Fabrication and characterization of high surface area nickel-deposited graphite substrates

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Abstract

In certain electrochemical battery cells, inefficiencies arise due to the formation of hydrogen from corrosion reactions at the anode. One way to reduce these inefficiencies is to operate the cell at high current densities, which is obtainable given a high cathode to anode surface area ratio; however, commercially available metal foams often do not provide sufficient surface area density (cm$^2$/g). Coating high-surface area materials in the appropriate metal is a premier alternative, but while methods to effectively coat two-dimensional substrates in metal through electrodeposition has been well documented, attempts to scale electrodeposition to three-dimensional coating to achieve high-surface area catalysts has encountered certain challenges. The formation of a pure metal crust on the outer surface area of the catalyst prevents the penetration of metal ions into the inner fibers of the material, resulting in a lower surface area density. This thesis describes simple, repeatable electrodeposition methods to increase the homogeneity of the nickel coating throughout highly porous graphite catalysts and prevent the formation of a metal crust. Parameters such as direct/pulsating current, ultrasonic vibration pretreatment, and varying electrodeposition solution concentrations were tested in order to optimize the electrodeposition procedure. Three techniques were used to characterize the post-synthesis surface condition including scanning electron microscopy, electron dispersive spectroscopy and cyclic voltammetry. The improved electrodeposition method led to nickel-coated graphite felt with a specific surface area of 620 cm$^2$/cm$^3$ and a surface area density of 7500 cm$^2$/g, achieving a 890% higher surface area and 4650% higher surface area density than commercially available nickel foams.

The proposed electrodeposition method provides high-surface area, full-volume coating of highly porous catalysts, applicable not only to electrochemical batteries but to any battery chemistry with an electrolyte that contains fuels, particularly flow batteries. The proposed methods to obtain effective full-coated, high-surface area catalysts have the potential to optimize outputted battery power and thereby revolutionize battery electrode fabrication.

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Title: Professor of Mechanical Engineering
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Chapter 1

Introduction

1.1 Objective

Due to its value as a component in numerous battery and fuel cell configurations, high surface area density nickel is a highly sought after material. In the context of electrochemical batteries, most require compactness and low system density, for which commercially available foams often to do not have sufficiently high surface area density. This is the source of the need for higher surface area density materials. This thesis explores the fabrication of high surface area density cathodes to increase the operating current densities of electrochemical batteries. Much research has been done to explore the fabrication of two-dimensionally metal coated cathodes but very little research has focused specifically the three-dimensional metal coating, in which the metal ions are deposited homogeneously on the outer and inner fibers of the catalyst matrix.

This thesis describes the fabrication of nickel-coated high-porosity 3 mm thick graphite matrices by nickel deposition on graphite substrates. We attempt to develop a simple, repeatable methodology to fabricate the high-surface area nickel-coated substrates. Towards this goal, we recommend a concentration regime for the electrolytic bath in which electrodeposition occurs, a current regime and a post-treatment process to optimize the mass transport of nickel ions to the inner fibers of the cathodic substrate.

After sample synthesis, analysis of the coated surface was analyzed using three techniques: (1) scanning electron microscopy (SEM), (2) energy-dispersive X-ray spectroscopy (EDS) and (3) cyclic voltammetry (CV). The surface microstructure, such as the the spatial arrangement, size and depth of penetration of the nickel deposits and elemental composition. Lastly, the magnitude of the increased effective surface-area of nickel-coated graphite substrates as compared to commercially available nickel foams was quantified.
The authors suggest further work for the successful integration of these high-surface area cathodes into electrochemical batteries.

1.2 Structure of Thesis

This thesis is structured as follows:

Chapter 1 highlights the overarching objectives and structure of the thesis.

Chapter 2 outlines the electrochemical kinetics of electrodeposition and the benefits of optimizing electrochemical battery efficiencies through the use of high-surface area cathodes, particularly in the context of an aluminum-permanganate battery technology.

Additionally, this chapter outlines prior research conducted on two-dimensional electrodeposition and previous attempts to scale up this procedure to three-dimensional coating.

Chapter 3 contains the electrodeposition fabrication methodologies that were tested and the characterization techniques used for post synthesis analysis of nickel-coated graphite surfaces.

Chapter 4 discusses the qualitative and quantitative results to compare the different electrodeposition fabrication methodologies, specifically comparing the surface area achieved by the best fabrication method to the surface area of commercially available nickel foams.

Chapter 5 summarizes the results obtained from the experiments and identifies the best fabrication methodology for nickel deposition on graphite.

Chapter 6 summarizes further work that needs to be completed in order to successfully integrate high-surface area cathodes by our select methodology into electrochemical battery technologies.

Chapter 7 contains any MatLAB or Arduino scripts utilized in our experimental setup and data analysis.
Chapter 2

Background

2.1 OpenWater Power’s aluminum-water-permanganate battery technology

In Professor Doug Hart’s Engineering System Design I class (2.013) taught in Fall 2013, students were tasked with designing a proof-of-concept (POC) prototype to integrate a novel power system into a REMUS 600 autonomous under-water vehicle (AUV). This power system is comprised of an aluminum oxidation and permanganate reduction reaction, patented by the startup OpenWater Power (OWP), involving aluminum, permanganate and water; this reaction is broken into two-half reactions denoted in Equation 2.1. Equation 2.1c denotes the overall oxidation reduction:

\[
\begin{align*}
\text{Anode:} & \quad \text{Al} + 4\text{OH}^- & \rightarrow & \text{Al(OH)}_4^- + 3\text{e}^- (-2.3 \text{ vs. SHE}) \\
\text{Cathode:} & \quad \text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- & \rightarrow & 4\text{OH}^- + \text{MnO}_2 (+0.6 \text{ vs. SHE}) \\
\text{Overall:} & \quad \text{Al} + \text{MnO}_4^- + 2\text{H}_2\text{O} & \rightarrow & \text{Al(OH)}_4^- + \text{MnO}_2
\end{align*}
\]

Permanganate is an advantageous oxidizer because, unlike most other oxidizers, the reactions involving permanganate do not produce hydrogen as a byproduct.

Figure 2.1 depicts a schematic of the internals of the prototype of the aluminum-water-permanganate battery technology that OWP is developing. The prototype of the chemical reactants: aluminum, permanganate ions (not shown) and water (not shown). The aluminum is stored as thin, vertical plates and composes the anode; the nickel catalyst matrix is the cathode of the battery.\(^1\) The anode and the cathode are electrically connected by wires and

\(^1\)Nickel was determined by OWP to be an optimal choice of metal for the catalyst matrix of the aluminum-water-
mechanically separated with a wire mesh. In order for electrons to flow through this circuit, the cathode and anode are suspended in a KOH and MnO₄ electrolyte solution.

Figure 2.1: Schematic of the internals of the scalable battery prototype containing the aluminum-water-permanganate reaction, as developed by OWP.

Bench-level experiments conducted by OWP researchers conclude that OWP’s unique two-step proposed discharge gives the battery technology a cell-level specific energy density of 1.2 MJ/L and system-level energy density of 0.9 ML/kg. Comparatively, the current REMUS 600 power system consists of a lithium ion battery with a specific cell-level energy density range of 0.5-0.9 ML/kg and system-level energy density of 0.4 ML/kg. Additionally, the current REMUS 600 has a cell-level energy density of 0.6 MJ/L and a cell-level power density of 1.4 W/L whereas the proposed electrochemical battery can reach a cell-level energy density and cell-level power density of 2.3 MJ/L and 5.3 W/L, respectively. OWP’s proposed aluminum oxidation reaction coupled with permanganate can generally improve the energy density of the current REMUS power supply by a factor of 2.25. Great, continued interest and financial backing for this project are provided by the Woods Hole Oceanographic Institute (WHOI), MIT Lincoln Laboratory and the Office of Naval Research (ONR) of the United States Navy.

The goal of optimizing the cell-level energy density of OWP’s aluminum-permanganate-water electrochemical battery was the initial motivation of the study we conducted to investigate the fabrication of high-surface area nickel-coated graphite substrates, as described in the subsequent sections of this report.

permanganate reaction outlined in Equation 2.1.

²At the cell-level only the volume of the reactants and products of the chemical reactions are considered. The material housing the reactions is not of the cell.

³Calculations conducted by 2.013 students and documented in the Fall 2013 2.013 Engineering Systems I Final Report titled, "Aluminum Permanganate-Driven Power System for the REMUS 600 Autonomous Underwater Vehicle." Please contact Katelyn Wolfenberger (wolfkat@mit.edu) for access to this document.
2.2 Achieving high electrochemical battery energy densities

OWP researchers state that their proposed electrochemistry has the potential of reaching a maximum theoretical energy density of 3.2 MJ/L for a closed system and 12 MJ/L for an open system \(^4\). The maximum theoretical energy densities were determined assuming the following: (1) an open-circuit voltage of 1.5 V, (2) negligible corrosion, (3) negligible mass and volume contributions from writing, reaction-enclosing housing, electrolyte, water intake and waste removal systems and (4) neutral system buoyancy. Optimizing the battery electrochemistry by implementing changes to the battery technology design and fabrication processes would allow the battery technology to operate near the theoretical maximum cell-level energy density and increase the battery’s outputted cell voltage. A more optimal design would allow 2.013 and OWP to create a power system to better meet 2.013’s sponsor’s goals of extending the range of the REMUS 600 to 30 days.

