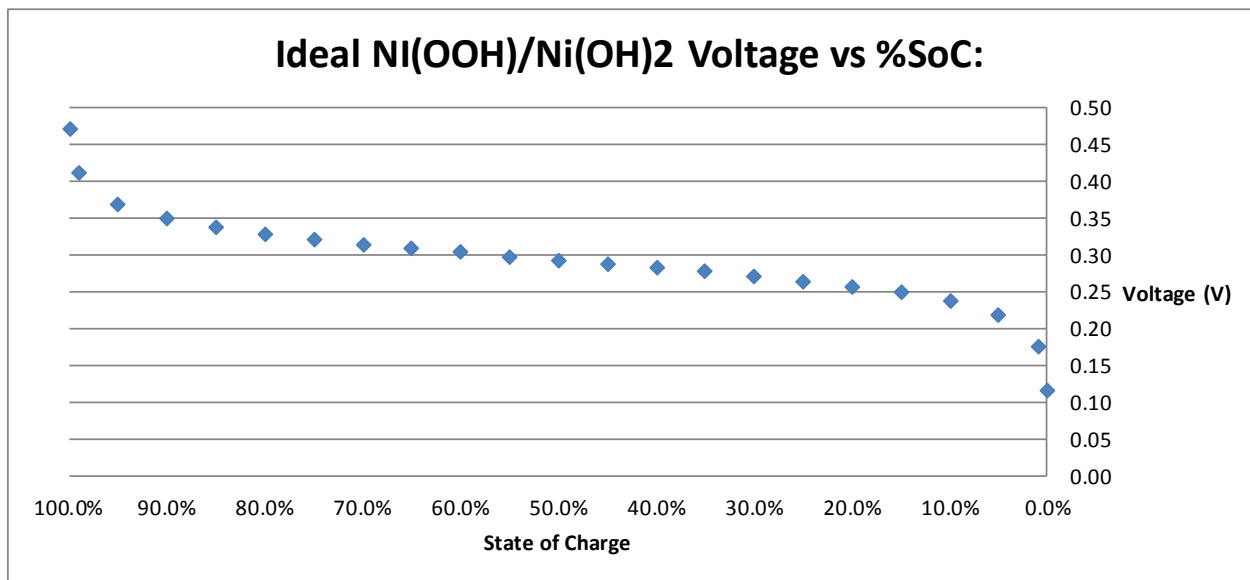


Figure 1.10: Ideal voltage profile of a $\text{Ni}(\text{OOH})/\text{Ni}(\text{OH})_2$ redox couple as a function of state of charge (%SoC).

When the system is at equilibrium, its voltage is governed by the Nernst equation and remains relatively flat between 10% and 90% SOC but changes rapidly as the system approaches either 100% or 0% SOC.

During the practical operation of a battery, the theoretical energy density described by equation 9 is not available due to three primary loss mechanisms. These mechanisms, ohmic losses, kinetic polarization, and mass transfer polarization all result in parasitic voltage losses in the battery and

therefore reduce the useful voltage, and thus energy, that can be delivered to an external load [8]. The remainder of this section will provide a brief overview of these loss mechanisms and suggest how certain physical properties of the Ni(OH)₂ electrodes developed here may impact the relative magnitude of each mechanism. Much of the work presented in Chapter 3 will be focused on characterizing ohmic, kinetic, and mass transport losses in an attempt to predict their relative impact on device energy and power density.

Ohmic losses, also known as IR losses, are the result of various sources of electrical resistance in the electrochemical system. The voltage drop due to ohmic losses is described by

$$V = I \cdot R_s \quad (12)$$

where I is the current supplied to an external load and R_s is the equivalent series resistance of the electrochemical system. Typically, R_s is a series combination of electrical resistance of the electrode and the solution resistance of the electrolyte solution [20]. As was mentioned previously, the electrodes developed here were designed to reduce electrical resistance by growing the Ni(OH)₂ active material directly on a nickel current collector. However, the high aspect ratio of the nanoflakes may minimize some of this benefit by increasing the distance electrons must travel to the nickel current collector. In terms of solution resistance, it is expected that the relatively high conductivity of the KOH electrolyte, the high porosity of the electrospun electrode and the geometry of the experimental set-up used in this work will minimize solution losses. Unfortunately, independent measurements of electrical and solution resistances were not possible due to limitations with instrumentation and sample size. However, a reasonably accurate measurement of R_s was done for all electrode samples using impedance spectroscopy and the results and implications for device performance will be discussed in section 3.3.

Kinetic polarization (η_k), also known as activation polarization or activation overpotential, is defined by

$$\eta_k = V - E \quad (13)$$

where V is the electrode potential and E is the reversible cell potential that is described by the Nernst equation [7]. The kinetic polarization can be thought of as a measure of energy required to drive a chemical reaction away from its equilibrium condition, for example when a battery is charged with an external voltage source or discharged at a certain current. Often the kinetic behavior, or voltage current relationship, of a redox couple in the absence of mass transport effects is described by the Butler-Volmer equation [7]

$$I = I_0 \cdot \left[e^{\frac{(1-\alpha) \cdot n \cdot F \cdot \eta_k}{R \cdot T}} - e^{\frac{\alpha \cdot n \cdot F \cdot \eta_k}{R \cdot T}} \right] \quad (14)$$

where the parameters n, F, R, T are the same as defined previously and the two exponential terms represent the contributions of the forward and reverse reactions for a given redox couple. The parameter α , known as the transfer coefficient is a measure of the energy barrier that must be overcome to drive a reaction in a forward or reverse direction [9]. While α typically has a value of ~0.5 for a one step, one electron reaction, it can deviate from this nominal value for multistep reactions and rough electrode geometries which is the case for the $\text{Ni(OH)}_2/\text{NiOOH}$ electrodes studied here [3] [7]. The parameter I_0 is known as the exchange current for the redox couple and is defined by

$$I_0 = F \cdot A \cdot K_0 \cdot C \quad (15)$$

where F is Faraday's constant, A is the electrode area, K_0 is the chemical reaction rate and C is the bulk concentration of the reacting species [9]. If a system is at equilibrium (ie. zero overpotential and rates of forward and backward reactions are roughly equal) the resulting

current is I_0 and thus the exchange current is a measure of the intrinsic rate of a chemical reaction. In terms of the Butler-Volmer equation, the larger the value of I_0 for a given redox couple, the lower the kinetic over potential required to supply a desired current [7]. It should be noted that the exchange current is often normalized to electrode area and expressed as the exchange current density, J_0 in units of A/cm^2 [9]. At small values of kinetic overpotential, a related figure of merit known as the charge transfer resistance R_{ct} can be defined as [9]

$$R_{ct} = \frac{R \cdot T}{I_0 \cdot F} \quad (16)$$

The charge transfer resistance can be a useful tool to extract an approximate value for the exchange current of an electrode and will be used as part of the impedance spectroscopy modeling presented in section 3.3. In contrast, at high values of electrode overpotential ($>100mV$), an electrode's redox couple is pushed far from equilibrium and the linear approximation used to derive the expression for R_{ct} is no longer valid [7][9]. Moreover, at high values of positive overpotential, the magnitude of the backward reaction is almost negligible and the Butler Volmer equation reduces to equation 17 [9]. By manipulating equation 17

$$i = i_0 \cdot e^{\frac{-\alpha \cdot n \cdot F \cdot \eta_k}{R \cdot T}} \quad (17)$$

we can arrive at equation 18

$$\eta_k = \frac{R \cdot T}{\alpha \cdot F} \cdot \ln i_0 - \frac{R \cdot T}{\alpha \cdot F} \cdot \ln i \quad (18)$$

which is known as the Tafel equation and describes the kinetic overpotential as a function of i_0 and the electrode current. To extract reasonable input values of i_0 and α for the Tafel equation, a procedure known as a Tafel analysis can be performed on data extracted from an electrode exposed to a potential step input. In the case of the electrodes developed here, a Tafel analysis

was done on cyclic voltammetry data recorded at different scan rates. It is assumed that the i_0 values measured in this work are proportional to the fundamental reaction rates of the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple. However, it is also anticipated that the large internal surface area provided by the nanoflake morphology will increase the value of i_0 and thus help to suppress the effect of kinetic polarization. The results of the Tafel analysis and estimated magnitude of the activation polarization for the Ni(OH)_2 test samples will be presented in section 3.2. Finally, an important figure of merit for the kinetic behavior of a redox couple is the kinetic time constant (τ_k), defined as the product of the an electrode's charge transfer resistance and double layer capacitance [2]. Like R_s , τ_k can be evaluated using impedance spectroscopy and will be the subject of some electrode characterization work discussed in section 3.3.

A third loss mechanism is mass transport polarization, also known as diffusion polarization or diffusion overpotential. As the chemical reaction at the electrode surface proceeds, the rate is governed by the kinetics of the redox couple. However, at high reaction rates, reactants at the surface of the electrode can become depleted such that the surface concentration is significantly below the bulk concentration. In order for the reaction to continue at this high rate, reactants must be transported from the bulk of the solution or the electrode to the electrode surface [9]. Given this limitation, designing a battery electrode for rapid mass transport is critical for maintaining high power performance. In general, mass transport in an electrochemical system is governed by three mechanisms; migration, diffusion, and convection and is described by the so-called Nernst Plank equation [9]. However, in most battery applications, mass transfer is dominated by diffusion, or material movement driven by a concentration gradient [8]. As such, we assume that the mass transport behavior for the

nanostructured electrode developed here is driven solely by diffusion. Fick's second law, also known as the diffusion equation is defined by

$$\frac{\partial C(x,t)}{\partial t} = D \left(\frac{\partial^2 C(x,t)}{\partial x^2} \right) \quad (20)$$

where $C(x,t)$ is the concentration of the diffusing species as a function of position and time and D is the species diffusion coefficient which has units of cm^2/s . An expression for $C(x,t)$ can be derived by applying a variety of mathematical techniques and relevant boundary conditions to equation 20. One widely studied solution to Fick's second law is that of a 1D flat electrode subjected to a potential step into a mass transport limited regime, also known as a Cottrell experiment [9]. In this scenario, the initial and boundary conditions define a depletion region for the diffusing species at time zero which expands into the bulk solution as t increases. The diffusion equation can be solved using a Laplace transform method and the solution in the time domain is [9]

$$C(x, t) = C^* \cdot \text{erf} \left[\frac{x}{2 \cdot (D \cdot t)^{1/2}} \right] \quad (21)$$

Here, C^* is the bulk concentration of the diffusing species and the argument inside the error function ensures that the diffusion layer, or the region where the concentration differs from the bulk concentration propagates away from the electrode surface at a rate proportional to $t^{-1/2}$. Further, the term in the denominator of the error function argument $(D \cdot t)^{1/2}$ has units of cm and is often referred to as the characteristic diffusion length L . This term expresses the distance a concentration profile propagates in a given time t and therefore is an important measure for the rate of mass transport in a given system [9]. This characteristic diffusion length can be rearranged slightly to provide an expression for the diffusion time constant (τ_d), or the time

required for a concentration profile to diffuse across a given length [2]. As mentioned in section 1.3, we assume that the species limiting the mass transport performance in Ni(OH)₂ electrodes will be the H⁺ ion, given its relatively low diffusion coefficient [4]. Therefore, a critical hypothesis to test is if the diffusion time constants for the electrodes developed here show any correlation to the Ni(OH)₂ nanoflakes thickness or with the power density of the device [13]. As will be shown in Chapter 2, our Ni(OH)₂ test samples have significantly different nanoflake morphologies. The EIS measurements summarized in section 3.3 were used to evaluate and compare diffusion time constants [2]. In the absence of kinetic polarization and ohmic losses, a mass transport overpotential can be defined as

$$\eta_{mt} = V - E \quad (22)$$

where V is the electrode voltage and E is the reversible electrode potential [9]. Additionally, an expression for mass transport overpotential can be derived as

$$\eta_{mt} = \frac{RT}{nF} \ln \left(\frac{i_l - i}{i_l} \right) \quad (23)$$

where R, T, n, and F are defined as before, i is the current flowing in the electrode and i_l is the limiting current of the system [9]. This expression demonstrates how mass transfer overpotential is a small effect when the system current is far from i_l but ramps up quickly as the limiting current is approached [9][8]. I_l can be defined as

$$I_l = n \cdot F \cdot A \cdot C^* \cdot m_0 \quad (24)$$

where n, F, A and C* are defined as before and m₀ is the mass transfer coefficient for the diffusing species and is defined as

$$m_0 = \frac{D}{\delta} \quad (25)$$

where D is the diffusion coefficient and δ is the diffusion layer thickness [9]. The diffusion layer thickness (δ) can be thought of as the distance between the electrode surface and the bulk solution concentration (C^*) and is hard to define precisely given the multiple mechanisms impacting $C(x,t)$ under most experimental conditions [9]. This uncertainty in the value of δ propagates back through equations 25 and 24, ultimately making it difficult to determine the precise value of mass transport overpotential for even a flat plate electrode. Given the added complexity of the highly porous and nanostructured electrodes developed here, we were not able to determine a reasonable value for mass transfer overpotential in this work. However, several efforts to evaluate the impact of mass transport on device performance were explored and will be presented in section 3.3. Ultimately, the task of characterizing battery electrode performance is focused on determining the relative magnitude of ohmic, kinetic and mass transfer losses as a function of operating voltage and current density. As described above, the governing equations for these mechanisms are relatively well understood for flat, smooth electrodes and the critical input parameters can be determined using an array of characterization techniques. Figure 1.11 shows an illustration of the behavior of the three loss mechanisms as a function of electrode discharge current. It should be noted that this simulation is meant as an example of loss mechanism behavior and is not necessarily representative of the polarization behavior of the electrodes developed in this work. As expected, ohmic losses increase linearly with current

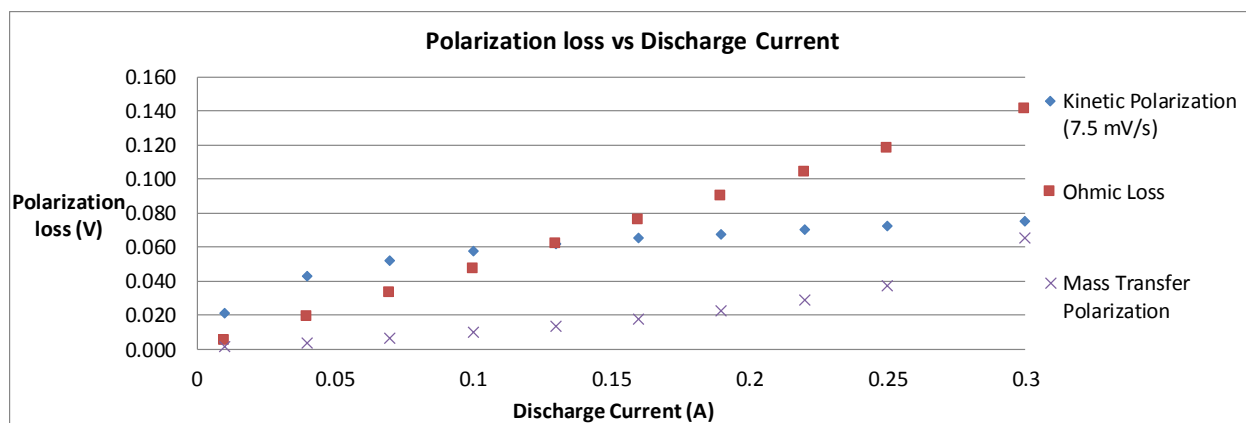


Figure 1.11: A simulation of the relative impact of ohmic, kinetic and mass transport losses as a function of discharge current. While linear ohmic loss, and logarithmic kinetic polarization tend to dominate at low currents, mass transport polarization can become significant at higher currents depending on the diffusion properties of rate limiting reactants, as discussed in [9].

and kinetic losses are logarithmic, initially increasing rapidly and then moderating at higher currents. As mentioned above, mass transfer polarization tends to be negligible at low currents but begins to increase exponentially as the system current approaches the limiting current of the electrode [8]. Finally, it must be noted that the theory reviewed in this section is technically only valid for a smooth, flat electrode, primarily because the governing differential equations were all solved using this geometric assumption [9]. Therefore, using this theory to interpret the characterization of nanostructured electrodes with a radically new geometry introduces an inherent source of error. However, it is assumed that existing theory provides a reasonable approximation of the electrochemical behavior of the devices developed here. In addition, elements of rough electrode theory will be used where appropriate to try and explain results which deviate from theoretical expected values.

1.5.3 Asymmetric Energy Storage Devices

Asymmetric storage devices, also known as hybrid devices, were first investigated in the 1990's with the goal of developing a storage solution that could provide the energy density of a battery with the power density of a supercapacitor [7]. A schematic for a typical asymmetric device is shown in Figure 1.12. The concept is to integrate a faradic or battery type electrode with an electrostatic or supercapacitor electrode into a single device.

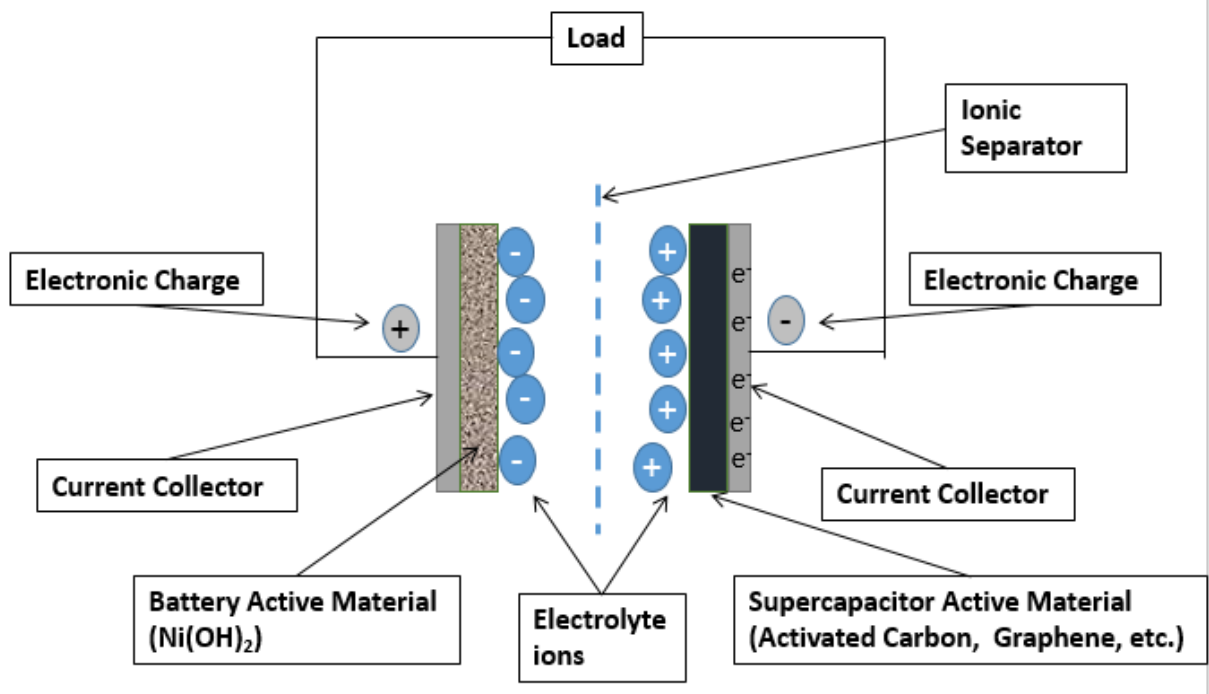


Figure 1.12: Asymmetric storage device. A battery electrode, ionic separator and supercapacitor electrode are combined into a single device. During charging and discharging, the battery electrode exchanges energy through a redox process while the supercapacitor electrode stores energy via the charging and discharging of a double layer. Adapted from [7].

One of the major advantages of asymmetric devices is that they overcome the “halving effect” on overall device capacitance, and thus improve energy density, experienced by symmetric supercapacitor devices[7]. This occurs because the battery-type electrode typically has a

significantly larger capacitance than the supercapacitor electrode. The overall device capacitance is roughly equivalent to a single supercapacitor electrode as per equation 1.6. The governing physical concepts and equations for asymmetric devices are the same as those for batteries and supercapacitors described in sections 1.5.1 and 1.5.2. In general, critical design criteria for asymmetric devices are as follows: [7]

- Both electrodes must have high power capacity. While this capability is inherent in the electrostatic storage mechanism of a supercapacitor electrode, it does require that the chemical reaction at the battery electrode be highly reversible and not limited by mass transport over the range of desired current densities.
- The available charge on each electrode should be approximately balanced. In practice, this typically means that the active mass of the supercapacitor type electrode is much larger than the battery electrode, given the relative energy density of the two systems.

Since Ni(OH)_2 and activated carbon electrodes can meet these requirements when combined with the appropriate active mass ratio and choice of electrolyte, they are commonly used to assemble asymmetric devices. For example, Yan et al developed a Ni(OH)_2 / graphene hybrid that yielded a performance of 77.8 Wh/kg at a power density of 174 W/kg [21]. A conceptual example of how the Ni(OH)_2 nanostructured electrodes developed here could be implemented in an asymmetric device is shown in Figure 1.13. As mentioned previously, two of the key design advantages are the integrated current collector and the high micro porosity of the electrode.

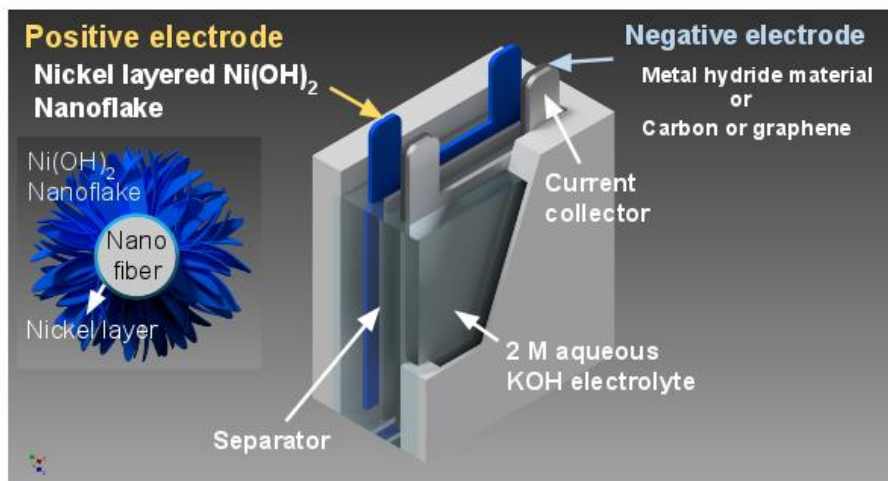


Figure 1.13: Conceptual design for asymmetric device constructed with electrospun Ni(OH)₂ electrodes developed here. Courtesy: Dr. J. Choi.

1.6 Relevant Literature

Historically, most research into Ni(OH)₂ based electrodes has been focused around improving their performance for conventional NiMH and NiCd battery applications. Recently however, a significant amount of research has been focused on developing nanotextured Ni(OH)₂ electrodes for use in asymmetric device storage applications. The electrodes developed in this work were designed to have three key advantages over other similar technologies that were surveyed in the relevant literature. Firstly, the aspect ratio of Ni(OH)₂ nanoflakes can be tuned easily by varying the concentration of one of the process chemistries used in the manufacturing process. This nanostructure tunability allows for the adjustment of both the surface area and thickness of the electrode active material and enables the researcher to investigate the impact of these parameters on overall electrode performance. Secondly, and somewhat related, the electrodes developed here have a very high internal surface area which enables most of the active material to be in direct contact with the electrolyte. This enables the electrode to achieve a high specific power as the majority of the Ni(OH)₂ to NiOOH material conversion is governed by the kinetics of Ni⁺² /

Ni^{+3} redox couple rather than the mass transport of the H^+ proton through the bulk of the active material. As the results of EIS measurements in Chapter 3 will demonstrate, the time constant of the kinetic process is approximately three orders of magnitude faster than that of the electrode mass transport behavior. Finally, the electrodes developed here can be manufactured using a relatively simple assembly process which does not require any electrochemical deposition, high temperature treatment, or use of exotic materials such as graphene. As such, it is anticipated that they will be relative low cost to produce if the technology can be successfully scaled to high volume. In many papers, authors refer to their devices as supercapacitors and therefore use either specific capacitance or volumetric capacitance as one of their key figures of merit. Perhaps the most relevant of these efforts is by Zhang *et al.*, who grew what they term as $\text{Ni}(\text{OH})_2$ nanoplatelets directly on electrospun carbon nanofibers [15]. Following similar logic as the device design in this work, these researchers were looking to leverage the high internal surface area of an electrospun scaffold and the opportunity to deposit the active material on a structure which acts as both a structural binder and current collector. When measured using a galvanic charge discharge at a current density of 1A/g in a solution of 2 molar KOH, the device achieved a specific capacitance of 2394 F/g based on the active mass of $\text{Ni}(\text{OH})_2$, or 667 F/g based on the total mass of the device. While this is an impressive result, the authors also claim that the maximum theoretical specific capacitance for $\text{Ni}(\text{OH})_2$ is 2082 F/g and do not explain why the measured result exceeds this maximum value. It should also be noted that the electrochemical measurements were performed with the electrospun electrode bonded to a glassy carbon current collector, perhaps indicating that the carbon nanofiber core is not conductive enough to act as an integrated current collector. In addition, the fabrication process requires a 1,500°C, N_2 treatment to effectively carbonize the electrospun nanofibers. This would likely add significant cost and

complexity to any future manufacturing process. Wang *et al.* pursued a more conventional approach to electrode design by growing Ni(OH)_2 nanoflakes on a graphene coated nickel foam current collector. This device exhibited a specific capacitance of 2161 F/g (active mass) at a current density of 3 A/g in 1M KOH when measured using a constant current discharge (GCD) technique. It was able to maintain a capacitance of 1520 F/g when tested at a high current density of 60 A/g [17]. The authors theorize that this strong capacitance retention at high current density is due primarily to the high electrical conductivity of the graphene layer deposited between the Ni(OH)_2 active material and the nickel foam current collector. The high power performance of this device is impressive, however it does come with significant manufacturing complexity and added capital cost as the graphene layer is grown using a high temperature chemical vapor deposition (CVD) step and the Ni(OH)_2 active material is deposited using an electrochemical process [17]. A similar approach to electrode design was taken by Yan *et al.* who synthesized a nanostructured Ni(OH)_2 / graphene composite which was then deposited on a nickel foam current collector [21]. This group measured the device performance using cyclic voltammetry and reported a specific capacitance of 2194 F/g (active mass) at a scan rate of 2 mV/s and a value of 895 F/g at a scan rate of 20 mV/s in 6M KOH. From a fabrication standpoint, this electrode design has an advantage over the method proposed by Wang [17] as it uses a simple wet chemistry process to fabricate the graphene / Ni(OH)_2 and does not require any high temperature steps. However, the resulting composite active material is then combined with a conductive additive and a binder in a mass ratio of (75% active material /20% conductive additive /5% binder) and deposited as an ethanol-based slurry onto a nickel foam current collector. While this assembly method is similar to that used in the fabrication of commercial battery and super capacitor electrodes, it has the obvious disadvantage of requiring the use of

significant amounts of non-active materials, which limit the specific energy of the overall device [8]. Table 1.2 summarizes the performance of the electrodes developed in this research and compares them to the alternative technologies that were discussed in this section.

Authors	Device Design	Performance at low current density <3A/g	Comments
Zhang <i>et al.</i> [15]	Ni(OH) ₂ nano-platelets grown on electro-spun and carbon nano-fibers	2,394 F/g (active mass) 667 F/g (total mass*) *not including mass of current collector	Active mass result is higher than theoretical capacitance limit and fabrication requires high temperature processing.
Yan <i>et al.</i> [18]	Ni(OH) ₂ / Graphene composite deposited on Ni foam current collector	2,194 F/g (active mass) Total mass not reported.	Ni(OH) ₂ / graphene composite is not used as fabricated. Rather it is crushed to a powder, combined with binders, and applied as a slurry to a nickel foam current collector.
Wang [17]	Ni(OH) ₂ nanoflakes grown on graphene coated nickel foam.	2,161 F/g (active mass) Total mass not reported.	Graphene deposition requires high temperature CVD fabrication.
This Work	Electrospun, nano structured Ni(OH) ₂ electrode with integrated current collector.	2,123 F/g (active mass) 1,040 F/g (total mass)	Process conducive to rapid scale up and low capital intensity.

Table 1.2: Comparison of device developed in this research project to similar work.

1.7 Chapter Summary

The work in this thesis was motivated by the increasing market demand for low cost, highly scalable energy storage technologies with both high energy and power densities. The electrodes developed here have the potential to meet this demand given their relatively simple assembly process and suite of advantageous product attributes such as very high internal surface area, nanoscale feature size and ability to incorporate functional materials. In this case, Ni(OH)₂ was

employed as the active energy storage material given its compatibility with nickel-coated, electro-spun nanowire technology and its extensive use in NiMH and NiCd batteries. Broadly speaking, the performance of these electrodes can be explained by measuring various electrical and electrochemical properties of the active materials using a standard electrochemical experimental setup. Measurement of these properties can determine the ohmic, kinetic and mass transport limitations of the system and thus allow for the development of performance models and clear directions to improve actual performance. However, it should be noted that much of present day electrochemical theory assumes a single, idealized, flat plate electrode geometry. Thus, it is likely that applying this theory to the nanostructured electrodes developed here may present some challenges and lead to some inaccuracies in predicting performance. Electrode performance and modeling approaches to account for deviations from ideal flat plate behavior will be explored in Chapter 3. The electrodes developed here compare favorably with similar systems presented in the literature, however it is often difficult to make direct comparisons with other research given the limited information that is often provided in the literature. The following chapter will summarize the electrode fabrication process, their physical properties and estimate key attributes such as porosity and internal surface area.

Chapter 2: Fabrication and Material Characterization of Electro spun and Nanostructured Ni(OH)₂ Electrodes

This chapter will provide an overview of the fabrication process for the nanostructured Ni(OH)₂ electrodes and outline the details of the experimental work conducted in this thesis. In addition, Chapter 2 will summarize the results of various material characterization tests used to evaluate electrode composition, size and morphology.

2.1 Electrode Fabrication Process

As was discussed in section 1.3, The nanostructured electrodes studied here were fabricated at the UBC AFM lab using a sequence of four process steps: Electrospinning, heat treatment, electroless nickel deposition and hydrothermal Ni(OH)₂ growth. The details of these process steps are outlined in Table 2.1. In the electrospinning step, a solution having a

Process Step	Chemistry	Time	Temperature	Other
Electrospinning	- Pd(C ₅ H ₇ O ₂) ₂ , 0.57% - PAN-Co-MA, 9.9% - DMF, 89.5%	Spin: 10.0 hrs Dry: 2.0 hrs	Spinning : 25°C Dry: 70°C	HV: 17.5 kV Humidity: 30%
Heat treatment	- Argon atmosphere	2.0 hrs	250°C	NA
Nickel plating	- NiCl ₂ , 3.89 g/L - C ₄ H ₄ Na ₂ O ₆ ·2H ₂ O, 25 g/L - NaOH, 3.5 g/L - N ₂ H ₄ , (64-65%), 0.1 g/L	0-6.0 hrs	40-90°C	NA
Ni(OH) ₂ growth	- NiSO ₄ ·6H ₂ O, 0.5 mol/L - NH ₄ OH, 0.9-1.8 mol/L	2.0 hrs	70°C	NA

Table 2.1: Fabrication process for Nanostructured Ni(OH)₂ Electrodes.

concentration of approximately 10% by weight of polyacrylonitrile (PAN) is diluted in DMF solvent and mixed with a 0.57% by weight palladium (II) acetylacetonate salt. This mixture is then loaded into a custom electrospinning apparatus and a randomly oriented mesh of nanowires is continuously deposited on an aluminum target over approximately 10 hours. The PAN mesh is then removed from the electrospinning tool and annealed in argon for approximately 2 hours at 250° C to prepare the nanowire surface for metallization. Next, the PAN mesh is immersed in a basic, nickel chloride (NiCl_2) and hydrazine (N_2H_4) solution and processed for 3 hours at 70° C to deposit approximately 100 nm of nickel metal onto the surface of the PAN nanowires. Next, the metalized nanowire mesh is rinsed with deionized water and transferred to a second solution of nickel (II) sulfate hexahydrate ($\text{NiSO}_4 (\text{H}_2\text{O})_6$) and ammonium hydroxide (NH_4OH) where the $\text{Ni}(\text{OH})_2$ nanoflakes are grown at 70° C for 2 hours. All the research samples were fabricated with prototype laboratory equipment. The lack of high temperature steps and relatively simple electrospinning and hydrothermal processing steps should enable a rapid manufacturing scale-up and relatively low-cost capital equipment.

