COPPER (II) HYDROXIDE NANORODS GROWN ON COPPER AND NICKEL PLATED NANOFIBRES FOR PSEUDOCAPACITOR ELECTRODES IN REGENERATIVE BRAKING

by

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Abstract

The threat of climate change has created a demand for superior energy storage devices. One application for them is regenerative braking in hybrid vehicles to reduce fuel consumption and greenhouse gas emissions. Instead of using brakes, the friction generated from turning electric motors charges batteries stops the vehicle. In turn, the batteries are used to accelerate the vehicle. Since braking time is short, batteries are imperfect for this application due to low rate of energy transfer (power). Supercapacitors are superior for power, but cost and amount of energy stored needs to be improved. In this study, Cu(OH)$_2$ nanorods grown on copper-nickel plated nanofibres (Cu(OH)$_2$ NGCuNiPN) were fabricated as electrodes for the pseudocapacitor application. The aim is to use nanofibres as a light weight support, the high conductivity of nickel for power and as a current collector, and Cu(OH)$_2$ nanorods for pseudocapacitance energy storage.

Cu(OH)$_2$ NGCuNiPN electrodes were fabricated by electrospinning, electroless plating, and wet-chemical Cu(OH)$_2$ nanorod growth. Polyacrylonitrile-co-methyl-acrylate/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibre sheets were fabricated with electrospinning. A heat treatment process converted Pd(C$_5$H$_7$O$_2$)$_2$ to Pd catalyst, which was necessary for electroless plating. Nickel was plated on the surface and through the thickness of the nanofibre sheet. Cu was plated on top of the Ni and converted to Cu(OH)$_2$ nanorods. X-ray photoelectron spectroscopy determined the wet-chemical method converted some nickel to nickel compounds (NiO, Ni(OH)$_2$, NiOOH) in addition to Cu(OH)$_2$ nanorod growth.
Electrochemical analysis determined Cu(OH)$_2$ nanorods reduced power density and did not affect energy density, but the nickel compounds improved energy density. Galvanic charge-discharge determined the specific energy and specific power densities of nickel plated nanofibres submerged in 3.75 M NaOH-0.3 M ammonium persulfate for 180 min were 13.2 Wh kg$^{-1}$ and 7892 W kg$^{-1}$ respectively at a current density of 28.8 A g$^{-1}$. Only 20% of capacitance was loss when current density was increased from 3.6 g$^{-1}$ to 28.8 A g$^{-1}$. Cyclic testing showed specific capacitance increased by 44% (330 F g$^{-1}$ to 476 F g$^{-1}$) after 1000 cycles. The increase in capacitance is likely due to the formation of additional nickel compounds under alkali conditions.
Lay Summary

Hybrid vehicles utilize regenerative braking to reduce fuel usage and greenhouse gas emissions. During braking, electric motors are turned to stop the vehicle instead of brakes, which charges batteries. Since braking time is short, supercapacitors are better than batteries for due to higher rate of energy transfer (power). Cu(OH)$_2$ nanorods grown on copper-nickel plated nanofibres were fabricated for the supercapacitor application. Chemical analysis determined Cu(OH)$_2$ nanorods growth solution also converted nickel into nickel compounds. Electrochemical analysis found Cu(OH)$_2$ nanorods did not improve energy capacity and reduced power, but the nickel compounds energy capacity. The energy and power densities of nickel plated nanofibre submerged in the growth solution were 13.2 Wh kg$^{-1}$ and 7892 W kg$^{-1}$ respectively when discharged at 28.8 A g$^{-1}$. Only 20% of energy was loss when the electrode was discharged from a slower to faster rate from 3.6 g$^{-1}$ to 28.8 A g$^{-1}$. 
Preface

A version of chapter 4 was published as conference proceedings for the Society of the Advancement of Materials and Process Engineering (SAMPE) in Long Beach, CA during May 23-26, 2014. I analyzed all the data and wrote the manuscript. Dr. Jungsu Choi, Yan Dong, and I conducted the experiments. Dr. Heejae Yang, Dr. Élőd Gyenge, and Dr. Frank Ko suggested corrections to improve the manuscript. Yip, G., Choi, J., Dong, Y., Yang, H., Gyenge, E., Ko, F. (2016) Amorphous Nickel-Phosphorus Nanofibers for Borohydride Electro-Oxidation, SAMPE 2016 – Long Beach CA – May 23-26/2016.

A version of chapter 4 and 5 was presented as a poster at the Pacific Centre for Advanced Materials and Microstructures on December 10, 2016 at The University of British Columbia.

Dr. Jungsu Choi developed the process to fabricate the activated nanofibres in Chapter 3 and 4. I was responsible for plating nickel on activated nanofibres initially and Dr. Choi was responsible for the optimization of nickel plating on activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ process.

Thermogravimetric analysis data in Chapter 4 was performed with the help from Ms Mijung Cho. X-ray photoelectron spectroscopy data in Chapter 4 was collected and partially analyzed by Dr. Ken Wong at the Interfacial Analysis & Reactivity Lab. Mr. Matt Dawson and I collected data for cyclic voltammetry and galvanic charge-discharge in Dr. John Madden’s Lab for Chapter 5. Mr Matt Dawson also gave advice and helped analyze some data. I collected all the rest of the experimental work and wrote the entire thesis.
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List of Symbols and Abbreviations

AFOLU = agriculture, forestry, and other land use
APS = ammonium persulfate
CH$_2$O = formaldehyde
Cu = copper
Cu(OH)$_2$ = copper(II) hydroxide
CuNiPN = Cu-Ni plated nanofibres
CuO = copper oxide
CuSO$_4$$\cdot$5H$_2$O = copper (II) sulfate pentahydrate
Cu(OH)$_2$ CNGCNPN = Cu(OH)$_2$ nanorods grown on Cu-Ni plated nanofibres
CV = cyclic voltammetry
DMF = N,N-dimethylformamide
EDLC = electric double layer capacitor
EDTA = ethylenediaminetetraacetic acid
EDX = energy-dispersive X-ray spectroscopy
EPB = electroless plating bath
EPS = electroless plating solution
GCD = galvanic charge discharge
N$_2$H$_4$ = hydrazine monohydrate
NaOH = sodium hydroxide
Ni = nickel
NiCl = nickel chloride
NiPN = nickel plated nanofibres