There are many challenges to reaching the ideal energy densities. For one, there is corrosion at the anode site that consists of the aluminum and water reacting independently of the anode/cathode circuit. Corrosion occurs because, naturally, aluminum is very chemically reactive. Additionally, OWP’s battery prototype, as depicted in Figure 1, is designed such that aluminum is electrically connected to nickel; the electronic connection between two metals of differing electrochemical properties (i.e. nickel is more inert than aluminum) causes galvanic effects to occur. The more chemically active metal atoms (i.e. atoms of aluminum) ionize and break into the surrounding water where they bond to oxygen ions to produce a dense aluminum oxide \((\text{Al}_2\text{O}_3)\) coating over the surface of the aluminum metal. This surface oxide thermally insulates the aluminum metal and it is this passivation layer that subsequently impedes the desired half reactions, outlined in Equations 2.1a and 2.1b. Inherent to the corrosion is the consumption and subsequent deterioration of mechanical surface properties of the aluminum metal. Given that these reactions utilize external electrical work, the battery technology efficiencies and decreasing battery power densities.

Furthermore, research studies conclude that pitting behavior between aluminum and water increases in moving water (Godard 1960). Therefore, if an electrochemical battery were to operate as an open system, in which water is continuously moving in and out of the cell housing, for an AUV power system, the effects of galvanic corrosion will be greater and thereby will cause the battery operate at an energy density even further from the theoretical maximum.

Coupled with the passivation of the aluminum metal is the generation of hydrogen gas at

---

\(^4\)Open seawater system means that seawater is actively entering and exiting the system during AUV operation. A closed seawater system is one in which (1) only gas byproducts are purged out of the reaction-enclosing housing and (2) no seawater enters or exits the system during AUV operation.
the anode site (Shrovan et al. 2011). The primary cathodic and anodic equations that govern the hydrogen evolution from aluminum corrosion are outlined in Equations 1 and 2. Overall, the reaction that occurs is denoted by Equation 2.2c if the aluminum reacts with water at a temperature lower than 70°C forming Al(OH)$_3^-$, otherwise a different aluminum hydroxide is formed, AlOOH, as outlined by Equation 2.2d.

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \quad \text{(Anode)} \tag{2.2a} \\
6\text{H}^+ + 6e^- & \rightarrow 42\text{H}_2 \quad \text{(Cathode)} \tag{2.2b} \\
2\text{Al} + 6\text{H}_2\text{O} & \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \quad \text{(Overall)} \tag{2.2c} \\
2\text{Al} + 2\text{H}_2\text{O} & \rightarrow 2\text{AlOOH} + 3\text{H}_2 \quad \text{(Overall)} \tag{2.2d}
\end{align*}
\]

It is important to inhibit hydrogen evolution as to increase the coulombic efficiency of the battery technology resulting from the consumption of the anode.

Michael Faraday studied electrolytic processes and determined that electrochemical corrosion processes are related to the flow of current; specifically, Faraday’s law states the proportionality between the corrosion current, $I_{\text{cor}}$, and the volume of hydrogen generated outlined by Equation 2.3 that is derived from Faraday’s laws of electrolysis and the ideal gas law:

\[
I_{\text{cor}} = \frac{zFPV}{tTR_0} \tag{2.3}
\]

in which the corrosion current is the difference between the net current that flows through the external circuit, $I$, and the magnitude of the dissolution of the anode (i.e. aluminum):

\[
I_{\text{cor}} = I - I_d \tag{2.4}
\]

$z$ is equivalent to the electrons consumed in the reduction of water to hydrogen, $F$ is Faraday’s constant, $P$ is the atmospheric pressure, $V$ is the volume of evolved hydrogen, $t$ is the time to collect $V$, $R_0$ is the universal gas constant and $T$ is the temperature in Kelvins.

Utilizing Faraday’s law, a relationship between the corrosion rate, $r$, and corrosion current density, $j_{\text{cor}}$ is as follows:
It is important to note that Equation 2.5 denotes a proportionality between the mass lost per unit area due to galvanic corrosion of the anode to the corrosion current density. More specifically, assuming that the cathodic process on both metals in the galvanic couple is diffusion-controlled, the dissolution of rate of the anode is proportional to the cathode-to-anode surface ratio (Mansfeld 1971); the net current density, \( j \), can be written in terms of the cathodic and anodic surface areas, \( A_{\text{cathode}} \), and \( A_{\text{anode}} \):

\[
J = \frac{A_{\text{cathode}}}{A_{\text{anode}}} \left( \frac{\Delta U}{R_{el} + R_{p,a} + R_{p,c}} \right) \tag{2.6}
\]

in which \( \Delta U \) is the difference of potential between the two electrodes, \( R_{el} \) is the electrolyte resistance, \( R_{p,a} \) and \( R_{p,c} \) is the polarization resistance at the anode and cathode, respectively. The relationship, outlined in Equation 2.6, denotes that a high cathode-to-anode surface area ratio will allow the cell to operate at high current densities; a very high cell current density is required to allow for high coulombic utilization, namely high discharge rate and minimal polarization during battery operation (Macdonald et al 1988).

Coupled with this increased current, Equation 2.3 subsequently denotes an increase in corrosion per unit anodic area. This thesis will primarily focus on more consistent, high-power operating capabilities of OWP’s water-activated aluminum-permanganate battery configurations as to engineer an integrated system with optimal projected energy density at the expense of low corrosion rates. High corrosion rates pose challenges for battery longevity; the conclusion of this thesis will highlight further research that would need to be conducted to further optimize for battery shelf-life.

### 2.2.1 Achieving a high cathode-to-anode surface area ratio

Although literature does not specify a desired cathode-to-anode surface area ratio for aluminum-permanganate reactions, OWP researchers investigated the aluminum oxidation and permanganate reduction dynamics; based on the current density outputs of prior battery incarnations, OWP researchers identified that a favorable cathode-to-anode surface area ratio is approximately on the order of \( 10^4 \) (McKay 2013).

The easiest and simplest way of increasing the surface area of an electrode is to increase the amount of material that is used in the reaction. Theoretically, one possibility is simply to
have many times more cathode material (in this case, nickel) than there is anode material (aluminum); however, this option is highly impractical when the goal, as it commonly is, is to have a small and compact battery. Ideally, the anode and cathode would be as small as possible, which means that the cathode would have a structure that provides a high surface area. High surface area systems can be attained by (1) fabrication of samples with a high surface-to-volume ratio or (2) fabrication of materials in which the void surface area is high compared to the volume of bulk support material. Given that a high surface area is one of the defining properties of porous materials, utilization of highly porous materials is a favorable material for electrochemical battery cathodes.

2.3 The role of nickel as cathodic material

Nickel is commonly used as a component of various battery configurations, with many commonly used configurations such as nickel-metal-hydride (NiMH). Nickel is often utilized as a catalyst or as part of a catalyst for the chemical reaction that drives the battery. For OWP’s aluminum-permanganate-water battery configuration, nickel was chosen as the cathode material due to its high corrosion and temperature resistance and its ability to act as a catalyst to help improve the reaction output.

The surface area density of current commercially available nickel foams are relatively low, ranging from 10 to 200 cm²/g (Recemat 2013). There are a large number of other non-metallic materials, including various foams and felts, that have considerably higher specific surface area, but would be made out of different materials. Graphite felt has a particularly high surface area, typically between 0.7 to 2000 m²/g (Floner et al 2007). However, graphite felt cannot be used as a cathode, since the cathode for this battery needs to be made of nickel, which acts doubly as both the cathode and the catalyst. In order to combine the structural benefits of high-surface area graphite felt and the chemical utility of nickel, we can coat the graphite felt with nickel through electrodeposition. This would produce a nickel-coated graphite substrate with the properties needed to function as the cathode of the battery, while concurrently offering an incredibly high surface area.

2.4 Electrodeposition technique for two-dimensionally coating materials

Two-dimensional techniques only allow coating of only the outer surface area of cathodic material via electrodeposition. Electrodeposition is the synthesis of composites from dissolved species by changing the oxidation states of the dissolved species using electricity.
Electrodeposition is a relatively low cost processing technique that enables user control of the composite morphology and thickness.

Extensive research has been conducted for two-dimensional electrodeposition coating methods; the procedure for coating a flat surface is well documented and straightforward. The procedure to two dimensionally coating materials utilizes a electrolyte solution that contains dissolved metal ions that will coat the cathodic material. The electrolyte contains other ions that permit the flow of electricity. Additionally, certain other substances, such as brightener, can also be mixed into the electrolyte in order to obtain the desired appearance of the coated cathodic material. The sample that is being coated, the anode, is placed in the solution connected to the positive side of a low voltage direct-current power source; the cathode is connected to the negative side to complete the circuit. Both the anode and the cathode are submerged in the electrolyte. As current flows through the circuit, electrochemical reactions occur at the interface between the electrode and the electrolyte. Bare metal ions expelled from the anode are present in the electrolyte in a hydrated state. With an applied potential, the ions are driven by a potential gradient towards the cathode. The bare metal ions combine with electrons on the surface of the cathode, become discharged and are now neutral atoms. These atoms eventually get adsorbed and result in layers over the substrate surface, thereby coating the cathodic material.