2.1.1 Experimental design for morphology characterization

With the baseline fabrication process described in section 2.1 established, the next goal was to attempt to find a correlation between the $\text{Ni}(\text{OH})_2$ nanostructure morphology and overall electrode performance. Through additional process development, it was discovered that variations in the molarity of ammonium hydroxide in the $\text{Ni}(\text{OH})_2$ growth process had a significant impact on the aspect ratio of the nanoflakes. Specifically, low NH_4OH concentrations tended to form longer, thinner flakes while higher concentrations formed shorter, wider flakes with a shorter distance between adjacent flakes. Based on this finding, three samples were manufactured with three different NH_4OH molarities and were used for the bulk of the

characterization work in this thesis. A naming convention and qualitative description of these samples is provided in Table 2.2 and a more rigorous characterization of the sample properties is described in the following sections of chapter 2.

Sample Name	Ammonium hydroxide concentration.	Expected nanoflake aspect ratio.	Expected nanoflake spacing
Sample_1 (S_1)	Low: ~0.9 M	High	High
Sample_2 (S_2)	Medium: ~1.4 M	Medium	Medium
Sample_3 (S_3)	High: ~1.8 M	Low	Low

Table 2.2: Description of experimental samples used in this thesis.

2.2 Physical characterization of Ni(OH)₂ electrode samples

Section 2.2 will provide a brief overview of the physical characterization of the nanostructured electrodes studied in this work. Section 2.2.1 will summarize the macroscopic dimensions of the test samples and section 2.2.2 will summarize SEM analysis used to determine electrode feature size on the micro and nanoscale. Section 2.2.3 will use this feature size information to provide estimates of sample surface area and porosity and section 2.2.4 will summarize the results of X-ray diffraction (XRD) measurements used to confirm material composition of the Ni(OH)₂ nanoflakes.

2.2.1 Electrode Dimensions

A precision ruler, a Mitutoyo digital barrel micrometer and a Mettler Toledo mass balance unit were used to characterize the dimensions and mass of the three test samples. This data is summarized in Table 2.3. It should be noted that the term “active mass” refers to the mass of nickel hydroxide contained in a test sample. Further, performance metrics such as specific

capacity or energy density presented in this work are quoted on an active mass basis. However, given that the mass of $\text{Ni}(\text{OH})_2$ is approximately 50% of the total sample mass, the reader can determine the sample performance based on total mass, by dividing the appropriate metrics by two. In addition, the wet mass of the device can be determined by including the mass of the electrolyte needed to charge the electrode fully to the total mass of the device, On the other hand, “volume” refers to the total sample volume, and therefore captures the space taken up by the device active material, nickel current collector, electrospun PAN binder and any free space, or porosity, inside the electrode.

	Length (mm)	Width (mm)	Thickness (μm)	Volume (cm^3)	PAN Mass (mg)	Nickel Mass (mg)	$\text{Ni}(\text{OH})_2$ Mass (mg)	Total Mass (mg)
S_1	10 +/-0.5	6 +/-0.5	61 +/- 0.5	0.0037 +/- 4.4×10^{-4}	0.83 +/- 12%	3.1 +/- 3%	3.3 +/- 3%	7.25 +/- 0.05
S_2	12 +/-0.5	6 +/-0.5	51 +/- 0.5	0.0037 +/- 4.5×10^{-4}	1.1 +/- 10%	3.6 +/- 3%	4.3 +/- 2%	8.95 +/- 0.05
S_3	12 +/-0.5	6 +/-0.5	44 +/- 0.5	0.0032 +/- 3.9×10^{-4}	0.97 +/- 9%	3.7 +/- 2%	3.5 +/- 3%	8.16 +/- 0.05

Table 2.3: Physical dimensions of test samples characterized in this work.

2.2.2 SEM analysis and nanostructure characterization

Test sample structure and morphology was studied with a scanning electron microscope (SEM, Model FEI Quanta 650). The working distance used for SEM imaging was approximately 5 mm and the accelerating voltage was 15 kV. Physical dimensions of key structural features, such as

Ni(OH)₂ nanoflakes and PAN nanowires were measured with the ImageJ software program (National Institute of Health, USA). Figure 2.1 shows the surface morphology of a

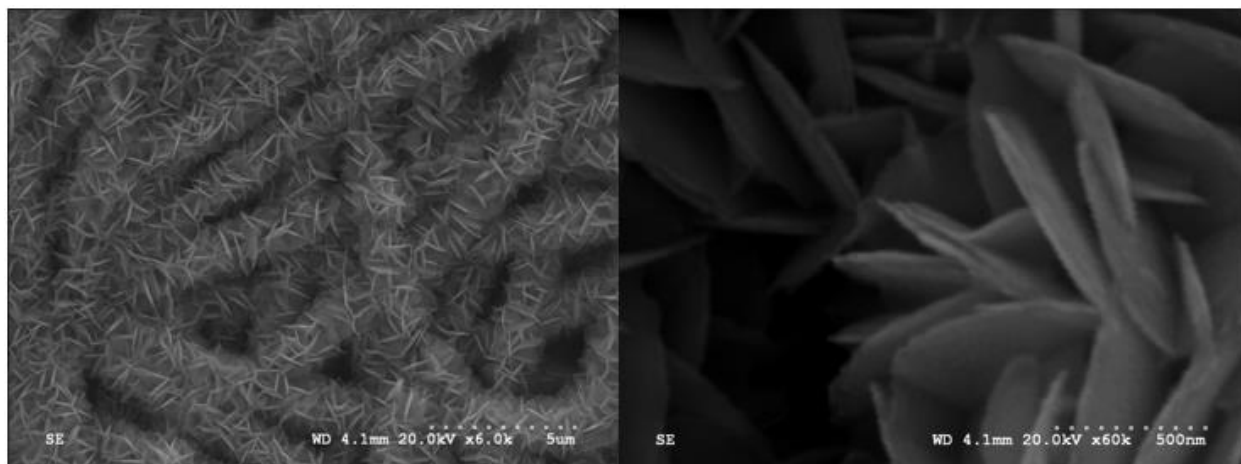


Figure 2.1: Low (left) and high (right) magnification SEM images of electrospun, nano-structured Ni(OH)₂ electrodes. On optimized samples, individual microwires are visible at low magnification with individual Ni(OH)₂ nanoflakes visible at high magnification.

typical electrode sample at low (left) and high (right) magnification. At low magnification, a random array of distinguishable micro wires is seen and while these wires appear to be closely packed together, many voids or spaces between adjacent wires can also be observed. At high magnification, individual Ni(OH)₂ nanoflakes can be seen to be secured at one end to the micro wire and appear to extend radially outward from the center of the wire. The high-magnification image also shows that the nanoflakes tend to have a very high aspect ratio, with their lengths being orders of magnitude larger than their thicknesses. To confirm that this structural pattern was consistent throughout the bulk of the electrode samples, a sample manufactured with the nominal process conditions (ie. Sample_2 process) was cut in half with a razor blade and the exposed surface was measured on the SEM. These cross-section images are shown in Figure 2.2 and based on the low-magnification image (left), we conclude that the structure of the micro-

wires is roughly consistent throughout the sample. Additionally, significant porosity or empty space is present within the electrode. The high magnification image (right) shows a cross

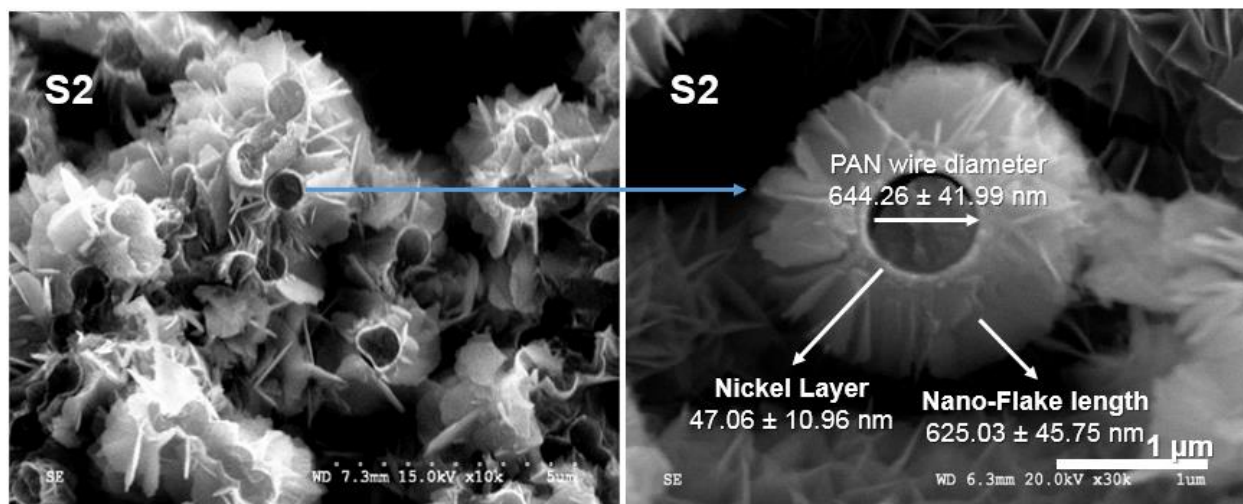


Figure 2.2: SEM cross section images of sample 2. The low magnification image (left) showing a consistent nanoflake structure in the bulk of the electrode and a high magnification (right) showing the relative dimensions of the PAN core wire, nickel metallization layer and Ni(OH)₂ nanoflake length that make up a single micro wire.

section view of an individual micro wire and the relative sizes of the 3 component materials that make up the electrode. The PAN core wire was found to be approximately 650 nm in diameter and as expected, was uniformly coated by approximately 50 nm of nickel. The Ni(OH)₂ nanoflakes had lengths of approximately 625 nm, and were confirmed to extend radially out from the center of the metallized core wire and be uniformly arrayed around its circumference. Surface SEM images of the three experimental samples (S1-S3) were then taken and measurements of the both the micro wire diameter and the nanoflake thickness were collected. These images are included in Figure 2.3 and show a trend of decreasing Ni(OH)₂ nanoflake aspect ratio, or length to thickness ratio, with increasing NH₄OH concentration. Specifically, Sample 1 was measured to have a flake thickness of approximately 9.5 nm and a micro wire

diameter of approximately $3.2\ \mu\text{m}$ while Sample 3 has a nanoflake thickness of roughly $18\ \text{nm}$ and a micro wire thickness of $1.36\ \mu\text{m}$. Along with this trend in decreasing aspect ratio, we also

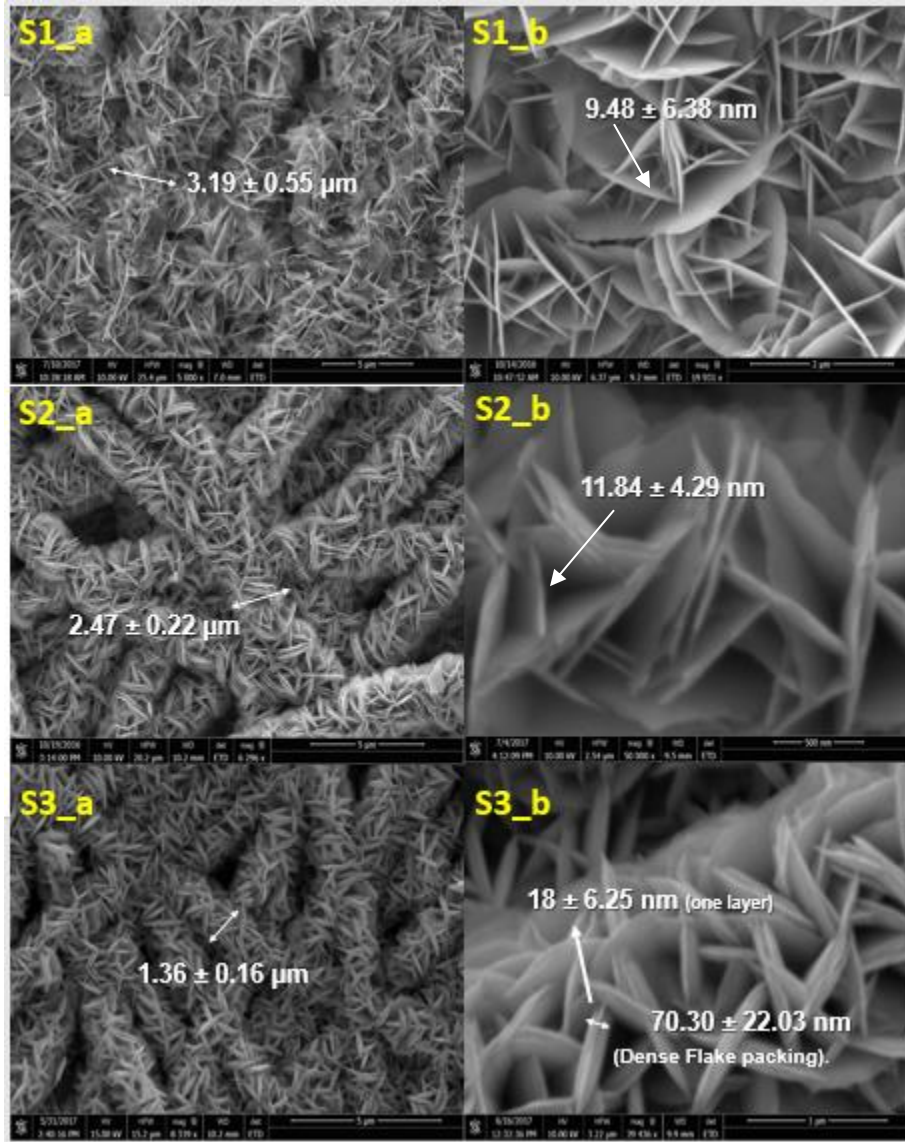


Figure 2.3: Surface SEM images of the three experimental samples characterized in this work. Two trends of decreasing nanoflake aspect ratio, and decreasing space between adjacent nanoflakes can be seen from Sample 1 to Sample 3.

observed a tendency towards decreasing spacing or pitch between adjacent nanoflakes. This effect is perhaps most visible in image S3_b where approximately 4 to 6 adjacent nanoflakes

appear to stack together in tight clusters of approximately 70 nm in thickness. The measured feature sizes for Samples 1-3 are summarized in Table 2.4 along with an estimate for the surface area to volume ratio of the Ni(OH)₂ nanoflakes on each sample. Given the observation from Figure 2.3 that the nanoflakes are uniformly distributed around the metalized core wire,

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect Ratio	Sample_3 Low Aspect Ratio
Micro wire diameter (μm)	3.2 +/- 0.5	2.5 +/- 0.2	1.4 +/- 0.2
Metallized (PAN+Ni) core wire diameter (nm)	691 +/- 53	691 +/- 52	691 +/- 52
Nanoflake length (nm) (annulus r ₂ -r ₁)	1249 +/- 301	880 +/- 136	334 +/- 106
Nanoflake annulus surface area (cm ²)	9.80 x 10 ⁻⁸ +/- 48%	4.97 x 10 ⁻⁸ +/- 30%	7.02 x 10 ⁻⁹ +/- 63%
Nanoflake thickness (nm)	9.48 +/- 6.38	11.84 +/- 4.29	18.00 +/- 6.25
Nanoflake annulus volume (cm ³)	4.6E x 10 ⁻¹⁴ +/- 115%	2.9 x 10 ⁻¹⁴ +/- 66%	6.3E x 10 ⁻¹⁵ +/- 98%
Nanoflake surface area to volume ratio	2.1 x 10 ⁺⁶ +/- 115%	1.6E x 10 ⁺⁶ +/- 66%	1.1 x 10 ⁺⁶ +/- 98%

Table 2.4: Physical dimensions and estimate of surface area to volume ratio for the samples characterized in this work. While a significant amount of uncertainty is present in these values due to accuracy limitation in SEM measurements, all samples have very high surface area to volume ratios; on the order of 10⁶ cm⁻¹.

surface area was estimated by calculating the surface area of an annulus with an outer radius equal to that of the sample micro wire and the inner radius equal to that of the metalized core wire. Correspondingly, the volume of a nanoflake was approximated by multiplying its thickness by the area of the annulus, as outlined in Figure 2.4. Based on the results shown

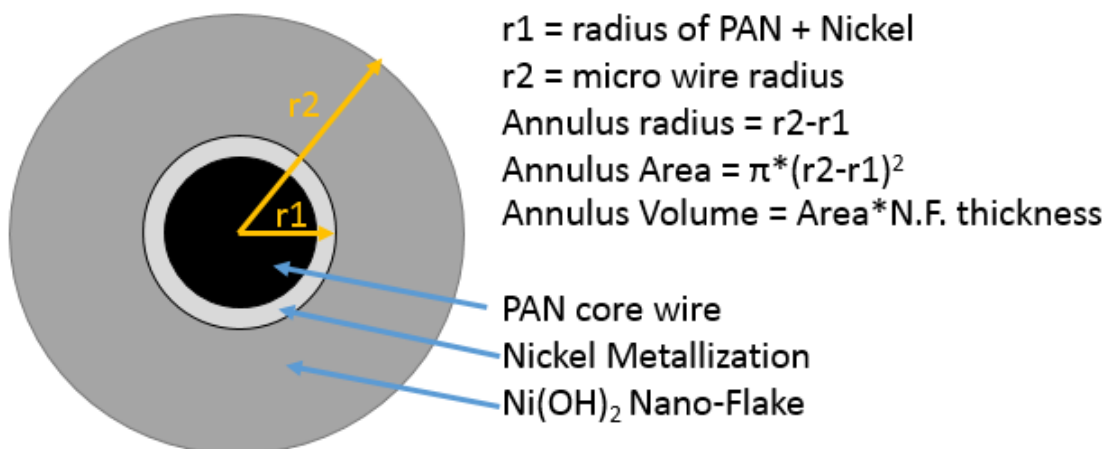


Figure 2.4: The array of Ni(OH)₂ nanoflakes around the metalized PAN core wire is approximated by an annulus. Nanoflake surface area and volume for experimental samples are then calculated using annulus area and flake thickness.

in Table 2.4, all three test samples have nanoflakes with very high surface area to volume ratios (SATVR); on the order of 10^6 cm^{-1} . In addition, there is a trend of decreasing surface area to volume ratio from Sample 1 to Sample 3 correlating with the trend of decreasing aspect ratio observed on the SEM images. It should be noted that the relative uncertainty in calculated values for surface area to volume ratio is relatively high (+/- ~100%) due primarily to accuracy limitations in evaluating various feature sizes on SEM images. In future studies, this uncertainty can likely be reduced by taking a larger number of SEM images and averaging the results or by taking higher resolution images with the aid of a TEM system. An important implication of the high surface area to volume ratio is that the majority of the active material is on the electrode surface. Thus, we assume that during electrode operation, the rate of charging and discharging of this surface material should be governed by the kinetics of the $\text{Ni(OH)}_2 \leftrightarrow \text{NiOOH}$ chemical reaction and any ohmic losses and should not be limited by the mass transport of the H^+ ions through the bulk of the nanoflakes. As was discussed in section 1.3, H^+ mass transport is often

the rate-limiting step in conventional flat plate $\text{Ni}(\text{OH})_2$ electrode designs [13] and some of the work presented in chapter 3 will attempt to validate this assumption. A final SEM image was taken on Sample 2 to investigate whether there was a change in surface morphology after a range of tests was performed. Figure 2.5 compares low magnification images of the surface morphology of Sample 2 before (left) and after (right) electrochemical testing. In general, the morphology seems largely unchanged with the diameter and orientation of the micro wires appearing similar in the two images. However, it does appear that there was some increase in the flake to flake spacing or pitch. This could have implications on the effective surface area of the electrode and therefore on electrode performance. This is also an area of potential future work where a series of high magnification SEM images taken pre and post cycling could confirm and study any significant changes in surface morphology.

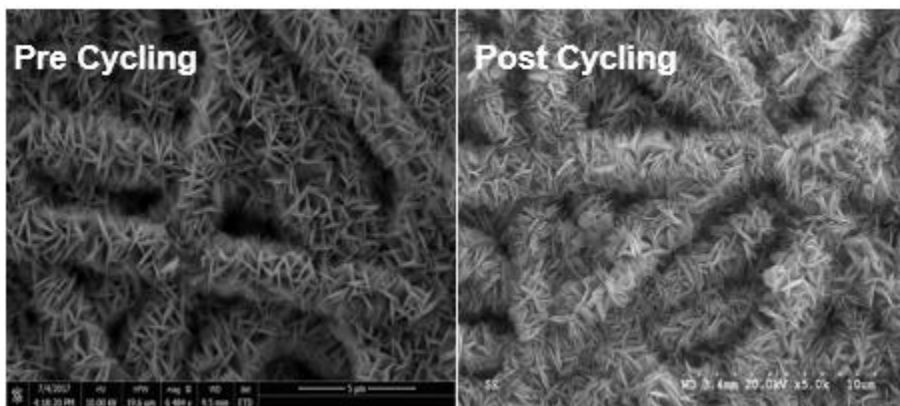


Figure 2.5: Low magnification SEM images of the surface morphology of sample 2 pre and post electrochemical characterization. Overall, the surface morphology appears largely unchanged although some increase in the spacing between adjacent nanoflakes appears visible.

2.2.3 Sample Surface Area and Porosity estimation

In addition to the work in the previous section to quantify the surface area and volume of individual nanoflakes, an attempt was made to estimate both the effective geometric surface area and porosity of the test samples. In the case of the surface area, an extension of the model in the previous section was developed where the mass of $\text{Ni}(\text{OH})_2$ active material in each test sample was assumed to be distributed in a square, flat plate with a thickness equal to the mean nanoflake thickness (t_{NF}). The dimensions of this idealized flat plate electrode are shown in Figure 2.6, and using the active mass (m) of the sample, the density of $\text{Ni}(\text{OH})_2$ and the

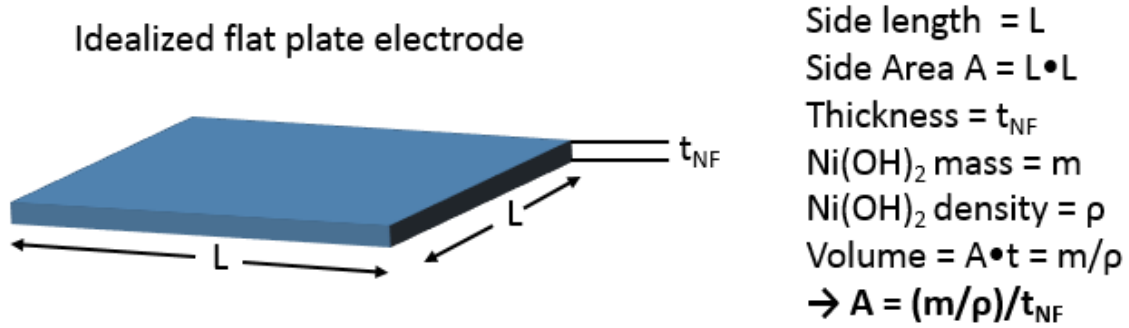


Figure 2.6: Model for an idealized flat plate electrode used to estimate the surface area of each test sample.

The plate is modeled to have a thickness equal to the mean nanoflake thickness and thus using the mass of active material and the density of $\text{Ni}(\text{OH})_2$ (4.1g/cm^3), a surface area can be calculated using equation 26.

nanoflake thickness, the area of one side of the plate was calculated. Then, an estimate for the geometric surface area of the electrodes was calculated using

$$\text{Surface Area} = (2 \cdot A) + (4 \cdot \sqrt{A} \cdot t) \quad (26)$$

and the results of the calculations are shown in Table 2.5. The second term on the right is an estimate of the flake edge area. As expected, the estimated geometric surface area of the

	Sample 1 High Aspect Ratio	Sample 2 Medium Aspect Ratio	Sample 3 Low Aspect Ratio
Ni(OH) ₂ mass (g)	0.0034 +/- 3%	0.0043 +/- 2%	0.0035 +/- 3%
Ni(OH) ₂ density (g/cm ³)	4.1	4.1	4.1
Nanoflake thickness (cm)	9.40 x 10 ⁻⁷ +/- 67.1%	1.2 x 10 ⁻⁶ +/- 36.1%	1.8 x 10 ⁻⁶ +/-34.7%
Area (cm ²)	865 +/- 70.1%	885 +/- 38.1%	470 +/- 37.7%
Estimated geometric surface area (cm ²)	1,730 +/- 70.1%	1,769 +/- 38.1%	950 +/- 37.7%
Measured surface area (cm ²)	1.22 +/- 13.3%	1.46 +/- 12.5%	1.46 +/- 12.5%

Table 2.5: The estimated geometric surface area of the test sample nanostructures is between ~500-1000x the measured surface area (length*width) of the test samples. The relatively large area uncertainty is a consequence of accuracy limitation in SEM measurements of nanoflake thicknesses.

test samples is significantly larger than the measured whole sample surface area, ranging from an approximate 1000 times increase for samples 1 & 2 and an approximate 500 times increase for sample 3. It should be noted that there is significant uncertainty in these numbers driven largely by accuracy limitations in the measurement of nanoflake thickness. These estimates will be compared against electrochemical measurement of sample surface area to be presented in Chapter 3. In the case of porosity, or the ratio of free space to electrode material, estimates were calculated for each sample using:

$$Electrode\ Porosity = 1 - \frac{PAN_{Vol} + Ni_{Vol} + Ni(OH)_2_{Vol}}{Sample\ Volume} \quad (27)$$

where the volumes of the constituent components were calculated from the measured mass and known density for PAN, nickel and Ni(OH)₂ and then compared as ratios to the measured

volumes of each sample. The results of these calculations are summarized in Table 2.6 and it was found that all three samples had significant porosity ranging from roughly 35 to 50%.

	Sample 1 High Aspect Ratio	Sample 2 Medium Aspect Ratio	Sample 3 Low Aspect Ratio
PAN Volume (cm ³)	7.0 x 10 ⁻⁴ +/- 12%	9.2 x 10 ⁻⁴ +/- 10%	8.2 x 10 ⁻⁴ +/- 9%
Ni Volume (cm ³)	3.4 x 10 ⁻⁴ +/- 3%	4.0 x 10 ⁻⁴ +/- 3%	4.1 x 10 ⁻⁴ +/- 2%
Ni(OH) ₂ Volume (cm ³)	8.3 x 10 ⁻⁴ +/- 3%	1.1 x 10 ⁻³ +/- 2%	8.5 x 10 ⁻⁴ +/- 3%
Porosity	49% +/- 18%	35% +/- 17%	34% +/- 17%

Table 2.6: Estimated porosity or percent empty space within each test sample. All samples are estimated to exhibit significant porosity ranging from approximately 35-50%.

It is not possible to determine how this porosity is distributed inside the electrode using this simple calculation. However, the porosity is assumed to be roughly homogenous given the random orientation of the PAN nanofiber scaffold and the distribution of voids observed in the SEM cross section images. While the surface area and porosity values presented here are admittedly rough estimates, they do confirm that nanostructured electrodes accomplished the two stated design goals of increasing the device internal surface area while maintaining significant porosity.

2.3 XRD analysis: Active material composition

X-ray diffraction analysis was used to determine the composition of the Ni(OH)₂ active material studied here. The XRD technique works by bombarding a material with a collimated beam of X-ray energy and measuring the intensity of diffracted rays which occur at various angles according

to the crystal structure of the sample. This diffraction pattern is then compared with the known pattern for a given material or range of materials that are expected to make up the sample under test. Our assumption was that this material was pure β -Ni(OH)₂ and that the composition did not change after numerous charge and discharge cycles during electrochemical testing. To validate this assumption, an electrode fabricated by the identical process used for sample 2 was measured on a XRD diffractometer immediately after fabrication and then again after approximately 100 charge / discharge cycles. The results are shown in Figure 2.7. The resulting diffraction

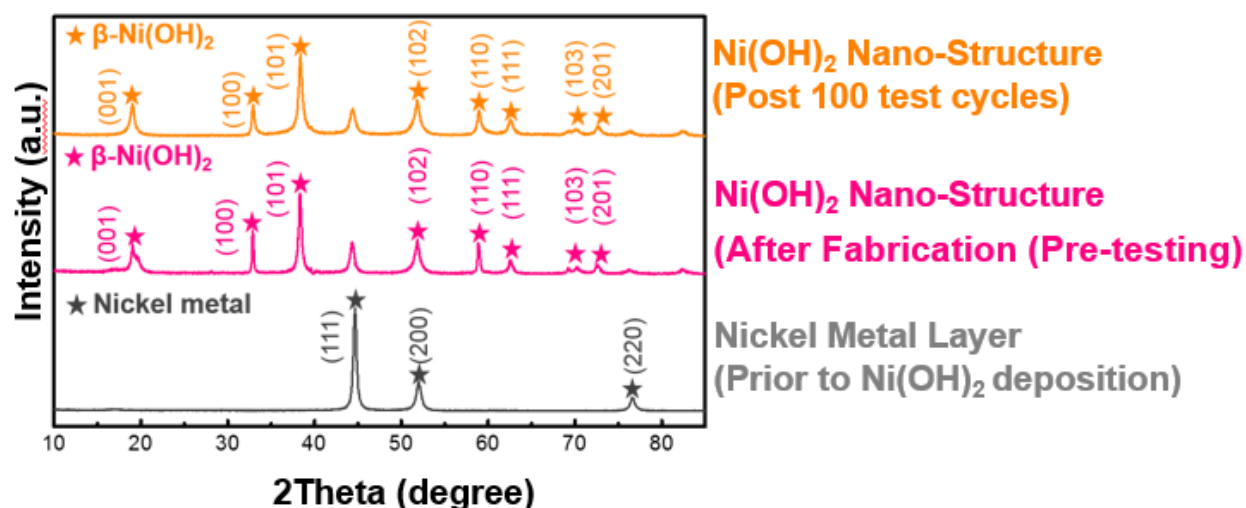


Figure 2.7: XRD analysis of Ni metal sample (grey), and Ni(OH)₂ electrode sample before and after charge/discharge cycling. The diffraction patterns are consistent with nickel and β Ni(OH)₂.

patterns for both the pre-cycling and post cycling Ni(OH)₂ samples were consistent with the β lattice configuration as expected. It is interesting to note that a small intensity peak associated with Ni metal was detected on both Ni(OH)₂ samples. However, it is not clear if this is due to small amounts of nickel being incorporated into the Ni(OH)₂ layer or rather the result of some of the X-ray energy penetrating through the active material and into the base nickel metallization.

2.4 Chapter Summary

The electrodes developed in this work were produced using a simple, 4 step fabrication process that requires no high temperature or vacuum processing and is compatible with roll to roll manufacturing. It was determined that by varying one of the process chemistries, the aspect ratio of Ni(OH)_2 nanoflakes could be tuned, which allow us to investigate the impact of the nanostructure morphology on electrode performance. Various metrology was employed to determine the surface area, thickness and weight of the electrodes while SEM images were used to estimate the size and shape of the Ni(OH)_2 nanoflakes and confirm that the nanostructure was consistent throughout the sample width. Electrode porosity was estimated using a combination of sample mass and density and was found to range between 35-50%. The geometric surface area of the electrodes was estimated using a combination of physical sample dimensions and nanoflake thickness measured using SEM and was found to range from 500-1,000 times the outer surface area of the test samples. In the next Chapter, a summary of electrical and electrochemical characterization tests will be presented and the performance of the three test samples will be summarized.

Chapter 3: Characterization and Modeling of Nanostructured Electrodes

This chapter will summarize the results of various electrochemical characterization tests which were used to determine the performance of $\text{Ni}(\text{OH})_2$ electrodes and investigate the physics underlying electrode operation. In addition, equivalent circuit models will be developed to explain electrode performance under different operating conditions and to extract various figures of merit which correlate to energy and power density.