PAN = polyacrylonitrile

PAN-co-MA = polyacrylonitrile-co-methyl-acrylate

Pd = palladium

Pd(C₅H₇O₂)₂ = palladium (II) acetylacetonate

C₄H₄KNaO₆·4H₂O = Potassium sodium L-tartrate tetrahydrate

SEM = scanning electron microscopy

C₄H₄Na₂O₆·2H₂O = Sodium L-tartrate dibasic dihydrate

TGA = thermogravimetric analysis

XPS = X-ray photoelectron spectroscopy

XRD = X-ray diffraction
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Dedication

*To my grandparents*
Chapter 1: Introduction

1.1 Motivation for the development of high energy and high-power supercapacitors for automotive applications

The impact of manmade climate change is a major concern in modern times due to the likelihood of many devastating environmental, economic, and geopolitical problems [1]. Extreme weather events, disruption of food production, and conflicts related to human migration are a few projected problems. Greenhouse gases (CO₂, CH₄, N₂O) are the drivers of climate change, which are separated by economic sectors in Figure 1. Electricity and heat production, AFOLU (agriculture, forestry, and other land use), industry, and transportation are the top contributors to greenhouse gas emissions, nevertheless reduction in emissions from all sectors will be necessary to minimize disasters.
Figure 1. Greenhouse gas emissions by economic sectors in 2010. Gigatonne of CO$_2$ equivalent (Gt CO$_2$-eq). Agriculture, forestry, and other land use (AFOLU) [1]. © Figure 1.7 from Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K. and Meyer, L. (eds.)]. IPCC, Geneva, Switzerland. By permission from publisher.

In terms of the transportation sector, there are efforts to reduce CO$_2$ emissions by the development of more fuel-efficient vehicles and alternative propulsion systems, such as batteries or fuel cell powered vehicles. Regardless of propulsion system, the reduction of weight and recapturing energy would further reduce fuel (electricity, hydrogen, gasoline) consumption. Hybrid vehicles recover energy with regenerative braking and reuses the energy for acceleration or to power the accessories of the vehicle [2]. In regenerative braking systems, the vehicles kinetic energy during braking is converted into other forms of energy and stored in energy
storage devices [3]. The amount of energy stored and the rate that energy transferred (power) are important factors to the regenerative braking system.

In a mechanical regenerative braking system, mechanical energy is stored with a flywheel that rotates during braking, storing kinetic energy. During acceleration, it rotates in the reverse direction, releasing kinetic energy back to the vehicle. The flywheel is fit for city driving where rapid acceleration and decelerations occur, since it supplies high power, but is unable to store vast amounts of energy due to friction rising between mechanical components [3]. There are also challenges for flywheel technology, such as safety concerns relating to flywheel damage, rapid energy dissipation in flywheels over time, and complexity of integration in the vehicle. There are no flywheel hybrid vehicles commercially available to the best of my knowledge.

In electrical regenerative braking systems (Figure 2), the rotating wheels mechanically spins electric motors to stop the vehicle and generate electricity, which are stored it in batteries or supercapacitors. Batteries and supercapacitors store more energy compared to flywheels, but are less efficient due to more energy conversion steps. During charging, mechanical energy is converted to electrical energy then to chemical/electrostatic energy. For discharging the reverse occurs.
Figure 2. Simplified regenerative braking system with a battery as an energy storage device [4].

Table 1 shows a comparison between capacitors, supercapacitors and batteries. In comparison, capacitors have the best power density, but worst energy density that is too low for the regenerative braking application. The main disadvantage for batteries is a relatively lower power density. Since braking last for a few seconds, the rate of energy storage must be high. Additional advantages to supercapacitors are higher cycle life and coulombic efficiency (less energy losses during operation). When comparing cost in terms of power, supercapacitors made by Maxwell Technologies were 6.25 times less expensive at $12 per kW compared to $75 per kW for Li-ion batteries; however, in terms of energy, supercapacitors were 32 times more expensive at $16 per Wh compared $0.5 per Wh for Li-ion batteries [5]. The reduction of $ per Wh without increasing $ per KW will increase usage of supercapacitor technology.
1.2 Supercapacitors

1.2.1 How supercapacitors work

A supercapacitor cell is displayed in Figure 3. Supercapacitors are generally comprised of two porous electrodes, a separator separating both electrodes, electrolyte, and if necessary two current collectors attached to the electrodes [6,7]. Charge is stored on the surface of the electrodes. The separator is an ion permeable and electrically insulative material that separates the two electrodes to prevent short circuit and allows ions from the electrolyte to pass through. The electrodes and separator are soaked with the electrolyte, which is an aqueous or organic solution. Aqueous electrolytes generally penetrate into the pores of the electrodes more effectively compared to organic electrolytes [8]; however, the breakdown voltages of organic electrolytes are higher. The breakdown voltages of aqueous and organic electrolytes are approximately 1 V to 4 V respectively [6,9], meaning supercapacitors with organic electrolytes are operated at higher

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<td>10⁻⁶ to 10⁻³</td>
<td>s to min</td>
<td>0.3–3 h</td>
</tr>
<tr>
<td>Charge time</td>
<td>10⁻⁶ to 10⁻³</td>
<td>s to min</td>
<td>1–5 h</td>
</tr>
<tr>
<td>Coulombic efficiency (%)</td>
<td>About 100</td>
<td>85–98</td>
<td>70–85</td>
</tr>
<tr>
<td>Cycle-life</td>
<td>Almost infinite</td>
<td>&gt; 500,000</td>
<td>about 1000</td>
</tr>
</tbody>
</table>
voltages, but aqueous electrolytes are generally lower in cost, safer to use (less toxic, non-flammable), and higher in ionic conductivity [8]. If the electrode has poor electrical conductivity, current collectors are required. The electrode material (usually a powder) is bonded to metallic current collectors with a polymeric binder. The polymeric binder reduces the charge capacity and increases the internal electrical resistance within the supercapacitor [10]. The mass of the current collector is significantly larger compared to the mass of the electrode powder material [7].

![Supercapacitor schematic](image)

**Figure 3. Supercapacitor schematic [6].** Fig. 4 from © A. González, E. Goikolea, J.A. Barrena, R. Mysyk, Review on supercapacitors: Technologies and materials, Renew. Sustain. Energy Rev. 58 (2016) 1189–1206. By permission from publisher.