**Critical variables in two-dimensional electrodeposition procedures**

Extensive research into two-dimensional coating through electrodeposition led to the identification of a specific set of parameters that had varying influence on the coating process. The factors with the strongest effect on the electroplating process are the chemical composition of the electroplating solution, the ratio of the compounds within the solution, and the concentration of the solution (Kopeliovich 2013). Most nickel electroplating solutions include some combination of nickel sulfate (NiSO$_4$·6H$_2$O), nickel chloride (NiCl$_2$·6H$_2$O), and boric acid (H$_3$BO$_3$). Certain less common additives are sometimes used for specific purposes, such as brightener for corrosion protection and high luster, or zinc sulfate (ZnSO$_4$) for a non-reflective surface. For each individual combination of constituents, the ratio of the components and the concentration of the overall solution are both vital factors when evaluating the effectiveness of the solution as an electrodeposition agent. This thesis primarily employs two of the more popular nickel electrodeposition solutions: the Watts solution, which includes NiSO$_4$, NiCl$_2$, and H$_3$BO$_3$ at fixed ratios, and the all-sulfate solution, which only includes NiSO$_4$ and H$_3$BO$_3$ (Kopeliovich 2013). Additional factors of the electrodeposition process include the temperature of the setup while running and the coating time (amount of time during which current is flowing). These factors are significant, but secondary to the
Many researchers conducted experiments in which nickel is the electrodeposited lattice onto particulate matter; these particulate matters included alumina (Ferkel et al. 1997 and Ciubotariu et al. 2008), carbon nanotubes (Chen et al. 2005), graphite (Wu et al. 2008), PTFE (Pena-Munoz et al. 1998), polyethylene (Hamid et al. 2002), tungsten carbide (Basu et al. 2004), silicon carbide (Benea et al. 2001, Hu et al. 2004), titanium dioxide (Chenthamarakshan et al. 2003, Spanou et al. 2009 and Hu et al. 2010), diamond (Wang et al. 2005 and Oghihara et al. 2009) and ruthenium dioxide (Vazquez-Gomez et al. 2007). These researchers sought to study and modify the physical and chemical properties of electroplated layers to get various surface characteristics; additionally, many of these researches sought to model the complex processes involved with the fabrication of these composite layers. The main objective of these papers was focusing primarily on obtaining high-volume of particular matter on the composite layers. In fact, few papers on the topic of electrodeposition focus on developing a technique that enables a single layer of uniformly dispersed electrodeposited lattice on particulate material. Additionally, very few papers focus on scaling up two-dimensional coating procedures to three-dimensional coating in which all exterior and interior of cathodic fibers contain a homogeneous, single-layer of metal ion deposit coatings. Electrodeposition methods to scale up this procedure to coat materials three-dimensionally have not been extensively researched and characterized.

2.5 Attempts at scaling electrodeposition up to achieve three-dimensional coating of porous materials

There have been very few attempts to study electrodeposition of nickel on three-dimensional structures. Documented unsuccessful attempts at developing techniques to scale up electrodeposition to three-dimensional coatings, particularly work done by Y.Z. Wan et al. of the Department of Materials Science and Engineering at Tianjin University that attempted to coat carbon fiber felt of 1.5 mm thickness, have highlighted two main challenges that prevent the homogeneity of three-dimensionally distributed metal ions on highly porous catalysts. Namely, the phenomena observed by researchers include: (1) the formation of a pure metal crust on the outer surface area of the catalyst and (2) the lack of penetration of metal ions into the inner fibers of the catalyst matrix. Both phenomena will be described in the subsequent subsections.

Of the few attempts to achieve three-dimensional coating of porous materials, fewer still have attempted to coat high surface area materials in nickel; however, certain experiments exhibited some levels of success, particularly the work done by Floner et al at the Laboratoire
de Sciences Chimiques de Rennes in 2007. Floner et al achieved a surface area density of 1 m²/g through the implementation of modifications of the standard electrodeposition process, including the choice of electrodeposition solution, coating run time, and the utilization of pulsating current, suggesting values or ranges for each property.

2.5.1 Formation of pure metal crust

Under the action of electric current, it is observed that the metal electrodeposition takes place primarily on the surface of the cathodic material. For the case of electroplating graphite, the inner fibers of the graphite are randomly oriented; therefore, the metal ions from the anode are prevented from approaching the inner fibers of the cathodic material and ultimately settle on the outer surface area of the graphite matrix. Once coated, the outer graphite fibers have a higher electrical conductivity than the uncoated inner graphite fibers and thereby act as a protective screen to the inner fibers (Wan et al 1997). Instead of running evenly through the whole sample, the current runs through the metal coated surface almost exclusively. This leads to the formation of a thick pure metal on the outer surface area of the catalyst matrix. This crust leads to a significant increase in the weight and volume of the cathode with very little relative gain in cathodic surface area, leading to a considerable loss in battery efficiency.

2.5.2 Lack of metal ions coating inner catalyst fibers

Due to the aforementioned metal crust formation, most of the current running through the sample is diverted through the metal crust. Since current is necessary for the metal ions to adhere to the sample being coated, a metal crust prevents the inner fibers from being sufficiently coated. Because of this, very little metal deposits penetrate deeper than 1-mm into a highly-porous catalyst matrix under the action of an electric current. This results in (1) virtually no coating of the inner fibers and (2) decreased homogeneity of potential distribution from the interior to exterior fibers of the cathodic material.

2.6 Ultrasound vibration as pretreatment or codeposition process

Many researchers cite the benefits of ultrasonic vibration of uncoated samples as a pretreatment and as a codeposition process during two-dimensional electroplating of pure metals. Electrodeposition under the influence of ultrasonic vibrations increase the mass transport. Researchers Kristof and Pritzker postulated that the evolution of hydrogen gas bubbles at solid microelectrodes creates drag force that results in a microjet oriented towards the
cathode surface that induces intense mixing and thereby improving the transport of bare metal ions to the cathode. Scientists claim, theoretically, ultrasonic radiation should supply a favorable charge-transfer reaction that would aid the adsorption of bare metal ions into the cathodic substrate (Sharma et al 2012). Lastly, ultrasound vibrations produce pressure waves that can aid the activation of electrode surfaces during electrochemical processes (Sharma et al 2012).

Specifically, Resrazi et al. demonstrated that ultrasound vibration increased the rate at which polytetrafluoroethylene particles deposited onto a gold catalyst matrix; Zheng and An proved that an ultrasonic treatment can improve the homogeneity of nanoAl₂O₃ in a NiZn alloy matrix. Lastly, Lee at al. determined that ultrasonic vibrations aided in the mass transport of Al₂O₃ and CeO₂ in a Cu substrate in a low concentrated electrolytic bath.

Therefore, there appears to be great potential for electrodeposition under ultrasonic vibrations to improve the quality of the deposit and the composite morphology for the specific case of nickel-deposited graphite substrates.

2.7 Electroplating under a pulsating current regime

There are additional parameters which are more specific to three-dimensional coating procedures, the most significant of which is the use of pulsating current (i.e. alternating current, AC) as opposed to direct current (DC). The theory behind the potential value of AC is the concept that since a three-dimensional structure requires considerably more coating than a two-dimensional structure, and furthermore that three-dimensional structures require the diffusion of metal ions throughout the sample in order to coat the inner fibers, the constant application of current leads to the depletion of metal ions surrounding the material being coated, impeding the coating process. When the metal ion concentration is low around the sample, any metal ions that diffuse towards the sample are immediately adhered to the surface, thickening the pure metal crust and leaving the inner part of the sample uncoated. In theory, periods of downtime allow for the metal ion concentration surrounding and within the sample to equalize, in an effort to prevent crust formation and increase coating penetration (Floner et al 2007). Specifically, Floner et al investigated the electrodeposition of nickel onto a graphite substrate under a pulsating current regime for the case of a graphite deposited into an electrolytic bath composed of NiSO₄ and H₃BO₃ in which the cathodic material is wrapped in an ionic exchange membrane and teflon plates; and in which the cathodic material, graphite felt, is never in contact with the electrolytic bath but rather, remains dry during the entire electrodeposition process. Additionally, Floner et al utilized a platinum grid as a counter electrode in a three electrode cell.
This report will, however, focus on determining whether a pulsating current regime can increase the homogeneity of nickel ion deposits onto a graphite catalyst matrix in an electrolytic bath composed of NiSO\(_4\) and H\(_3\)BO\(_3\) in which the cathodic material is fully submerged in electrolytic solution and achieve similar results without utilizing additional mechanical components such as an exchange membrane and teflon plates, a situation that is deemed considerably simpler.
Chapter 3

Experimental Details

3.1 Initial Setup and Experimentation Period

An electrochemical cell was formed in an open chemistry beaker at room temperature; the beaker was filled with approximately 80 mL of electrodeposition solution. The electrodeposition solution used initially was a concentration suggested by literature, of 0.05M NiSO₄ and 0.25 H₃BO₃ (Floner et al 2007). Chemical electrodeposition of nickel was carried out in this electrochemical cell. The working electrodes consisted of 21 cm² of pure nickel plate (of thickness 0.58mm) parallel to the highly-porous graphite felt of volume 0.729 cm³ with a thickness of 3mm. (The graphite felt was cut down to appropriate thickness using bandsaw by MIT Central Machine Shop.) Boric acid was purchased from Silk Road LLC, while nickel sulfate was purchased from SS Chemicals. Graphite felt, with 99.9% porosity, was purchased from Alfa Aesar.

![Diagram](image)

Figure 3.1: Graph detailing the effect of increasing run time on coating penetration.
The coating procedure involved sonicating a sample of graphite felt, suspending it and the nickel sheet in the electrodeposition solution through use of an alligator clip, and connecting the nickel sheet and graphite felt to a DC power supply through a MOSFET. The MOSFET is connected to an Arduino, the combination of which allows for the regulation of the DC power supply in order to turn it on and off periodically, as shown in Figure 3.1.

The samples were then left to coat until a current passed through them for 45 minutes, as suggested by literature (Floner et al. 2007). Samples coated using AC had active current through them for a period of 30 seconds, followed by a recovery period of 120 seconds (Floner et al. 2007). This resulted in a total procedure time of 3.75 hours for samples coated using AC, and a total procedure time of 45 minutes for samples coated using DC.

Certain samples were not sonicated before the coating procedure, in order to study the effects of sonication on the coating procedure. After noting that there was effectively no penetration on non-sonicated samples, all future samples were sonicated.

A significant portion of this first experiment involved feasibility experiments and tests to determine the appropriate base setup.

### 3.2 Procedure Refinery Period

After the initial experimental setup was deployed, numerous experiments involving various deviations from the original electrodeposition procedure were developed, assessed, and implemented, with the hopes of furthering the goal of improving the electrodeposition procedure. This period was used to both discover and develop improvements and to eliminate certain major inconsistencies.