3.1 Galvanic Charge Discharge

3.1.1 Introduction to measurement technique and figures of merit

Galvano-static charge discharge (GCD), also known as cyclic chronopotentiometry, is a technique used to characterize the response of an electrochemical system to constant charge and discharge currents. The measurement applies a constant current to a test sample located at the working electrode of a test apparatus and then measures the voltage response at the reference electrode [9]. In the case of the electrodes developed here, the application of a constant charging current will oxidize the active material and $\text{Ni}(\text{OH})_2$ will be converted to NiOOH according to the chemical processes described in section 1.3. During charging, the system voltage will change according to the relative concentration of $\text{Ni}(\text{OH})_2$ and NiOOH at the electrode surface, as predicted by the Nernst equation (Eq 10). However, the voltage recorded at the reference electrode will not be the reversible electrode potential, but rather a value offset by ohmic losses and the kinetic overpotential required to drive the forward reaction at the desired rate [9]. During a constant current discharge, the conversion process is reversed and the measured electrode voltage will be polarized from the reversible electrode potential in the opposite direction. This effect can be seen in Figure 3.1 which shows the voltage vs time relationship for a complete 10mA galvanic charge and discharge cycle for sample 1.

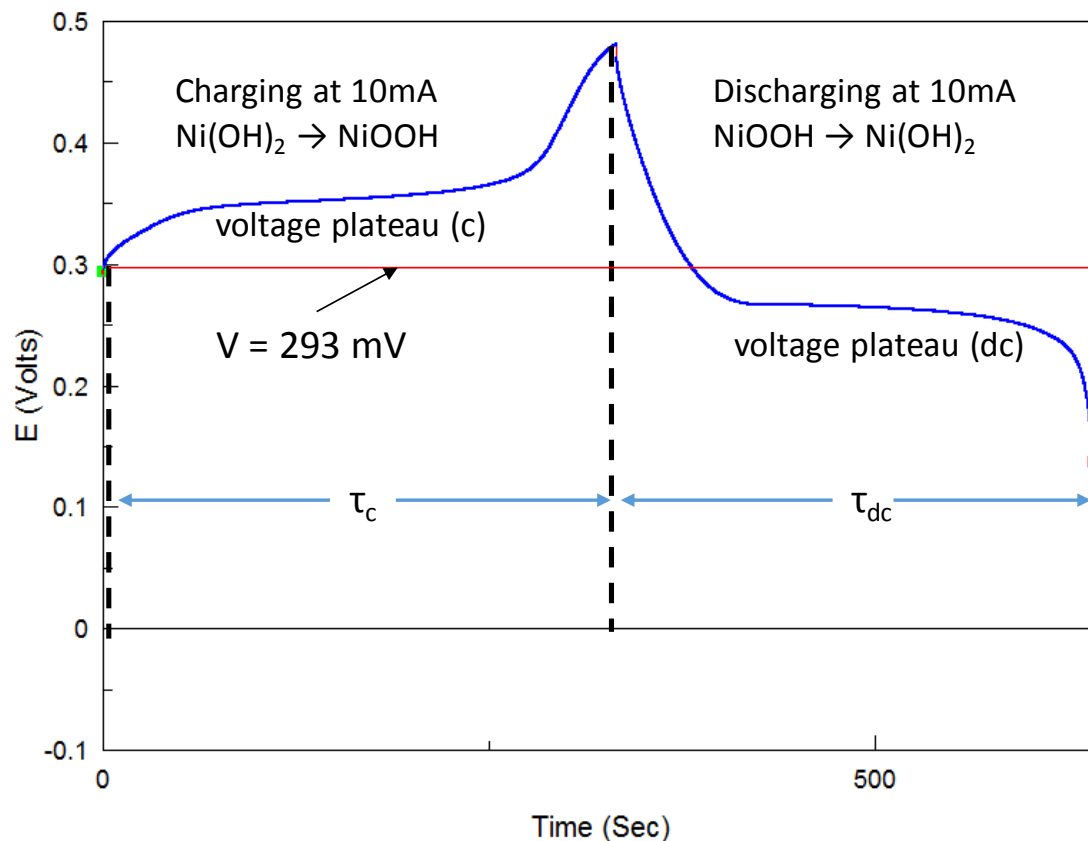


Figure 3.1: Example of a Galvanic Charge / Discharge (GCD) curve where a constant current is applied to a test sample and the voltage response is recorded as a function of time. During the charge cycle, (left half of the figure) Ni(OH)_2 is converted to NiOOH and the reverse process occurs during the discharge cycle (right half of figure). Note that $\tau_c \sim \tau_{dc}$ indicates a reversible reaction and that the charge and discharge voltage plateaus are polarized above and below $\sim 293 \text{ mV}$, the standard reduction potential of the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple. Electrode performance was measured using an Ag/AgCl ref electrode in 2M KOH .

The Nernstian behavior of the charge and discharge curves is clear as the two voltage plateaus are roughly symmetrical about $\sim 293 \text{ mV}$, the standard reduction potential of the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple [8]. Figure 3.1 also illustrates the rapid increase or decrease in electrode voltage near the ends of the charge and discharge processes respectively. As discussed in section 1.5.2, this rapid increase in voltage is due to one of two mechanisms. Either the active material is completely oxidized/reduced per equation 11 or one or several of the reactants are

depleted due to mass transport limitations which results in a rapidly increasing concentration overpotential [8][9]. The latter mechanism occurs when the reaction is driven at GCD currents which exceed the so-called limiting current (i_l) which was defined in section 1.5.2. A key figure of merit for GCD curves is tau (τ) which is defined as the time lapse between the onset of a constant current and the peak of the rapidly increasing voltage region [9]. In Figure 3.1, the values of tau for the 10mA charge (τ_c) and discharge (τ_{dc}) curves are highlighted and are approximately equal. This symmetry in charge and discharge time indicates that the forward and reverse reaction rates of the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple are similar and that the reaction is highly reversible [9]. There are three primary figures of merit that will be extracted from the GCD experiments conducted here. The first of these is capacity, or the amount of charge in coulombs that can be extracted from the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple. Typically, battery electrode capacity is reported on a mass basis in units of mA•h/g and in the case of Ni(OH)_2 the maximum theoretical capacity can be calculated as follows [8]

$$(96,485 \text{ C/mol} / 92.7 \text{ g/mol}) / 3600 \text{ s/h} = 289 \text{ mA}\cdot\text{h/g}$$

A second figure of merit is electrode capacitance. As was mentioned in section 1.5.1, this metric is slightly problematic as the Ni(OH)_2 storage mechanism is clearly electrochemical and not electrostatic, as is the case for a traditional supercapacitor electrode material. However, given that many of the research groups in this space report capacitance, the performance of the devices developed here will also be reported on a specific (F/g) and volumetric (F/cm^3) basis. As is the case with other groups reporting this metric, the GCD curves will be approximated by a straight line and the electrode capacitance will be calculated as

$$C = i / \left(\frac{dv}{dt} \right) \quad (28)$$

where i is the GCD current, dv and dt are the voltage range and time required to fully charge or discharge the device [15][7]. Based on the specific voltage window used in these experiments, which will be discussed in more detail in the next section, the maximum theoretical capacitance for the $\text{Ni}(\text{OH})_2$ electrodes developed here can be calculated as follows:

$$C = 289\text{mA}\cdot\text{h/g}\cdot 3600\text{ s/h} / 0.048\text{ V} = 2190\text{F/g}.$$

The third and perhaps most important metric extracted from the GCD measurements is the device energy density. Energy density for a battery active material was defined in section 1.5.2 by equation 6 and is typically reported in units of $\text{W}\cdot\text{h/kg}$ or $\text{W}\cdot\text{h/L}$. However, given the shape of the GCD curves, energy was calculated according to

$$E = q \cdot V = i \cdot \int v(t)dt \quad (29)$$

where i is the device current and $v(t)$ is the voltage as a function of time. In this work, the integral was evaluated numerically using a trapezoidal integration technique implemented in a MATLAB script. The voltage used is versus the Ag/AgCl reference electrode, which is a common technique found in relevant literature and can effectively probe the $\text{Ni}^{+2}/\text{Ni}^{+3}$ redox couple that is storing / releasing energy in these electrodes. Finally, device power density was calculated by dividing the energy calculated from the GCD curves by the discharge time and presented in both a specific (W/kg) and volumetric (W/L) basis. Results for all three figures of metric are presented in section 3.3 below.

3.1.2 Experimental set up

All electrochemical measurements presented in this work were conducted using a three-electrode experimental configuration which is shown in Figure 3.2. Measurements were done using a SI 1247 electrochemical interface (Solatron Industries) or a 4827 impedance analyzer (Solartron

Industries) and analyzed using Core_view and Z_view visualization and modeling software [22][23].

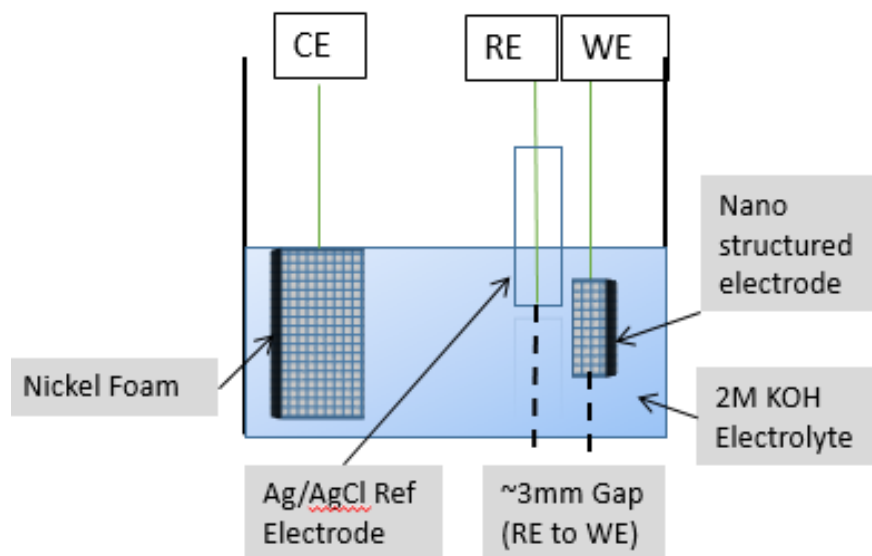


Figure 3.2: Diagram of 3 electrode measurement set up used for the GCD, CV and EIS tests in this work.

Nanostructured $\text{Ni}(\text{OH})_2$ samples were used as the working electrode while high surface area nickel foam and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. 2M KOH was used as the electrolyte solution for all tests. All efforts were made to minimize the uncompensated resistance between the working and reference electrodes [9][10].

A three-electrode measurement technique operates by using the device to be tested as the working electrode and measuring the device's response to various voltage or current excitations at the reference electrode. Current for the system is supplied by the counter electrode and flows to the working electrode through an ionically conductive electrolyte [9][10]. In this work, $\text{Ni}(\text{OH})_2$ test samples were held in position using stainless steel clips to minimize contact resistance between the sample and the test apparatus and to avoid any parasitic reactions with the electrolyte. Saturated Ag/AgCl reference electrodes sourced from BASi Scientific were used for

all measurements and were calibrated against a known good reference sample prior to testing. High surface area nickel foam was used as a counter electrode and a two molar potassium hydroxide (2M KOH) solution was used as the electrolyte. Prior to measurements, all electrical connections were cleaned and sanded to remove any debris or chemical residue and the electrical apparatus was measured with a digital multimeter to verify that electrical resistance was minimized. In addition, care was taken to reduce and standardize the distance between the reference electrode and the working electrode to minimize the impact of uncompensated solution resistance on the measurements.

Test sequence: All three test samples underwent the following test sequence:

- **Burn in Test:** 20 cycles of cyclic voltammetry where the sample was cycled at a scan rate of 20 mV/s between a voltage range of 0 to 0.6 volts. Characterization data was not extracted from this test. Rather it was used to prepare each electrode for the subsequent measurements by activating the Ni(OH) surface flooding the inner volume of the electrode with electrolyte.
- **CV measurement:** 4 individual CV measurements were performed at different scan rates. Details will be discussed in section 3.2
- **GCD measurement:** A sequence of GCD measurements were taken over a range of discharge currents. Details are discussed below in this section.
- **EIS measurement:** A single EIS measurement was performed at a specific state of charge (%SOC) and bias voltage. Details will be discussed in section 3.3

In the case of GCD measurements, each sample was put through an identical test protocol where it was first charged to a known %SOC and then discharged at sequentially higher rates to determine performance as a function of current density. As described in section 3.1, during

charging, Ni(OH)_2 was converted to NiOOH with an applied current of 10 mA over a voltage window of 0 to 0.48 Volts. These charge parameters were determined empirically and were selected to charge each sample to approximately the same %SOC without causing any change in NiOOH composition, which can occur with over charging [24]. During the discharge portion of each GCD cycle, samples were converted back to Ni(OH)_2 over the identical voltage range at discharge currents ranging from 10 to 300 mA. The output response of sample voltage as a function of time was recorded by the instrumentation and the performance metrics of electrode capacity and energy density as functions of current density were calculated and will be discussed below in section 3.1.3. Figure 3.3 shows an example of GCD curves for

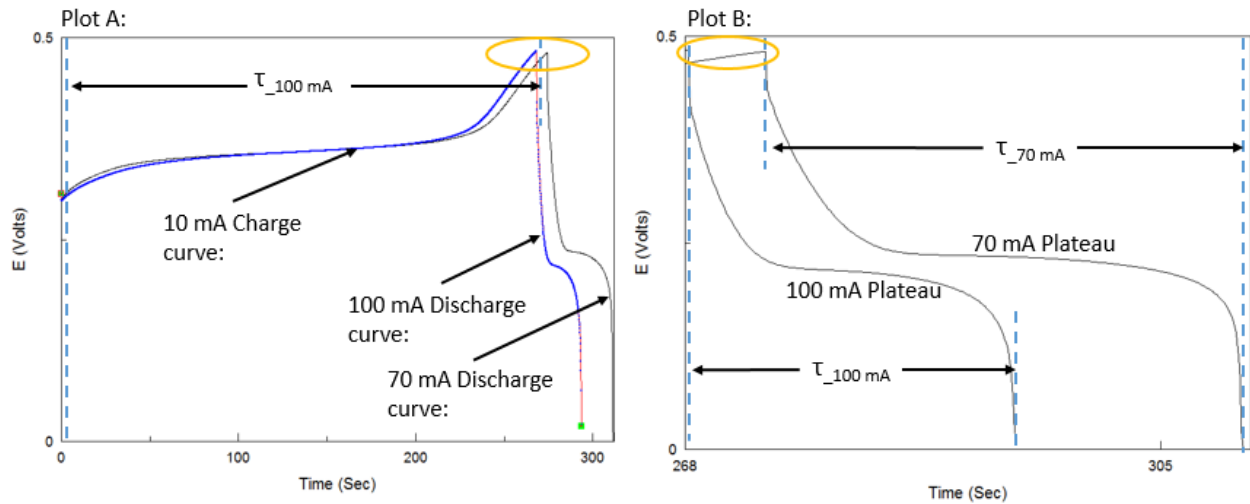


Figure 3.3: Plot A shows GCD curves for Sample 1 being charged at 10mA but discharged at two different currents, 70 and 100mA. While it was assumed that all samples were charged to the identical %SoC, the small horizontal offset between charge curves highlighted in the yellow circle indicates there may be some uncertainty in sample %SOC prior to discharge. Plot B is a zoomed image of the 100mA and 70mA discharge curves. Note the different values of discharge times (τ_{dc}) for the two discharge currents and the vertical offset between the 70 mA and 100 mA voltage plateaus, due to different magnitudes of electrode polarization [8].

Sample 1 testing at different discharge rates. Plot A demonstrates how the 10 mA charge curves are nearly identical while there are clear differences between the 100 mA and 70 mA discharge curves. While it is assumed in this work that all samples achieved the identical %SoC prior to every discharge test, we did observe small variations in sample charge time. An example of this variation is highlighted in the yellow circles in both plot A and plot B. While this variation was observed to be small ($\sim 2\%$), it may have had an impact on the sample %SoC after charging and thus introduced a small amount of uncertainty into the capacity and energy density values calculated from the discharge curves [13]. Plot B illustrates a clear difference in the magnitude of discharge times (τ_{dc}) for the 70 mA and 100 mA discharge curves due to the different rates of chemical conversion at different current densities. In addition, plot B shows a clear vertical offset of voltage plateaus between the two discharge currents. This offset is the result of different magnitudes of electrode polarization, again stemming from different discharge current densities and will be explored more deeply in subsequent sections of this chapter.

3.1.3 Summary of results

The capacity and capacitance performance for all three test samples are plotted as functions of current density in Figure 3.4. The data is reported on an active mass basis for discharge

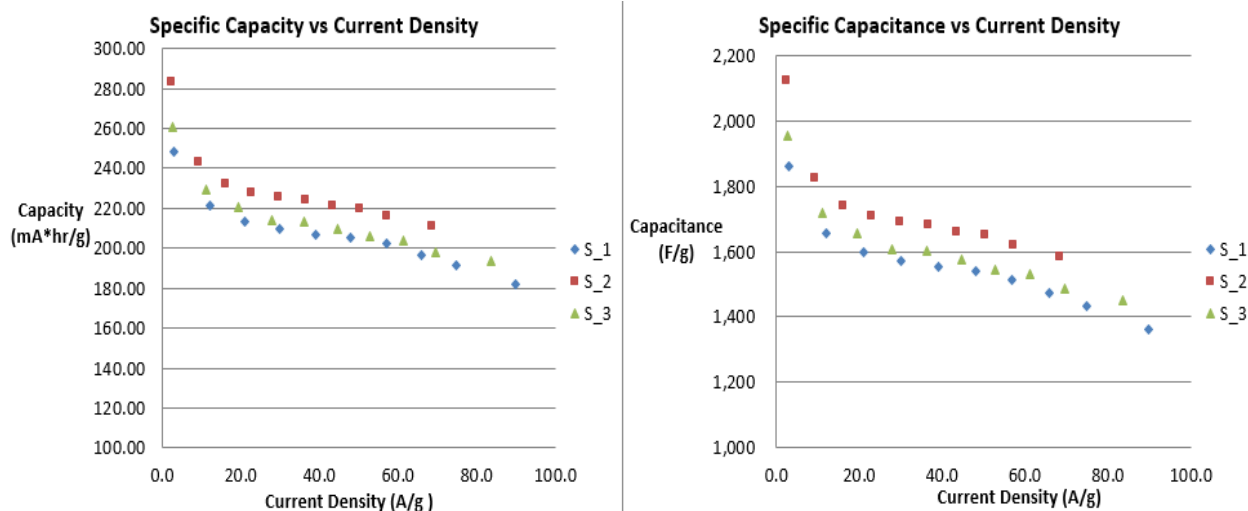


Figure 3.4: Plots of specific capacity (left) and specific capacitance (right) as a function of current density.

Results are reported on an active mass basis for discharge currents of 10 to 300mA. To estimate results on a total mass basis, values can be divided by 2. While S_2 gave the best results of the three samples, all curves have a similar shape characterized by a sharp initial drop and relatively shallow negative slope at higher current densities. Source data is shown in Appendix A.1.

currents ranging between 10-300 mA which translates to current densities of 2-90 A/g depending on the sample mass. If the reader is interested in estimating sample performance on a total mass basis, the reported values can be divided by 2 as roughly 50% of the electrode mass is $\text{Ni}(\text{OH})_2$ while the other 50% is a combination of nickel and PAN. While all samples have impressive performance, sample 2 recorded the highest capacitance and capacity over the full range of discharge currents. Precise values of sample performance at the lowest (10 mA) and highest (300 mA) discharge currents on both mass and volume bases are summarized in Table 3.1.

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect Ratio	Sample_3 Low Aspect Ratio
Specific capacitance (F/g) @ low current density	1862.9 +/- 5%	2123.5 +/- 4%	1954.9 +/- 5%
Specific capacitance (F/g) @ high current density	1362.4 +/- 5%	1586.2 +/- 4%	1450.0 +/- 5%

Volumetric capacitance (F/g) @ low current density	1697.5 +/- 14%	2536.1 +/- 14.3%	2215.5 +/- 14.3%
Volumetric capacitance (F/g) @ high current density	1241.5 +/- 14%	1894.4 +/- 14.3%	1643.4 +/- 14.3%
Specific capacity (mA•h/g) @ low current density	248.4 +/- 5%	283.1 +/- 4%	260.6 +/- 5%
Specific capacity (mA•h/g) @ high current density	181.66 +/- 5%	211.49 +/- 4%	193.2 +/- 5%
Capacity loss over current range	26.9% +/- 10%	25.3% +/- 8%	25.8% +/- 10%

Table 3.1: Summary of test sample performance at lowest (10 mA) and highest (300 mA) discharge currents.

Sample 2 had highest capacitance and capacity on both volumetric and active mass bases with Sample 1 having the lowest values of the group. Uncertainty values were driven primarily by accuracy limitations in sample mass and volume measurements.

At a 10 mA discharge rate, sample 2 recorded a specific capacity of 283 mA•h/g +/- 4% which is nearly 98% of the theoretical value for Ni(OH)₂. In addition, sample 2 had a volumetric capacitance of 2,500 F/cm³ +/- 14.3% which is impressive considering the sample volume includes the space required for the electrode binder, current collector and a porosity of approximately 35%. This value also compares favorably with experimentally determined values of volumetric capacitance of activated carbon in 6M KOH, which can range from 300-500 F/cm³, depending on its average pore size [7] It is not immediately clear why the capacity values of S_3 and S_1 are lower than S_2. Some of the variation is likely due to measurement uncertainty. It is also possible that sample morphology may play a role, however it is not possible to make this claim without performing additional tests that will be reviewed in subsection sections. It should be noted that on a volumetric capacitance basis, S_1 measures significantly lower than S_2 and S_3. This could be a result of having a significantly higher porosity (~50% vs 35%) which likely results in less active material being contained within the sample volume. An additional figure of merit listed in Table 3.1 is capacity loss over current

range, which is defined as the ratio between the capacity measured with a discharge current of 300 mA and the capacity measured at a 10 mA discharge. Effectively, this parameter is a measure of the charge, or the number of coulombs, that can be extracted at different rates of discharge. Since capacity is one of the two factors that determines energy density, capacity loss is a partial measure of an electrode's energy density as a function of discharge rate and therefore one indicator of power density. As the data in Table 3.1 shows, all three samples were measured to have a similar amount of capacity loss ranging from 26.9% on S_1 to 25.3% on S_2. In addition, as Figure 3.4 illustrates, all three samples exhibited a similar pattern of capacity loss as a function of current density, characterized by a steep initial drop and then a more gradual rate of decline at higher current densities. Roughly speaking, all three test samples lose approximately 50% more absolute capacity when they are discharged at 40 mA compared to 10 mA than when they are discharged at 160 mA compared to 40 mA. This non-linear rate of capacity loss with current density can be partially explained by examining how the time required to discharge the electrode (τ_{dc}) varies with current. Figure 3.5 shows a plot of τ_{dc} as a function of current density. Obviously, we expect τ_{dc} to decrease as higher currents drive a fast rate of NiOOH

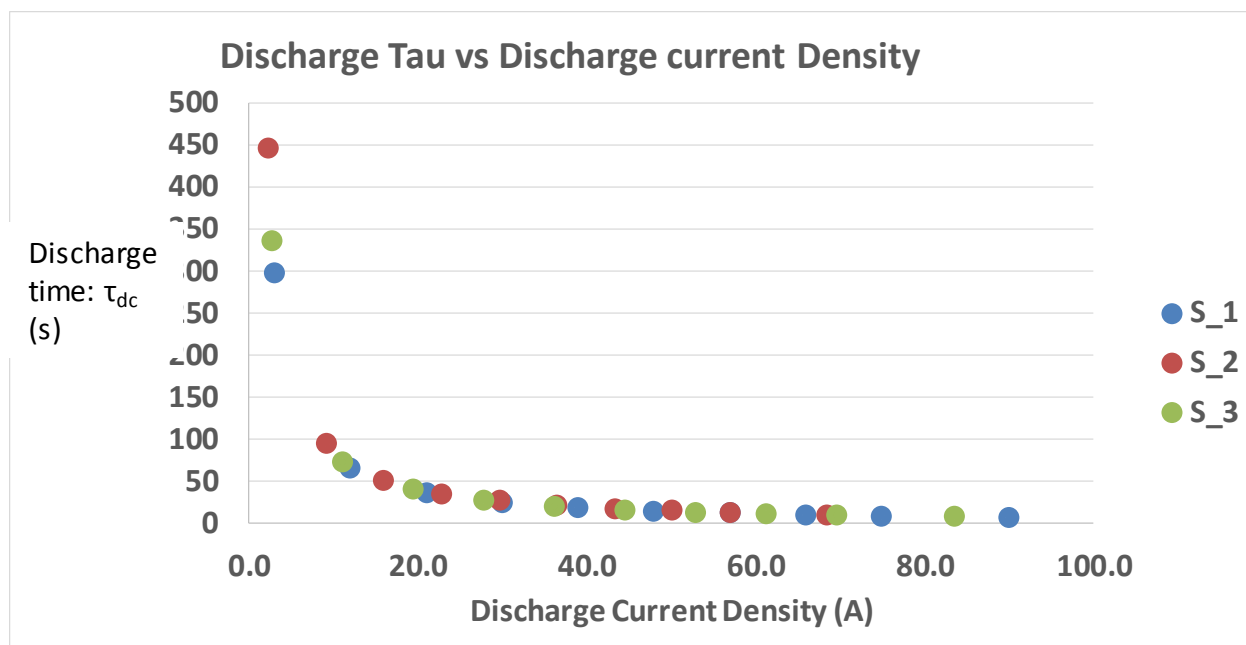


Figure 3.5: A decrease in discharge tau (τ_{dc}) is expected with increasing current density. However, the data indicates that some components of the active mass require a significantly longer discharge time than others. For example, it requires 447 seconds to extract 4.47 coulombs of charge from S_2, but only 11 seconds to extract 3.34 coulombs, or approximately 75% of the total.

chemical conversion. However, τ_{dc} is also decreasing at higher currents as less charge is being extracted from the test samples. For example, at a 10 mA discharge rate, τ_{dc} is 447 seconds and 4.47 coulomb of charge is extracted from S_2. However, at a discharge current of 300 mA, 3.34 coulombs of charge are extracted from the same sample in approximately 11 seconds. This data implies that a small portion of the electrode's active mass has a time constant on the order of 100 seconds while much of the Ni(OH)_2 material has a time constant on the order of <10 seconds.

One possible hypothesis for this effect is that certain sections of the nanostructured electrodes are becoming mass transport limited at high rates of discharge. It is conceivable that either thicker regions of Ni(OH)_2 nanoflakes or regions deep inside the electrode could have large mass transport time constants due to long characteristic diffusion lengths. Interestingly, the fact that

all three samples have similar amounts and rates of capacity loss with current suggests that this effect may not be correlated to mean nanoflake aspect ratio or thickness. We will leave this topic for the moment but additional analysis will be presented in later sections of Chapter 3 to attempt to explain this phenomenon. Sample energy and power performance calculated on both an active mass and volume basis are shown in the Ragone plots in Figure 3.6. Overall, the performance is impressive with Sample 2 achieving

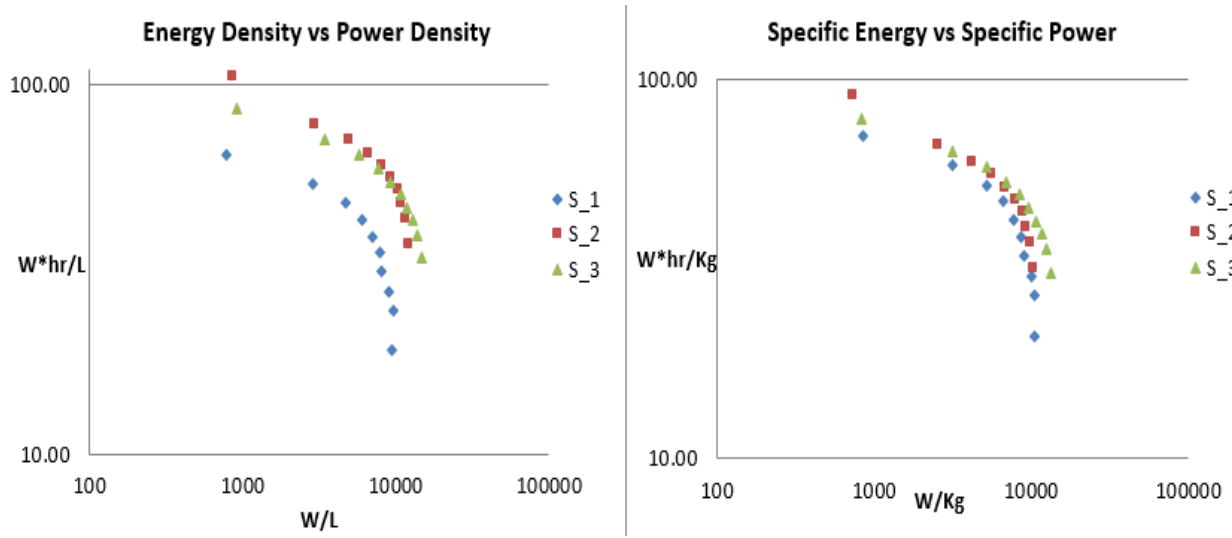


Figure 3.6: Ragone plots for energy and power density (left) and specific energy vs specific power (right).

Specific energy and energy density appear correlated to the capacity values presented in Table 3.1 with the performance ranking as follows: $S_2 > S_3 > S_1$. S_3 recorded the highest power density and specific power, while S_1 recorded the lowest values for both metrics.

an energy density of 90.4 W•h/kg (+/- 4%) and specific power of 727.6 W•h/kg (+/- 4%) a 10 mA discharge rate. In addition, at 300 mA, S_2 maintained a specific energy of 31.1 W•h/kg (+/- 4%) and achieved a specific power of 10,284 W/kg (+/- 4%). This is an order of magnitude increase in device power with only a 3x decrease in energy. It is difficult to compare these performance results to commercial devices given the radically different geometry and integrated current collector of the electrodes developed here. However, this power performance is on par

with commercial supercapacitor devices and the specific energy performance is roughly equivalent to commercial NiMH batteries [7][8]. Precise values of sample energy and power performance at the lowest (10 mA) and highest (300 mA) discharge currents on both mass and volume bases are summarized in Table 3.2. Looking at a sample to sample performance comparison, energy density and specific energy seem correlated to electrode capacity

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect Ratio	Sample_3 Low Aspect Ratio
Specific Energy at low current (W•h/kg)	71.0 +/- 5%	90.4 +/- 4%	78.4 +/- 5%
Specific Energy at high current (W•h/kg)	21.1 +/- 5%	31.8 +/- 4%	30.68 +/- 5%
Specific Power at low current (W/kg)	857.2 +/- 5%	727.6 +/- 4%	837.5 +/- 5%
Specific Power at high current (W/kg)	10,434.1 +/- 5%	10,284.6 +/- 4%	13,258.5 +/- 5%
Energy Density at low current (W•h/L)	64.7 +/- 14%	105.7 +/- 14.3%	86.6 +/- 14.3%
Energy Density at high current (W•h/L)	19.2 +/- 14%	37.2 +/- 14.3%	33.9 +/- 14.3%
Power Density at low current (W/L)	781.1 +/- 14%	851.3 +/- 14.3%	925.4 +/- 14.3%
Power Density at high current (W/L)	9507.6 +/- 14%	12,032.3 +/- 14.3%	14,650.7 +/- 14.3%
Specific Energy Loss over Current Range	70.3% +/- 10%	64.9% +/- 8%	60.9% +/- 10%

Table 3.2: Summary of specific and volumetric energy and power performance at low and high discharge currents. While energy density tracks capacity with S_2 recording the highest values and S_1 the lowest, power performance deviates from this trend with S_3>S_1>S_2 on a mass basis and S_3>S_2>S_1 on a volume basis.

performance with S_2 performing best and S_1 performing worst. However, in terms of power performance, S_3 performed best on both a mass and volume basis. This may be partially explained by reviewing the final metric in Table 3.2, specific energy loss over current range.