A simplified depiction of the charge-discharge cycle in electrostatic capacitors are shown in Figure 4. The charge-discharge cycle in electrostatic capacitors are similar to supercapacitors with difference in mechanism of charge-discharge on the surface of electrodes, which will be explained in Section 1.2.2 and 1.2.3. In Figure 4A, the battery is charging the capacitor, in which the positive terminal of the battery attracts electrons from the electrode connected to the positive terminal, causing the surface of the electrode to become positively charged. In Figure 4B, the
negative terminal repels electrons to the surface of the electrode connected to negative terminal of the battery, causing the electrode to become negatively charged. The capacitor becomes fully charged when attraction of the electrons is equal between the positively charged electrode and the positive terminal of the battery. In Figure 4C, the supercapacitor is discharged. The positive electrode repels electrons in the negative electrode causing electrons to move across the circuit to power the light bulb. Charges are neutralized at the positive electrode. The electrons stop moving across the wire when enough positive charges are neutralized and there is insufficient repulsive force to move the electrons across the circuit.

![Figure 4. Charge-discharge cycle of capacitor: (a) capacitor charging, (b) capacitor fully charged, (c) capacitor discharging [11]. Adapted from Capacitors and capacitance © David Santo Pietro (https://www.khanacademy.org/science/physics/circuits-topic/circuits-with-capacitors/v/capacitors-and-capacitance). CC BY-NC-SA 3.0 US](image)

One main difference between electrostatic capacitors and supercapacitors is the use of porous electrodes and electrolyte instead of solid electrodes. The role of the electrolyte is important for the attraction of charges on the surfaces of porous electrodes. When the
supercapacitor is charged the anions of the electrolyte are concentrated on the positive electrode, while cations are concentrated on the negative electrode [6,10]. The anions and cations become more mixed as the supercapacitor discharge.

The specific capacitance \( (C_{\text{specific}}) \) and specific energy density \( (E_{\text{specific}}) \) in a supercapacitor are described by the following equations:

\[
C_{\text{specific}} = \frac{I \Delta t}{M \Delta V}
\]
\[
E_{\text{specific}} = \frac{C \Delta V^2}{2}
\]

Where \( I \) is current, \( \Delta V \) is cell voltage, \( M \) is the mass of the active material, \( \Delta t \) is discharge time.

The specific average power density \( (P_a) \) and maximum instantaneous power \( (P_{\text{max}}) \) are described by the equation:

\[
P_a = \frac{E_{\text{specific}}}{\Delta t}
\]
\[
P_{\text{max}} = \frac{\Delta V^2}{4RM}
\]

Where \( R \) is the internal resistance of the capacitor, which is related to the electrical resistance of the electrodes and current collectors. If the mass of the active material is replaced with total weight of the supercapacitor, the overall energy density can be lowered by 50% [12]. Energy density can be lowered 75% for the combination of total weight and non-ideal operating conditions. Therefore, normalization by active material mass can be misleading.
Different mechanisms of charge storage occur, depending on the active material on the electrode. Supercapacitor energy storage can be separated into two categories, electric double layer and pseudocapacitance.

1.2.2 Electric double layer capacitors (EDLC)

Electric double layer capacitors (EDLC) stores charge electrostatically (charge stored on the surface of electrodes). Figure 5a displays the surface of a charged positive EDLC electrode. A Helmholtz double layer or interface is formed between the surface and the anions of the electrolyte [6–8]. On negative EDLC electrodes, cations in the electrolyte form a Helmholtz double layer. EDLC electrodes stores more charge or energy compared to solid electrodes in electrostatic capacitors due to higher surface area. Current collectors are usually not required for EDLC electrodes since they are usually composed of electrically conductive materials.

Typical electrode materials for EDLC are high surface area carbon materials, such as activated carbon, carbon nanotubes, and graphene. Activated carbon is a form of carbon that has been processed to form a porous structure. Carbon nanotubes are tube allotropes of carbon with a cylindrical nanostructure that have diameters as small as 1 nm. Graphene is another allotrope of carbon that is a 2-dimensional material in the atomic scale. Porous carbon fibres are micro-meter diameter sized carbon fibres that was processed to make its surface porous. Table 2 depicts a range of specific capacitances for different EDLC electrode materials.
Table 2. Specific capacitance of EDLC electrodes.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Specific Capacitance (F/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>100-340</td>
<td>[6,9]</td>
</tr>
<tr>
<td>Carbon nanotubes powder</td>
<td>20-130</td>
<td>[6]</td>
</tr>
<tr>
<td>Graphene</td>
<td>100-250</td>
<td>[6,7,13]</td>
</tr>
<tr>
<td>Porous carbon fibre</td>
<td>60-287</td>
<td>[6,8]</td>
</tr>
</tbody>
</table>

1.2.3 Pseudocapacitors

Pseudocapacitors utilizes fast redox reactions on the surface of the electrode to store energy [6,7] (Figure 5b). More energy is stored in pseudocapacitors compared to EDLC due to the use of chemical energy storage, but at the cost of power, charging time, and durability. The main difference between batteries and pseudocapacitors is the active material in batteries is in bulk, whereas the active material in pseudocapacitors is on a high surface area substrate. Pseudocapacitor active materials are usually composed of poor electrical conductors, in which current collectors are required. Table 3 depicts a range of specific capacitances for pseudocapacitor electrode materials.
Figure 5. (a) charge storage on the surface of a positive EDLC electrode (b) mechanism of energy storage on the surface of a pseudocapacitor electrode [14]. Figure 2 from © J.W. Long, D. Bélanger, T. Brousse, W. Sugimoto, M.B. Sassin, O. Crosnier, Asymmetric electrochemical capacitors—Stretching the limits of aqueous electrolytes, MRS Bull. 36 (2011) 513–522. doi:10.1557/mrs.2011.137. By permission from publisher.

Table 3. Specific capacitance of pseudocapacitors.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Specific Capacitance (F/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrous RuO₂</td>
<td>208-1340</td>
<td>[6,10,13]</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>81-382</td>
<td>[10,13]</td>
</tr>
<tr>
<td>NiCo₂O₄</td>
<td>678-1400</td>
<td>[13]</td>
</tr>
<tr>
<td>Ni(OH)₂</td>
<td>1040-2646</td>
<td>[13]</td>
</tr>
<tr>
<td>MnCo₂O₄</td>
<td>346</td>
<td>[13]</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>1300</td>
<td>[13]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>597-1272</td>
<td>[9,13]</td>
</tr>
<tr>
<td>Cu(OH)₂</td>
<td>750</td>
<td>[15]</td>
</tr>
</tbody>
</table>
1.2.4 Challenges for supercapacitors

Based on this section of the literature review, the challenges related to supercapacitors can be summarized in the following:

- Cost per watt-hour of supercapacitors is significantly higher compared to batteries
- Polymeric binder, which attaches active material to current collector reduces charge capacity and increase internal electrical resistance
- Overall energy density and power density can be significantly lower due to the mass of other components in the supercapacitor compared to active material mass

Focus will be on addressing these challenges associated with supercapacitors. Here we attempt to fabricate low cost pseudocapacitors electrodes (due to higher energy capacity) that does not require external current collectors and polymeric binders with novel fabrication techniques, such as electrospinning and electroless plating, which are discussed in sections 1.3.1 and 1.3.2 respectively.