#### 3.2.1 Current Density

Various current densities were run between the working electrodes in our initial experimental procedures, ranging from 0.05 mA/mm$^3$ to 0.5 mA/mm$^3$. It was observed that high current densities led to the formation of a visibly thicker crust, while low current densities led to little penetration. This resulted in reaffirmation of the current density suggested by literature of 0.17 mA/mm$^3$ (Floner et al. 2007).

#### 3.2.2 Graphite Suspension

Previously, the graphite felt was suspended in the solution using an alligator clip. This led to the graphite felt being coated to only be partially submerged in the electrodeposition
solution. This led to difficulties determining the volume of submerged graphite felt, which in turn led to inconsistencies in determining the appropriate current to apply to the electrodeposition setup. After the testing of various wires and other forms of suspension, nickel foam was determined to be the optimal method of graphite suspension, primarily due to its combination of durability and conductivity, in addition to eliminating potential impurities due to the introduction of a foreign metal into the electrodeposition system, as illustrated in Figure 3.2.

![Figure 3.2: Schematic illustrating the implementation of nickel felt as a sample suspension system right, allowing the immersion of the graphite felt in the electrolyte without contaminating the electrolyte or exposing the alligator clip to the electrolyte.](image)

### 3.2.3 Alternating and direct current

Another experiment was designed to detect the differences between pulsating/alternating current (AC) and direct current (DC). Multiple samples were coated using both direct and alternating current, after which they were inspected thoroughly.

Samples were run with on- and off-pulse of time durations previously suggested by researchers at the Laboratoire des Sciences Chimiques de Rennes in Rennes Cedex, France. Table 3.1 summarizes their experimental conditions in regards to current densities of graphite felts of various thicknesses.

Given that we are interested in nickel-coating 3 mm-thick graphite felt, according to Table 3.1, we experimented with a 120 second off-pulse.

The DC samples consistently exhibited a strong, thick nickel crust enveloping the graphite felt samples alongside extremely low nickel coating penetration, barely penetrating the sur-
Table 3.1: Experimental conditions for nickel electrodeposition of graphite felt of various thicknesses by Floner et al.

<table>
<thead>
<tr>
<th>Felt thickness ( \delta ) (mm)</th>
<th>[Ni(^{2+})] ( \text{mol L}^{-1} )</th>
<th>On-pulse ( \tau ) (s)</th>
<th>Off-pulse ( t ) (s)</th>
<th>pH</th>
<th>Current efficiency ( I ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta &lt; 2^a )</td>
<td>(&lt;1^a)</td>
<td>( \tau &lt; 1^a )</td>
<td>( t &lt; 60^a )</td>
<td>4.5(^a)</td>
<td>100(^b)</td>
</tr>
<tr>
<td>1(^b)</td>
<td>1(^b)</td>
<td>1(^b)</td>
<td>30(^b)</td>
<td>4.5(^b)</td>
<td>70(^b)</td>
</tr>
<tr>
<td>2 &lt; ( \delta &lt; 6^a )</td>
<td>(&lt;0.1^a)</td>
<td>( 1 &lt; \tau &lt; 30^a )</td>
<td>( 60 &lt; t &lt; 120^a )</td>
<td>5(^a)</td>
<td>70(^b)</td>
</tr>
<tr>
<td>3(^b)</td>
<td>0.05(^b)</td>
<td>30(^b)</td>
<td>120(^b)</td>
<td>5(^b)</td>
<td>70(^b)</td>
</tr>
<tr>
<td>( \delta &gt; 6^a )</td>
<td>(&lt;0.01^a)</td>
<td>( \tau &gt; 15^a )</td>
<td>( t &gt; 180^a )</td>
<td>5.5(^a)</td>
<td>20(^b)</td>
</tr>
<tr>
<td>6(^b)</td>
<td>0.01(^b)</td>
<td>30(^b)</td>
<td>180(^b)</td>
<td>5.5(^b)</td>
<td>20(^b)</td>
</tr>
</tbody>
</table>

* General experimental conditions.

** Typical examples.

face. The low nickel coating penetration likely stems from the thick crust that developed through the procedure. The AC samples, in comparison, had no nickel crust and exhibited nickel coating penetration past the outer surface. Visual inspection affirmed that the AC method had superior results. All future samples were coated through the AC method.

### 3.2.4 Electrodeposition run time

Additional tests were run to test the validity of the 3.75 hours run time suggested by literature (Floner et al 2007). Multiple test samples were coated using coating times ranging from 45 minutes to 3 days, with a minimum of three samples taken per time period. As shown in Figure 3.3, the increase in nickel coating penetration was minimal after 24 hours. Furthermore, after 24 hours, a thick nickel crust formed more strongly along the outer fibers of the samples. Subsequently, all future samples were coated for a total run time of 24 hours.
Ultrasonic vibration pretreatment

A ultrasonic cleaning tank was used to carry out the ultrasonic agitation of cut, pre-nickel-coated graphite samples, before the samples were thrown into an electrolytic bath to carry out electrodeposition. The ultrasonic generator is of model Branson 2210R-MT Ultrasonic Cleaner with a frequency of 47Khz and a maximum capacity of 90W. Select samples were pretreated for 10 minutes.

3.2.5 Determining optimal concentration regime via binary search

After the implementation of the optimization detailed in the previous section, the electrodeposition solution suggested by literature, an all-sulfate mixture of 0.05M NiSO₄ and 0.25 H₃BO₃, did provide sufficient nickel coating penetration, often not penetrating past half the depth of the 3 mm thick graphite specimen. Samples coated using commercially purchased Watts nickel coating solution achieved significant, but not complete, nickel coating penetration, on the order of 80%. Using general suggested ranges for an all-sulfate nickel electroplating solution, the ratio of NiSO₄ to H₃BO₃ was fixed and a binary search was started in order to test various concentrations of all-sulfate solution in an attempt to improve upon the results produced by using the commercially available premixed solution (Kopeliovich 2013).
A binary search is a particular method of optimization used when trying to find the optimal parameter within a certain range. Binary searches primarily involve testing the two extremes of the range along with the average of the two. The worst performing parameter is discarded, and the parameter that is the average of the two remaining parameters is further tested. This process is continued until the optimal parameter appears. The binary search’s primary benefit is that it considerably speeds up the optimization process by reducing the amount of parameters that need to be tested.

Solutions A, B, and C, as detailed in Table 3.2 were mixed for the purpose of testing various concentrations of an all-sulfate solution. Solutions A and B are composed of the two extremes of the molar concentrations of NiSO₄ and H₃BO₃. Samples A and B were composed of an electrolytic bath of 1.5M NiSO₄, 0.46M H₃BO₃ and 2.6M NiSO₄ and 0.46M H₃BO₃, respectively. Sample C is composed of an electrolytic bath of the midway molar concentrations of the two extremes, thereby is of 2.0M NiSO₄, 0.61M H₃BO₃.

<table>
<thead>
<tr>
<th>Solution</th>
<th>NiSO₄(M)</th>
<th>H₃BO₃(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>0.46</td>
</tr>
<tr>
<td>C</td>
<td>2.0</td>
<td>0.61</td>
</tr>
<tr>
<td>B</td>
<td>2.6</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 3.2: Table detailing the molar concentrations of NiSO₄ and H₃BO₃ that compose the electrolytic bath. These concentrations are the parameters for the primary binary search.

If samples fabricated in an electrolytic bath of a given two concentration regimes repeatedly possess superior surface morphology than samples fabricated from the other concentration regime, the binary search would narrow in which the former two concentration regimes become the new extremes and a new concentration regime composed of the halfway molar concentrations of both NiSO₄ and H₃BO₃ would be examined. The binary search would be continued repeatedly, with each subsequent pair of search parameters continuously refining the optimal concentration regime.

### 3.3 Characterization Techniques

Three characterization techniques were utilized to analyze the morphology, microstructure and elemental composition of nickel-deposited graphite substrates: (1) scanning electron microscope (SEM), (2) energy-dispersive X-ray spectroscopy (EDS) and (3) cyclic voltammetry (CV).
3.3.1 Scanning Electron Microscope (SEM)

SEM is a microscopy technique that utilizes a focused beam of high-energy electrons to create a raster scan of a selected area of the solid sample surface. The high-energy atoms interact with atoms at the surface of the specimen; the electron-sample interaction generates signals to produce a high-resolution two-dimensional image. Given that SEM micrographs have a large depth of field, the image has a three-dimensional appearance that is beneficial for studying the specimen surface topology. Additionally, SEM micrographs readily depict the spatial arrangement of materials that compose the specimen, the sizes of metal deposits on the substrates and approximate depth at which the deposits penetrated. Selected areas to analyze can range from 1 cm to 5 μm in width with magnifications of 10 to 500,000 times and spatial resolution of 5nm at an accelerating voltage of 20 kV.

Microscopic studies were conducted using a JEOL 6010LA SEM at the MIT Institute for Soldier Nanotechnologies (ISN). Micrographs were captured using an accelerating voltage, which dictates the depth of penetration of the high-energy electrons into the specimen, of 5kV to 15kV to obtain optimal resolution of the specimen surface.

3.3.2 Energy-dispersive X-ray spectroscopy (EDS)

SEM is primarily used to produce micrographs, however, has the capability to be used for element mapping if an X-ray spectrometer is coupled to the SEM machine. The ISN JEOL 6010LA SEM is equipped with an energy-dispersive detector that is capable of running energy-dispersive X-ray spectroscopy (EDS) to study the elemental composition of specimen.