This parameter is defined as the ratio between the energy measured at 300 mA and 10 mA discharge currents. It captures the energy loss due to the combination of capacity reduction and parasitic voltage losses stemming from either ohmic resistance or kinetic / mass transport induced overpotential. While the specific energy loss for all three samples is within experimental uncertainty, the absolute values are roughly correlated to sample power performance with S_3 losing the least energy at 60.9% and S_1 losing the most at 70.3%. Finally, when we compare sample capacity loss to sample energy loss, we see that on average the samples lose rough 25% of their capacity over the range of discharge currents but roughly 65% of their energy. This indicates that while capacity loss is significant, voltage loss due to ohmic resistance or electrode polarization is a larger contributor to device energy loss and high-power performance. An initial attempt to quantify the magnitude of sample voltage loss as a function of current density is presented in the next section.

3.1.4 Polarization curves.

As mentioned in section 1.5.2, when an electrode is driven away from equilibrium, it becomes polarized due to ohmic, kinetic and mass transport losses [8][9]. One way to quantify the combined magnitude of these voltage losses as a function of electrode current is by plotting a polarization curve [8][13]. For all test samples, the midpoint value from the voltage plateau of each discharge curve was recorded and then graphed versus discharge current. Figure 3.7

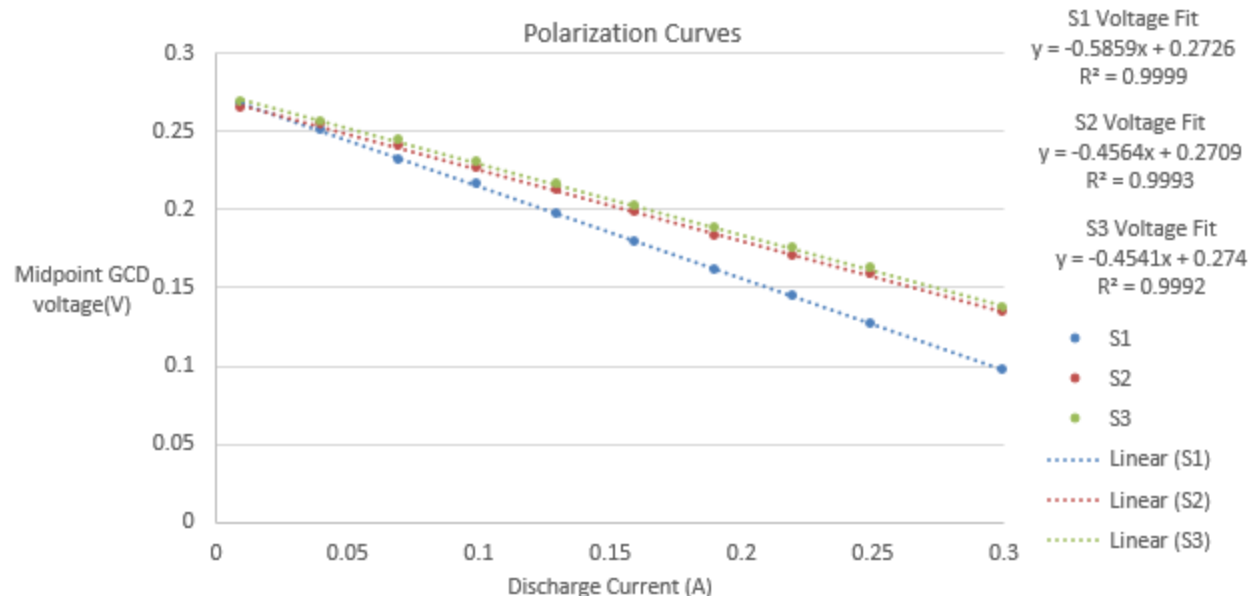


Figure 3.7: Polarization curves for Samples 1-3. Midpoint values from the voltage plateau of every discharge curve were captured and plotted as a function of current. All three curves were linear indicating polarization losses are likely a combination of ohmic resistance and kinetic overpotential. The slope of the S_1 curve is significantly larger than the slopes of S_1 and S_2, suggesting a partial explanation of poor power performance.

shows the resulting polarization curves. A simple regression analysis confirms all three curves are linear, indicating voltage losses for all three samples are consistent with ohmic resistance and kinetic overpotential [8]. Note the absence of a sharp increase in polarization at high discharge currents, which would indicate the presence of mass transfer polarization as discussed in section 1.5.2. The slope of the S_1 curve is significantly higher than the S_2 and S_3 curves. This result may provide a partial explanation for the low power performance of S_1 and the fact that this sample had the highest specific energy loss over the current range while having similar capacity losses to the other two samples. While the polarization curves of S_2 and S_3 are nearly identical, the slope of S_3 is slightly lower than that of S_2. This may provide some insight as to why S_3 performed slightly better in terms of energy loss while S_2 exhibited

slightly less capacity loss. However, given the experimental uncertainty attributed to these parameters, S_2 and S_3 exhibit effectively the same level of device performance. The next step in this analysis is to perform additional measurements to try and determine how much of this polarization loss can be attributed to ohmic, kinetic and potentially mass transport mechanics. Section 3.2.3 will present a Tafel analysis aimed at quantifying sample kinetic performance. Section 3.3.3 will review EIS measurements that will quantify sample ohmic resistance and provide estimates of mass transport properties.

3.2 Cyclic Voltammetry

3.2.1 Overview of technique, equipment set up and goals of characterization.

Cyclic Voltammetry (CV), is commonly used to characterize the general behavior of an electrochemical system. The technique applies a linear voltage scan rate (v in units of V/s) which ramps the system voltage in one direction over a defined voltage window and then immediately reverses the scan rate and ramps the voltage in the opposite direction [9]. During the voltage sweep, the system's current response is recorded as a function of time and the resulting data is typically presented as an $I \cdot V$ plot. For each of the three test samples in this work, CV curves were generated by sweeping the sample voltage between 0 and 600 mV. Measurements were recorded at four different sweep rates (1 mV/s, 2.5 mV/s, 5 mV/s, and 7.5 mV/s) and two cycles were captured for every measurement to ensure data repeatability. The experimental set up was identical to that described in Section 3.1.1 with the test sample located at the working electrode, the voltage set by the reference electrode and the data captured by a SI 1247 Electrochemical interface. Two CV curves for sample 1, recorded at a scan rate of 7.5 mV/s are shown below in Figure 3.8 below. The two curves are nearly identical indicating an acceptable level of experimental reliability. At the outset of the experiment, the voltage is swept

in a positive direction starting from an initial value of 0 Volts. As Figure 3.8 illustrates, the system current is approximately static at low voltages as the electrode double layer is charged

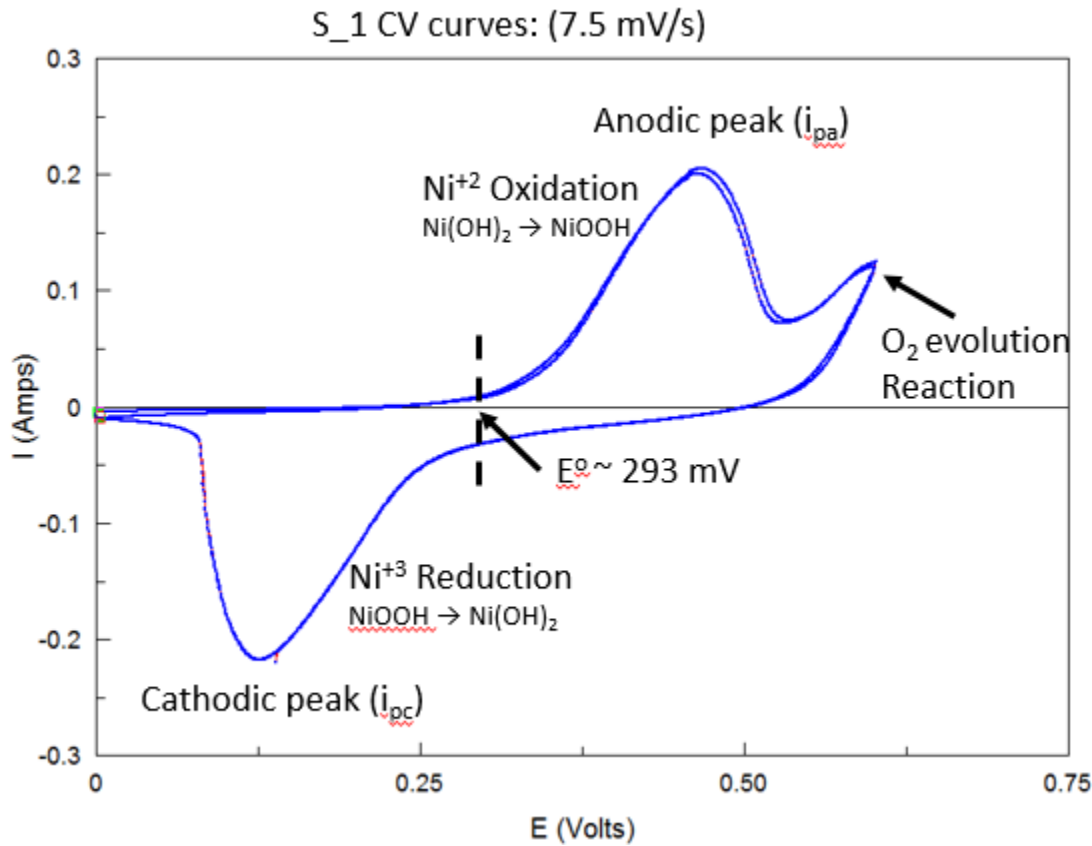


Figure 3.8: CV curve for S_1 recorded at a scan rate of 7.5 mV/s over a voltage range of 0 to 600 mV. As the voltage is swept in the forward and reverse directions, the current will remain approximately static until the standard reduction potential E° is reached and the current begins to rise dramatically [9]. The oxidation and reduction peaks are centered at roughly $E^\circ = 293$ mV, consistent with the theoretical value for the $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ redox couple [8]. The onset of an O_2 evolution reaction can be observed at approximately 0.55 Volts, highlighting the edge of the electrochemical stability window for an aqueous electrolyte.

according to equation 28. However, as the system voltage approaches the standard reduction potential of $\text{Ni}(\text{OH})_2$, the current begins to rise rapidly as a kinetic overpotential drives the oxidation of Ni^{+2} and $\text{Ni}(\text{OH})_2$ is converted into $\text{Ni}(\text{OOH})$ [8]. As the voltage is increased further, it is assumed that the reaction begins to deplete any limiting reactants at the electrode surface and

a concentration gradient begins to form as the reaction becomes mass transport limited [9]. As described in section 1.5.2, this concentration gradient provides the driving force for the diffusion of reactant material to the electrodes. As Figure 3.8 demonstrates, the system current continues to increase with increasing voltage until the current hits a maximum or peak value (I_{pa}) and then begins to decline. This current peak and decline is consistent with the time evolution of the solution to the diffusion equation in a Cottrell experiment, which was described by equation 21 in section 1.5.2. The peak current on the CV curve corresponds to the maximum value of the concentration gradient between the depleted electrode surface and the region of bulk concentration. The subsequent decline in current corresponds to the decrease in concentration gradient as the diffusion layer thickness extends outward from the electrode surface at a rate proportional to $1/t^{1/2}$ [9]. While it is assumed from theory that the mass transport limiting species in this system is the H^+ ion [13], work in the next section (3.2.2) will attempt to confirm this assumption and make an estimate of the diffusion coefficient. It should be noted that a secondary rise in current associated with the onset of an O_2 evolution reaction can also be observed at approximately 0.55 Volts. This behavior highlights the edge of the electrochemical stability window for the aqueous electrolyte used in this work. As Figure 3.8 also illustrates, as the scan rate is reversed and the voltage is swept from 600 mV to zero, the reverse reaction occurs and Ni^{+3} is reduced as $NiOOH$ is converted back to $Ni(OH)_2$. It is also clear that the oxidation and reduction peaks are roughly symmetric about $V = 293$ mV which is consistent with the theoretical value for the standard reduction potential (E°) of the $Ni(OH)_2 / NiOOH$ redox couple [8]. As mentioned previously, CV curves for each sample were generated at multiple scan rates and the results are shown below in Figure 3.9B and two significant effects were

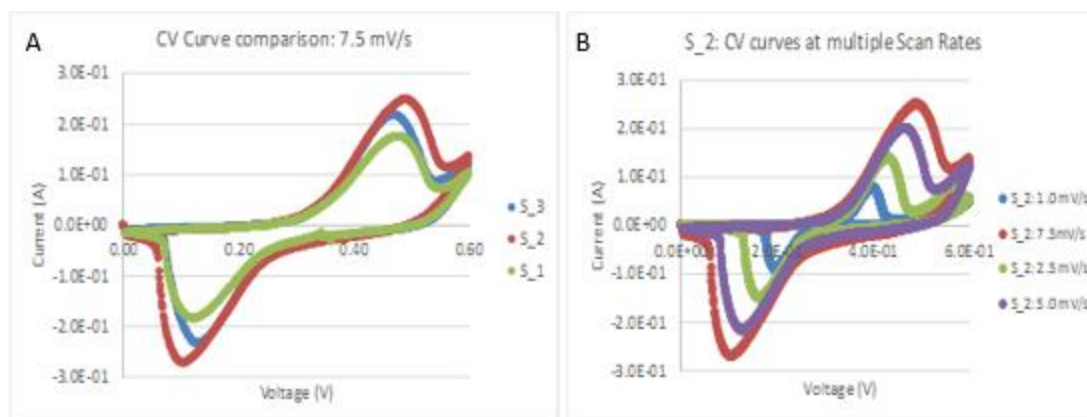


Figure 3.9: A comparison of CV curves (left) for all three test samples at 7.5 mV/s scan rate shows a roughly similar electrochemical response. A plot of S_2 CV curves (right) at 4 different scan rates illustrates increasing capacitive and peak currents correlated to increasing in scan rate [9].

observed. Firstly, the peak currents move up and to the right or down and to the left with increasing scan rate for the oxidation and reduction processes respectively. This effect is due to a combination of the presence of series resistance in the system and the dependence of peak current on scan rate which will be demonstrated in the next section [9]. Secondly, the vertical current offset between the forward and reverse CV curves increases with increasing scan rate. This effect is somewhat consistent with the charging and discharging of an electrochemical double layer, since the magnitude of the measured capacitance is proportional to the applied scan rate (dv/dt), as expressed by equation 28 in section 1.5. However, the magnitude of this effect appears to be far larger than can be attributed to each sample's double layer capacitance which was estimated using an EIS measurement and will be presented in section 3.3.3. We will leave this point for now but return to it in section 3.2.3 where we will discuss the details of a Tafel analysis, which requires a proper accounting of double layer capacitance in order to estimate various aspects of electrode kinetic behavior [10]. Figure 3.9A plots the CV curves for all three test samples measured with the same scan rate of 7.5 mV/s. A glance at the plots indicates all

three samples have roughly the same curve shape and thus exhibit similar electrochemical characteristics. Differences between sample curves, such as peak height and slope are likely due to differences in sample mass or electrical properties which will be discussed in more detail in the following sections. The main conclusion drawn from this section is that even though the nanostructured electrodes developed here have a novel surface morphology, their electrochemical behavior is largely consistent with the established performance of a $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ redox couple [8]. In the next two sections, the CV data discussed above will be used to extract device parameters, which may provide insight on both mass transport and kinetic performance.

3.2.2 Determination of diffusion coefficients.

As mentioned in the previous section, it is assumed that the current peak and decay behavior observed on CV curves is a result of mass transport control during this segment of the measurement. It was shown in section 1.5.2 that the solution to the diffusion equation in the case of a potential step into mass transport control (essentially a CV experiment) will have $1/t^{1/2}$ dependence (see equation 21). It follows that the peak current in a CV experiment should be proportional to the square root of the CV scan rate ($v^{1/2}$ - in units of $\text{V}^{1/2}/\text{s}^{1/2}$) [18][9]. The trend of increasing peak current with increasing scan rate illustrated in Figure 3.9B supports the assumption that our electrodes become mass transport limited at the peak of the CV curves. To confirm this assumption, the peak anodic and cathodic currents for all three test samples were plotted as a function of $v^{1/2}$. An example plot using the peak anodic currents for Sample 2 is shown below in Figure 3.10 and confirms a linear relationship between i_{pa} and $v^{1/2}$. We do note that this plot has a Y-intercept that is slightly offset from zero and while this is unexpected, it is

thought to be an artifact of the uncompensated resistance in the test circuit leading to a slight shift in the peak of the CV curves. It can be shown that the peak current for a reversible reaction

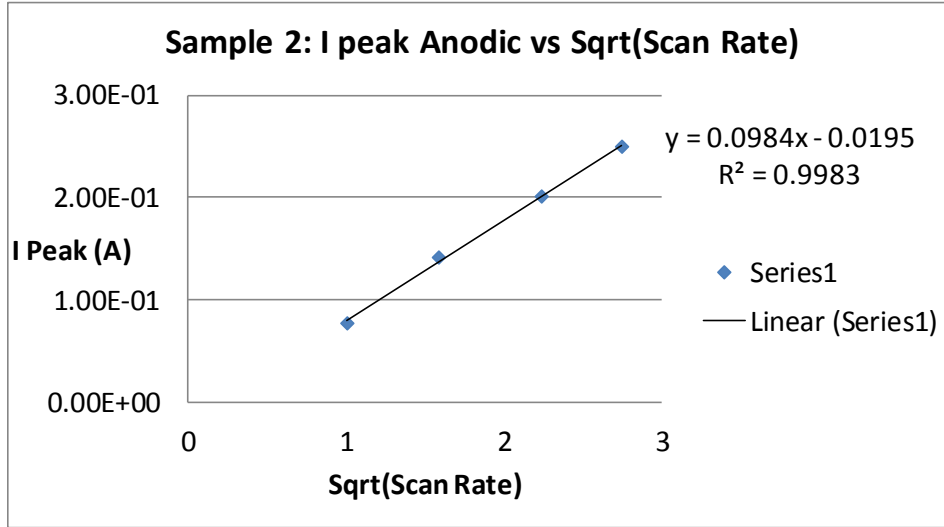


Figure 3.10: Plot of peak cathodic current (I_{pc}) vs $v^{1/2}$ for Sample 2. The linear relationship confirms that the electrode current is under mass transport control at peak currents. Similar plots for S_1 and S_3 confirm the same result and can be found in Appendix B1.

under mass transport control can be expressed as

$$i_p = \left(2.69 \times 10^5 \cdot n^{\frac{3}{2}} \cdot A \cdot D^{\frac{1}{2}} \cdot C^* \cdot v^{\frac{1}{2}} \right) \quad (30)$$

where n , D , C^* and v are as defined previously and A is the real surface area of the electrode [9].

It must be noted that this equation is strictly only valid for a smooth, flat electrode in 1 dimension. Here we assume this equation is still valid for the nanostructured electrodes developed in this work as they consist of many flat, smooth nanoplates, as illustrated by the SEM images in Chapter 2. Equation 30 can be rearranged to arrive at an expression for D , the diffusion coefficient for the mass transport limiting species. Using the peak cathodic currents from the sample CV curves and making some key assumptions for A and C^* , we can estimate a

value for a diffusion coefficient [25]. Clearly, a critical assumption is: which species becomes limiting under mass transport control conditions. Based on the background theory on Ni(OH)_2 electrodes discussed in section 1.3, we assume there are two candidates:

1. H^+ ion: The majority of Ni(OH)_2 electrode theory asserts that proton diffusion through the electrode solid solution is what drives mass transport control [6]. Several research groups have also attempted to calculate the H^+ diffusion coefficient and some of these results will be discussed below.
2. OH^- ion: As equation 1 and 2 illustrate, the hydroxide ion is an essential component in the chemical conversion of Ni(OH)_2 and combines with the H^+ at the electrode surface to form water. In addition, assuming a 2M KOH concentration and 35-50% sample porosity, there is only 10-15% of the OH^- required to complete the reaction initially inside the test samples. To fully convert all the electrode active mass, approximately 85-90% of the required OH^- ions must be transported to the reaction sites from the bulk solution outside the electrode.

Without knowing which one (or both) of these candidates was the mass transport limiting species, we calculated diffusion coefficients for both ions. The input parameters for S_2 are in Table 3.3 and data for S_1 and S_3 can be found in Appendix B2.

Sample_2: Diffusion Coefficient Calculations - Cathodic Peak:					
Proton (H+) limited					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	9.11E-02	1.51E-01	2.17E-01	2.71E-01	
Eff. Surface Area (cm ²)	1195.00	1195.00	1195.00	1195.00	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (M/cm ³)	0.044	0.044	0.044	0.044	
Diff Coeff (cm ² /s)	4.10E-14	4.51E-14	4.66E-14	4.83E-14	4.53E-14
Hydroxide ion (OH-) limited					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	9.11E-02	1.51E-01	2.17E-01	2.71E-01	
Eff. Surface Area (cm ²)	1.46	1.46	1.46	1.46	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (mol/cm ³)	0.002	0.002	0.002	0.002	
Diff Coeff (cm ² /s)	1.35E-05	1.48E-05	1.53E-05	1.59E-05	1.5E-05

Table 3.3: Sample 2 calculations of ionic diffusion coefficient for H⁺ and OH⁻ using equation 30. Note that assumptions for ion concentration and surface area yield dramatically different results.

Clearly, there is a dramatic difference between the Sample 2 calculated values of D with the H⁺ value being approximately 4.9×10^{-14} cm²/s and OH⁻ being roughly 1.5×10^{-5} cm²/s. This nine order of magnitude difference between these values is the result of key assumptions for two of the input parameters to equation 30:

- Surface Area.
 - For the H⁺ ion, we assumed a value for the real surface area of the nanostructure which was extracted from an EIS measurement. The details of this measurement will be discussed in section 3.3 but for the moment, we only note that this technique yields the most accurate value of surface area. For S_2, the surface area was determined to be 1,195 cm².
 - In the case of the OH⁻ ion, we assumed a value equal to the outer surface area of each sample electrode. This value was chosen because the majority of the OH⁻

consumed in the reaction must diffuse into the electrode from the surrounding bulk solution. For S_2, the surface area was determined to be 1.46 cm²

- Molar concentration
 - A value 0.044 mol/cm³ was assumed for the mobile H⁺ ion concentration as this is a value frequently quoted in literature [4] [13]. It is stoichiometrically equivalent to the nickel hydroxide concentration and therefore can be calculated by dividing Ni(OH)₂ density by its molecular weight.
 - The OH⁻ concentration was assumed to be 2 M as this was the concentration of the KOH electrolyte.

Based on these assumptions, the calculated values for H⁺ and OH⁻ diffusion coefficients for all three test samples are listed in Table 3.4. The last column of this table also includes a

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio	Range quoted in literature
H ⁺ diffusion coefficient (cm ² /s)	2.56 x 10 ⁻¹⁴ +/- 3.66%	4.53 x 10 ⁻¹⁴ +/- 12.11%	2.29 x 10 ⁻¹⁴ +/- 9.8%	3.0 x 10 ⁻⁸ to 3.4 x 10 ⁻¹³ [4]
OH ⁻ diffusion coefficient (cm ² /s)	1.03 x 10 ⁻⁵ +/- 13.6%	1.49 x 10 ⁻⁵ +/- 12.5%	1.14 x 10 ⁻⁵ +/- 12.5%	5 x 10 ⁻⁵ [7]

Table 3.4: Summary of calculations and quoted values of diffusion coefficients for OH⁻ and H⁺ ions. Note that the calculated value for the OH⁻ is on the same order of magnitude as the theoretical value while calculated values for the H⁺ ion are an order of magnitude less than the predicted range.

range of quoted values of D for H⁺ and OH⁻. Looking at the OH⁻ results, we see that values for all three samples are similar and of the same order of magnitude as a typical value for the hydroxide ion diffusion coefficient in a KOH electrolyte [7]. However, no correlation to the nanoflake aspect ratios or electrode porosity values calculated in Chapter 2 is apparent. For the H⁺ ion results, the values for all three samples are again similar to each other, ranging from 1.42 x 10⁻¹⁴ cm²/s to 4.53 x 10⁻¹⁴ cm²/s. However, these values are an order of magnitude smaller

than the low end of the quoted range for proton diffusion coefficients in the $\text{Ni(OH)}_2 / \text{NiOOH}$ solid solution [4]. In their excellent paper on the mass transport and kinetic properties of nickel hydroxide, Ta *et al* highlight the relatively wide range of published proton diffusion coefficients (3×10^{-8} to $3.4 \times 10^{-13} \text{ cm}^2/\text{s}$). They cite the use of different fabrication techniques leading to different film densities and porosity, the use of different measurement techniques (CV, EIS and Pulse current) and challenges in accurately measuring nanometer scale films as possible reasons for the lack of consistency between published works [4]. It is possible that some of these factors could be a cause for the very low values measured here. However, it is also possible that the use of CV peak currents is not a valid technique in this instance due to the nanostructure of our electrodes. At this point we will leave this topic as we can't conclusively say which, or either of these results is valid. However, we will return to this subject in section 3.3.4 where we will use an EIS technique to determine diffusion time constants for the test samples and use these values and the mean nanoflake thickness measured in Chapter 2 to estimate diffusion coefficients.

3.2.3 Kinetics: Tafel analysis and kinetic overpotential

The focus of this section will be an attempt to describe the electrochemical kinetic properties of the nanostructured electrodes developed here using information extracted from CV measurements. As was mentioned in Section 1.5, the Tafel equation (eq. 18 – restated below)

$$\eta_k = \frac{R \cdot T}{\alpha \cdot F} \cdot \ln i_0 - \frac{R \cdot T}{\alpha \cdot F} \cdot \ln i \quad (18)$$

describes the kinetic overpotential or polarization as a function of current that is either extracted or delivered to the electrode [9]. Using a procedure known as Tafel analysis, we can generate a so called Tafel plot of kinetic overpotential vs the logarithm of applied current. From the linear region of this plot, we can extract the following Tafel parameters:

- i_0 : the electrode exchange current which was defined previously by equation 15 in section 1.5.2. and is determined by the y-intercept of the Tafel plot. Exchange currents are presented as a function of area (A/cm^2) and electrode exchange current densities can range from $10^{-3} A/cm^2$ to $10^{-9} A/cm^2$ [9].
- b : the Tafel slope (mV/decade) defined by

$$Tafel\ slope = \frac{\alpha \cdot F}{2.3 \cdot R \cdot T} \quad (31)$$

where the variables are as defined previously and the factor of 2.3 is an artifact of the conversion from base e to base 10 in the calculation. From the Tafel slope, we can extract the $RT/\alpha F$ term seen in the Tafel equation above. A typical value for the Tafel slope is 118 mV/decade, assuming a value of 0.5 for α [9].

- Alpha (α): The reaction transfer was defined previously in section 1.5.2 and has a typical value of 0.5 for a 1-step, 1 electron reaction [7].

The procedure to generate a Tafel plot is a series of steps to correct a measured CV curve for various measurement artifacts. The basic procedure is as follows and the progression of each step is show in Figure 3.11:

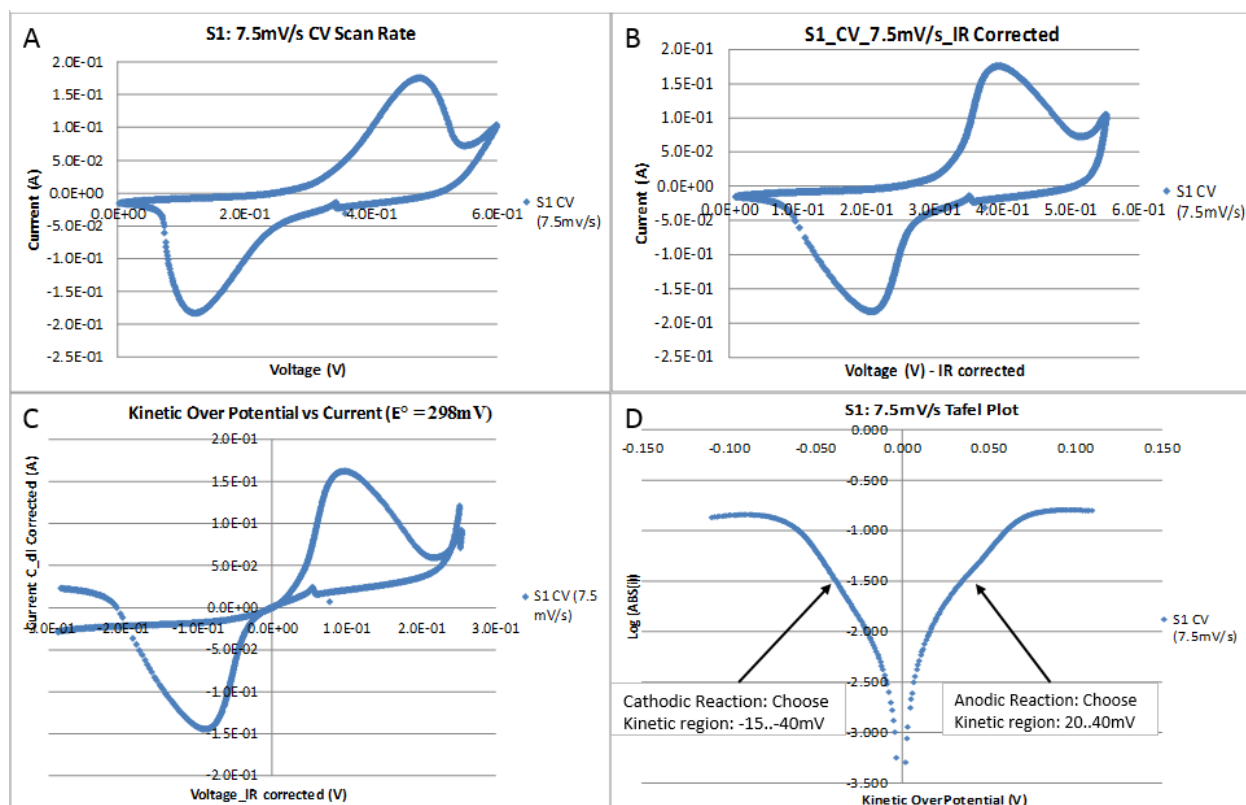


Figure 3.11: Summary of Tafel analysis for S_1 extracted from CV curve with 7.5 mV/s scan rate measurement. The sequence of plots outlines procedure of Tafel analysis. Tafel slope, i_0 and α were extracted from the linear section of the cathodic branch of Figure D.