1.3 Metalized nanofibres

Metalized fibres are polymer fibres with metals bonded on its surface, which have the combined properties of the fibres and the metal. Some properties of metalized fibres are light weight, flexibility (dependent on amount of bonded metal), and electrical conductivity. Examples of commercially available metalized fibres are X-static® [16] (silver bonded fibres for antimicrobial garments) and Aracon® [17] (nickel bonded Kevlar® fibres for electromagnetic shielding and smart fabrics). The commercially available metalized fibres are in the micro-meter diameter range. Metalized nanofibres (defined as fibres in the diameter range between 1 nm to
1000 nm due to various phenomena observed this range [18]) can improve performance and add unique properties. The larger surface area and smaller pore size of nanofibres allows for additional applications, such as transparent conducting electrodes [19] (copper bonded nanofibres), water filtration [20] (palladium-zeolite bonded nanofibres), and energy storage [21,22] (nickel infused carbon nanofibres). In terms of supercapacitors, the larger surface area allows for more charge stored on the surface of EDLC and increased active surface area for redox reactions for pseudocapacitors.

In this work, the metalized nanofibres will act as a current collector, which will replace the solid metal current collector to reduce mass of the overall pseudocapacitor. Electrospinning and electroless plating are discussed for the fabrication of the metallized nanofibres.

1.3.1 Electrospinning

There are several methods for generating nanofibres, but none matches the simplicity of the electrospinning process. Electrospinning uses electrostatic forces to draw micro or nano diameter sized fibres from polymer solutions [23–25]. The experimental electrospinning set up is shown in Figure 6. The experimental set up consist of: a high voltage power supply, a needle and syringe containing a polymer solution, a fixed grounded target, a syringe pump. The high voltage power supply is connected to a needle, which applies a potential between the polymer solution and the target, causing fibres to be drawn out of the polymer melt. The syringe pump continually pushes polymer solution out the needle as a voltage is simultaneously applied to the needle from the high voltage power supply. At a certain voltage, the electric field strength overcomes the surface tension of polymer solution at the tip of the needle forming a Taylor cone and producing a jet. The jet goes through many bending instabilities, including stretching before reaching the
grounded target. The stretching of the jet encompasses a cone shape area where the solvent evaporates from the polymer. The dried fibres reach the grounded target and are collected as nonwoven randomly orientated fibres.


Various fillers can be added to the electrospinning polymer solution to enhance the properties of the fibres. For instance, the additions of carbon nanotubes enhance the mechanical properties of carbon nanofibres [24] and the addition of magnetite allows the nanofibres to have electromagnetic interference shielding capabilities [26]. Catalytic fillers were added to the polymer solution to catalyze the electroless plating reactions in this work (Section 1.3.2).

1.3.1.1 Polyacrylonitrile (PAN)

Polyacrylonitrile (PAN) is a thermoplastic polymer that can be easily electrospun [27,28]. Heating PAN nanofibres under inert gas is necessary to fabricate metallized nanofibres (Section 2.2.1) PAN does not decompose at temperatures up to 300°C [29] under inert gas atmospheres.
Xiao et al. reported the structural evolution of PAN under stabilization in N\textsubscript{2} at 2 °C/min to 240°C for 2 h [30] and it can be separated into 3 phases. The first is the initiation phase, where C in the triple bond of nitrile (CN) forms C-O in OH and C=NH forms. Next is the cyclization phase, where an equilibrium or tautomerism between C=N or C=C is formed. In the last step, dehydrogenation causes the structure to become fully conjugated. The cyclization reaction converts the PAN into a stable ladder polymer by holding the molecules in the fibre together and increases stiffness [31]. The mass fraction of CN consumed during stabilization was approximately 80%.

![Figure 7. Systematic of reactions of PAN up to 240°C in N\textsubscript{2} gas [30]. Figure 5 from © S. Xiao, H. Lv, Y. Tong, L. Xu, B. Chen, Thermal behavior and kinetics during the stabilization of polyacrylonitrile precursor in inert gas, J. Appl. Polym. Sci. 122 (2011) 480–488. doi:10.1002/app.33656. By permission from publisher.](image-url)
1.3.2 Electroless plating

Electroless plating is the reduction of metal ions with a reducing agent to form a metal film [32]. The oxidation, reduction, and overall reaction of electroless copper (Cu) deposition with formaldehyde (CH2O) [33–35] is used as an example (Table 4):

Table 4. Oxidation, reduction, and overall reactions of Cu electroless plating.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E° (V vs SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation: CH2O + 3OH⁻ → HCOO⁻ + 2H2O + 2e⁻ (pH = 14)</td>
<td>1.07</td>
</tr>
<tr>
<td>Reduction: Cu²⁺ + 2e⁻ → Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>Overall: Cu²⁺ + CH2O + 3OH⁻ → Cu + HCOO⁻ + 2H2O (pH = 14)</td>
<td>1.41</td>
</tr>
</tbody>
</table>

The overall standard redox potential is positive, indicating the reduction of Cu ions to metallic Cu is thermodynamically favorable.

Even though the reduction of Cu²⁺ by CH2O is thermodynamically feasible, electroless plating baths are more complex. The essential contents of electroless plating baths (EPB):

- Source of metal ions
- Complexing agent
- Reducing agent

The source of metal ions is usually water-soluble metal salts, such as copper sulfate or nickel chloride. The type of anion (SO₄²⁻, Cl⁻) formed from the dissolution of metal salts can affect the concentration limits of metal salts and plating rates of the EPB [34,36].
Undesired precipitation of the metal occurs in the EPB due the thermodynamic feasibility of metal reduction thus, a complexing agent is required to depress the free metal ion content [34]. The complexing agent forms bonds with the free metal ions, which prevents precipitation of the metal (Figure 8b). Common complexing agents for Cu electroless plating are ethylenediaminetetraacetic acid (EDTA) or tartrate. The strength of the complex generally depends on the number of bonds formed with the metal ion (6 bonds for EDTA). The rate of electroless plating can be significantly reduced or not proceed at all if the complex is too strong or if there are insufficient free metal ions due to high complexing agent concentration. The actual reduction half reaction that occurs for the Cu-EDTA complex shows the reduction to Cu and the dissociation of EDTA to EDTA$^+$ [33,37]:

$$[\text{CuEDTA}]^{2-} + 2e^- \rightarrow \text{Cu} + \text{EDTA}^{4-}$$

Figure 8. (a) EDTA molecular structure. (b) EDTA bind to metal ion [38].
The reducing agent is responsible for the reduction of the metal ions to the metal. Common reducing agents for Cu electroless plating are formaldehyde, hypophosphite, and hydrazine. The substrate must be able to catalyze the reducing agent by oxidizing the reducing agent to initiate the electroless plating process. After initial catalysis, the reduced metal catalyzes the reaction. The catalyst activity required to initiate electroless plating varies depending on type of reducing agent and catalyst used [39].