EDS operates on the principle that each chemical element has a unique atomic structure, according to the Rutherford-Bohr model, and therefore provides a unique set of peaks on an X-ray emission spectrum. Electrons are located in electron shell bound to the atom’s nucleus and each shell denotes a discrete energy level. During EDS, a high-energy beam of electrons is bombarded on a specific area of the specimen; this incident beam excites the electrons located in the outer (or, possibly inner) electron shell and removes the electron from the shell, creating a vacancy. Subsequently, another electron from a higher-energy state falls into this vacancy. The difference in energy between the higher-energy shell and the lower-energy shell where the electron was originally positioned is released in the form of X-ray light. The energy of a particular X-ray emission is characteristic of the difference in energy of the two shells and of the unique atomic structure of the chemical element from which they were emitted.

Once the incident X-ray strikes the detector, a charge pulse is created that is related to
the energy in a particular X-ray emission. Energy-dispersive spectrometers employ pulse height analysis that are able to convert the charge pulse into voltage signals, which, too, is related to the X-ray energy; these voltage signals are then sent to a pulse processor capable of measuring the signals that subsequently generates a display of the data. Ultimately, a histogram of X-ray energy vs. signal strength (i.e. the number of X-rays received and processed by the detector) is produced.

The signal strength is dependent upon the relative concentration of a particular element in a specimen so a comparison between the relative concentration of elements that compose a specimen can be analyzed.

Each of the EDS histograms were generated with a stationary electron beam on a spot size of greater than 50 mm. Therefore the generated spectra is from an entire scan area of the SEM which provides localized elemental information.

Additionally, the EDS histograms were taken when the specimen surface was in focus at an optimum working distance of 10 mm. Deadtimes of 10% to 20% were utilized to maximize output rates for a given scan area.

### 3.3.3 Cyclic voltammetry (CV)

CV is a characterization technique that utilizes known reaction voltage potential of reactions to determine the surface area of tested samples. CV involves the interaction of three electrodes: a working electrode, a counter electrode, and a reference electrode. These electrodes are placed within an electrolyte, as depicted in Figure 3.4. The working electrode consists of the sample being tested. The reference electrode allows the measurement of the voltage difference between the electrolyte and the working electrode. The counter electrode completes the circuit, allowing current to run through the working electrode.

By measuring the current and factoring in the volume of the working electrode, the current density of the working electrode can be extracted. This process is repeated with a sample of the same material with known surface area, typically a flat plate or wire, as the working electrode. After the execution of the CV procedure, data such as that in Figure 3.5 is analyzed. The trough in the graph represents the voltage at which a specific, known reaction occurs, causing current to flow through the working electrode. This reaction differs depending on the combination of electrodes and the chemical composition of the electrolyte. Measuring the current at the trough and factoring in the surface area of the sample gives a conversion factor, with units of \( \text{m}^2/\text{A} \). After performing the same procedure for the desired sample with an unknown surface area made of the same material as the benchmark test, the same reaction will occur at the same voltage level. The extraction of the current density from the
CV data allows for the calculation of the specific surface area ($cm^2/cm^3$) of the sample.

The setup used for performing cyclic voltammetry in this experiment utilized platinized titanium as the counter electrode, 0.5M KOH as the electrolyte, and the nickel coated graphite felt samples being tested as the working electrode. The tests were conducted using a Bio-Logic SP-50 potentiostat, utilizing the reaction detailed in Equation 3.1. The cyclic voltammogram of nickel wire, as depicted in 3.6 nickel wire was used as a benchmark for calculating the specific surface area of nickel-coated graphite felt.

$$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^- \quad (3.1)$$
Figure 3.5: Example of the raw data resulting from CV.

Figure 3.6: Cyclic voltammogram of nickel wire, taken to use as calibration to find the specific surface area of coated samples of graphite felt.
3.3.4 Correlation to determine bulk support material

The sample with known surface area used in this experiment was a sample of nickel wire, for which the resulting cyclic voltammogram is shown in Figure 3.6. The resulting calibration constant is 5.29 cm²/mA.
Chapter 4

Results and Discussion

4.1 Direct v. alternating current

4.1.1 Coating of outer graphite fibers

Figure 4.1 contains SEM micrographs of two different fibers located at the edge of a nickel-coated graphite felt fabricated utilizing a direct current in an electrolytic bath of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$. The samples were treated with ultrasonic vibration (the effects of which are concretely outlined in the subsequent subsection titled, "Ultrasonic vibration pretreatment.") An EDS histogram of the scan areas of the right SEM micrograph of Figure 4.2 is contained in 4.2. A typical scan area contains a high signal strength for nickel X-ray emissions; a typical edge fiber is composed of approximately 93.87 ± 0.78% nickel by mass.

![SEM micrographs of outer pretreated graphite fibers coated utilizing direct current. Electrodeposition occurs with an electrolytic bath of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$. Images acquired by Ian McKay.](image)

Figure 4.1: SEM micrographs of outer pretreated graphite fibers coated utilizing direct current. Electrodeposition occurs with an electrolytic bath of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$. Images acquired by Ian McKay.
Figure 4.2: EDS histograms of the outer fibers of pretreated graphite fibers coated utilizing direct current. Electrodeposition occurs with an electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃. Histogram acquired by Ian McKay.

Given that the EDS depicts that a high concentration of nickel deposited on the outer fibers of samples treated with direct current, we conclude that there is a tendency for the nickel deposits to concentrate on the fibers located on the outer surface area of the graphite matrix. Both micrographs in Figure 4.1 depict a high concentration of large, irregular clusters of nickel on the surface of the fibers. Important to note is that the nickel deposits are not coating the surface of the fiber homogeneously; instead, the nickel deposits tend to concentrate in clusters along the fiber surface. The micrograph to the left depicts a buildup of deposit that is roughly 80 μm in height (i.e. 80 μm protruding perpendicularly from the surface of the graphite fiber); the micrograph to the right depicts nickel deposits of diameter of approximately 3 μm along the axis of a fiber.

The existence of such large, jagged clusters on the outer fiber of a sample indicates there is a thick nickel crust on the the outer surface area of the sample. Such a pure metal crust formation is far from ideal in the context of three-dimensionally metal-coating porous material for the purpose of adding effective cathodic surface area; the thicker nickel crust on the outer fibers adds bulk to the substrate with no corresponding increase in efficiency, decreasing the surface area density of the sample.

To compare these results, Figure 4.3 contains SEM micrographs of the outer fibers of pretreated nickel-coated graphite felt samples that have been fabricated through alternating current in an identical bath of 1.5M NiSO₄ and 0.46M H₃BO₃. The surface morphology of the samples depicted in Figure 4.3 exhibit a smooth and coating, especially when compared to Figure 4.1; these coated graphite fibers are, on average, 55 μm in diameter, as compared to the typical 25 μm thick uncoated graphite fiber. Therefore, a pulsating current applies a
more homogeneous metal-coat along the axis of a graphite fiber.

Figure 4.3: SEM micrographs of outer pretreated graphite fibers coated utilizing alternating current. Electrodeposition occurs with an electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃.

The corresponding elemental composition of the scan area of the left of the SEM micrograph in Figure 4.3 is contained in Figure 4.4. A typical scan area of a outer fiber for samples fabricated with a pulsating current produces a weaker signal strength for nickel; on average, a sample fabricated with a pulsating current is composed of approximately 85.17 ± 1.12% nickel by mass, less than the average nickel composition of samples fabricated with a direct current. Given the same anodic material size and electrodeposition run time, samples fabricated with a pulsating current are composed of less nickel on the outer fibers than samples fabricated with a direct current.

Figure 4.4: EDS histogram of the outer fibers of pretreated graphite fibers coated utilizing pulsating current. Electrodeposition occurs with an electrolytic bath of
4.1.2 Coating of inner graphite fibers

Figure 4.5 contains SEM micrographs of the inner fibers of specimen fabricated with both a direct and alternating current in an identical electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃. The inner fibers of the specimen fabricated under a pulsating and direct current regime contain small widely-dispersed nickel deposits. The specimen fabricated with a direct current have 0.1 μm wide nickel ion deposits that are approximately 10 μm apart whereas specimen fabricated under a pulsating current have ion deposits that are more densely arranged; the ion deposits for the samples fabricated with a pulsating current are 1 μm wide and approximately 3 μm apart.

![SEM micrographs of inner pretreated graphite fibers coated utilizing a direct current (left) and an alternating current (right). Electrodeposition occurs with an electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃.](image)

The more sparse spatial arrangement of metal deposits on the specimen electroplated with a direct current may appear to be subtle compared to the less sparse spatial arrangement of metal deposits on the specimen electroplated with a pulsating current however these differences are more readily apparent in the quantified elemental composition of each of the specimen’s respective scan areas. The elemental composition of each of the respective scan areas of the inner fibers is contained in Figure 4.6. The inner fibers of specimen fabricated under a direct current regime are composed of only 34.98 ± 3.25% nickel by mass whereas the inner fibers of a specimen fabricated under a pulsating regime are composed of 91.59 ± 3.45% nickel by mass.

A pulsating current prevents the buildup of metal ions on the outer surface area of a porous catalyst matrix, specifically in the context of the electrodeposition of nickel ions onto a graphite catalyst matrix. Specifically, the pulsating current prevents the outer graphite fibers from having a high electrical conductivity and allowing the current in the electrodeposition
setup to continue to run throughout the fibers of the matrix, as opposed to exclusively only through the metal-coated fibers at the edge of the specimen. Therefore, a pulsating current enables a higher concentration of nickel ions to penetrate into a 1.5 mm depth and coat the inner fibers of the specimen, enabling the fabrication of a high surface area catalyst.

4.2 Ultrasonic vibration pretreatment

4.2.1 Coating of outer graphite fibers

Figure 4.7 contains SEM micrographs of the outer fibers of nickel-coated graphite felt samples in which the graphite felts were not treated under ultrasonic agitation. The image on the left is a micrograph of the synthesized composite structure as a result of nickel electrodeposition of graphite felt in an all-sulfate bath of 1.5M NiSO₄ and 0.46M H₃BO₃. Both specimens were fabricated via nickel electrodeposition under a pulsating current.