- Step 1: The starting point is a standard CV curve as shown in Figure 3.11A
- Step 2: A correction for all sources of series resistance in the CV measurement (electronic, solution etc.) is applied by subtracting the equivalent voltage drop from each point in the CV curve. For the analysis shown here, the total series resistance (R_s) was measured for each sample using an EIS technique that will be discussed in section 3.3.2. the R_s corrected CV curve is shown in Figure 3.11B.
- Step 3: The CV curve is shifted in the x-axis such that it is symmetric about the anodic and cathodic halves of the curve. Typically, this shift is equal to the reversible cell potential (293 mV in the case of $\text{Ni}(\text{OH})_2$) for the electrode material however, for all

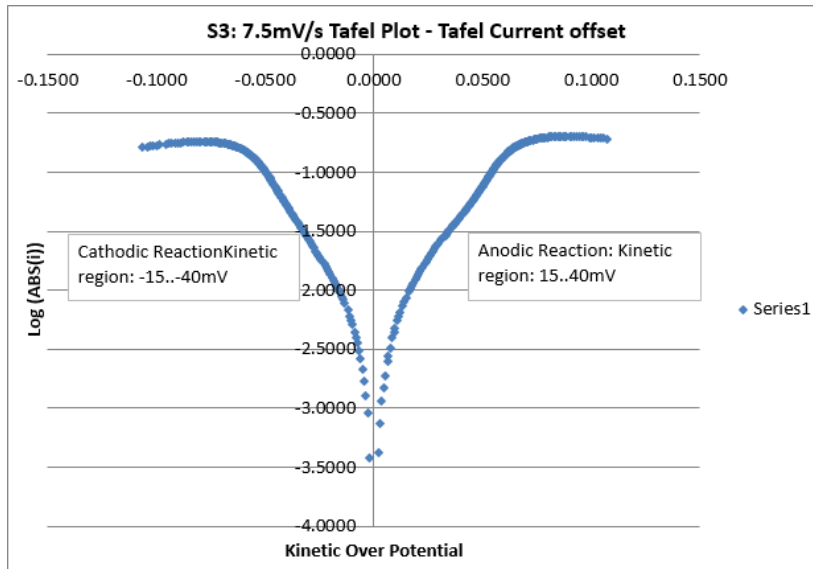
three test samples, the voltage shift was found to be 298 mV. We assume this 5mV shift from theory is due to a systematic error in the reference electrode. In addition to the shift in the voltage axis, the CV curve is corrected for the charging and discharging effects of a sample's double layer capacitance. This is done by applying an offset current to the CV curve such that the anodic and cathodic parts of the CV curve are equal at the equilibrium cell potential (0 volts in Figure 3.11C). The assumption is that any gap between the forward and reverse CV curves at E^0 is caused by stored energy in the sample double layer since at zero overpotential, there should be no net faradic processes charging/discharging the sample. However, as mentioned in the previous section, when we review the value of the currents required to eliminate offset at the equilibrium potential, we find that they are significantly higher than what would be expected based on the measured values of double layer capacitance of each of the samples. Table 3.5

	S_1	S_2	S_3
Tafel Offset current (A)	0.052	0.069	0.058
Calculate Tafel Capacitance (F)	6.9	9.2	7.8
EIS measured C_{dl} (F) (Randles model)	0.022	0.024	0.029
Calculated C_{dl} current (A)	1.65×10^{-4}	1.80×10^{-4}	2.18×10^{-4}

Table 3.5: Comparison of capacitance values calculated using Tafel offset currents for each sample vs estimation of double layer capacitance (C_{dl}) extracted from an EIS measurement. Clearly the values derived from the two methods are significantly different and the source of the discrepancy is unclear. compares the capacitance values equivalent to the Tafel offset current, calculated using equation 32 and assuming a CV scan rate (dv/dt) of 7.5 mV/s, double layer capacitance

$$i(t) = C \cdot \frac{dv}{dt} \quad (32)$$

values extracted from an EIS measurement that will be discussed in Section 3.3.3. There is a 2 order of magnitude difference between these capacitance values and thus some cause to question using the Tafel offset current to generate any meaningful kinetic parameters. However, when a full Tafel analysis was performed using a current offset derived from the EIS C_{dl} measurements, the resulting Tafel plots were of poor quality with significant asymmetry between the anodic and cathodic branches (see Figure 3.12) and more concerning, the lack of a defined linear region for the cathodic branch.



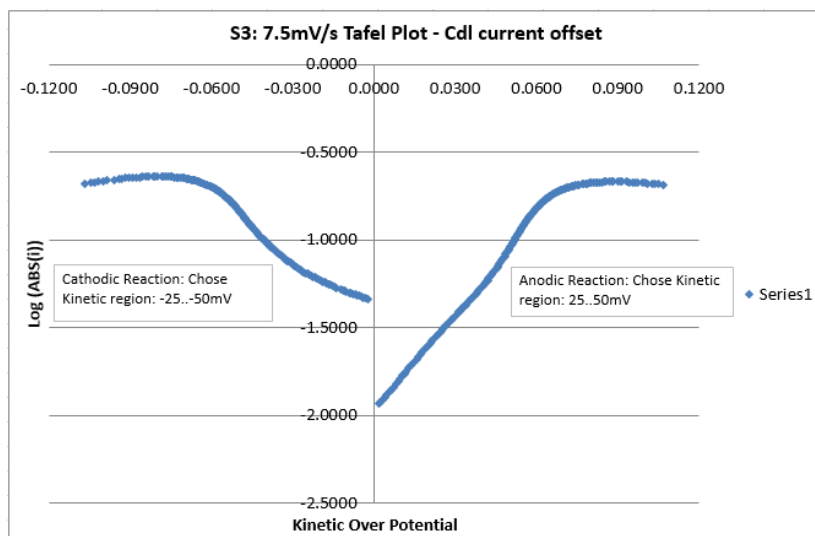


Figure 3.12: Tafel plots derived using Tafel offset current (top) and a C_{dl} current offset (bottom) derived from an EIS measurement. Note the significant asymmetry in the bottom plot in addition to the lack of a defined linear region on the cathodic branch.

While there is no obvious explanation for the discrepancy between the actual (ie Tafel) and expected (C_{dl}) offset currents, we hypothesize that there is additional faradic energy stored after the anodic charge cycle, (ie pseudocapacitance) that is creating the appearance of excessive double layer capacitance in each sample. Given the obvious problems with the Tafel plots derived using the small C_{dl} offset currents, it was decided to present and discuss an analysis based on plots derived from the larger Tafel offset currents in this thesis. We will leave this topic here but note that this point has no clear explanation and is a potential source of uncertainty in the analysis that follows.

- Step 4: We generate the Tafel plot (Figure 3.11D) of kinetic over potential vs $\log(\text{abs}(i))$ which consists of two branches, one for the cathodic (oxidation) and anodic (reduction) section of the CV curves. The linear regions of each branch are the voltage ranges where the sample is under kinetic control and the non-linear roll off at higher overpotential on

each branch indicates the onset of mass transport effects. The kinetic parameters presented here were extracted from the cathodic branch so that they correlate with the data extracted from the Galvanic discharge curves presented in section 3.1. The Tafel slope and i_0 values were extracted using a linear fit between the over potentials of 15 and 40mV. The α parameters were derived from equation 18 using simple algebra.

The Tafel analysis outlined above was performed on CV curves of all three samples for two different CV scan rates (1m V/s and 7.5 mV/s) and the data is presented in Table 3.6.

	S_1 (7.5 mV/s)	S_1 (1.0 mV/s)	S_2 (7.5 mV/s)	S_2 (1.0 mV/s)	S_3 (7.5 mV/s)	S_3 (1.0 mV/s)
Tafel slope (b) (mV/decade)	36.0 +/- 10%	29.9 +/- 10%	33.8 +/- 10%	31.3 +/- 10%	33.7 +/- 10%	30.1 +/- 10%
RT/ α F	0.016 +/- 10%	0.013 +/- 10%	0.015 +/- 10%	0.014 +/- 10%	0.015 +/- 10%	0.013 +/- 10%
ϕ_{CPE}	0.74	0.74	0.70	0.70	0.76	0.76
RT/ α F* ϕ_{CPE}	0.012 +/- 10%	9.6 x 10 ⁻³ +/- 10%	0.01 +/- 10%	9.8 x 10 ⁻³ +/- 10%	0.011 +/- 10%	9.9 x 10 ⁻³ +/- 10%
α	1.64 +/- 10%	1.97 +/- 10%	1.72 +/- 10%	1.89 +/- 10%	1.72 +/- 10%	1.93 +/- 10%
I_0 (A)	2.8 x 10 ⁻³ +/- 10%	6.5 x 10 ⁻⁴ +/- 10%	3.2 x 10 ⁻³ +/- 10%	8.7 x10 ⁻⁴ +/- 10%	3.4 x 10 ⁻³ +/- 10%	7.7 x 10 ⁻⁴ +/- 10%
J_0 (A/cm ²)	2.5 x 10 ⁻⁶ +/- 13.6%	5.9 x 10 ⁻⁷ +/- 13.6%	2.7 x 10 ⁻⁶ +/- 22.1%	7.3 x 10 ⁻⁷ +/- 22.1%	2.3 x 10 ⁻⁶ +/- 19.8%	5.2 x 10 ⁻⁷ +/- 19.8%

Table 3.6: Summary of Tafel analysis output for 1.0mV/s and 7.5 mV/s CV measurements. The absolute parameters for the Tafel slopes, and thus derived values for α , are significantly different from those predicted by theory. However, comparing the results across all three test samples, we see minimal variation, suggesting that the same chemistry and similar kinetics are occurring on all samples. We also note that there are small differences between kinetic parameters derived at different CV scan rates (1 mV/s vs 7.5 mV/s) for each sample which is a source of concern with the data as Tafel parameters should be independent of scan rate. We theorize these variations are an artifact of the electrode nanostructure.

Row 1 of Table 3.6 outlines the Tafel slopes for each sample. The first observation is that these values deviate significantly from the expected value of 118 mV/decade, ranging from 30 to 36

mV/decade. While the reason for this deviation is not clear, we speculate that it is either due to the influence of the sample nanostructure or an error in the analysis and we will explore possible explanations for the deviation later in this section. A second observation is that while the Tafel slope values deviate from theory, there is relatively little variation between samples, indicating that similar chemistry and kinetic behavior is likely occurring at all three electrodes. Thirdly, we observe a small difference in sample Tafel slope values extracted at different CV scan rates. It is interesting to note that the difference in slope as a function of scan rate is most pronounced in S_1, which has the highest nanoflake aspect ratio (~100:1) of all three test samples. According to both the Tafel and Butler-Volmer equations, there is no influence of scan rate on Tafel slope or kinetics more broadly and again we assume this signal is an artifact of the sample nanostructure or due to an error in the analysis. Since the values for the transfer coefficient (α) are calculated from the Tafel slope values using equation 31, they are also significantly different from the expected value of 0.5. Values range from approximately 1.6 to 2.0 for all samples and are as expected, inversely proportional to Tafel slope values. Shifting to the values for exchange current (i_0), we see a similar dependence on scan rate for each sample with values measuring approximately an order of magnitude higher at 7.5 mV/s vs 1/0 mV/s. There is also a weak signal that the i_0 values for S_1 are significantly higher than those for S_2 and S_3 for both scan rates, possibly indicating slightly inferior kinetics with this sample. However, given the level of uncertainty in the analysis, we mention this only as an observation and note that additional EIS measurements discussed in section 3.3.2 will attempt to confirm this signal. To compare the results of these measurements to generally accepted values, it is instructive to normalize the i_0 values by sample area. Values for sample exchange current density (j_0) were calculated using estimations of real sample surface area extracted from EIS measurement covered in section 3.3.2.

J_0 data is shown in row 6 and range from 2.3×10^{-6} to 7.3×10^{-7} A/cm² depending on sample number and CV scan rate. While exchange current densities on the order of 10^{-6} A/cm² are not unreasonable for chemical processes with moderate kinetic rates [9], other published work on Ni(OH)₂ electrodes has quoted higher values of j_0 ranging from 10^{-4} A/cm² [13] and 10^{-3} A/cm³ [4]. However, it should be noted that in both these cases, experiments and simulations were conducted on thin, flat plate electrode geometries. At this point, it seems appropriate to discuss potential causes for the significant discrepancy between the electrodes measured here and accepted values for electrode kinetics. Based on the data, we propose three possibilities. First, the samples could be affected by one or more errors in the experimental technique or analysis procedure. The discrepancy of the capacitive offset current discussed previously is one example of a potential source of error in the analysis. Second, it could be that Tafel analysis is not applicable to the porous, nanostructured electrodes developed here and cannot be used to predict kinetic behavior. This is not unreasonable since several of the governing equations assume a smooth and flat electrode. Third, the electrode nanostructure could lead to non-uniform kinetic behavior that is difficult to interpret with a conventional Tafel analysis. It is clear from the high magnification SEM images presented in section 2.1, that there is a distribution of nanoflake geometries and aspect ratio on each test sample. In one interpretation, each nanoflake could behave like an individual electrode with a unique surface area, leading to a distribution of exchange currents, given the dependence of i_0 on electrode area [9]. A distribution in exchange currents would also lead to a distribution in kinetic time constants, perhaps explaining the variation of extracted i_0 values with CV scan rate [9][2]. An approach to quantify the impact of nanoflake size and shape distribution on various sample properties is presented later in this thesis in section 3.3.1 and if the reader requires more background at this point, they are encouraged to

review that section before proceeding any further. This approach uses an EIS measurement to record the frequency response of the nanostructure electrode and then uses an equivalent circuit model comprised of capacitive phase elements to interpret the result. While the details of this analysis will be presented in section 3.3.1, we note that associated with a capacitive phase element is parameter phi (ϕ_{cpe}) which approximates the dispersion of $R_s \cdot C_{dl}$ time constants on rough or non-uniform electrode surfaces [2]. In the work of Tamas *et. all* on electrochemistry on fractal surfaces, the authors note that when the Tafel slope (b) associated with the kinetic polarization of a flat, smooth electrode is compared with the slope extracted from a flat electrode with a rough surface, the Tafel slopes differ by an amount $b \cdot \phi_{cpe}$ [26]. Given this result, a “ ϕ_{cpe} corrected” Tafel slope was calculated for each test sample and the values are shown in row 4 of Table 3.6. Since all the values of ϕ_{cpe} are less than 1, making this correction reduces the magnitude of the term $RT/\alpha F$ in the Tafel equation, which suppresses the kinetic overpotential, for a given electrode current. Given the evidence that Tafel analysis values can be influenced by deviations from smooth and flat electrode surfaces, the values derived in the analysis above were used to estimate the kinetic polarization using equation 18 and the results are presented in Figure 3.13. As expected, the weak effect of scan rate on Tafel slope propagates through the

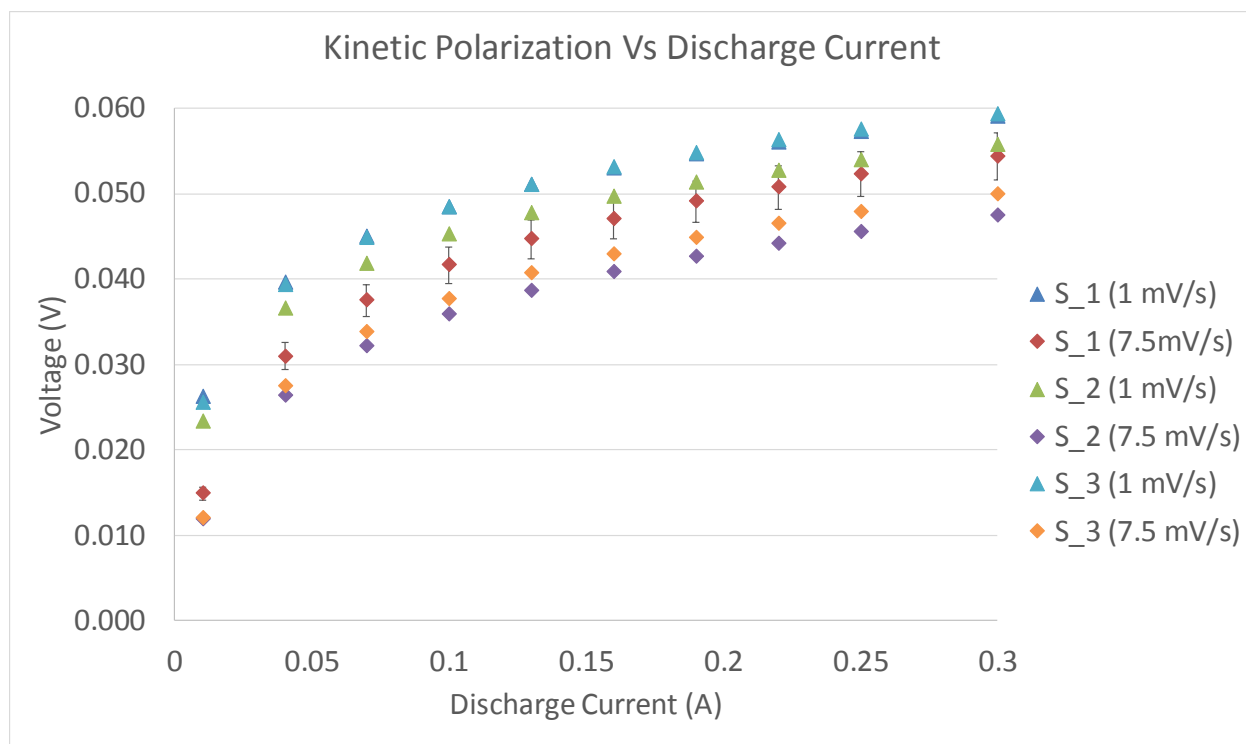


Figure 3.13: Plot of sample kinetic polarization at both high and low scan rates, evaluated at the current set points used in the Sample GCD measurements presented in section 3.1.3. The artifact of weak dependence on scan rate is present as expected from the form of the Tafel equation. However, the curve shape is as expected and there are minimal differences between samples, with the notable exception of S_1 measure at high scan rate.

calculation and is present in the Kinetic polarization curves. However, the shape of the curves is as expected and there is minimal difference between all three samples (~ 10 mV) over the range of operating current, with the possible exception of S_1 measured at 7.5 mV/s. Given this

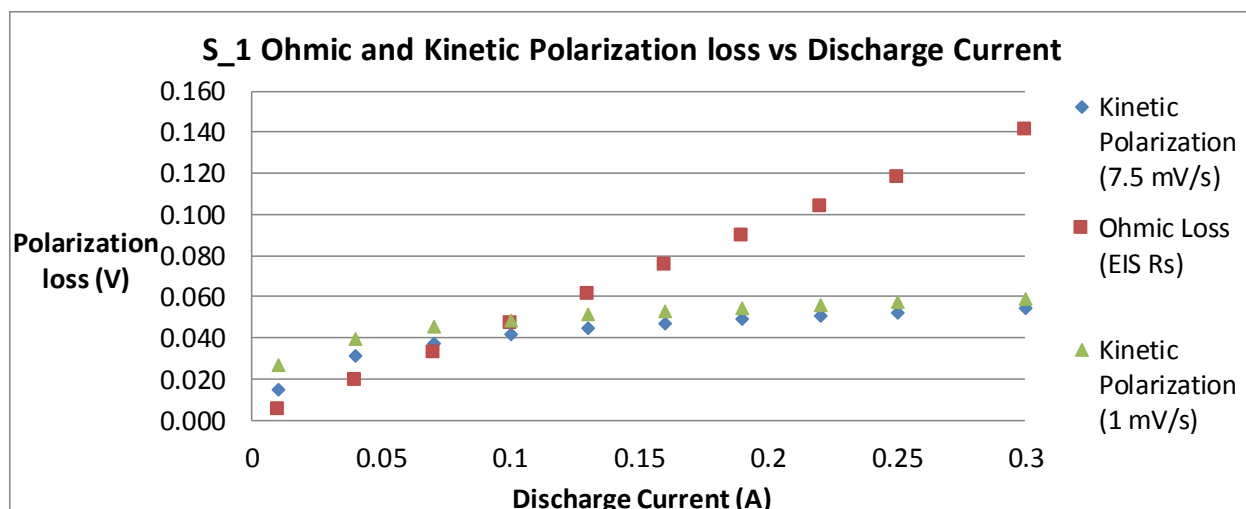


Figure 3.14: Plot of ohmic and kinetic polarization for S₁. Curve shapes are as expected, with Kinetic loss dominating at low currents and ohmic losses dominating at high currents. Kinetic parameters were extracted from a Tafel analysis while ohmic or series resistance (R_s) was extracted from an EIS measurement.

result, the next logical step is to combine the calculated effects of the ohmic and kinetic polarization losses to determine how closely they can model the shape and slope of the actual polarization curves extracted from GCD measurements and presented in section 3.1.4. Figure 3.14 plots the modeled ohmic and kinetic polarization curves for S₁ where the kinetic data is the same presented above from the Tafel analysis and the ohmic data is generated from the sample R_s value extracted from EIS measurements that will be presented in section 3.3.2.

Finally, Figure 3.15 below shows a comparison of actual and predicted polarization curves for S₁. Actual curves were extracted from GCD measurements and presented in section 3.1.4.

Predicted curves are constructed from the sum of the ohmic losses and the kinetic losses, extracted at both slow (1.0 mV/s) and fast (7.5 mV/s) scan rates. The top graph displays the predicted values using uncorrected kinetic parameters and the modeled curves have reasonable accuracy compared to the actual values, overestimating the actual polarization curve by approximately 30 mV at high discharge currents. The bottom graph displays predicted curves

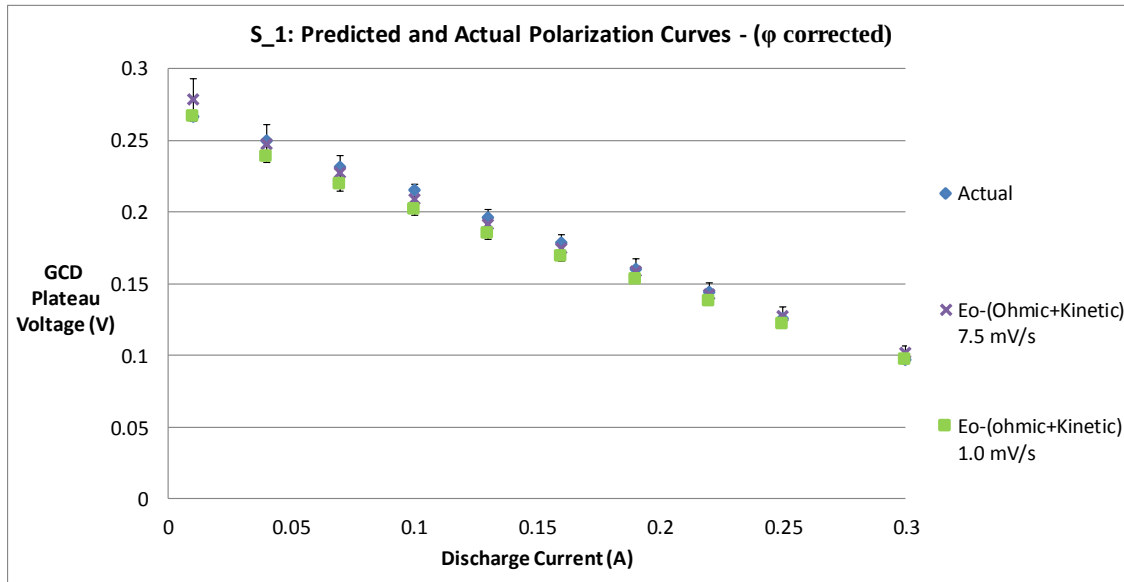
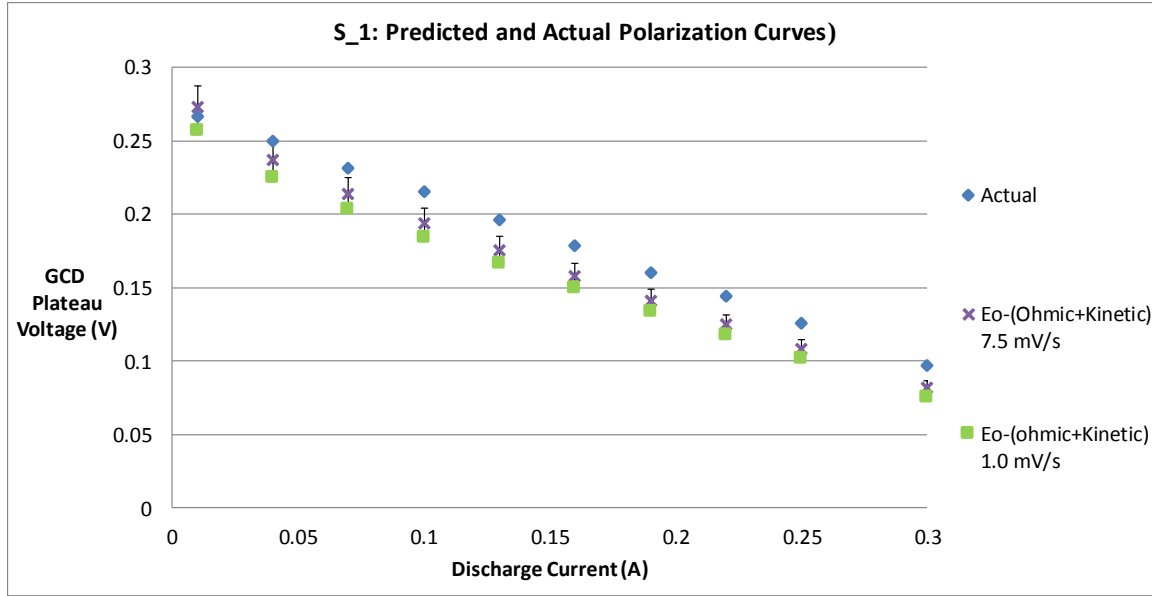


Figure 3.15: Comparison of actual and predicted polarization curves for S_1. Actual curves were extracted from GCD measurements and presented in section 3.1.4. The top graph displays the predicted values using uncorrected kinetic parameters and the modeled curves have reasonable accuracy compared to the actual values, overestimating the actual polarization curve by approximately 30mV at high discharge currents. The bottom graph displays predicted curves that incorporate ϕ_{cpe} corrected kinetic parameters. The bottom graph shows good agreement between actual and predicted values for S_1 at both CV scan rates. Similar results are seen for both S_2 and S_3 using both corrected and uncorrected kinetic parameters.

that include ϕ_{cpe} corrected kinetic parameters. The bottom graph shows very good agreement between actual and predicted values for S_1 at both low and high CV scan rates, with predicted values within +/- 10mV of the actual values. Very similar results are seen for both S_2 and S_3 using corrected and uncorrected kinetic parameters and the data for these samples is shown in Appendix B1. In summary, the sample kinetic parameters extracted from CV curves using a Tafel analysis had significant deviations from expected values. In addition, we observed a weak dependence of kinetic parameters on CV scan rate which is not predicted by conventional electrochemistry. As discussed, it is likely that the deviation is due to experimental or modeling errors, limitations of conventional Tafel analysis or the effects of the electrode porosity and nanostructure making interpretation of the kinetic data non-trivial. However, when these kinetic parameters were used in conjunction with modeled values for sample ohmic losses to predict the sample polarization curves extracted from GCD experiments, we found reasonable agreement between actual and predicted values. Further, when the kinetic polarization values were corrected by CPE parameters that serve as a proxy for the effect of sample nano structure on sample kinetic behavior, we saw very good agreement between modeled and experimental values of sample polarization across a wide range of discharge currents. Recommendations for future work will be presented in section 4.2 and will focus on strategies to determine the root cause of abnormal kinetic parameters measured here and to determine the effects of electrode porosity and nanostructure on electrochemical kinetics of Ni(OH)_2 electrodes.

3.3 EIS measurements: Overview of technique and goals of characterization

Electrical Impedance Spectroscopy (EIS) can be used to characterize an electrochemical system and to develop equivalent electrical circuit models of the system's behavior [2]. The technique applies a sinusoidal input signal and then records the system's response as this signal is swept across a defined frequency range. In the case of the samples measured here, a 5mV peak to peak amplitude signal was swept across a frequency range of 10 kHz to 3 MHz. In addition, the voltage of each sample was controlled by the measurement system to a set point of 269 mV. This voltage bias was chosen as it corresponded to the open circuit voltage of the Ni(OH)_2 electrode material at approximately 10% state of charge. To ensure that all three samples were measured at the same SOC, and thus the same electrochemical condition, each was subjected to an identical 10 mA GCD conditioning cycle prior to the start of the EIS measurement sequence. The experimental set up was identical to that described in Section 3.1.1 with the test sample located at the working electrode, the voltage set by the reference electrode and the data captured by a SI 1247 Impedance and gain / phase analyzer. The output of an EIS measurement is the impedance of the test sample as a function of frequency [2]. This frequency response can be modeled as an equivalent circuit where various electrical components, typically resistors, capacitors and certain specialized elements represent the ohmic, kinetic and mass transport properties of an electrochemical system [2]. Moreover, the variability of the test sample as a function of frequency can provide clues as to what type of electrochemical behavior, for example kinetic or mass transport, dominates at which frequency ranges. EIS measurements can be used to estimate the time constants of kinetic and diffusion processes [2]. Typically, the results of an EIS measurement are presented either as plots of impedance vs frequency, known as complex impedance plots or magnitude and phase angle vs frequency, otherwise known as magnitude or

phase Bode plots respectively. Complex impedance and Bode phase plots for all three test samples are displayed in Figure 3.16 below. Examining the complex impedance plot, all three samples exhibited a similar frequency response, characterized by a truncated semi-circle at high

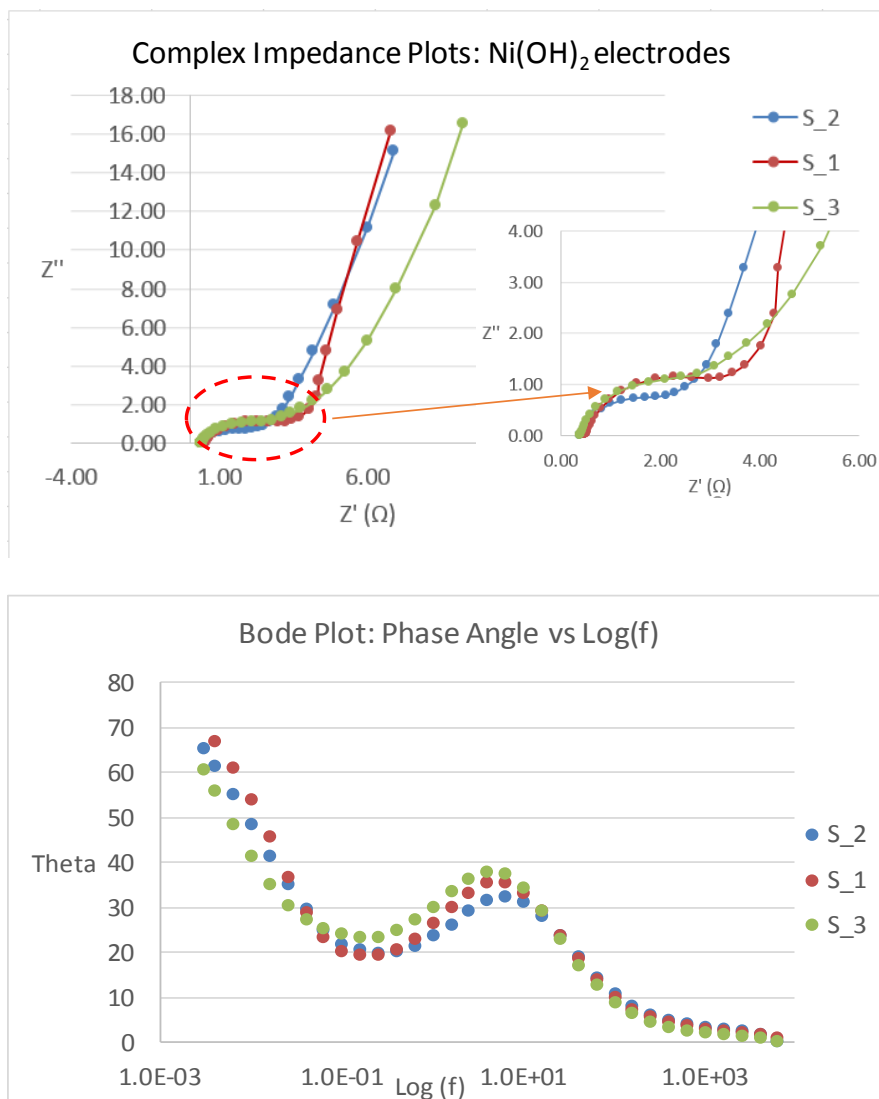


Figure 3.16: EIS results for all three test samples. The shape of the complex impedance plots (top figure) are characteristic of a typical battery electrode [8]. The response of each sample shows a truncated semi-circle at high frequency, which indicates kinetic control of the electrode at this frequency range. At lower frequencies, the plots for all three samples transition to a roughly linear positive slope, characteristic of mass transport control [2]. Note the apparent trend of decreasing slope with increasing sample number, possibly correlating

to the trend in nanoflake aspect ratio. The bode phase plot is included here as sample phase angle will be a significant experimental parameter and will be discussed in subsequent sections. The bode magnitude plots for all test samples are included in the appendix for completeness.

frequency and a transition to a region of roughly linear positive slope as the scan frequency decreases. This EIS response is typical of a battery electrode, where the truncated semi-circle indicates kinetic control of the system at high frequencies or shorter time scales and the quasi-linear section is representative of mass transport control at lower frequencies or longer time scales [8][2]. Two observations can be noted from the complex impedance plots. Firstly, the fact that the semi-circular kinetic region is truncated, rather than fully formed is an indication of the relative magnitudes of the kinetic and mass transport time constants [2]. This point will be discussed in more detail in later sections but for now we state that the relative time scale of these two regimes and how quickly a system transitions from one to the other can have an impact on the power density of the electrode. Secondly, the slope of the low frequency regime on the complex impedance plot shows a trend with sample number, with S1 having the highest slope and S3 having the lowest. Given that the nanoflake aspect ratio was tuned from high to low using different $[\text{NH}_4\text{OH}]$ across the three samples, this trend could indicate a correlation between aspect ratio and the mass transport properties of the electrodes. To quantify these observations and extract various figures of merit from the EIS spectra, several equivalent circuit models were created using custom Corrware's software platform Zview [23]. Specifically, the goal of these models was to estimate the following for each electrode sample:

- Surface area and the relative distribution of nanoflake aspect ratio.
- Magnitudes of Ohmic and kinetic resistances (as defined in section 1.1)
- Kinetic and mass transport time constants.