1.3.2.1 Electroless plating on plastics

Among the many methods to coat metals on polymers [40], electroless plating is well suited for nanofibres due the immersion of it into liquid EPB, which allow metals to be plated in complex shapes and through the thickness of the nanofibre substrate. Hydrogenation-dehydrogenation intermediate reactions occurs in all electroless plating oxidation reactions, which is initiated by catalyst [32,41]; therefore, electroless plating reactions only proceeds with hydrogenation-dehydrogenation catalyst. To plate on non-catalyst such as PAN nanofibres, the surface of the substrate must be coated with a suitable catalyst. The most popular method is to dip-coat polymer surfaces with palladium colloidal particles in water. This solution contains in a mixture of palladium chloride, stannous chloride, and hydrochloric acid solution where palladium ions (Pd²⁺) are reduced to form metallic palladium (Pd) by stannous ions (Pd²⁺) [32,40,42].

\[
Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd
\]

However, in the case of nanofibres substrates, uniform distribution and loose colloidal palladium leads to potential challenges. Non-uniform colloidal palladium distribution leads to
non-uniform electroless plating of the metal on the substrate and loose colloidal palladium leads to precipitation of the reduced metal. Therefore, another method to uniformly coat catalyst on the surface of the nanofibre substrate without loose colloidal particles is proposed for this work (Section 2.2.1).

1.4 Cu(OH)$_2$ nanorods

Xu et al. demonstrated that Cu(OH)$_2$ nanorods and CuO nanosheets can be utilized as pseudocapacitor electrodes [15]. The specific capacitance of Cu(OH)$_2$ nanorods, CuO nanosheets-Cu(OH)$_2$ nanorod mixture and CuO nanosheets are 511.5, 78.44 and 30.36 F g$^{-1}$, respectively, at a current density of 5 mA cm$^{-2}$ indicating that Cu(OH)$_2$ nanorods were the superior for the application compared to CuO.

Copper (II) hydroxide (Cu(OH)$_2$) and copper oxide (CuO) nanostructures are fabricated by four general methods: thermal oxidation [43], direct resistive heating [44], direct plasma oxidation [43,45], wet chemical [15,43,46–55]. In the thermal oxidation process CuO nanowires are grown from Cu heated in an air or oxygen atmosphere [43]. Cu is usually heated between 400$^\circ$C to 600$^\circ$C to promote oxidation. In direct resistive heating, electrical current is put through the Cu substrate to heat both the Cu and oxygen surrounding it to promote oxidation [44]. The temperature to promote oxidation range from 400$^\circ$C to 700$^\circ$C. The direct plasma oxidation method forms CuO nanorods by utilizing oxygen in the plasma state to heat and oxidize Cu substrates [43,45]. Temperatures that surrounds the Cu substrate ranges from 680$^\circ$C to 720$^\circ$C. Formation of Cu(OH)$_2$ and CuO nanostructures can also be achieved by submersion of Cu in liquid chemical solutions (wet-chemical method) to precipitate or grow nanostructures.
Nanostructures can be precipitated or grown at room temperature usually with a solution containing sodium hydroxide (NaOH).

PAN degrades at temperatures above 300°C [29–31]; therefore, the wet chemical method is best suited for polymer substrates, since the formation of Cu(OH)$_2$ and CuO nanostructures are at room temperature unlike the other methods. Prior work utilized a simple method to grow nanostructures by immersing Cu foil in a solution containing NaOH and ammonium persulfate (APS, (NH$_4$)$_2$S$_2$O$_8$) to obtain Cu(OH)$_2$ nanorods [15,47,52,56,57] and CuO nanosheets [15,48,56,57]. The formation of the type of nanostructure depends on the concentration of reactants and reaction time. For example, Zhang et al. immersed Cu foil in a 1.25 M NaOH-0.05 M APS solution for 30 min to form Cu(OH)$_2$ nanorods[57], but longer submersion times and higher NaOH-APS concentrations formed CuO nanosheets. The reaction for Cu(OH)$_2$ nanorod and CuO nanosheets growth are as follows:

$$\text{Cu} + 4\text{OH}^- + (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{Cu(OH)}_2 + 2\text{SO}_4^{2-} + 2\text{NH}_3 + 2\text{H}_2\text{O}$$

$$\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O}$$

The mechanism for the formation of Cu(OH)$_2$ nanorods and CuO nanosheets with NaOH and APS is explained by Zhang et al. [57]. Cu is continuously oxidized and dissolved by APS. The Cu$^{2+}$ forms bonds with OH$^-$ and forms Cu(OH)$_2$ chains in a structure that forms a sheet in the (010) plane. Hydrogen bonds allows the sheets to stack and form a crystal. Crystal growth rate can be described by the Bravais-Friedel-Donnay-Harker method, which states that crystal growth rate is inversely proportional to lattice-plane spacing ($d_{hkl}$). The planar distance of
Cu(OH)$_2$ crystal for (1 0 0), (0 1 0), (0 0 1) are 2.9471, 10.5930, 5.2564 Å [57,58] meaning growth will be fastest in the [1 0 0] direction, allowing nanorods to form.

Figure 9. Cu(OH)$_2$ nanorods grown from metallic Cu. Scale bar = 1 µm.

1.5 Objectives

The European Commission Seventh Framework Programme set goals for supercapacitors for automotive applications. The performance targets are 20 kW/kg power density, 10 Wh/kg energy density, and cost target of 10 €/kW (approx. $14 CAD/kW) [59].