Both specimen depicted in Figure 4.7 show an approximately 80 µm-thick, uniform deposit of nickel ions on the outer fibers of the graphite matrix. Comparatively, each fiber of the graphite matrix is approximately 20 µm-thick.

To quantify the amount of nickel within these designated scan areas, EDS X-ray spectra were measured and displayed in Figure 4.8. The specimen that was fabricated via electrodeposition in lower concentrations of NiSO₄ and H₃BO₃ had an approximate signal strength of 3.2x10⁴ counts of nickel in which nickel constitutes 88.42 ± 2.18% of the mass of the specimen by volume. In this sample, carbon generated approximately 1.3x10⁴ counts of carbon,
constituting only 2.03 ± 0.45% of the total mass. The sample fabricated via electrodeposition in higher concentrations of NiSO₄ and H₃BO₃ had a higher signal strength, totaling to 4.8x10⁴ counts of nickel in which the nickel constitutes 91.09 ± 3.16 % of the mass of the specimen by volume. Contrarily, in this sample, carbon constituted only 1.41 ± 0.32% of the total mass.

Figure 4.7: SEM micrographs of outer graphite fibers without ultrasonic vibration pretreatment. Electrodeposition occur under a pulsating current regime with an electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃ (left) and 2.6M NiSO₄ and 0.73M H₃BO₃ (right).

Figure 4.8: EDS histograms of outer graphite fibers without ultrasonic vibration pretreatment fabricated in an under a pulsating current regime with an electrolytic bath of 1.5M NiSO₄ and 0.46M H₃BO₃ (left) and 2.6M NiSO₄ and 0.73M H₃BO₃ (right).

Figure 4.9 contains SEM micrographs of outer fibers of nickel-coated graphite felt samples in which the graphite felts were pretreated under ultrasonic agitation for 10 minutes. Both specimen were fabricated under a pulsating current regime. The graphite samples were then subjected to identical experimental procedures as the samples without ultrasonic pretreatment; specifically, the micrographs denote specimen that were synthesized via nickel
electrodeposition in a all-sulfate bath of 1.5M NiSO₄ and 2.6M NiSO₄ and 0.73M H₃BO₃, respectively. The micrograph to the left depicts a slightly less homogeneous coating of nickel deposits on the outer fibers of graphite. The thickness of this coating is approximately 45 μm-thick, less than the thickness of the coating for the specimen without ultrasonic vibration pretreatment. The generated X-ray spectrum for this specimen is incorporated in the left X-ray spectrum of Figure 4.10. The specimen fabricated in an lower concentration of nickel salts is composed of 80.63 ± 4.13% of nickel by mass, less than the amount of nickel that composed the specimen fabricated in the same settings but without the ultrasonic pretreatment.

The micrograph to the right of Figure 4.9 is of a lower magnification; however, it depicts less of a deposit of nickel on the outer fibers of the graphite matrix. Additionally, these nickel ion deposits are less concentrated along the axis of the graphite fibers. Each of the nickel deposits are discrete, rounded and approximately 5 μm in diameter. The X-ray spectrum generated by this specimen, as depicted in the image to the right of Figure 4.10, states that this specimen is composed of 86.61 ± 3.20% of nickel by mass.

We repeatedly observe that the ultrasonic pretreatment prevents the formation of a pure nickel crust on the outer fibers of the graphite.

4.2.2 Coating of inner graphite fibers

Figure 4.11 contains SEM micrographs of the cross section of nickel-coated graphite felt fabricated with no ultrasonic vibration pre-treatment and two different electrolytic concentration regimes: 1.5M NiSO₄ and 0.46M H₃BO₃ (left) and 2.6M NiSO₄ and 0.73M H₃BO₃ (right).

We repeatedly observe that the ultrasonic pretreatment prevents the formation of a pure nickel crust on the outer fibers of the graphite.
SEM micrographs depict the inner fibers of the specimen coated with small (approximately 2 μm in diameter), discrete, widely dispersed deposits of nickel ions; each nickel deposit is roughly 20 μm apart from the adjacent deposit. This indicates that there is very little adsorption of the nickel ions into the fibers located approximately 1.5 mm into the depth of the original 3 mm thick graphite sample.

Images contained in Figure 4.12 are the X-ray spectra of the inner fibers of the aforementioned, unpretreated samples. For the specimen formed in an electrolytic bath of lower concentrations, the specimen approximately $81.81 \pm 2.12\%$ of nickel by mass. The specimen formed in an electrolytic bath of higher concentrations, the specimen is approximately $34.75 \pm 1.40\%$ of nickel by mass.
Figure 4.12: EDS histogram of inner graphite fibers without ultrasonic vibration pretreatment fabricated under a pulsating current regime in an electrolytic bath of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$ (left) and 2.6M NiSO$_4$ and 0.73M H$_3$BO$_3$ (right).

Figure 4.13 contains an SEM micrograph of a typical nickel-coated inner fibers of specimen that had been pretreated with ultrasonic agitation, in an electrolytic bath composed of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$. The fibers of this specimen are coated with discrete, rounded deposits. However, these pretreated samples have large nickel deposits; each nickel deposit is 10 $\mu$m in diameter and less spaced out, with each deposit, on average, 15 $\mu$m apart. There is more adsorption of nickel into the inner fibers of the pretreated specimen.

Figure 4.13: SEM micrograph of inner fibers of specimen with ultrasonic vibration pretreatment fabricated in electrolytic bath of 1.5M NiSO$_4$ and 0.46M H$_3$BO$_3$.

Figure 4.14 details the composition of a typical inner fiber of the aforementioned pretreated specimen; the inner fibers of the pretreated specimen are composed of 92.90 ± 2.68% nickel by mass, equating to a signal strength of 3.9x10$^4$ counts.
The specimen without ultrasonic agitation pretreatment, as compared with the specimen that were pretreated, have a higher deposit of nickel ions on the outer fibers of the graphite matrix than the adsorption of nickel ions into the inner fibers. Without ultrasonic agitation, the nickel ions were adsorbed primarily by the outer fibers of the graphite matrix causing the outer-most fibers to become at least four times as thick as uncoated fibers; these thick nickel-coated outer fibers covered any bulk space in the material, disabling effective mass transport of the nickel ions into the inner fibers of the matrix. Effectively, the outer fibers act as a protective screen to the inner fibers. Conversely, with ultrasonic agitation, the nickel-coated outer fibers are not as thick because less nickel ions are adsorbed by the outer fibers. There is more bulk space in which the nickel ions can effectively pass through to reach the inner fibers and thereby the pretreated samples have a higher concentration of metal in the inner fibers of the matrix.

We repeatedly observe that ultrasonic agitation pretreatment of the graphite specimen before nickel electrodeposition increases the homogeneity of potential from the inner to the outer fibers of the graphite.

4.3 Electrolytic bath concentration regime

4.3.1 Coating of outer fibers using primary binary search parameters

Figure 4.15 contains EDS histograms of samples nickel-coated via electrodeposition in an electrolytic bath of Solution A (1.5M NiSO₄, 0.46M H₃BO₃), Solution B (2.6M NiSO₄, 0.73M H₃BO₃) and Solution C (2.0M NiSO₄, 0.61M H₃BO₃) under a pulsating current, as outlined
in Table 3.2. Both specimen were pretreated with ultrasonic sonication for 10 minutes. The X-ray spectra generated determined that the outer fibers of the specimen fabricated in an electrolytic bath of Solution B generated the weakest signal strength and was determined to be composed of only 86.61 ± 1.32% of nickel by mass; additionally, the outer fibers of the specimen fabricated in an electrolytic bath of Solution A and C was determined to be 91.49 ± 2.52% and 94.38 ± 2.41% of nickel by mass.

We conclude that graphite-nickel composite specimen fabricated in electrolytic baths of lower concentrations of NiSO$_4$ and H$_3$BO$_3$ (specifically between 1.5M and 2.0M NiSO$_4$ and between 0.46M and 0.61M H$_3$BO$_3$) contain less nickel on the fibers on the edge of the graphite matrix than specimen fabricated in electrolytic baths of higher concentrations (specifically, 2.6M NiSO$_4$ and 0.73M H$_3$BO$_3$).
4.3.2 Coating of inner fibers using primary binary search parameters

Figure 4.16 contains pictures that depict the surface morphology of the inner specimen fibers of the specimen fabricated in electrolytic bath of Solution A and C had nickel ion deposits of approximately 1 μm that were roughly 10 μm and 8 μm apart. Specimen fabricated with Solution B, however had a less nickel ion deposits along the axis of the fibers, roughly 35 μm apart, on average.

Figure 4.16: SEM micrographs of pretreated specimen fabricated in an electrolytic bath of 1.5M NiSO$_4$, 0.46M H$_3$BO$_3$ (upper, left), 2.0M NiSO$_4$, 0.61M H$_3$BO$_3$ (upper, right) and 2.6 NiSO$_4$, 0.73M H$_3$BO$_3$ (bottom) under a pulsating current.

Figure 4.17 contains the X-ray spectra of the scan areas contained in Figure 4.16 of the inner fibers of the nickel-deposited graphite specimen of Solutions A, C and B. The inner fibers of the specimens fabricated with Solution A or Solution C had the highest signal strengths; Solution A populated a total of approximately 6.6x10$^4$ counts of nickel and specimen fabricated from Solution C populated approximately 1.9x10$^4$ counts of nickel. Whereas,
specimen fabricated from Solution B only accumulated a signal strength corresponding to $4 \times 10^2$ counts of nickel. Specimen fabricated by an electrolytic bath composed of Solution A, C and B generated a composite structure that is composed of $94.97 \pm 2.67\%$, $93.29 \pm 5.40\%$ and $81.74 \pm 3.14\%$ of nickel by mass, respectively.