- Diffusion coefficient and diffusion lengths for the rate limiting mass transport species.

Ultimately, the goal of this work was to determine if the estimates of these sample parameters extracted from the EIS spectrum exhibited any correlation to the trends in electrode performance data that was summarized in sections 3.1 and 3.2. Two modeling approaches were taken, both of which employed a complex, non-linear, least squares method to fit the EIS data. [2][23]. The first of these was to employ Constant Phase Elements (CPE) in conjunction with several resistive elements, to model the kinetic and mass transport properties of the electrodes. A CPE is effectively a non-ideal capacitor, whose impedance Z_{cpe} is described by [7]

$$Z_{CPE} = \frac{1}{T \cdot (j\omega)^\varphi} \quad (33)$$

where the parameter T describes the magnitude of the element's capacitance, j is the imaginary unit, ω is the system frequency, and the parameter φ is an ideality factor ranging between 0 and 1. $\varphi=0$ would represent a purely resistive, or real response and $\varphi=1$ would represent a purely capacitive or imaginary response [7]. CPEs are frequently used to model the behavior of electrochemical interfaces and the specifics of the model used here will be discussed below in section 3.3.1. The second approach was to apply a Randles circuit model to the EIS spectrum of each sample. Randles circuits are perhaps the most common way of modeling the EIS response of a battery electrode where resistive elements are used to capture the effects of ohmic and kinetic losses and an ideal capacitor is used to model the response of the electrode's double layer [9]. To capture the mass transport effects of the electrode in the frequency domain, a Randles circuit incorporates a Warburg element, whose impedance is described by

$$Z_W = \frac{m_0}{\sqrt{\omega}} \cdot (1 - j) \quad (34)$$

where m_0 is the mass transport coefficient as described in section 1.6, ω is the system frequency and j is the imaginary unit [2]. The Warburg impedance can be derived by solving Fick's law in the frequency domain, assuming a concentration gradient that is induced by the voltage oscillations of the EIS measurement and appropriate boundary conditions [2]. As such, a Warburg element is a frequency domain representation of the Cottrell behavior and the $1/t^{1/2}$ rate dependence of mass transfer phenomena that was described in section 1.6. The results of the Randles circuit modeling performed here are described in section 3.3.2 below.

3.3.1 CPE equivalent circuit model results

As mentioned in the previous section, constant phase elements are commonly used to characterize electrode-solution interfaces. In practice, such interfaces will often deviate from ideality due to non-uniformities in electrode shape or defects in the material surface, which make modeling with a non-ideal capacitor appropriate [3] [2]. Physically, CPE behavior can arise from a distribution of time constants τ associated with electrode surface non-uniformity. Considering how a non-uniform surface would impact the electrochemical double layer, this time constant can be defined by

$$\tau = R_s \cdot C_{dl} \quad (35)$$

where R_s is the solution resistance between the electrode surface and the reference electrode and C_{dl} is the double layer capacitance of a portion of the electrode surface [2]. Given the broad distribution of nanoflake morphology observed on the sample surface and bulk SEM images presented in Chapter 2, it seems reasonable that this morphology distribution could result in such a distribution of double layer time constants [3]. In this interpretation, each $\text{Ni}(\text{OH})_2$ nano-flake could be thought of as its own nano-electrode, with a slightly different kinetic and mass transport response than others distributed through the sample. Assuming this interpretation, the equivalent

circuit shown in Figure 3.17 was used to model each sample's frequency response, with resistive elements R_s and R_{ct} used to capture constant ohmic and kinetic losses and the element CPE_{dl} was used to capture the distribution of nanoflake double layer capacitances. A second constant

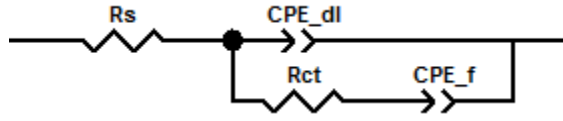
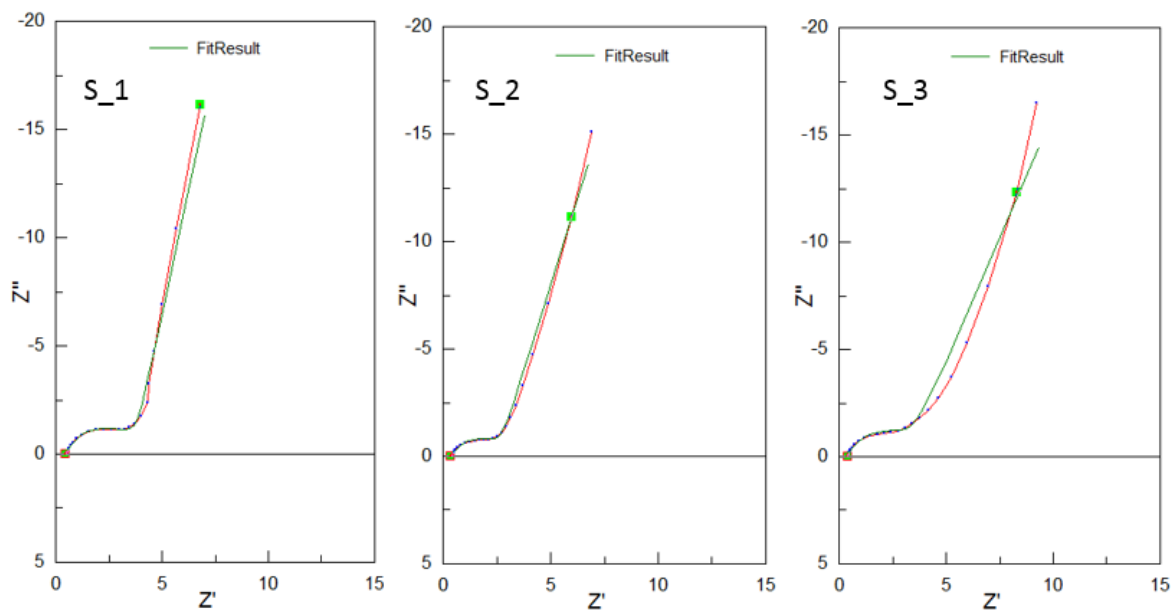


Figure 3.17: Equivalent circuit for CPE model. The assumed distribution of each sample's double layer capacitances and mass transport pathways are modeled with the Constant Phase elements CPE_{dl} and CPE_f respectively. R_s and R_{ct} are as defined previously and represent the ohmic and kinetic resistances in the electrodes respectively.

phase element, CPE_f was used to model the mass transport response of each sample. As mentioned in the previous section, mass transport effects are often modeled using a Warburg element, which is effectively a constant phase element with a value of $\phi = \frac{1}{2}$. However, in this model we assume that a distribution in nanoflake morphologies could lead to a distribution in mass transport pathways, and thus a distribution in diffusion time constants which could be captured by a CPE representation [7] [2]. The results of the model fitting for all the three samples are shown in Figure 3.18. with the sample frequency response outlined in red and the



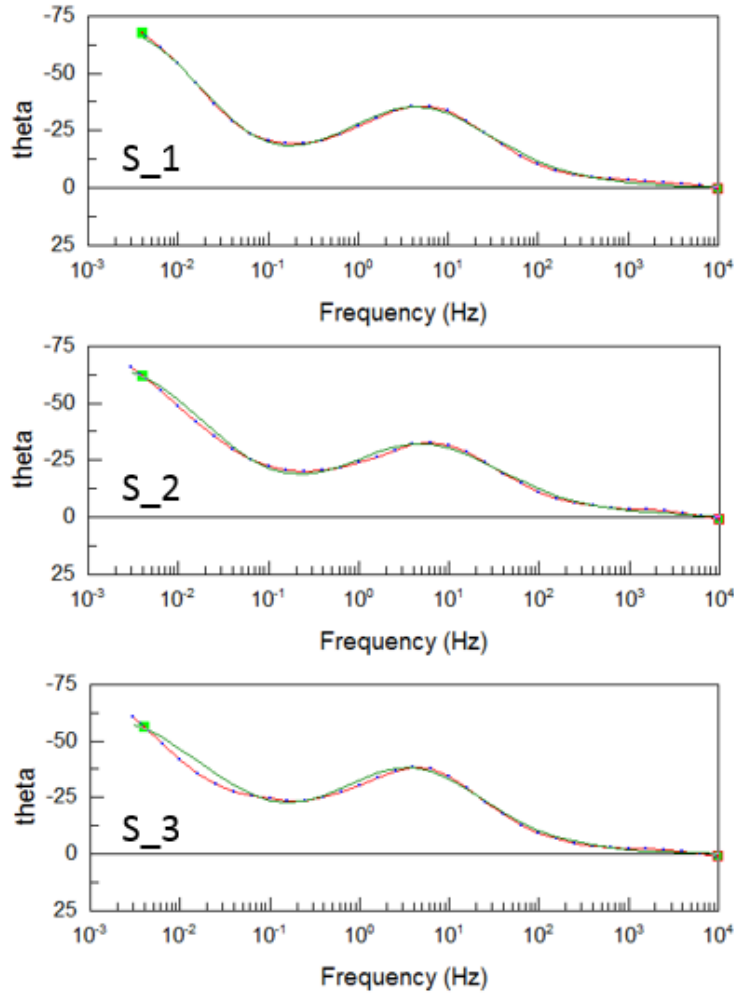


Figure 3.18: CPE Model output showing modeling of the sample frequency response in red and the CPE based equivalent circuit model in green. In general, the model fits appear reasonable for all three samples. Qualitatively, the CPE models appear to yield reasonable fits of the experimental data for all three test samples. Further, these models were used to estimate several figures of merit for each sample and the results are summarized in Table 3.7. The first

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Series Resistance $R_s(\Omega)$	0.49 +/- 6.7%	0.38 +/- 8.5%	0.39 +/- 8.4%
Kinetic Resistance $R_{ct}(\Omega)$	3.60 +/- 12.4%	2.54 +/- 17.6%	3.23 +/- 13.6%

CPE _{dl_T} (F)	0.07 +/- 4.2%	0.10 +/- 2.9%	.09 +/- 3.2%
CPE _{dl_P} (ϕ)	0.74 +/- 5.3	0.70 +/- 5.6%	0.76 +/- 5.1
C _{dl} (F)	0.021 +/- 5.6%	0.023 +/- 4.2%	.030 +/- 4.3%
Real Surface Area (cm ²)	1,036.8 +/- 6.0%	1,133.7 +/- 4.2%	1475.4 +/-4.3%
CPE _{f_T} (F)	1.44 +/- 0.8%	1.64 +/- 0.7%	1.14 +/- 1.08%
CPE _{F_P} (ϕ)	0.87 +/- 2.4%	0.82 +/- 2.5%	0.74 +/- 2.8%

Table 3.7: Figures of merit extracted from CPE based equivalent circuit models. The Rs (series resistance) value for S1 is higher than those for S2 and S3, indicating a higher value of ohmic resistance and correlating with the trend in polarization curves shown in section 3.1.2. The values of ϕ for each sample's CPE_{dl} parameter are significantly <1, suggesting a broad distribution in double layer time constants [2]. Estimates of the real surface area were calculated using double layer capacitance values derived from several model parameters. Finally, note the trend of decreasing CPE_{F_P} values (exponent ϕ) with sample number, possibly indicating a correlation between the distribution of mass transport time constants and nanoflake aspect ratio [3][2].

row of Table 3.7 summarizes the CPE model output for Rs, the total series resistance measured for each sample. It should be noted that this value is an aggregate of the contributions of electrical, solution resistances in the test set up [9]. We observe that the Rs value of S₁ is significantly higher than those for S₂ and S₃, indicated that the total series resistance of this sample is higher than the other two. This correlates with the trend in the slope of the sample polarization curves and sample power density performance which was detailed in section 3.1.2. Model output values for sample kinetic resistance (row two of Table 3.7) do not exhibit any apparent correlation to sample aspect ratio. It is possible that there is a weak correlation to the kinetic parameters that were extracted via the Tafel analysis detailed in Section 3.2.3. S₁ has the highest R_{ct} value of the three samples which is consistent with S₁ having the lowest i₀ values

(see Table 3.4 in section 3.2.3). However, given that the sample R_{ct} values are equivalent to each other within the range of model uncertainty, we can not state anything beyond what was concluded from the calculated values of i_0 in section 3.2.3; that all three samples exhibit similar kinetic behavior. Shifting to the values of the CPE_{dl} exponents (shown in row three of Table 3.7), we note that while there is no clear pattern in this model value among the test samples, all of the values are <0.8 , indicating a significant deviation from ideality [2]. In the interpretation used here, we assume that these exponent values ranging from 0.7 to 0.76 confirm a significant distribution in double layer time constants which is consistent with the observed distribution in nanoflake morphology and the resulting deviation from a smooth electrode surface. We recall that these exponent values were used as correction factors for the Tafel slope parameters calculated in section 3.2, in an attempt to capture the impact of a rough or highly non uniform electrode surface on sample kinetic parameters [26]. In addition, these exponent values and the model outputs the CPE_T parameter, R_s , and R_{ct} values, were used to estimate the double layer capacitance for each sample. The C_{dl} values were calculated according to

$$C_{dl} = T^{\frac{1}{\varphi}} \cdot \left(\frac{1}{R_s} + \frac{1}{R_{ct}} \right)^{1-\frac{1}{\varphi}} \quad (36)$$

and range from 21 mF for S_1 to 30 mF for S_3 [2]. Using a generally accepted capacitance/area value of 40 μ F/cm² for a typical electrochemical double layer [9], estimates of the real surface area of each sample were calculated and are summarized in row 6 of Table 3.5. These values range from 1,036 cm² on S_1 to 1475 cm² on S_3 and while the sample set is admittedly small, it is interesting to note that sample surface area increases as nanoflake aspect ratio decreases.

When these surface area values derived from EIS measurements are compared with the sample geometric surface area estimates derived in Section 2.2.3, we find that the values are of the same

order of magnitude, and in the case of S_1 and S_2, are equivalent to within measurement uncertainty. This result gives some confidence that an EIS measurement is a reasonable method to measure the real surface area of the nanostructured electrodes developed here. Finally, while the physical meaning of the CPE_f_T parameter is somewhat difficult to interpret in this model, we note that the CPE_F_P values (exponent ϕ) are all <1 , indicating non-ideal mass transport behavior. Further, we note that the value of the CPE_f exponent decreases across all three test samples from 0.87 on S_1 to 0.74 on S_3. Given the CPE interpretation assumed here, this trend could indicate a widening of the distribution of mass transport time constants with decreasing nanoflake aspect ratio [3][2]. Overall, we can state that the CPE model predictions for sample series and kinetic resistance were consistent with previous results determined using GCD and CV techniques. In addition, sample surface area estimates derived from CPE_dl parameters were reasonable when compared with estimates calculated using nanoflake feature sizes extracted from SEM measurements. Further, CPE_f values indicated a possible correlation between nanoflake aspect ratio and sample mass transport behavior which will be explored in more depth in the following section.

3.3.2 Randles Equivalent Circuit model Results.

As discussed in section 3.3.1, a Randles model was also employed to analyzed sample EIS data as this is the equivalent circuit representation most commonly applied to battery electrodes. The Randles circuit used here is shown in Figure 3.19. Like the CPE model discussed in the previous section, the elements R_s and R_{ct} capture the respective series and kinetic resistance in the sample

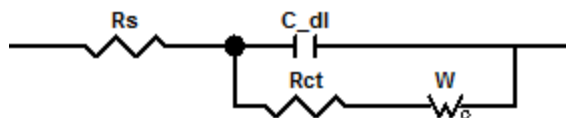


Figure 3.19: Equivalent circuit for Randles model. R_s and R_{ct} are as defined previously and represent the ohmic and kinetic resistances in the electrodes respectively. The C_{dl} term captures the double layer capacitance of the sample while the Warburg element W models the mass transport behavior.

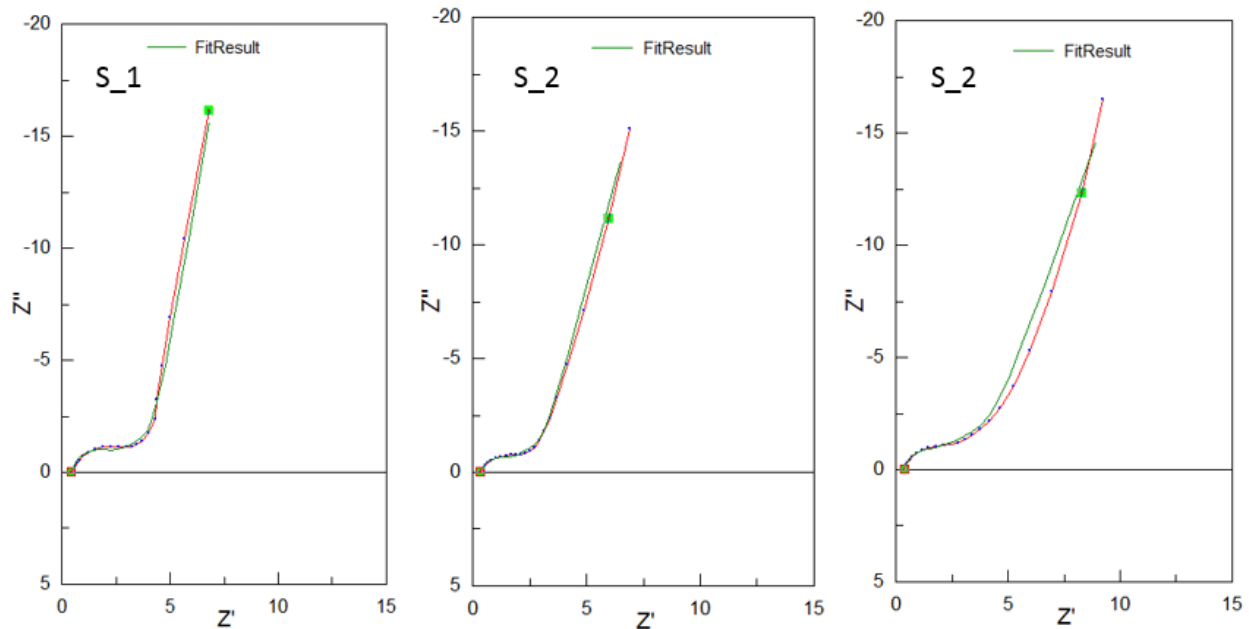
electrodes. However, in contrast to the CPE model, an ideal capacitor, C_{dl} was used to approximate the double layer capacitance of the test samples. This element was selected partly due to a limitation in the allowable number of degrees of freedom permitted by the Z-view modeling software and partly to compare modeling results using ideal and non-ideal capacitive elements [22] [2]. Finally, a Warburg element was used to capture the mass transport behavior of the test samples. To employ the most appropriate type of Warburg element in the equivalent circuits, the following assumptions were made about the mass transport properties of the Ni(OH)_2 nanostructured electrodes:

- As mentioned previously, the species limiting the mass transport performance in Ni(OH)_2 electrodes will be the H^+ ion diffusing in the Ni(OH)_2 / NiOOH solid solution. This assumption is supported by most of published literature on Ni(OH)_2 electrodes and by the Randles circuit modeling results that are presented later in this section.
- The H^+ ions are subject to finite diffusion conditions as opposed to semi-infinite diffusion since the Ni(OH)_2 nanoflakes are obviously of finite thickness [2]. Following this, we assume reflective boundary conditions as it is not physically possible for the H^+ ions to diffuse beyond the Ni metal current collector at the base of the Ni(OH)_2 nanoflakes. Together, these boundary conditions require the use of a so called Warburg open element in the Z-view modeling software [22].

- The mass transport behavior can be most accurately modeled by a generalized Warburg element where the exponent ϕ_w can deviate from a fixed value of $1/2$. This assumption is appropriate given how the phase angle for all three samples never achieves 90 degrees in the low frequency limit of a bode phase plot and correspondingly deviates from a slope of 1 in low frequency limit of a complex impedance plot (see Figure 3.20) [2].

Additionally, the modeling results from section 3.3.2 where the CPE_f exponent term was <1 for all three test samples and correlated to decreasing nanoflake aspect ratio suggest complicated and perhaps multi-dimensional diffusion pathways which are often modeled with a generalized Warburg element [2].

Given these assumptions, the results of the model fitting for all the three samples are shown in Figure 3.20. with the sample frequency response outlined in red and the model fit



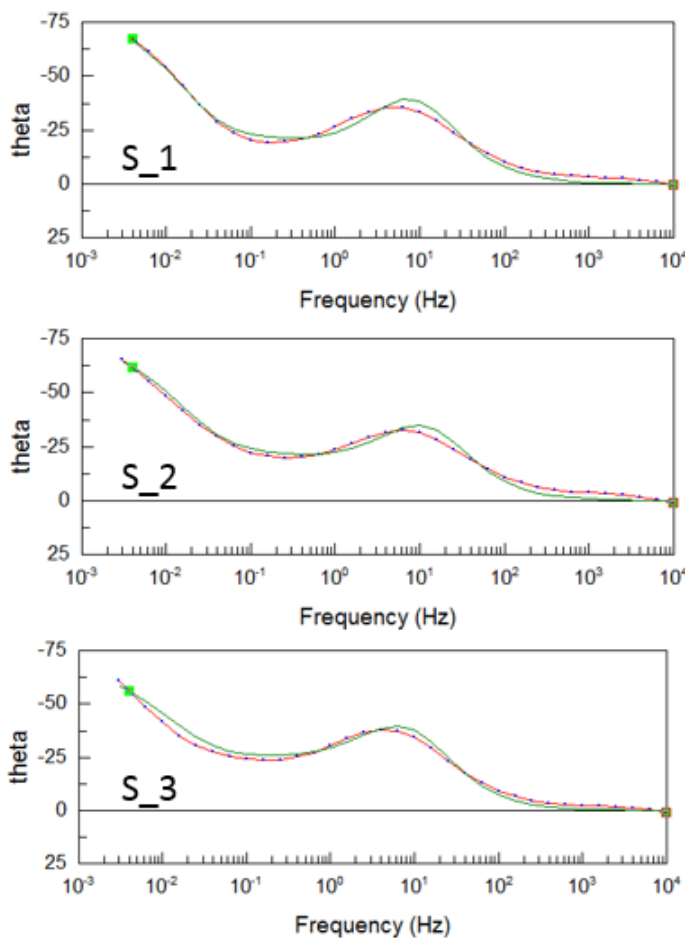


Figure 3.20: Randles circuit model outputs showing the sample frequency response in red and the equivalent circuit model in green. In general, model fits appear reasonable for all three samples.

in green. Qualitatively, the Randles Circuit models appear to yield reasonable fits of the experimental data for all three test samples. Further, these models were used to estimate several figures of merit for each test sample and the results are summarized in Table 3.8.

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Series Resistance $R_s (\Omega)$	0.520 +/- 1.3%	0.413 +/- 8.0%	0.408 +/- 7.6%
Kinetic Resistance $R_{ct} (\Omega)$	1.54 +/- 4.8%	0.88 +/- 4.5%	0.95 +/- 4.1%

Double layer Capacitance C_{dl} (F)	0.022 +/- 3.7%	0.024 +/- 12.1%	0.029 +/- 9.8%
Real Surface Area (cm ²)	1,105 +/- 3.7%	1,195 +/- 12.1%	1,470 +/- 9.8%
Kinetic time constant: τ_k (s) $\tau_k = \frac{1}{(R_{ct})*(C_{dl})}$	0.03 +/- 8.5%	0.02 +/- 16.6%	0.03 +/- 13.9%
Warburg R: “Diffusion resistance” (Ω)	6.0 +/- 10.5%	4.9 +/- 9.1%	7.4 +/- 5.8%
Warburg T: Diffusion time constant: τ_d (s)	13.3 +/- 14.5%	14.9 +/- 0.1%	21.9 +/- 5.6%
Warburg P: (exponent ϕ_w)	0.44 +/- 2.9%	0.42 +/- 5.0%	0.39 +/- 5.3%

Table 3.8: Figures of merit extracted from Randles equivalent circuit models. Like the CPE Model, the R_s value (Row 1) for S1 is higher than those for S2 and S3, indicating a higher value of ohmic resistance and correlating with the trend in sample polarization curves. R_{ct} values (Row 2) are significantly different from those extracted from the CPE model but appear weakly correlated to sample I_0 values extracted from a Tafel analysis. Values of double layer capacitance (C_{dl} -Row 3) are equivalent to those extracted from the CPE model and were used to estimate a real surface area for each sample. Time constants for both kinetic and diffusion processes were calculated and differ by approximately 3 orders of magnitude. Finally, note the trend of decreasing Warburg P values (exponent ϕ) with sample number, suggesting increasingly non-uniform diffusion behavior with decreasing nanoflake aspect ratio [3][2]. However, it must be noted that the significance of this trend is weak given the modeling uncertainties associated with each value of ϕ_w .

Row 1 of Table 3.8 summarize the Randles model output for R_s , the total series resistance measured for each sample. Like the values extracted from the CPE model, the R_s value of S_1 is significantly higher than those for S_2 and S_3 and again correlates with the trend in the slope of the sample polarization curves. Model output values for sample kinetic resistance, R_{ct} (Row 2) are significantly different compared with those extracted from the CPE model. However, they do exhibit a weak, inverse correlation to the exchange current values extracted via the Tafel analysis detailed in Section 3.2.3, as predicted by equation 16. Table 3.9 displays the sample R_{ct}

extracted from the Randles model and the exchange current values (I_0) extracted from the Tafel analysis at both high and low CV scan rates. S_1 has significantly higher R_{ct} values and significantly lower I_0 values (at both scan rates) when compared with both S_2 and S_3.

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Kinetic Resistance R_{ct} (Ω)	1.54 +/- 4.8%	0.88 +/- 4.5%	0.95 +/- 4.1%
Exchange Current I_0 (A) (Tafel analysis @ $v=1.0\text{mV/s}$)	6.1×10^{-4} +/- 10%	8.7×10^{-4} +/- 10%	7.7×10^{-4} +/- 10%
Exchange Current I_0 (A) (Tafel analysis @ $v=7.5\text{mV/s}$)	2.8×10^{-3} +/- 10%	3.2×10^{-3} +/- 10%	3.4×10^{-3} +/- 10%

Table 3.9: Comparison of Kinetic resistance (R_{ct}) values extracted using EIS and exchange current (I_0) values extracted using a Tafel analysis of CV data. S_1 has significantly higher R_{ct} and lower I_0 compared to S_2 and S_3. This correlation lends credibility to the results of the Tafel Analysis and to the prediction that S_1 will have higher kinetic losses and thus lower energy retention at high current densities compared with the other two samples.

This correlation suggests that there is some physical validity to the results derived from the Tafel analysis even though there was significant uncertainty associated with the extracted kinetic parameters. By extension, one of the key predictions of the Tafel analysis, that S_1 had significantly higher kinetic polarization as a function of applied current (see Figure 3.12 in section 3.2.3), is more credible given that a significant difference in S_1 kinetic behavior was identified by two independent characterization techniques. The combination of higher R_s and R_{ct} values for S_1 compared with S_2 and S_3 is consistent with the observed trends in energy retention at high current density and polarization curve slope presented in sections 3.1.3 and 3.1.4 respectively. Shifting to the values of double layer capacitance (Row 3 in Table 3.8), we note that the C_{dl} values range from 22 mF for S_1 to 29 mF for S_3 and are equal to those extracted using the CPE model to within experimental uncertainty. These values were used to

estimate the real surface area for all three test samples using the generally accepted value of $40\mu\text{F}/\text{cm}^2$ [9] for a typical double layer capacitance. The sample surface areas ranged from $1,105\text{ cm}^2$ on S_1 to 1470 cm^2 on S_3. When these surface area values are compared with the sample geometric surface area estimates derived in Section 2.2.3, we find that the values are the same order of magnitude, and in the case of S_1 and S_2, are equivalent to within measurement uncertainty. This result, along with the similar result extracted from the CPE model, gives confidence that an EIS measurement is a reasonable method to measure the real surface area of the nanostructured electrodes developed here. Finally, rows 6-8 in Table 3.8 summarize the 3 figures of merit associated with the Warburg circuit element. The first of these is the Warburg_R term which can be interpreted as a diffusion resistance [22]. The second parameter is Warburg_T term, or the diffusion time constant (τ_d) defined as

$$\tau_d = \frac{L^2}{D} \quad (37)$$

where L is the diffusion length and D is the diffusion coefficient. We recall that this relationship is derived from a solution of Fick's second law as outlined in section 1.5. The extracted diffusion time constant values range from 13.3s for S_1 to 21.9s for S_3 and notably are roughly correlated to nanoflake thickness or to aspect ratio more generally. It is theorized that this correlation is a consequence of thicker $\text{Ni}(\text{OH})_2$ nanoflakes resulting in a longer effective length which the H^+ ions need to diffuse through to fully charge and discharge the device. We will leave this point for a moment but return to it later in this section and discuss in more detail. It is interesting to compare the magnitude of the sample diffusion time constants to that of the kinetic time constants, τ_k which are defined by

$$\tau_k = \frac{1}{R_{ct} \cdot C_{dl}} \quad (38)$$

where R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance [2]. The τ_k values are similar for all three samples, ranging from 0.02s on S_2 to 0.03s for S_1 and S_3. The values do not appear to correlate to nanoflake aspect ratio or other physical attributes of the test samples, but they are approximately 3 orders of magnitude smaller than the diffusion time constants and thus are likely not limiting the electrode discharge times summarized in section 3.2. While it is anticipated that the chemical reaction kinetics of $Ni(OH)_2$ are much faster than the mass transport properties, it does highlight the advantages of the nanostructured electrode developed here where most of the active material is located on the electrode surface rather than in the bulk, and thus subject to material conversion rates on the order of tens of milliseconds. This difference in scale between the kinetic and diffusion time constants perhaps offers an indication as to the source of electrode capacity loss at high currents. As was reported in section 3.3.1, the majority (~75%) of sample storage capacity (coulombs) could be discharged at high rates in ~7-11 seconds for all three samples. However, to extract the remaining ~25% of electrode charge, the samples had to be discharged at much lower rates over times ranging from ~300-450 seconds. Based on the relative magnitudes of the kinetic and diffusion time constants and the high internal surface area of the nanostructured electrodes, it seems logical that the rate of charge/discharge of most of the $Ni(OH)_2$ active material is not limited by the relatively high speed kinetics. However, some proportion of the active material, perhaps in the center or base of the nanoflake structures may be limited by the rate of H^+ mass transport and thus require discharge times on the order of tens or hundreds of seconds. An additional EIS model which incorporates multiple Warburg elements to represent different sections or thicknesses of the $Ni(OH)_2$ electrode is presented in Appendix A and the reader is encouraged to review this material if interested. The third and final figure of merit of a Warburg element is the “P term” or

exponent ϕ_w and the extracted values ranged from 0.44 on S_1 to 0.39 on S_3. As the values were all <0.5 , the data validates the assumption of using a generalized Warburg element to model the nanoflake morphology. In addition, the apparent trend in the extracted values seems to be correlated to nanoflake aspect ratio, suggesting that as the nanoflakes become shorter and wider, the mass transport is becoming less uniform or perhaps occurring through several different diffusion pathways [2]. Based on these trends of increasing τ_d and decreasing ϕ_w with decreasing nanoflake aspect ratio, a simplified conceptual model for the electrode mass transport mechanism is proposed in Figure 3.21. It is hypothesized that the primary

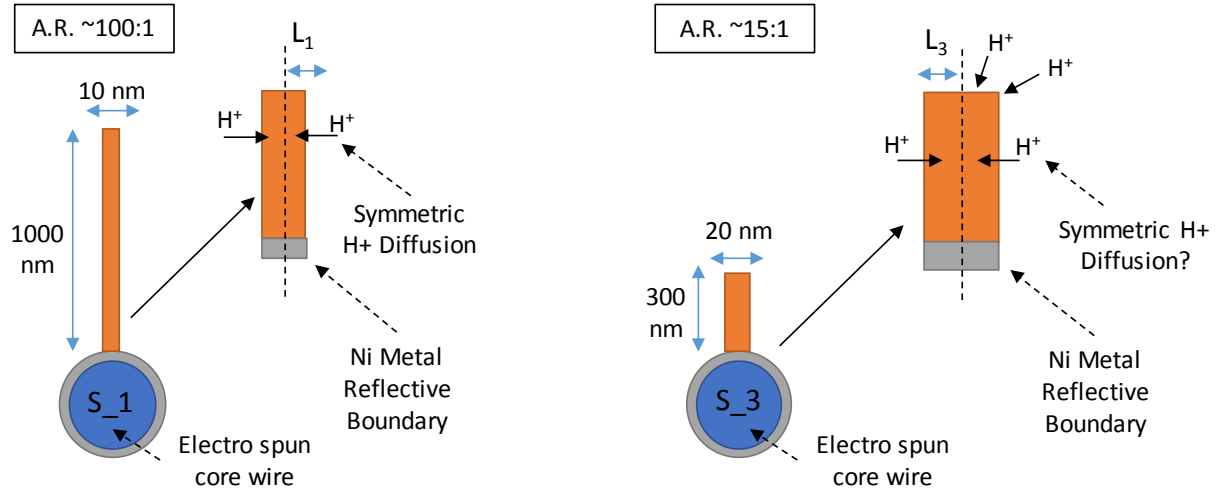


Figure 3.21: Simplified conceptual model for H^+ mass transport through $Ni(OH)_2$ nanoflakes. We theorize that the majority of H^+ ions diffuse symmetrically from both sides of a nanoflake. As the aspect ratio decrease, the nanoflakes become wider, perhaps increasing the horizontal diffusion lengths (L_1 and L_3), leading to larger diffusion time constants. Also, as the aspect ratio gets smaller, some H^+ ion could diffuse into the bulk from multiple directions (perhaps vertically?) leading to more complex diffusion pathways consistent with the trend of smaller value of ϕ_w .

mass transport mechanism during charging or discharging is H^+ ions diffusing into the bulk $Ni(OH)$ symmetrically from both sides of a nanoflake. As the aspect ratio decreases, the

nanoflakes become wider which we assume increases the effective diffusion lengths of the H⁺ ions. These diffusion lengths are represented by L_1 and L_3 in Figure 3.18, where each is taken to be $\frac{1}{2}$ the thickness of the mean nanoflake thickness for each sample and thus $L_1 < L_2 < L_3$. It follows that as this diffusion length increases from S_1 to S_3, the diffusion time constant measured by the EIS technique would also increase, per equation 35. Also, as the aspect ratio falls or as the density of nanoflake packing density increases, as was observed on the high magnification SEM images presented in Chapter 2, some H⁺ ions could diffuse into the Ni(OH)₂ bulk from multiple directions leading to more complex diffusion pathways consistent with the trend of a smaller value of ϕ_w . Given the magnitude and observed trend of diffusion time constant with nanoflake aspect ratio, these values can be used to extract estimates for the H⁺ diffusion coefficient using equation 37. For values of diffusion length, we used half the value of the nanoflake thickness extracted via SEM image for each sample, consistent with the conceptual mass transport model discussed above. The results of this calculation are shown in Table 3.10.