The objective of this work focuses on the fabrication and characterization of high performance pseudocapacitor electrodes made from low cost materials for the regenerative braking application. The target performance of the pseudocapacitor electrodes are:

- Specific power density of 20 kW/kg
- Specific energy density of 10 Wh/kg
A composite composed of nanofibre coated with electroless plated Ni and Cu(OH)$_2$ nanorods grown on its surface is proposed. Using metalized electrospun nanofibres as a current collector would reduce the overall mass of the supercapacitor and could allow it to achieve power performance target. The metalized electrospun nanofibres would also be the carrier for active materials, which offers other benefits: high surface area, mass reduction, reduction of active materials. Growth of Cu(OH)$_2$ nanorods by utilizing the wet chemical method would be a simple way to further the increase energy density to achieve the energy performance target.

Electrospinning is utilized to fabricate nanofibres and a catalytic filler was added to the spinning solution to initiate electroless plating. Electroless plating allows for the fabrication of metalized nanofibres, since this technique can deposit metal on the complex shape of nanofibres sheets without the use of performance depreciating polymer binders. Ni and Cu were chosen for the plated metals due to their abundance and low cost at 2.51 USD [60] and 4.67 USD [61] respectively as of Jan 8, 2017. Cu is plated on top of the Ni then converted into Cu(OH)$_2$ nanorods by the wet chemical process (section 1.4).
Chapter 2: Materials and Experimental Methods

2.1 Materials

Nickel chloride (NiCl, Sigma-Aldrich), sodium L-tartrate dibasic dihydrate (C₄H₄Na₂O₆·2H₂O, Sigma-Aldrich), hydrazine monohydrate (64-65%, N₂H₄, Sigma-Aldrich), sodium hydroxide (NaOH, Sigma-Aldrich), copper (II) sulfate pentahydrate (CuSO₄·5H₂O, BDH Chemicals), potassium sodium L-tartrate tetrahydrate (C₄H₄KNaO₆·4H₂O, Alfa Aesar), formaldehyde (CH₂O, 37% solution, J.T Baker), polyacrylonitrile-co-methyl-acrylate (PAN-co-MA, MW=100000, Scientific Polymer Products Inc.), palladium (II) acetylacetone (Pd(C₅H₇O₂)₂, 99%, Sigma-Aldrich) N,N-dimethylformamide (DMF, Anachemia Chemicals Inc.), and ammonium persulfate (APS, BDH Chemicals) were utilized without any modifications.
2.2 Preparation process

Figure 10 shows a schematic depicting the fabrication steps for Cu(OH)$_2$ nanorods grown on Cu-Ni plated nanofibres (Cu(OH)$_2$ NGCuNiPN).

![Figure 10](image)

Figure 10. A schematic depicting the fabrication steps of Cu(OH)$_2$ NGCuNiPN: (a) electrospinning of PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres, (b) activation of as spun PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres by heat treatment, (c) electroless plating of Ni on activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres, (d) electroless plating of Cu on Ni plated on nanofibres, e) growth of Cu(OH)$_2$ nanorods on Cu-Ni plated nanofibres by wet-chemical method.

2.2.1 Preparation of activated nanofibres

Electrospinning solution was prepared by stirring Pd(C$_5$H$_7$O$_2$)$_2$ in DMF at 90°C until all the Pd(C$_5$H$_7$O$_2$)$_2$ was fully dissolved. PAN-co-MA was added afterwards and stirred vigorously at 90°C for at least 12 h and cooled to room temperature before electrospinning with NEU Nanofibre Electrospinning Unit (Kato Tech Co., Ltd, Japan) on aluminum foil. The mass distribution of Pd(C$_5$H$_7$O$_2$)$_2$, PAN-co-MA, and DMF in the electrospinning solution was 0.57%, 9.94%, and 89.49%. A voltage of 17.5 kV was applied to the spinning electrospinning solution. The formed nanofibres were cut into 50 mm by 50 mm sheets and dried in an oven at 90°C overnight.
Figure 11. (a) PAN-co-MA/ Pd(C₃H₇O₂)₂/DMF electrospinning solution. (b) Electrospinning chamber.

Figure 10b shows the activation phase. Activation in electroless plating means to convert the substrate into catalysts capable of initiating the electroless plating reaction. The dried nanofibres were heated in a tube furnace at 250°C for 2 h at a heating rate of 1°C per min in argon and furnace cooled.

2.2.2 Electroless plating of Ni on activated nanofibre sheets

Figure 10c shows Ni electroless plating on activated nanofibres. Table 5 shows the composition and operating conditions of the Ni EPB. The Ni electroless plating solution (EPS) was produced by stirring NiCl₂, C₄H₅Na₂O₆·2H₂O, and NaOH. in DI water at room temperature in the order presented. EPS is the solution prior to the addition of the reducing agent and EPB is the solution with the addition of the reducing agent.

The activated nanofibres were cut into 25 mm by 25 mm sheets. 15 mL of Ni EPS was placed in a cylindrical 30 mL bottle and the reducing agent, N₂H₄ was pipetted into Ni EPS. The cut nanofibres were placed vertically into the Ni EPB. Electroless Ni plating was conducted in an
oven heated at 70°C for 180 min. The Ni plated nanofibres (NiPN) were placed into the Cu plating solution instantly after Ni plating. If Cu plating was not desired NiPN were rinsed with distilled water and dried at room temperature.

Table 5. Composition and operating conditions of Ni EPB.

<table>
<thead>
<tr>
<th>Ni Electroless Plating Solution (g L⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl</td>
<td>3.89</td>
</tr>
<tr>
<td>C₄H₄Na₂O₆·2H₂O</td>
<td>25</td>
</tr>
<tr>
<td>NaOH</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reducing Agent (mL mL⁻¹ Ni Electroless Plating Solution)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂H₄ (64-65%)</td>
<td>.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (⁰C)</td>
<td>60</td>
</tr>
<tr>
<td>Plating Time (min)</td>
<td>180</td>
</tr>
<tr>
<td>Plating solution volume (mL)</td>
<td>15</td>
</tr>
</tbody>
</table>

2.2.3 Electroless plating of Cu on Ni plated nanofibre sheets

Figure 10d shows Cu electroless plating on the NiPN. Table 6 shows the composition and operating conditions of the Cu EPB. The Cu EPS was produced by dissolving C₄H₄KNaO₆·4H₂O, CuSO₄·5H₂O, and NaOH in DI water at room temperature in the order presented. 15 mL of Cu EPB was placed in a cylindrical 30 mL bottle and the reducing agent, CH₂O was pipetted into Cu EPS. The NiPN were placed vertically in the EPB. Electroless Cu plating was conducted at room temperature for times ranging between 8 to 240 min. The Cu-Ni plated nanofibres (CuNiPN) were rinsed with distilled water and dried at room temperature.
Table 6. Composition and operating conditions of Cu EPB.