Figure 4.17: EDS histograms of pretreated specimen fabricated in an electrolytic bath of $1.5 \text{M} \text{NiSO}_4$, $0.46 \text{M}\text{H}_3\text{BO}_3$ (upper,left), $2.0 \text{M} \text{NiSO}_4$, $0.61 \text{M}\text{H}_3\text{BO}_3$ (upper,right)and $2.6 \text{M} \text{NiSO}_4$, $0.73 \text{M}\text{H}_3\text{BO}_3$ (bottoms) under a pulsating current.

Specimen fabricated from Solution A and C contain a higher concentration of nickel deposits at a depth of 1.5 mm than specimen fabricated by Solution B. Thereby, the optimal concentration regime for nickel deposition onto a graphite matrix is between $1.5 \text{M}$ and $2.0 \text{M} \text{NiSO}_4$ and $0.46 \text{M}$ and $0.61 \text{M}\text{H}_3\text{BO}_3$. 
4.3.3 Refining the primary binary search

Coating of outer fibers with refined binary search parameters

To refine the binary search, the new concentration extremes are 1.5M and 2.0M NiSO₄ and 0.46M and 0.61M H₃BO₃. Solution D was synthesized as containing half of the concentrations of the two new extremes for both NiSO₄ and H₃BO₃; Solution D is comprised of 1.7M NiSO₄ and 0.54M H₃BO₃. Table 4.1 details the molar concentrations of the new parameters for the refined binary search. All aforementioned specimen were fabricated via nickel electrodeposition under a pulsating current and underwent an ultrasonic vibration pretreatment for 10 minutes.

<table>
<thead>
<tr>
<th>Solution</th>
<th>NiSO₄(M)</th>
<th>H₃BO₃(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>0.46</td>
</tr>
<tr>
<td>D</td>
<td>1.7</td>
<td>0.54</td>
</tr>
<tr>
<td>C</td>
<td>2.0</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Table 4.1: Table detailing the molar concentrations of NiSO₄ and H₃BO₃ that compose the electrolytic bath. These concentrations are the parameters for the refined binary search.

Figure 4.18 contains an SEM micrograph as well as the X-ray spectrum produced from a scan area of the outer fibers of a nickel-coated graphite matrix via electrodeposition in an electrolytic bath of Solution D. The specimen is fabricated under a pulsating current regime and were pretreated before electrodeposition. The outer fibers of these specimen are coated with large nickel deposits of approximately 3 µm and are very closely arranged with each nickel deposits roughly 1 µm within the neighboring deposit. The spatial arrangement of these nickel ion deposits on these outer fibers is much more dense than on outer fibers of specimen fabricated in the either Solution A, B or C, contained in Figure 4.16. It is important to note that the nickel ion deposits do not coat the entirety of the surface area of the fiber, yet such a high concentration of nickel is achieved by large, closely spaced, discrete nickel ion deposits. Therefore, a pure metal crust is never formed, and this prevents the buildup of a large potential on the outer fibers of the nickel-coated graphite matrices fabricated in an electrolytic bath of Solution D.

Indeed, the EDS histogram, also contained in Figure 4.18, validates that the dense spatial arrangement of the nickel ion deposits gives rise to a specimen composed of a larger percentage of nickel. A typical scan area of an outer fiber of specimen fabricated utilized solution D is approximately 97.52 ± 1.24% of nickel by mass, the highest concentration of nickel of
any samples fabricated with any other methodology outlined in this study.

Thereby, it appears that the electrolytic bath composed of a concentration of \( \text{NiSO}_4 \) and \( \text{H}_3\text{BO}_3 \) midway between the refined binary search parameters of 1.5M and 2.0M \( \text{NiSO}_4 \), 0.46M and 0.61M \( \text{H}_3\text{BO}_3 \) is the most ideal for achieving a high concentration of nickel ions on the outer fibers of a graphite matrix without the formation of a pure metal crust that subsequently would create a protective screen over the inner fibers of the matrix.

### Coating of inner fibers with refined binary search parameters

Figure 4.19 contains an SEM micrograph and the X-ray spectrum produced from specimen fabricated via nickel electrodeposition in an electrolytic bath of Solution D. The specimen were fabricated under a pulsating current regime and were pretreated before electrodeposition. The fibers located at approximately a 1.5 mm depth into the 3 mm thick graphite matrix are densely coated with nickel deposits with each deposit roughly 5 \( \mu \text{m} \) apart, however each nickel deposits is very small, less than 1 \( \mu \text{m} \) in diameter. Additionally, each nickel deposit is not rounded and does not protrude far perpendicularly from the surface of the fiber. The resulting X-ray spectrum, also contained in Figure 4.19, confirms specimen fabricated in Solution D are composed of very little nickel; a typical scan area of the inner fibers are only approximately 46.51 ± 4.30% nickel by mass.

The very low nickel composition in the inner fibers of the nickel-graphite composites fabricated with Solution D, despite an incredibly high, homogeneous concentration of nickel on the outer fibers of the matrix is most likely because (1) a total electrodeposition time of 24 hours is not adequate or (2) the anodic surface area was not adequate enough. Given
that the inner fibers are densely coated with nickel ions, there is an affinity for nickel ions to penetrate 1.5 mm into the graphite matrix and densely coat the entire axis of the inner fibers, however the remaining nickel ions of the anodic material did not become electrically attracted to those deposits already contained in the inner fibers of the matrix to subsequently allow these deposits to grow in size. Therefore, the nickel deposits in the inner fibers were only 1 μm in diameter. This may be because there was not enough time for the remaining nickel ions to leave the anodic material and subsequently coat the inner fibers of the graphite or because there were no nickel ions on the anodic surface. The latter hypothesis is plausible because it was observed that the anodic surface condition was poor; the anodic material showed severe pitting post specimen-synthesis.

4.3.4 Quantifying specific surface area of nickel-graphite composites of primary and refined binary search parameters

Specimen that were fabricated in an electrolytic bath of concentrations pertaining to the new parameters of the refined binary search were analyzed via CV to quantify the fabricated specimens’ specific surface area. Figure 4.20 depicts the cyclic voltammogram resulting from samples of specimen fabricated from electrolytic bath of Solution A, D and C.
Figure 4.20: Cyclic voltammogram of specimen fabricated in an electrolytic bath of 1.5M NiSO₄, 0.46M H₃BO₃ (Solution A), 2.0M NiSO₄, 0.61M H₃BO₃ (Solution C) and 1.7M NiSO₄, 0.54M H₃BO₃ (Solution D) and of commercially available nickel foam of 500 μm pore size.

The nickel-graphite substrates fabricated from an electrolytic bath concentration of Solution C had the lowest specific surface area, 460 cm²/cm³, and subsequently produced the lowest surface area density, 5600 cm²/g. Substrates fabricated in lower concentration regimes, namely Solution A and D, have specific surface areas of 570 and 6320 cm²/cm³ and surface area densities of 6900 and 7500 cm²/g, respectively; thereby, specimen fabricated in an electrolytic bath of 1.7M NiSO₄, 0.54M H₃BO₃ had specific surface area densities of approximately 890% and surface area densities of 4700% that of readily available commercially available nickel foams.

The specimen fabricated via nickel electrodeposition of Solution D was composed of the highest nickel by mass in the outer fibers, however it had the lowest nickel by mass in the inner fibers, of all other specimen fabricated with any other methodology of this report. The significant surface area added from the homogeneous coating of the outer fibers offset the poor surface roughness achieved by the deposition of nickel into the inner fibers of the graphite matrix. We hypothesize that with either a higher electrodeposition time or anodic material of a higher surface area were utilized in the experimental setup, there would be sufficient resources to further increase the specific surface area of the specimen. Thereby, we hypothesize that nickel-deposited graphite matrices can achieve a specific surface area much greater than 7500 cm²/g.
Lower concentration regimes are ideal for nickel coating a three-dimensional highly porous substrate such as graphite felt. The sample coated using Solution D resulted in a 8.8% increase in specific surface area and surface area density over Solution A. In the context of the binary search, specimen fabricated in Solution D resulted in a higher specific surface area and surface area density than those fabricated in Solution A, both of which are higher than specimen fabricated in Solution C, suggests that the ideal concentration lies somewhere between the concentration regimes of Solution A and D, which is a range of 1.5 - 1.7 M NiSO₄, and 0.46-0.54 M H₃BO₃. However, due to the fact that the samples coated using Solution A and those coated using Solution D are very similar in specific surface area and surface area density (<10%), it is possible that the ideal concentration regime for nickel-coating graphite is below the concentration regime of Solution A, 1.5 M NiSO₄ and 0.46 M H₃BO₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (cm²/cm³)</th>
<th>Surface Area Density (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Foam</td>
<td>16-69</td>
<td>37.6-161</td>
</tr>
<tr>
<td>Solution A</td>
<td>569</td>
<td>6930</td>
</tr>
<tr>
<td>Solution D</td>
<td>616</td>
<td>7490</td>
</tr>
<tr>
<td>Solution C</td>
<td>462</td>
<td>5620</td>
</tr>
</tbody>
</table>

Table 4.2: Table summarizing the results of the analysis of the CV data, comparing the results to commercial nickel foam.

This is likely because high concentrations of nickel ions surrounding the sample being coated during the coated procedure increases the amount of nickel that adheres to the outer surface of the sample, thereby increasing the density of the nickel crust. A low concentration of nickel ions around the sample being coated helps prevent the formation of nickel crust in that specific manner.
Chapter 5

Conclusion

The purpose of this experiment was to develop a repeatable methodology for simply and reliably coating graphite with nickel felt, primarily through the study and analysis of alternate/direct current, ultrasonic vibration pretreatment, and electrodeposition solution concentration.