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Diffusion coefficient (cm ² /s) EIS Method	1.7 x 10 ⁻¹⁴ +/- 148.7%	2.4 x 10 ⁻¹⁴ +/- 72.3%	3.7 x 10 ⁻¹⁴ +/- 81.0%
Diffusion coefficient (cm ² /s) CV Method	2.5 x 10 ⁻¹⁴ +/- 3.7%	4.5 x 10 ⁻¹⁴ +/- 12.1%	2.3 x 10 ⁻¹⁴ +/- 9.8%

Table 3.10: Diffusion coefficients calculated using data extracted from CV and EIS methods. Significantly, the values are the same order of magnitude for each sample and slightly beyond the high end of what has been reported in the literature for the diffusion coefficient of H⁺ in a Ni(OH)₂NiOOH solid solution [4]. The uncertainties for the EIS method are high as the calculation incorporates the high uncertainty from nanoflake SEM images.

It is interesting that the values of diffusion coefficient calculated using a combination of EIS and SEM data are of the same order of magnitude as the values calculated using CV data for each test

sample. While these values are one order of magnitude above the high end of what has been reported in the literature for the diffusion coefficient of H^+ in $Ni(OH)_2$, the fact that two different measurement techniques produced similar results lends some credibility to the assumption that the H^+ ion is the mass transport limiting species in the electrodes developed here. Obviously, a somewhat reciprocal calculation using equation 35 can be performed to impute the nanoflake thickness for each sample using the diffusion coefficient extracted from CV measurements and the τ_d values to calculate the value of L . The data for this exercise is shown in Table 3.11 and

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
*Characteristic Diffusion Length (nm)	5.83 +/- 9.1%	8.22 +/- 6.1%	7.08 +/- 7.7%
**Imputed nanoflake thickness (nm)	11.7 +/- 9.1%	16.4 +/- 6.1%	14.2 +/- 7.7%
Measured Nanoflake thickness (nm)	9.48 +/- 6.38%	11.84 +/- 4.29%	18.00 +/- 6.25%

Table 3.11: Comparison of measured values of sample nanoflake thickness and values calculated using H^+ diffusion coefficients extracted from CV curves and τ_d values extracted from EIS measurements.

perhaps unsurprisingly given the previous result, the calculated nanoflake values are all within 50% of the values measured by the SEM. In summary, we can state that the Randles model predictions for series resistance were consistent with values extracted from the CPE model. Kinetic resistance values were significantly different from those in the CPE model but were weakly correlated to exchange current values extracted using Tafel analysis, lending credibility to the reaction kinetic figures of merit derived in section 3.2.3. Taken together, the sample trends in R_s and R_{ct} are consistent with trends identified in both sample polarization curves and energy retention at high current densities. Sample surface area estimates derived from C_{dl} parameters were reasonable when compared with estimates calculated using nanoflake

feature sizes extracted from SEM measurements. Values for diffusion time constants correlated to nanoflake aspect ratio and were used to calculate values for sample diffusion coefficients and nanoflake thickness with reasonable accuracy. Finally, kinetic time constants were found to be approximately three orders of magnitude smaller than those for mass transport and thus are likely not the mechanism limiting the charge and discharge times of the sample electrodes.

Chapter 4: Conclusion

This chapter will summarize the key findings of this research effort and suggest some possible directions for future work.

4.1 Summary of Key Results

The electrochemical properties of nanostructured nickel hydroxide electrodes developed using a new method were characterized. This method involves the in-situ growth of high aspect ratio Ni(OH)_2 nanoflakes on a metalized nanowire scaffold. The first step in this assembly process involves the electrospinning of 700 nm diameter, polymer nanofibers to form a highly porous structure. The polymer nanofiber material is doped with a proprietary salt that allows for the chemical deposition of nickel directly onto the fibers in a subsequent process. The final manufacturing step involves the chemical growth of the Ni(OH)_2 nanoflakes directly on the metalized nanowires, such that the electrode active material is in intimate contact with the highly porous current collector. Ni(OH)_2 nanostructured electrodes constructed with this method had good performance, providing a specific energy of 90 $\text{W}\cdot\text{h/kg}$ at a specific power of 727 W/kg and maintained a specific energy of 32 $\text{W}\cdot\text{h/kg}$ at a power density of 10 kW/kg . Although direct comparisons between technologies are sometimes difficult due to differences in measurement techniques and how results are presented, the electrodes developed in this work compare favorably with results published on similar types of energy storage devices. These comparisons are summarized in Table 4.1, which is the information from Table 1.2, presented in section 1.6.

Authors	Device Design	Performance at low current density <3A/g	Comments
Zhang <i>et al.</i> [15]	Ni(OH)_2 nano-platelets grown on electro-spun and carbon nano-fibers	2,394 F/g (active mass) 667 F/g (total mass*) *not including mass of current collector	Active mass result is higher than theoretical capacitance limit and fabrication requires high temperature processing.

Yan <i>et al.</i> [18]	Ni(OH) ₂ / Graphene composite deposited on Ni foam current collector	2,194 F/g (active mass) Total mass not reported.	Ni(OH) ₂ / graphene composite is not used as fabricated. Rather it is crushed to a powder, combined with binders, and applied as a slurry to a nickel foam current collector.
Wang [17]	Ni(OH) ₂ Nanoflakes grown on graphene coated nickel foam.	2,161 F/g (active mass) Total mass not reported.	Graphene deposition requires high temperature CVD fabrication.
This Work	Electrospun, nano structured Ni(OH) ₂ electrode with integrated current collector.	2,123 F/g (active mass) 1,040 F/g (total mass)	Process conducive to rapid scale up and low capital intensity.

Table 4.1: Table 1.2 from Section 1.6 showing the comparison between the performance of the electrodes

developed here and similar technologies identified in a literature search. It is important to note that the three main advantages of this work are electrodes with a tunable nanostructure, a very high internal surface area, and a simple manufacturing process.

It is important to highlight three key benefits of the electrode design presented here. First, the aspect ratio of the nanoflakes can be tuned by adjusting the ammonium hydroxide concentration during the Ni(OH)₂ growth process. This allows the electrode designer to determine the impact of nanostructure morphology on various macro properties, such as energy or power density, and optimize the nanostructure for performance. Second, the electrodes are highly porous (~50%) and are estimated to have a very high internal surface area (~1450 cm²) which allows for excellent wetting of the active material with the electrolyte. In addition, the combination of a tunable nanostructure with a high internal surface area is likely an enabling feature for the high power densities exhibited by these devices and will be discussed in more detail later in this section. Finally, the electrodes can be constructed using a relatively simple, three step

manufacturing process that doesn't require any high temperature processing or exotic materials such as graphene which are currently prohibitively expensive for industrial applications. While these properties make this electrode design attractive from both scientific and commercial perspectives, one drawback is the fundamental limitation of energy density associated with Ni(OH)_2 active material. Ni(OH)_2 has a moderate specific capacity of 289 mA•h/g, relatively low reduction potential of 0.49 V and the requirement for an aqueous electrolyte with a limited electrochemical stability window (~1.6 V). This restricts the ability of Ni(OH)_2 based devices to compete with the energy density of lithium based storage technologies that can leverage that material's high specific capacity (~3,860 mA•h/g) and reduction potential (-3.1V) [8]. However, understanding how an optimized electrode nanostructure of any composition can impact electrode performance and specifically electrode power density, can very likely be applied to improving the designs of emerging lithium- and sodium-based energy storage technologies. Using a range of characterization techniques, we were able to develop a basic understanding of how the Ni(OH)_2 electrode nanostructure impacted device performance. Using XRD and SEM techniques, the electrode active material was successfully identified, and the surface and bulk morphology of the nanostructure quantified to a first approximation. The electrochemical behavior of the nanostructure was interrogated using cyclic voltammetry measurements and parameters extracted from CV curves were used to quantify the kinetic behavior of each test sample. While the predicted values for kinetic polarization appeared reasonable when compared to measured values, other figures of merit extracted in this analysis, such as the Tafel slope and transfer coefficient varied significantly from those predicted by theory. We hypothesize that part of this deviation is due to the difficulty of interpreting the kinetic behavior of the Ni(OH)_2 nanostructure using theory developed assuming flat and smooth electrode geometries. Galvanic

charge and discharge measurements were able to quantify the performance of the test samples across a wide range of discharge rates. In addition, these GCD measurements were used to extract polarization curves for each sample which helped to quantify both sample to sample variation and performance at low and high current densities. Samples lost 60-70% of their energy density over the range of discharge rates measured here and the majority of this energy loss was attributable to parasitic voltage losses caused by electrode polarization. Ohmic losses were found to be the most significant factor of this polarization loss at high rates of discharge and some suggestions for future work to understand the key contributors to ohmic loss are presented in section 4.2 below. Equivalent circuit models were developed to interpret sample frequency responses measured using electrical impedance spectroscopy. Double layer capacitance values extracted from EIS measurements (see Table 3.7 and Table 3.9) provided reasonable estimates of the real surface area of the electrode nanostructure. The EIS models were successful in both augmenting the understanding of sample ohmic and kinetic properties determined using CV and GCD analysis as well as interrogating the mass transport behavior of the electrodes. Based on a good correlation between values on the order of $10^{-14} \text{ cm}^2/\text{s}$ for diffusion coefficients extracted using both EIS and CV measurements, we were able to conclude that the mass transport limiting species in the system is indeed the H^+ diffusing in the $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ solid solution. The models derived from EIS measurements also yielded values for mass transport (τ_d) and kinetic (τ_k) time constants which determine electrode behavior over different time scales and provide a possible explanation of electrode capacity loss at high rates of discharge. Specifically, values for the kinetic time constants were in the range of 0.02-0.03s and were approximately 3 orders of magnitude faster than the diffusion time constants which were on the order of 15 seconds. Given the high internal surface area of the electrodes and the

high surface area to volume ratio of the $\text{Ni}(\text{OH})_2$ nanoflakes, we conclude that the majority of the $\text{Ni}(\text{OH})_2$ to NiOOH material conversion is governed by the kinetics of $\text{Ni}^{+2} / \text{Ni}^{+3}$ redox couple rather than the mass transport of the H^+ proton through the bulk of the active material. It follows that this combination of high-speed kinetics and electrode nanostructure is the primary driver for the high power densities recorded for all test samples. However, as was reported in section 3.3.1, while the majority (~75%) of nanostructured electrode capacity could be discharged in approximately 7-11 seconds, the remaining ~25% of capacity required 300-450 seconds to discharge at much lower currents. We hypothesize that this behavior is due to a mass transport limitation in the nanostructure, perhaps in the center or base of the $\text{Ni}(\text{OH})_2$ nanoflakes, where the active material is the thickest in one or perhaps multiple spatial dimensions. In such a region, the effective diffusion length for the H^+ ion would be longer than the mean nanoflake thicknesses recorded by SEM measurements and multiple diffusion pathways could exist, as was suggested by the Warburg exponent values (ϕ_w) in the Randles EIS model. Thus, a complete charge/discharge of an electrode would require enough time for the H^+ to diffuse fully through this thicker section of active material. It is recommended that validating this hypothesis of H^+ mass transport impacting sample power density be one of the directions for future work with the $\text{Ni}(\text{OH})_2$ nanostructured electrodes developed here.

4.2 Future work

Broadly speaking, there are two directions for future work that could be undertaken to explore the electrodes developed in this work more deeply. The first recommendation would be an effort to improve the scientific, and specifically the electrochemical, understanding of the electrode behavior. A more complete understanding of the fundamental limitations (ie kinetic and mass transport) of the $\text{Ni}(\text{OH})_2$ nanostructure would allow for more accurate modeling of electrode

performance. In addition, this effort would likely accelerate the pace of electrode improvement as research work could be targeted at overcoming these limitations through changes in nanostructure composition, geometry, or fabrication. The second recommendation would be to work on initial reliability, manufacturability and device integration testing. This effort should be completed to confirm the commercial viability of this technology and to enable the rapid production scale up of this technology once a market opportunity is identified. Suggestions for specific work on both these directions will be discussed briefly below.

4.2.1 Work to improve Scientific understanding and device performance:

One of the central questions in this work is how electrode porosity and nanostructure impact energy and power density. While several reasonable figures of merit for ohmic, kinetic and mass transport behavior were extracted for each test sample, there are several areas where experimental results deviate from accepted theory. We hypothesize that one significant source of this deviation could be due to the unique nanostructures developed here, as the electrochemical behavior may not be able to be interpreted using theory developed assuming smooth and flat plate electrodes. Thus, it seems reasonable to design a series of experiments to try and quantify the impact of both porosity and nanostructure on electrode performance. Specifically, it is recommended that these experiments independently vary both parameters from low to high, such that at the low end of the experimental range, the test samples would approximate a smooth and flat Ni(OH)_2 electrode. In the case of porosity, this would require tuning several process parameters in the electrospinning process to modify the density of the nanofiber web so that at very high fiber densities, the resulting porosity of the nanostructure electrodes would be minimized. In the case of the Ni(OH)_2 nanostructure, a combination of process time and ammonium hydroxide concentration could be used to tune the aspect ratio of the nanoflakes from

the relatively high levels explored in this work (~1000:1) to very low or perhaps even negligible levels. At the low end of this aspect ratio spectrum, we would essentially have cylindrical Ni(OH)₂ nanowires that would approximate a smooth electrode. A very similar approach was taken by Tamas *et al.* where the group modified the surface roughness of platinum wires and was able to measure significant changes in electrochemical kinetic parameters, such as the value of the Tafel slope, using CV and step potential experiments [26]. While the standard set of electrochemical tests (CV, GCD, EIS, potential step) would be used to characterize the various electrode structures, the following metrology tools would be required to evaluate nanostructure feature size and material properties:

1. A TEM system to provide high resolution images of the electrode nanostructure and nanoflake aspect ratio. While the SEM measurements used in this work were very helpful in characterization, much greater levels of accuracy and precision in feature size and geometry are needed to accurately model sample electrochemical properties. The high resolution of a TEM system would be especially helpful in quantifying thinner and thicker regions of the Ni(OH)₂ nanoflakes and helping to validate the hypothesis of H⁺ mass transport limitations in thick regions of active material.
2. A XPS system to characterize electrode material properties and clearly distinguish Ni metal from Ni(OH)₂ and conclusively determine if the nanostructures are formed from Alpha or Beta Ni(OH)₂ or some combination of the two. This is important to determine as each polymorph of Ni(OH)₂ has a unique specific capacity, and thus a test sample's maximum theoretical capacity would depend on its composition.

A second focus of any future work should be to quantify the specific sources of ohmic loss in the electrode. Ohmic losses were clearly significant in reducing electrode power density and

therefore identifying their root cause should provide pathways to improve performance. It is likely that total ohmic losses are some combination of 3 mechanisms: electronic resistance, solution resistance and ionic resistance, or the solution resistance associated with the porosity of the electrode. Given the high porosity of the test samples and the relatively high ionic conductivity of 2M KOH, the expectation is that electronic resistance will dominate. However, the following experiments should be performed to determine the relative contribution of each resistance mechanism:

1. Electrical resistance could be measured on dry samples using a 4-wire measurement technique, where current is injected across the sample by two probes and the resulting voltage drop measured by two additional probes. In addition to using this technique on freshly prepared samples, it could be used on samples which are at various states of charge to validate the theory that the electrical resistance changes as the material converts from Ni(OH)_2 to NiOOH [8].
2. Solution resistance can be measured by using either an EIS or GCD technique in a 3 electrode set up to extract the total ohmic resistance in the system, and then subtracting the electrical and ionic resistance to determine the solution resistance. It is recommended that this technique be done at several concentrations of electrolyte (e.g. 2M, 4M and 6M) to confirm the linearity of the measurement.
3. Electrode Ionic resistance can be measured using an EIS technique and a 4-wire ionic resistance apparatus. In this measurement, ionic current is forced through the porous membrane by two electrodes immersed in the KOH electrolyte along with the test sample and the resulting voltage drop is measured by two reference electrodes. One difficulty with this experiment is that it requires test samples significantly larger than can currently

be manufactured. However, with improvements to process control and $\text{Ni}(\text{OH})_2$ nanoflake uniformity, it is possible that such samples could be manufactured in the future. If samples were to become available, it is recommended that measurements of ionic resistance be completed over a range of electrode porosities to see if a correlation can be detected.

4.2.2 Tasks required for early stage commercialization

Prior to investing significant funds to commercialize the nanostructured electrodes developed here, the following activities should be completed. The work suggested below should help to significantly de-risk the eventual manufacturing scale up, which is often where advanced technologies experience significant cost overruns and delays in time to market.

1. Optimize the baseline recipe and determine key process variables. S_2 and S_3 performed better than S_1 in terms of energy and power density. While this is a small data set, the results of the characterization work detailed in Chapter 3 suggest moving the baseline manufacturing process to one with a higher concentration of ammonium hydroxide (between 1.4 and 1.8 M/L) and then performing additional tests to window the performance around this new baseline. Design of experiment (DOE) and statistical process control (SPC) techniques could be employed to systematically determine the optimum process window and minimize the variability in the manufacturing process. In addition, exploring an electrode design space with higher active material loading (longer $\text{Ni}(\text{OH})_2$ growth times) and higher concentration of KOH electrolyte to lower solution resistance is also recommended as these may increase both energy and power density. Additionally, it is worth exploring whether cobalt nanoparticles could be incorporated in the $\text{Ni}(\text{OH})_2$ nanostructure. Doping $\text{Ni}(\text{OH})_2$ with cobalt is occasionally used to increase

the electrical conductivity of commercial battery electrodes and we assume that since this technique has been adopted by industry, it has a high likelihood of improving the performance of the electrodes developed here [8]. Finally, it is recommended that some minimal system of quality inspection and control be implemented for all process materials and equipment. Material contamination was thought to be one of the major contributors to poor yield and process instability during this development project.

2. Efforts should be taken to protect any intellectual property derived from the development efforts associated with this or future projects. Typically, this is accomplished by filing patents in commercially significant regions. However, it may be prudent in some cases to retain some IP as a trade secret to minimize the diffusion of critical manufacturing or process engineering knowledge to potential competitors.
3. Marathon testing: Some level of charge / discharge cycling of the electrodes should be done to quantify any capacity fade and identify the root causes of any performance degradation. Initially, a 1,000-cycle test should be performed at a moderate GCD current (perhaps 100 mA) and electrode capacity, coulombic efficiency and polarization loss for each cycle should be recorded. While the 1,000 cycle is somewhat arbitrary, it seems like a reasonable number in order to generate results in a relatively short amount of time while still pushing the device far beyond what is normally done in R&D scale bench testing. SEM images of the samples should be taken before and after cycling to determine if any physical damage or modification is happening to the electrode nanostructure. If minimal degradation is seen after a 1K cycling test, then subsequent tests should increase the cycle count to a point where either significant degradation in

power or energy density is observed in order to identify likely failure modes or reliability risks.

4. Building device prototypes: a prototype Ni(OH) battery could be constructed by integrating the nanostructured electrodes developed here with a conventional ionic separator, metal hydride counter electrode and KOH electrolyte. These “off the shelf” components can be acquired from multiple industrial suppliers, such as Sigma-Aldrich, and will have very well-defined performance characteristics which could provide a means to isolate the performance of the nanostructured electrode in a complete device. Building and testing such a device is perhaps the most effective way to determine the commercial viability of the technology developed here as it allows direct comparisons with existing technology and will expose any practical limitations of the nanostructured electrodes that may not be apparent during typical bench scale R&D testing.
5. Cost modeling: A simple cost model should be built to identify the major components of both product cost and capital cost needed to scale the product to high volume manufacturing.
 - a. On the product cost side, the goal should be to determine if the overall cost structure will be competitive with incumbent technologies and at what scale. Ideally the product has enough of a performance advantage over incumbent technologies that early stage customers would be willing to pay a premium for the product until it can be cost-reduced through scale. The product cost modeling exercise should also identify key cost drivers which the design team can then focus on reducing as part of future development efforts. In addition, it should be clearly understood which of the key cost components can be reduced through

innovation and which will naturally be reduced as the product scales to higher volumes. While this distinction seems trivial, it is very important as the strategies for addressing these high cost components are significantly different; some costs can be scaled out while others must be designed out.

- b. While it is often difficult to estimate the capital cost required to scale a nascent technology into volume production given uncertainties about the cost of production tooling and facilities costs, it is an important exercise for any hardware technology as significant cash, and therefore debt or equity will be required to bring the technology to market. Where possible, similar types of manufacturing equipment can be used as proxies to estimate the cost of manufacturing. Tooling and utility usage rates (ie electricity, gases, chemicals) can be estimated from those used in the prototype assembly process. Special emphasis should be put on equipment that requires complex manufacturing technology or uses process chemicals that are either dangerous or toxic to human health or the environment. These manufacturing tools will likely add significant cost and efforts should be made early in the product development cycle to see if they can be simplified or eliminated.
6. Market validation study: Once significant progress has been made on the five tasks outlined above, the development team should begin to engage with relevant industry players who might be interested in acquiring the technology or funding further research. Aside from the obvious financial benefits, the main goals of this activity are to validate the perceived advantages of this technology, confirm that these advantages are valuable to potential customers and to determine product market fit. Given the relatively simple

assembly process, high energy and power density and integrated structure of the electrodes here, it is likely that this technology could find applications in products ranging from mobile electronics to electric cars.

Bibliography

- [1] S. S. Zumdahl, *Chemical principles*. Houghton Mifflin, 2009.
- [2] A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*. 2002.
- [3] T. Pajkossy, “Impedance of rough capacitive electrodes,” *J. Electroanal. Chem.*, vol. 364, no. 1–2, pp. 111–125, 1994.
- [4] K. P. Ta, “Mass Transfer and Kinetic Phenomena at the Nickel Hydroxide Electrode,” *J. Electrochem. Soc.*, vol. 145, no. 11, p. 3860, 1998.
- [5] L. JM Energy Co., “Comparison with various electric storage devices Pioneer of lithium ion capacitor JM Energy Co., Ltd.” [Online]. Available: http://www.jmenergy.co.jp/product_compare.html. [Accessed: 06-Jul-2017].
- [6] V. Srinivasan, J. W. Weidner, and R. E. White, “Mathematical models of the nickel hydroxide active material,” *J. Solid State Electrochem.*, vol. 4, no. 7, pp. 367–382, 2000.
- [7] F. Béguin and E. Frackowiak, *Supercapacitors*. 2013.
- [8] H. O. F. Batteries, D. E. Library, and T. M. Companies, *Handbook of batteries*. 2004.
- [9] A. J. Bard, L. R. Faulkner, N. York, C. @bullet, W. Brisbane, and S. E. Toronto, *ELECTROCHEMICAL METHODS Fundamentals and Applications*. 1944.
- [10] D. Bizzotto, *Chem 517 Course Notes*. .
- [11] X. Luo, J. Wang, M. Dooner, and J. Clarke, “Overview of current development in electrical energy storage technologies and the application potential in power system operation,” *Appl. Energy*, vol. 137, pp. 511–536, 2015.
- [12] F. Ko, “Nanofiber Technology,” pp. 233–244, 2006.
- [13] J. W. Weidner, “Effect of Proton Diffusion, Electron Conductivity, and Charge-Transfer Resistance on Nickel Hydroxide Discharge Curves,” *J. Electrochem. Soc.*, vol. 141, no. 2,

- p. 346, 1994.
- [14] E. M. Rus, D. M. Constantin, L. Oniciu, and L. Ghergari, “Structural and Electrochemical Characteristics of Sintered Nickel Electrodes,” *Croat. Chem. Acta*, vol. 72, no. 1, pp. 25–41, 1999.
 - [15] L. Zhang, Q. Ding, Y. Huang, H. Gu, Y. E. Miao, and T. Liu, “Flexible Hybrid Membranes with Ni(OH)₂ Nanoplatelets Vertically Grown on Electrospun Carbon Nanofibers for High-Performance Supercapacitors,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 40, pp. 22669–22677, 2015.
 - [16] A. Motori, F. Sandrolini, and G. Davolio, “Electrical properties of nickel hydroxide for alkaline cell systems,” *J. Power Sources*, vol. 48, no. 3, pp. 361–370, 1994.
 - [17] L. Wang, X. Li, T. Guo, X. Yan, and B. K. Tay, “Three-dimensional Ni(OH)₂ nanoflakes/graphene/nickel foam electrode with high rate capability for supercapacitor applications,” *Int. J. Hydrogen Energy*, vol. 39, no. 15, pp. 7876–7884, 2014.
 - [18] J. Yan, W. Sun, T. Wei, Q. Zhang, Z. Fan, and F. Wei, “Fabrication and electrochemical performances of hierarchical porous Ni(OH)₂ nanoflakes anchored on graphene sheets†,” *J. Mater. Chem.*, vol. 22, no. 23, p. 11494, 2012.
 - [19] J. A. Witt, D. R. Mumm, and A. Mohraz, “Microstructural tunability of co-continuous bijel-derived electrodes to provide high energy and power densities,” *J. Mater. Chem. A*, vol. 4, no. 3, pp. 1000–1007, 2016.
 - [20] H. Kleemann, “Theory of the Impedance of Electron Diffusion and Recombination in a Thin Layer,” pp. 325–333, 2010.
 - [21] J. Yan *et al.*, “Advanced asymmetric supercapacitors based on Ni(OH)₂/graphene and porous graphene electrodes with high energy density,” *Adv. Funct. Mater.*,

- vol. 22, no. 12, pp. 2632–2641, 2012.
- [22] S. Analytical, *Impedance / Gain-Phase Analyzer. Operating Manual.* .
- [23] I. Scribner Associates, *CorrWare Operating Manual.* .
- [24] K.-H. Young *et al.*, “Fabrications of High-Capacity Alpha-Ni(OH)₂,” *Batteries*, vol. 3, no. 1, p. 6, 2017.
- [25] C. Zhang, “The Anodic Oxidation of Nickel in Alkaline Media Studied by Spectroelectrochemical Techniques,” *J. Electrochem. Soc.*, vol. 134, no. 12, p. 2966, 1987.
- [26] T. Pajkossy, “Electrochemistry at fractal surfaces,” *J. Electroanal. Chem.*, vol. 300, no. 1–2, pp. 1–11, 1991.

Appendix A Additional EIS modeling results using multiple Finite Warburg Elements

The following section is an extension of the EIS measurement and modeling work that was presented in section 3.3.2. Specifically, an alternative configuration of a Randles circuit model is proposed as a hypothesis to explain the electrode capacity loss at high rates of discharge thought to be associated with H^+ mass transport limits. It must be noted at the outset that this work is preliminary due to time constraints and may include errors in the modeling or analysis.

However, this work is included for completeness and may provide some additional insight to the nanostructured electrodes developed here and inform directions of future work. As was reported in section 3.3.1, while the majority (~75%) of nanostructured electrode capacity could be discharged in approximately 7-11 seconds, the remaining ~25% of capacity required 300-450 seconds to discharge at much lower currents. We hypothesize that this behavior is due to a mass transport limitation in the nanostructure, perhaps in the center or base of the $Ni(OH)_2$ nanoflakes, where the active material is the thickest in one or perhaps multiple spatial dimensions. In such a region, the effective diffusion length for the H^+ ion would be longer than the mean nanoflake thicknesses recorded by SEM measurements and multiple diffusion pathways could exist, as was suggested by the Warburg exponent values (ϕ_w) in the EIS model presented in section 3.2.2. A conceptual model for this situation is presented in Figure A1 where we hypothesize that the $Ni(OH)_2$ nanoflakes have two distinct regions, a high aspect ratio and thus relatively thin “flake” region and a thicker “base layer” region that exists at the interface of the nanoflake and the nickel current collector. In this conceptual picture, H^+ ions can diffuse symmetrically through the flake region during charging and discharging and have a diffusion length L_1 , which is

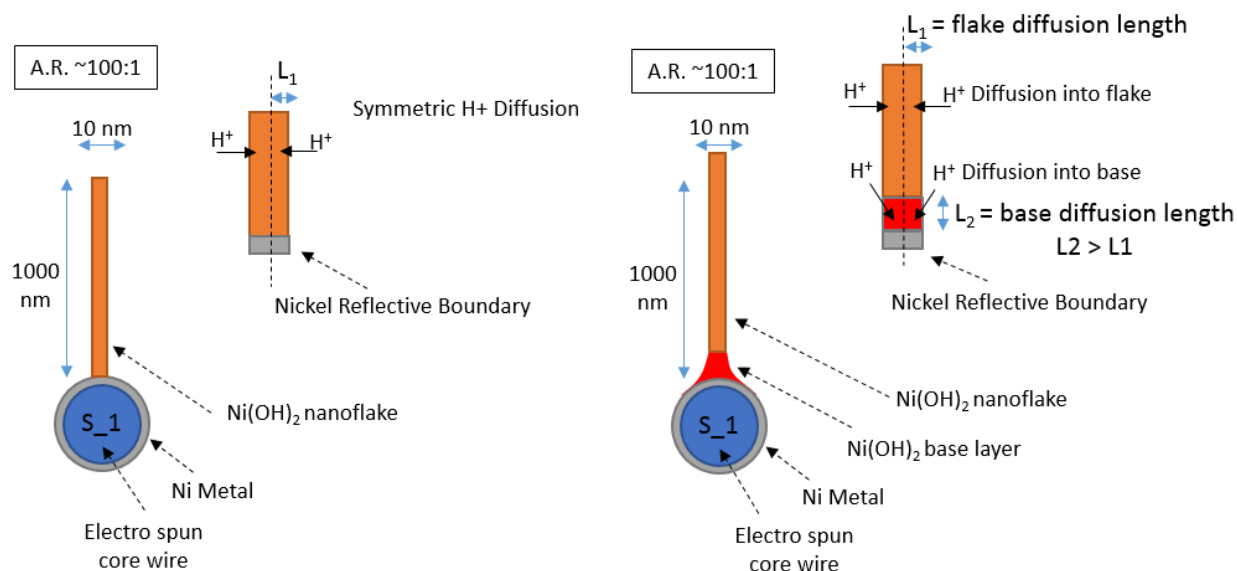


Figure A.1: On the left side of the figure a simplified view of the electrode nanostructure is shown, with high aspect ratio $\text{Ni}(\text{OH})_2$ nanoflakes extending radially outward from a nickel coated PAN core wire. On the right side of the figure, a more complex nanostructure is envisioned. Here, the $\text{Ni}(\text{OH})_2$ nanoflakes are hypothesized to have both a thin “flake” region with a characteristic H^+ ion diffusion length of L_1 and a thicker “base layer” region with a diffusion length L_2 . In this model, L_2 is significantly greater than L_1 and thus will require a longer time to charge and discharge under mass transport limited conditions..

equal to one half of the nanoflake thickness recorded by the SEM measurements presented in section 2.2 or approximately 6-8 nm. In addition, H^+ ions can diffuse into a base region which is characterized by a diffusion length L_2 and is imagined to be significantly larger than L_1 . Since L_2 is larger than L_1 , the active material in the base region would take longer to charge / discharge than material in the flake region under mass transport limited conditions. Under such conditions, this material would not be accessible to store or release energy at charge / discharge times that exceeded the H^+ diffusion time constant in this region and would result in the electrode exhibiting a lower effective capacity. To model this conceptual picture, a modified Randles circuit outlined in Figure A.2 was employed to fit the EIS data for all three electrode test

samples. Similar to the equivalent circuit model presented in section 3.2.2, the elements R_s and R_{ct} capture the respective series and kinetic resistance in the electrode while the C_{dl} element captures the effect of the electrochemical double layer.