<table>
<thead>
<tr>
<th>Cu Electroless Plating Solution (g L⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>Plating solution volume (mL)</td>
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2.2.4 Cu(OH)₂ nanorod growth

Figure 10e shows the growth of Cu(OH)₂ nanorods on CuNiPN by wet-chemical method. The CuNiPN were submerged vertically in a solution containing NaOH and APS at molar concentrations with the ratio of 1 M NaOH:0.08 M APS. The submersion time ranged from 30 min to 240 min. Cu(OH)₂ nanorods grown on Cu-Ni plated nanofibres (Cu(OH)₂ NGCuNiPN) were rinsed with distilled water and dried at room temperature after growth.

2.3 Characterization techniques

2.3.1 Thermogravimetric analysis

The suitable heat treatment temperature to fabricate activated nanofibres was determined by thermogravimetric analysis (TGA, TA Instruments Q500). As spun nanofibres were dried in an oven at 100°C before analysis from room temperature to 500°C at a rate of 10°C/min under nitrogen atmosphere. The gas flow rate was 40 mL min⁻¹.
2.3.2 Scanning electron microscope (SEM)

Morphology was studied with scanning electron microscope (SEM, FEI Quanta 650). The working distance used for SEM imaging was approximately 5 mm and the accelerating voltage was 15 kV. Diameters were measured with ImageJ software (National Institutes of Health, USA). Average and standard deviation calculation measurements were made with a minimum of 30 measurements.

2.3.3 X-ray diffraction (XRD)

Molecular structure was studied with X-ray diffraction (XRD). XRD patterns were obtained using an X-ray diffractometer (Rigaku, Japan) with Cu Kα (λ = 1.540) radiation over Bragg angle ranging from 3° to 90° at a scan rate of 1°/min.

2.3.4 X-ray photoelectron spectroscopy (XPS)

Chemical analysis was studied with X-ray photoelectron spectroscopy (XPS, Leybold Max200) with Al Kα X-ray source. The pass energy used for survey and narrow scan measurements were 192 eV and 48 eV respectively. The analyzed area in all samples were 4 mm by 7 mm.

2.3.5 Four probe resistivity measurement

Electrical conductivity was measured using a power supply (Xantrex XDL 35-5P DC Power Supply) and voltmeter (Agilent U1272A) attached to home built four-point probes. The home built four-point probe consisted of four strands of exposed tinned Cu wire (E-Z Hook, USA) lined up in parallel across a glass slide and held in place by electrical tape. The inner
probes/wires were attached to the voltmeter and the outer probes or wires were attached to the power supply. The resistance (R) is calculated according to Ohm’s law:

\[ R \ (\Omega) = \frac{V}{I} \]

Where \( V \) is the voltage between the potential probes and \( I \) is the constant current supplied by the power supply of 0.5 A. The electrical conductivity (\( \sigma \)) is calculated by:

\[ \sigma \ (s/cm) = \frac{l}{wt} \times \frac{1}{R} \]

Where \( w \) is the width of the nanofibre sheet, \( t \) is the thickness of the nanofibre sheet, and \( l \) is the distance between the two potential probes or wires. The nanofibres sheets were cut into a width of 4 mm. Thickness of the nanofibre sheets were obtained with a thickness gage (543-783, Mitutoyo, Japan) and the distance between the two potential probes was 20 mm.

### 2.3.6 Electrochemical Measurements

Electrochemical tests were conducted on a three-electrode electrochemical cell using a potentiostat (Solartron 1287) controlled by CorrWare software (Scribner Associates Inc.). The nanofibre sheets acted as the working electrode, carbon paper as the counter electrode, and Ag/AgCl electrode as reference electrode. All working electrodes were cut to 12 mm by 6 mm. All electrochemical measurements were conducted in 2 M KOH. The solution was made by dissolving KOH pellets (Fisher Scientific) in DI water. Cyclic voltammetry (CV) measurements were conducted at varying scan rates in the potential window between 0 to 0.6 V. Galvanotactic
charge-discharge (GCD) measurements were conducted at varying currents between the potential range of 0 to 0.5 V.

Capacitor performance of nanofibre electrodes were evaluated with the galvanic discharge measurement. The specific capacitance ($C_{specific}$), energy density ($E_{specific}$), and average power density ($P_a$) were calculated with the equations:

$$C_{specific} = \frac{i\Delta t}{\Delta V M}$$

$$E_{specific} = \frac{C_{specific} \Delta V^2}{2}$$

$$P_a = \frac{E_{specific}}{\Delta t}$$

Where $i$ is current, $\Delta V$ is discharge potential range, $M$ is the mass of the active material, $\Delta t$ is discharge time.
Chapter 3: Preparation and Characterization of Cu(OH)$_2$ Nanorods Grown on Cu-Ni Plated Nanofibres

3.1 Introduction

Coating the surface of nanofibres with metals provides many fabrication challenges as stated in Section 1.3.2.1. The process explained in Section 2.2 attempts to overcome these challenges to fabricate Cu(OH)$_2$ nanorods grown on Cu-Ni plated nanofibres. In Chapter 3, the nanofibre materials fabricated from each step of the Cu(OH)$_2$ NGCuNiPN fabrication process were analyzed and characterized with various characterization techniques, such as SEM and XRD. Cu(OH)$_2$ NGCuNiPN was investigated with varying mass of plated Cu, growth solution concentration, and growth time. XPS was utilized to identify the chemical composition of the activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres and the effect of the nanorod growth solution on NiPN.

3.2 As spun PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres

After electrospinning, the appearance of as spun PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibre sheet was white coloured in the macro scale (top left of Figure 12a). SEM images (Figure 12 a and b) of as spun PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres indicates that the nanofibres are uniform and smooth on the surface. The average diameter of the as spun PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres is 722 ±56 nm.
3.3 Activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres

After heat treatment at 250$^\circ$C for 2 h with a heating rate of 1$^\circ$C/min in argon, the activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibre sheet turned from white to brown (top left of Figure 13a). SEM images of the surface of activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres (Figure 13 a and b) indicates that the nanofibres are uniform in shape. The average diameter of activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres is 667±47 nm. Cross-sectional SEM images of the activated nanofibre sheet is shown in Figure 14. The mass and thickness of the 25 mm by 25 mm activated nanofibre sheet is 10.9 ± 1.0 mg and 44.3 ±5.7 µm respectively. The conversion of Pd(C$_5$H$_7$O$_2$)$_2$ to metallic Pd was verified in Section 3.9.1.
Figure 13. SEM image of activated PAN-co-MA/Pd(C$_3$H$_7$O$_2$)$_2$ nanofibres: (a) scale bar = 4 µm, (b) scale bar = 1 µm.