Samples coated utilizing direct current resulted in $93.87 \pm 0.78\%$ nickel by mass on the outer fibers, while samples coated through alternating current had only $85.17 \pm 1.12\%$ nickel by mass on the outer fibers, indicating the formation of considerably less metal crust on samples that are coated through alternating current.

Experiments performed in order to determine the benefit of ultrasonic vibration pretreatment on coated samples resulted in non-pretreated samples having inner fibers of $34.75 \pm 1.40\%$ nickel by mass and pretreated samples' inner fibers having $92.90 \pm 2.68\%$ nickel by mass, indicating that ultrasonic vibration pretreatment leads to considerably higher penetration of nickel coating through at least a $1.5$ mm depth of the graphite matrix.

A binary search executed on the range of electrolytic bath concentrations of $1.5$-$2.6M$ NiSO$_4$ and $0.46$-$0.73M$ H$_3$BO$_3$ resulted in a solution of $1.7M$ NiSO$_4$ and $0.54M$ H$_3$BO$_3$ giving the best results, leading to a specific surface area of $616 \text{ cm}^2/\text{cm}^3$ and a surface area density of $7490 \text{ cm}^2/\text{g}$.

The experiments executed as part of this report suggest an optimal electrodeposition coating procedure for coating graphite felt with nickel. For a sample of graphite felt approximately $3$ mm in thickness, the graphite felt must be pretreated with ultrasonic vibration and fabricated in an electrodeposition solution comprised of $1.7M$ NiSO$_4$ and $0.54M$ H$_3$BO$_3$ by suspending in graphite felt in the electrolytic bath using nickel foam (can be substituted with other conductive materials). Secondly, both electrodes must have a pulsating current run through
the circuit, specifically a 17 A/cm³ on-pulse for 30 and an off-pulse (i.e. 0 A/cm³) for 120 seconds, followed by a rest period of 120 seconds, for a total run time for 24 hours.

Compared to typical commercially available nickel foams, the nickel coated graphite felt produced using this method results in a 890% increase in specific surface area (cm²/cm³) and a 4650% increase in surface area density (cm²/g). We hypothesize that the specific surface area of nickel-deposited graphite can be further increased by fabricating the composites with a higher electrodeposition time or an anodic material of higher surface area.
Chapter 6

Future Work

We briefly mention the future work that should be accomplished in order to further refine the electrodeposition methodology of full-volume nickel-coating of 3 mm thick graphite felt for the purposes of fabricating very high surface area substrates. Additionally, we highlight experimentation that would be required to integrate high surface area catalysts into OWP’s aluminum-permanganate-water electrochemical battery and subsequently into all electrochemical battery technologies. Additionally, we briefly mention experiments that would need to be conducted in order to quantify the increase in battery current densities from utilizing high surface area cathodes.

6.1 Increasing electrodeposition time and anodic surface area

Experiments to investigate the increase in surface area of anodic material and the increase electrodeposition run time of nickel electrodeposition onto graphite substrates fabricated in an electrolytic bath of $1.7\text{M NiSO}_4$ and $0.54\text{M H}_3\text{BO}_3$ should be conducted to investigate if these parameters will increase the penetration of nickel ion deposits into the fibers at a 1.5 mm depth $a$ of graphite matrix to further optimize the overall specific surface area of the nickel-graphite substrate. As mentioned previously, an increase in either electrodeposition run time or surface area of anodic material could potentially fabricate nickel-graphite substrates of specific surface area greater than $616 \text{cm}^2/\text{cm}^3$.

6.2 Further refining electrolytic bath concentration regime

Experimentation would need to be orchestrated to further refine the binary search for the optimal concentration regime for which to nickel-coat graphite felt. Additionally, the elec-
trolytic composition we investigated was only of NiSO₄ and H₃BO₃ however, a binary search could be applied to different compositions of electrodeposition solution (i.e. solution that contain different nickel salts than the ones utilized in the experiments outlined in this report), in order to find the optimal concentration for each distinct composition and compare them accordingly.

6.3 **Integrating high-surface area cathodic material to electrochemical battery prototypes**

A bench-top battery prototype of the aluminum-permanganate-water battery technology would need to be constructed to quantify the improvement in specific battery parameters utilizing high-surface catalysts fabricated by the methodology outlined in this thesis report as the cathodic material; subsequently compare these parameters to those obtained when the battery operates with commercially available nickel foams as the cathodic material. This bench-top prototype would contain the cathodic material and anodic material (i.e. aluminum) into a compact corrosive-resistant housing with an electrolytic bath consisting of KMnO₄ and KOH. Using this prototype, experiments would need to be executed to analyze the battery operation and longevity over an extended duration of time; the battery current density and hydrogen evolution at the anode-site would be mapped over time to determine the effect of high-surface area cathodes on battery operation as compared to a battery cell that utilized commercially available nickel foams as the cathodic material.

Additionally, the authors suggest integrating a high-surface area nickel-coated catalyst into other flow batteries that utilize nickel as the cathodic material and investigating the battery operation improvement as compared to current commercially available nickel foams to determine if the theoretical nine-times greater battery current density is experimentally achieved.

6.3.1 **Quantifying battery corrosion rates with high-surface area catalysts**

The experimentation carried out to maximize the specific surface area of cathodic material to achieve a consistent high-power battery operation is at the expense of a low corrosion rate. Equation 2.5, discussed in the Background section of this report, denotes that a high cathode-to-anode surface area ratio is proportional to the rate of dissolution of the anode. A bench-top prototype should also map battery electrode degradation over total battery operation time
6.4 Extrapolating fabrication methodology to other metal-coated matrices

We suggest investigating utilizing the same electrodeposition fabrication methodology outlined in this report to metal-coat any high porosity catalyst matrix for other electrochemical battery configurations for consistent, optimal, high-power battery operation.
Chapter 7

Appendix

7.1 MatLAB script for CV analysis

%sample names and volumes/areas in cm^3 or cm^2

samplename1 = 'Ni Foam 500um pore size';
v1 = 1.16*1.64*.62;
samplename2 = 'Ni–C Sample # 48';
v2 = .4*.6*.8;
samplename3 = 'Ni–C Sample # 34';
v3 = .6*.6*.45;
samplename4 = 'Ni–C Sample # 14';
v4 = .5*.5*.37;
samplename5 = 'Ni plate';
a5 = 3*2.54*2;
samplename6 = 'Clean felt';
v6 = .6*9*.5;

% get data
column_format = '%d %d %d %d %f %f %f %f %f %f %f %f %f %f';

fid_data_1 = fopen('1106mmx160mm.602mm_NiFoam_WE__Pt–Ti_CE__SCE_ref__05M_KOH_350rpm__CV_2_C01.txt');
data_1 = textscan(fid_data_1,column_format,'HeaderLines',53);

fid_data_2 = fopen('no48.4mmx6mmx8mm_Niplated_graphite_felt_WE__Pt–Ti_CE__SCE_ref__05M_KOH_350rpm__CV_2_C01.txt');
data_2 = textscan(fid_data_2,column_format,'HeaderLines',53);

fid_data_3 = fopen('no34.6mmx6mmx405mm_Niplated_graphite_felt_WE__Pt–Ti_CE__SCE_ref__05M_KOH_350rpm__CV_3_C01.txt');
data_3 = textscan(fid_data_3,column_format,'HeaderLines',53);
fid_data_4 = fopen('no14.5mmx5mmx307mm_Niplated_graphite_felt_WE___Pt-Ti_-CE___SCE_ref___05M_KOH_350rpm___CV_3_C01.txt');
data_4 = textscan(fid_data_4,column_format,'HeaderLines',53);

fid_data_5 = fopen('30mmx5mm_NiSheet_WE___Pt-Ti_CE___SCE_ref___05M_KOH_350rpm___CV_3_C01.txt');
data_5 = textscan(fid_data_5,column_format,'HeaderLines',53);

fid_data_6 = fopen('6mmx9mmx5mm_graphite_felt_WE___Pt-Ti_CE___SCE_ref___05M_KOH_350rpm___CV_3_C01.txt');
data_6 = textscan(fid_data_6,column_format,'HeaderLines',53);

ewel = data_1{8}; i1 = data_1{9}; %ece1 = data_1{12};
ewe2 = data_2{8}; i2 = data_2{9}; %ece2 = data_2{12};
ewe3 = data_3{8}; i3 = data_3{9}; %ece3 = data_3{12};
ewe4 = data_4{8}; i4 = data_4{9}; %ece4 = data_4{12};
ewe5 = data_5{8}; i5 = data_5{9}; %ece4 = data_4{12};
ewe6 = data_6{8}; i6 = data_6{9}; %ece4 = data_4{12};

subplot(1,3,1)
plot(ewel, i1/v1, ewe2, i2/v2, ewe3, i3/v3, ewe4, i4/v4)
xlabel('V vs. SCE')
ylabel('mA/cm^3')
title('Porous Ni Structures in .5M KOH @20mV/s')
legend(samplemname1, samplemname2, samplemname3, samplemname4)

subplot(1,3,2)
plot(ewe6, i6/v6)
xlabel('V vs. SCE')
ylabel('mA/cm^3')
title('Unplated felt for comparison')
legend(samplemname5)

subplot(1,3,3)
plot(ewe5, i5/a5)
xlabel('V vs. SCE')
ylabel('mA/cm^2')
title('Flat Ni plate for comparison')
legend(samplemname6)

7.2 Arduino script for pulsating current

int MosPin = 12;
void setup()
{
    pinMode(MosPin, OUTPUT);
}

void loop()
{
    digitalWrite(MosPin, HIGH);
    delay(30000);
    digitalWrite(MosPin, LOW);
    delay(120000);
}
Chapter 8

Works Cited


Recemat, BV. *Data Sheet: Nickel Foam.* 2013.