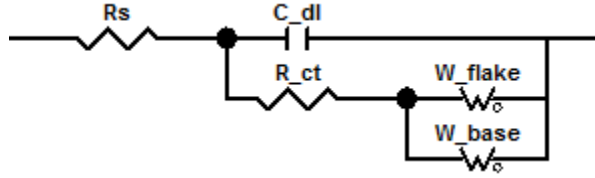


Figure A.2: Equivalent circuit for Randles model employing two finite Warburg elements arrayed in parallel. R_s and R_{ct} are as defined previously and represent the ohmic and kinetic resistances in the electrodes respectively. The C_{dl} term captures the double layer capacitance of the sample while the two finite Warburg elements capture the mass transport behavior of the hypothesized base and flake structures.

Two finite Warburg elements, representing the mass transport behavior of the $Ni(OH)_2$ flake and base regions are included in the circuit and are arranged in parallel as it is assumed that both these regions will charge / discharge simultaneously in a working electrode. Using this modeling approach would allow for each Warburg element to have a unique diffusion time constant. In addition, employing two finite Warburg elements assumes that each corresponds to a single diffusion pathway for each of the flake and base regions in the $Ni(OH)_2$ nanostructure. This is in contrast to the single, general Warburg element that was presented in section 3.2.2 and is typically associated with multiple or complex diffusion pathways [2]. Given these assumptions, the results of the model fitting for all the three samples are shown in Figure A.3. with the sample frequency response outlined in red and the model fit in green

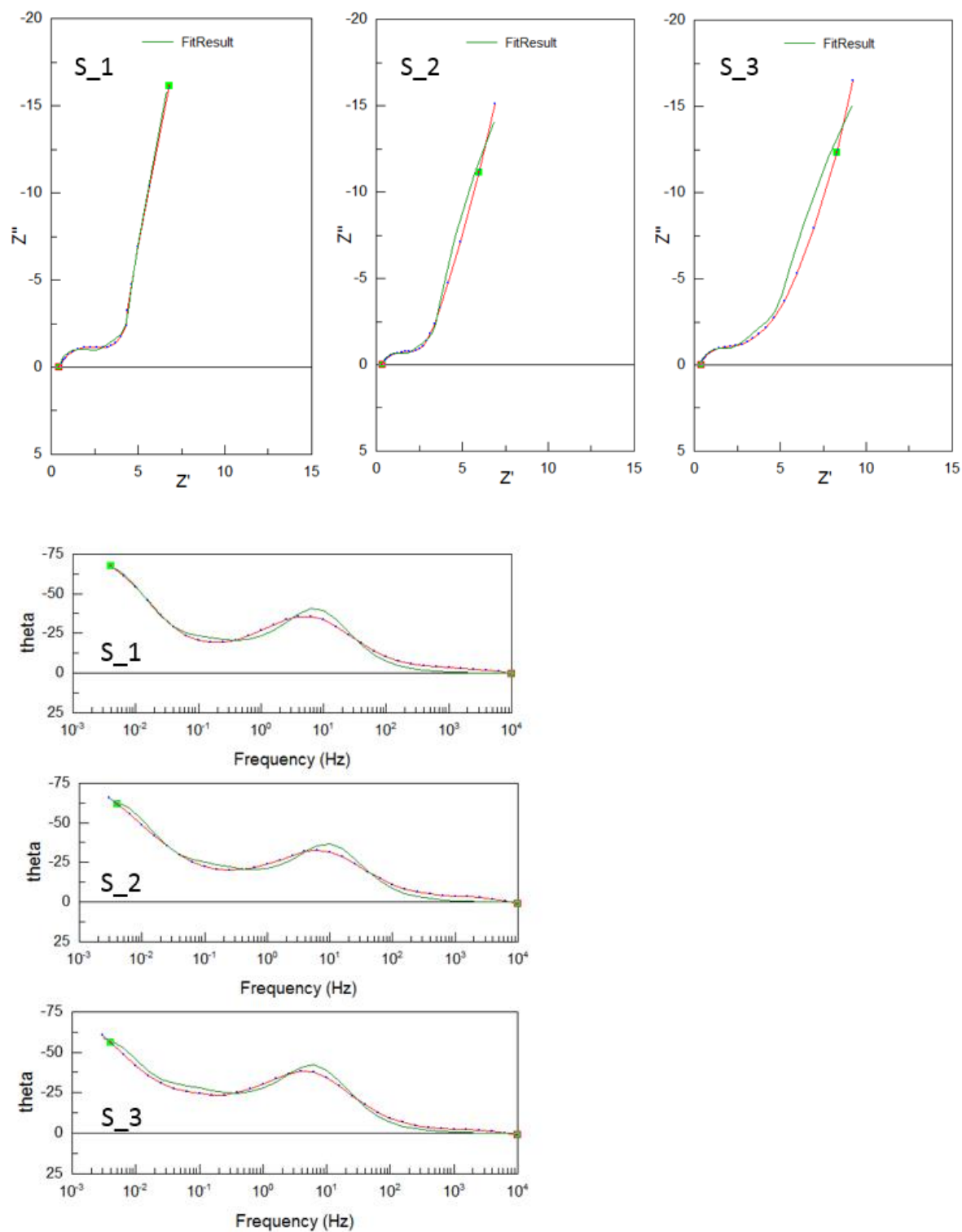


Figure A.3: Modified Randles circuit model outputs showing sample frequency response in red and the equivalent circuit model in green. The model fits appear reasonable for all three samples.

Qualitatively, the double Warburg Circuit models appear to yield reasonable fits of the experimental data for all three test samples. Further, these models were used to estimate several figures of merit for each test sample and the results are summarized in Table A.1.

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Series Resistance R_s (Ω)	0.52 +/- 6.3%	0.41 +/- 7.9%	.041 +/- 7.9%
Kinetic Resistance R_{ct} (Ω)	1.73 +/- 2.3%	1.11 +/- 3.5%	1.45 +/- 2.7%
Double layer Capacitance C_{dl} (F)	0.023 +/- 12.6%	0.026 +/- 11.3%	0.032 +/- 9.0%
Real Surface Area (cm^2)	1145 +/- 12.6%	1280 +/- 11.3%	1608 +/- 9.0%
Kinetic time constant: τ_k (s) $\tau_k = \frac{1}{(R_{ct}) * (C_{dl})}$	0.040 +/- 14.9%	0.028 +/- 14.8%	0.046 +/- 11.7%
Nano-Flake: Warburg R: “Diffusion resistance” (Ω)	7.9 +/- 5.7%	7.9 +/- 5.7%	15.14 +/- 2.9%
Nano-Flake: Warburg T: Diffusion time constant: τ_d (s)	14.8 +/- 0.1%	18.3 +/- 0.1%	27.2 +/- 0.04%
Nano-Flake: Warburg P: (exponent ϕ_w)	0.5	0.5	0.5
NiOH ₂ Base: Warburg R: “Diffusion resistance” (Ω)	137.3 +/- 0.02	144.1 +/- 0.01	131.9 +/- 0.02
NiOH₂ Base: Warburg T: Diffusion time constant: τ_d (s)	150.9 +/- NA	765.0 +/- NA	783.6 +/- NA
NiOH ₂ Base: Warburg P: (exponent ϕ_w)	0.5	0.5	0.5

Table A.1: Figures of merit extracted from a modified Randles equivalent circuit model employing two finite Warburg elements. Similar to the CPE and Randles models presented in section 3.2, the R_s value (Row 1) for S1 is higher than those for S2 and S3, indicating a higher value of ohmic resistance and correlating with the trend in sample polarization curves. Values of double layer capacitance (C_{dl} -Row 3) are equivalent to those extracted from previous models and were used to estimate a real surface area for each sample. Interestingly, the two finite Warburg elements produced significantly different values for diffusion time constants (τ_d). Values for the “flake elements ranged from 14-27 seconds are were roughly equivalent to values extracted from the

Randles circuit presented in section 3.3.2. However, values generated for the base Warburg element were an order of magnitude larger, ranging from ~150-780 seconds. It is important to note that the model was not able to output uncertainty values for the base diffusion coefficient. This model limitation likely indicates a higher degree of uncertainty with these values. Finally, kinetic time constants for each test sample were calculated and found to be similar to the values extracted from the Randles model presented in section 3.3.2.

Row 1 of Table A.1 summarize the Randles model output for R_s , the total series resistance measured for each sample. Like the values extracted from the CPE and Randles model in section 3.3.2, the R_s value of S_1 is significantly higher than those for S_2 and S_3 and again correlates with the trend in the slope of the sample polarization curves. Similarly, values for double layer capacitance, charge transfer resistance and derived values of sample surface area and kinetic time constants were roughly equivalent to those extracted from the Randles model in section 3.3.2. However, it is interesting to note that the diffusion time constants (τ_d) for the two finite Warburg elements produced significantly different values. Values for the “flake” elements ranged from 14-27 seconds, correlated to the observed trend in nanoflake thickness measured by SEM, and were roughly equivalent to values extracted from the Randles circuit presented in section 3.3.2. However, values generated for the base Warburg element were an order of magnitude larger, ranging from ~150-780 seconds. It is important to note that the model was not able to output uncertainty values for the base diffusion coefficient. This model limitation likely indicates a higher degree of uncertainty with these values. While this result should be taken as preliminary, it is consistent with the hypothesis that there are be two distinct regions in the electrode nanostructure with different mass transport time constants. Given these values of (τ_d), most of the material in the flake region could be charged or discharged in 10-20 seconds. However, it would take 150-700 seconds to fully convert the active material in the base region. Significantly, the relative orders of magnitude of these two diffusion constants are roughly consistent with the

GCD analysis presented in section 3.3.1, where the majority (~75%) of electrode capacity could be discharged in approximately 7-11 seconds while the remaining ~25% of capacity required 300-450 seconds to discharge. Following from this result, an attempt to determine the approximate thickness of both the Ni(OH)₂ flake (L1) and base (L2) regions was done using the appropriate diffusion time constants extracted from the EIS model and estimates of sample diffusion coefficient extracted from CV measurements presented in section 3.1.3. The data for this exercise is shown in Table A.2 and the calculated values for the Ni(OH)₂ flake thickness

	Sample_1 High Aspect Ratio	Sample_2 Medium Aspect ratio	Sample_3 Low Aspect ratio
Diffusion coefficient (cm ² /s) CV Method	2.5 x 10 ⁻¹⁴ +/- 3.7%	4.5 x 10 ⁻¹⁴ +/- 12.1%	1.7 x 10 ⁻¹⁴ +/- 9.8%
Nano-Flake: Warburg T: Diffusion time constant: τ_d (s)	14.8 +/- 0.1%	18.3 +/- 0.1%	27.2 +/- 0.04%
*Characteristic Diffusion Length (nm)	6.16 +/- ~1%	9.02 +/- ~1%	7.79 +/- ~1%
**Imputed nanoflake thickness (nm)	12.32 +/- ~1%	18.04 +/- ~1%	15.58 +/- ~1%
Measured Nanoflake thickness (nm)	9.48 +/- 6.38%	11.84 +/- 4.29%	18.00 +/- 6.25%
Ni(OH) ₂ Base: Warburg T: Diffusion time constant: τ_d (s)	150.9 +/- NA	765.0 +/- NA	783.6 +/- NA
Ni(OH)₂ Base Thickness (nm)	19.65 +/- %	58.84 +/- %	42.33 +/- %

Table A.2: Comparison of measured values of sample nanoflake thickness and values calculated using H⁺ diffusion coefficients extracted from CV curves and τ_d values for the flake and base regions extracted from EIS measurements. Imputed nanoflake thicknesses are within 50% of values measure with an SEM for each test sample. Calculated values for the hypothetical Ni(OH)₂ base structure range from approximately 20-60 nm.

were determined to be within 50% of the values measured by SEM for each of the three test samples. Calculated values for the Ni(OH)₂ base thicknesses ranged between 20-60 um which is again consistent with the hypothesis of the base region being thicker than the flake region and

thus requiring a longer time to charge / discharge under mass transport limited conditions where H^+ ions are the diffusing species. Given that the results of this double finite Warburg model were somewhat consistent with sample measurement data, it is proposed that additional analysis that builds off this model and conceptual picture could be a possible direction for future work.

Appendix B Galvano-static Charge / Discharge (GCD) data for all Samples

Sample_1: GCD Calculations											
Current (A)	0.01	0.01	0.04	0.07	0.1	0.13	0.16	0.19	0.22	0.25	0.3
Delta V (V)	0.5	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Delta t (s)	420.6	298.21	66.36	36.59	25.16	19.11	15.41	12.77	10.71	9.19	7.27
Capacitance (F)	8.41	6.21	5.53	5.34	5.24	5.18	5.14	5.05	4.91	4.79	4.54
Cs (F/g) (Total Mass)	1160.28	856.93	762.76	736.01	722.99	713.88	708.51	697.21	677.07	660.20	626.72
Cs (F/g) (Active Mass)	2,522	1,863	1,658	1,600	1,572	1,552	1,540	1,516	1,472	1,435	1,362
Cv (F/cm ³)	2,298	1,697	1,511	1,458	1,432	1,414	1,403	1,381	1,341	1,308	1,241
Capacity (Coulombs)	4.206	2.98	2.65	2.56	2.52	2.48	2.47	2.43	2.36	2.30	2.18
Energy /cell (J)	1.102	0.8532	0.7089	0.6313	0.5686	0.5112	0.4617	0.4125	0.361	0.3216	0.253
Energy Eff (%)	64.64%	70.7%									
Columbic Eff (%)	98.40%	94.2%									
Energy / Cell (Wh/cm ³)	0.083644	0.0647	0.0538	0.0479	0.0432	0.0388	0.035	0.0313	0.0274	0.0244	0.0192
Energy Density (Wh/L)	83.64	64.70	53.80	47.90	43.20	38.80	35.00	31.30	27.40	24.40	19.20
Power / cell (W)	0.00262	0.0029	0.0104	0.0172	0.0219	0.0255	0.0288	0.0297	0.0332	0.0350	0.0348
Power Density (W/cm ³)	0.716	0.781	2.84	4.71	5.98	6.97	7.87	8.11	9.07	9.56	9.51
Power Density (W/L)	715.9	781.1	2841.5	4712.8	5983.6	6967.2	7868.9	8109.3	9071.0	9558.2	9507.6
Specific Energy (Wh/Kg)	91.80	71.01	59.04	52.57	47.41	42.58	38.41	34.35	30.07	26.78	21.07
Cell Power (W)	0.0026	0.0029	0.0104	0.0172	0.0219	0.0255	0.0288	0.0297	0.0332	0.0350	0.0348
Specific Power (W/kg)	785.69	857.18	3118.44	5172.03	6566.72	7646.18	8635.68	8899.55	9955.02	10489.68	10434.09
Current Density (A/g) active	3.00	3.00	11.99	20.99	29.99	38.98	47.98	56.97	65.97	74.96	89.96
Current Density (A/cm ³)	2.73	2.73	10.93	19.13	27.32	35.52	43.72	51.91	60.11	68.31	81.97

Sample_2: GCD Calculations											
Current (A)	0.01	0.01	0.04	0.07	0.1	0.13	0.16	0.19	0.22	0.25	0.3
Delta V (V)	0.5	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Delta t (s)	626.3	447	96	52.35	36	27.4	22.15	18.390	15.8	13.65	11.13
Capacitance (F)	12.53	9.31	8.00	7.63	7.50	7.42	7.38	7.28	7.24	7.11	6.96
Cs (F/g) (Total Mass)	1399.55	1040.50	893.85	853.00	837.99	829.14	824.95	813.34	809.12	794.34	777.23
Cs (F/g) (Active Mass)	2,916	2,168	1,862	1,777	1,746	1,727	1,719	1,694	1,686	1,655	1,619
Cv (F/cm ³)	3411.2	2536.1	2178.6	2079.1	2042.5	2020.9	2010.7	1982.4	1972.1	1936.1	1894.4
Capacity (Coulombs)	6.263	4.47	3.84	3.6645	3.6	3.562	3.544	3.4941	3.476	3.4125	3.339
Energy /cell (J)	1.649	1.397	1.034	0.9396	0.8647	0.8029	0.7424	0.6898	0.6304	0.5756	0.4915
Energy Eff (%)	62%	64%									
Columbic Eff (%)	94%	95%									
Energy / Cell (Wh/cm ³)	0.1248	0.1057	0.0783	0.0711	0.0655	0.06077	0.05619	0.05221	0.04772	0.04357	0.0372
Energy Density (Wh/L)	124.80	105.70	78.30	71.10	65.50	60.77	56.19	52.21	47.72	43.57	37.20
Power / cell (W)	0.0026	0.0031	0.0108	0.0180	0.0241	0.0293	0.0335	0.0375	0.0399	0.0422	0.0442
Power Density (W/cm ³)	0.717	0.85	2.94	4.89	6.55	7.98	9.13	10.22	10.87	11.49	12.03
Power Density (W/L)	717.4	851.3	2936.3	4889.4	6550.0	7984.4	9132.5	10220.6	10872.9	11491.0	12032.3
Specific Energy (Wh/Kg)	106.67	90.35	66.93	60.77	55.99	51.94	48.03	44.63	40.79	37.24	31.80
Cell Power (W)	0.0026	0.0031	0.0108	0.0180	0.0241	0.0293	0.0335	0.0375	0.0399	0.0422	0.0442
Specific Power (W/kg)	613.16	727.63	2509.76	4179.21	5598.60	6824.64	7805.96	8736.00	9293.61	9821.91	10284.63
Current Density (A/g) active	2.33	2.33	9.31	16.29	23.28	30.26	37.24	44.23	51.21	58.19	69.83
Current Density (A/cm ³)	2.72	2.72	10.89	19.06	27.23	35.40	43.57	51.74	59.91	68.08	81.70

Sample_3: GCD Calculations											
Current (A)	0.01	0.01	0.04	0.07	0.1	0.13	0.16	0.19	0.22	0.25	0.3
Delta V (V)	0.5	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Delta t (s)	483.7	336.9	74.1	40.76	27.71	21.24	16.97	14	11.98	10.25	8.33
Capacitance (F)	9.67	7.02	6.18	5.94	5.77	5.75	5.66	5.54	5.49	5.34	5.21
Cs (F/g) (Total Mass)	1185.54	860.14	756.74	728.45	707.47	704.96	693.22	679.13	672.90	654.23	638.02
Cs (F/g) (Active Mass)	2,763	2,005	1,764	1,698	1,649	1,643	1,616	1,583	1,569	1,525	1,487
Cv (F/cm ³)	3,054	2,216	1,949	1,876	1,822	1,816	1,786	1,749	1,733	1,685	1,643
Capacity (Coulombs)	4.837	3.369	2.964	2.8532	2.771	2.7612	2.7152	2.66	2.6356	2.5625	2.499
Energy /cell (J)	1.2953	0.9881	0.8113	0.7363	0.6764	0.6245	0.5767	0.5283	0.49072	0.4482	0.387
Energy Eff (%)	61%	69%									
Columbic Eff (%)	92.60%	91.60%									
Energy / Cell (Wh/cm ³)	0.1135	0.0866	0.0711	0.06451	0.0593	0.0547	0.0505	0.0463	0.043	0.0393	0.0339
Energy Density (Wh/L)	113.50	86.60	71.10	64.51	59.30	54.70	50.50	46.30	43.00	39.30	33.90
Power / cell (W)	0.0027	0.0029	0.0109	0.0181	0.0244	0.0294	0.0339	0.0377	0.0409	0.0437	0.0464
Power Density (W/cm ³)	0.84	0.93	3.45	5.70	7.70	9.27	10.71	11.91	12.92	13.80	14.65
Power Density (W/L)	844.7	925.4	3454.3	5697.6	7704.1	9271.2	10713.0	11905.7	12921.5	13802.9	14650.7
Specific Energy (Wh/Kg)	102.71	78.37	64.34	58.38	53.67	49.50	45.70	41.90	38.91	35.57	30.68
Cell Power (W)	0.0027	0.0029	0.0109	0.0181	0.0244	0.0294	0.0339	0.0377	0.0409	0.0437	0.0464
Specific Power (W/kg)	764.47	837.45	3126.02	5156.24	6972.02	8390.21	9695.04	10774.40	11693.70	12491.34	13258.52
Current Density (A/g) active	2.86	2.86	11.43	20.00	28.57	37.14	45.71	54.28	62.85	71.42	85.70
Current Density (A/cm ³)	3.16	3.16	12.63	22.10	31.57	41.04	50.51	59.97	69.44	78.91	94.70

Figure B1. Electrode performance data for all three test samples extracted from GCD measurements. Material is in reference to results presented in section 3.1

Appendix C CV Appendix

C.1 CV Appendix: S2 and S3 Predicted vs Actual Polarization curves

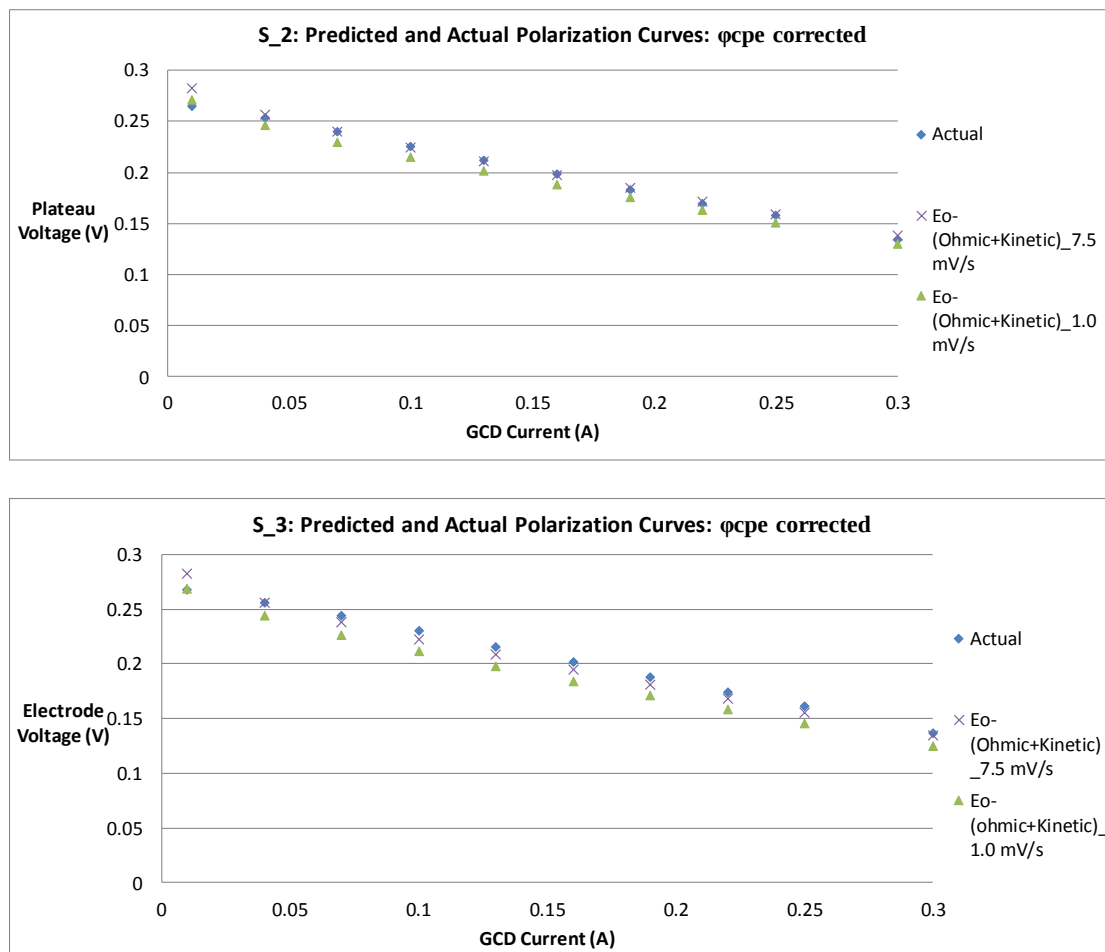
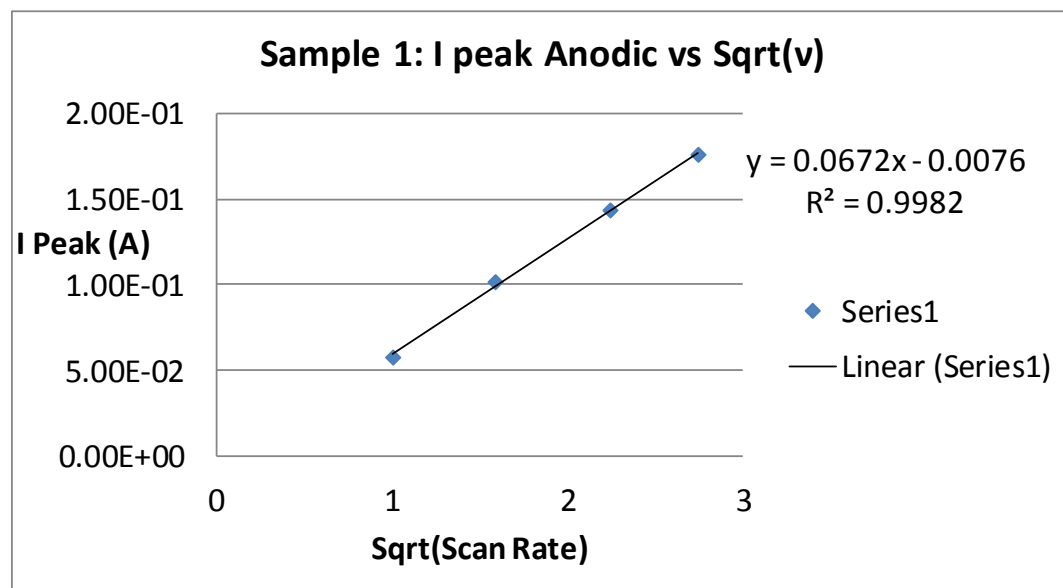


Figure C1. Electrode performance data for all three test samples extracted from GCD measurements. Material is in reference to results presented in section 3.2

C.2 Summary Data for diffusion coefficient extraction from CV measurements

Sample _1					
Diffusion Coefficient Calcs (H+)					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	6.67E-02	1.04E-01	1.49E-01	1.83E-01	
Eff. Surface Area (cm ²)	1105.00	1105.00	1105.00	1105.00	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (M/cm ³)	0.044	0.044	0.044	0.044	
Diff Coeff (cm ² /s)	2.57E-14	2.52E-14	2.55E-14	2.59E-14	2.56E-14
Diffusion Coefficient Calcs (OH-)					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	6.67E-02	1.04E-01	1.49E-01	1.83E-01	
Eff. Surface Area (cm ²)	1.22	1.22	1.22	1.22	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (M/cm ³)	0.002	0.002	0.002	0.002	
Diff Coeff (cm ² /s)	1.03E-05	1.01E-05	1.03E-05	1.04E-05	1.03E-05



Sample_3					
Diffusion Coefficient Calcs (H+)					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	8.07E-02	1.33E-01	1.90E-01	2.33E-01	
Eff. Surface Area (cm ²)	1470.00	1470.00	1470.00	1470.00	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (M/cm ³)	0.044	0.044	0.044	0.044	
Diff Coeff (cm ² /s)	2.13E-14	2.30E-14	2.35E-14	2.37E-14	2.29E-14
Diffusion Coefficient Calcs (OH-)					
Scan Rate (mV/s)	1	2.5	5	7.5	
Peak Cathodic Current (A)	8.07E-02	1.33E-01	1.90E-01	2.33E-01	
Eff. Surface Area (cm ²)	1.46	1.46	1.46	1.46	
# Electrons (n)	1	1	1	1	
H+ Molar Conc. (M/cm ³)	0.002	0.002	0.002	0.002	
Diff Coeff (cm ² /s)	1.06E-05	1.15E-05	1.17E-05	1.18E-05	1.14E-05

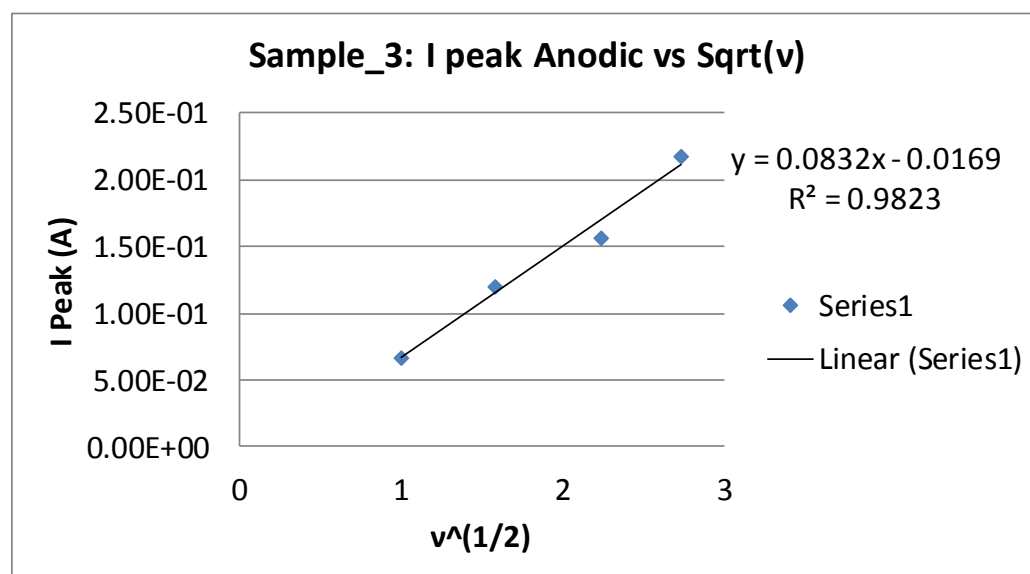


Figure C2. Electrode performance data for all three test samples extracted from GCD measurements. Material is in reference to results presented in section 3.2