Figure 14. (a) Cross-sectional SEM images of activated PAN-co-MA/Pd(C$_3$H$_7$O$_2$)$_2$ nanofibres: (a) scale bar = 30 µm, (b) scale bar = 4 µm.

3.4 Electroless Ni plating on activated nanofibres

Figure 15a and b shows SEM images of NiPN. The activated nanofibres transformed from brown to gray (top left of Figure 15a). SEM images of NiPN shows the nanofibres are uniformly plated with Ni (Figure 15a) and the higher magnification image shows a rough spiky
morphology (Figure 15b). The average diameter of NiPN is 813±64 nm. The total (Ni + nanofibres) and Ni mass for 25 mm by 25 mm sized sheets are 35.0 ± 1.1 mg and 23.5 ± 0.8 mg respectively. The average thickness of NiPN increased to 47.3 ± 8.1 µm.

Figure 15. SEM image of NiPN: (a) scale bar = 5 µm, (b) scale bar = 1 µm.

Cross-sectional SEM images of NiPN (Figure 16) shows nanofibres in the cross section are also plated with Ni. The diameter of NiPN near the surface and at the core of the nanofibre sheet is similar at 757±57 nm and 746 ±29 nm respectively (Figure 16b and c).
Figure 16. Cross-sectional SEM images of NiPN: (a) entire cross section, scale bar = 20 µm. (b) core of the nanofibre sheet, scale bar = 4 µm, (c) near the surface of the nanofibre sheet, scale bar = 4µm, (d) core of the nanofibre sheet, scale bar = 1µm, (e) near the surface of the nanofibre sheet, scale bar = 1µm.
3.5 Electroless Cu plating on Ni plated nanofibres

Cu electroless plating was applied to NiPN immediately after Ni electroless plating. Figure 17a, b, c, and d shows SEM images of CuNiPN at plating times of 8, 30, 60, and 240 min respectively. At 8 min of Cu electroless plating, the surface of the nanofibres changed from a spiky Ni surface (Figure 15b) to small circular Cu particles (Figure 17a). The nanofibre diameter and circular Cu particles increased in size with electroless Cu plating time. At 8 min Cu electroless plating time, the average diameter of the CuNiPN was within the standard deviation of Ni plated nanofibres. The physical appearance of CuNiPN changes to the colour of Cu with increasing plating time; however, the Cu colour is not uniform throughout the entire surface of the nanofibre sheet for plating times past 8 min (top left of SEM images in Figure 17).
Figure 17. SEM images of CuNiPN with varying Cu electroless plating times: (a) 8 min, (b) 30 min, (c) 60 min, (d) 240 min. Scale bar = 1 µm.

The mass of plated Cu on the 25 mm by 25 mm NiPN with increasing time is displayed in Figure 18. The plated Cu mass at 8, 15, 30, 60, 120, 180, and 240 min are 2.0, 9.4, 13.0, 15.2, 18.1, 18.7, and 19.1 mg respectively. The amount of plated Cu out of the EPB was calculated by comparing the mass of Cu$^{2+}$ ions dissolved in the EPB and the mass of Cu plated on the NIPN. The rate of Cu electroless plating was faster initially as 68% of the Cu$^{2+}$ ions were plated within the first 30 min. The lower Cu plating rate at longer times could be attributed to the decrease in the reducing agent and Cu$^{2+}$ ions in solution over time. The decrease in Cu$^{2+}$ ions was shown
from the colour of Cu EPB becoming lighter and clearer over time. At the end of 240 min of Cu electroless plating, nearly 100% of the Cu\(^{2+}\) ions were converted to metallic Cu.

![Figure 18. Mass of plated Cu vs. time on 25 mm by 25 mm NiPN.](image)

SEM images of CuNiPN with a 60 min plating time is shown in Figure 19a, b, and c. The average diameter at the core of the cross section is 741 ± 41 nm (Figure 19d), which is thinner than the average diameter on the surface of 1042 nm (Figure 17c), indicating more Cu was plated on the surface of the CuNiPN sheet compared the core. This could be due to a difference in concentration of Cu\(^{2+}\) ions on the surface compared to the core, since Cu\(^{2+}\) ions are reduced to metallic Cu initially on the surface before diffusing to the core. This did not occur in electroless Ni plating due to plating conditions at elevated temperatures, which could promote the diffusion of Ni ions into the core of the activated nanofibre sheet.
Figure 19. Cross-sectional SEM images of CuNiPN with 60 min plating time. Scale bar = (a) 40 µm, (b) 4 µm, (c) 400 nm.
3.6 Cu(OH)$_2$ nanorod growth

3.6.1 Cu(OH)$_2$ nanorod growth with varying plated Cu mass

Figure 20 shows SEM images of Cu(OH)$_2$ NGCuNiPN grown in 1.25 M NaOH-0.1 M APS solution for 30 min with varying mass of plated Cu. The mass of Cu plated used to grow nanorods are specified at the end of “Cu(OH)$_2$ NGCuNiPN” for section 3.6.1. For example, Cu(OH)$_2$ NGCuNiPN-2.7 indicates Cu(OH)$_2$ NGCuNiPN was grown with 2.7 mg of Cu. The number of Cu(OH)$_2$ nanorods increased with Cu mass and the colour of the Cu(OH)$_2$ NGCuNiPN sheets changes from gray to light blue accordingly (top left of SEM images in Figure 20). Cu(OH)$_2$ nanorods completely covered the NiPN at Cu mass above 2.7 mg. The nanorods in Cu(OH)$_2$ NGCuNiPN-19.1 appeared to cluster together at the tips (Figure 20d), which was also observed in previous work [48] and indicated that growth at large amounts of Cu altered the morphology of the nanorods. The diameter of the Cu(OH)$_2$ nanorods are not significantly different with varying Cu plating mass as standard deviations overlap.
Figure 20. SEM images of Cu(OH)$_2$ NGCuNiPN grown with varying masses of plated Cu: (a) 2.7 mg, (b) 7.7 mg, (c) 10.4 mg, (d) 19.1 mg. Scale bar = 4µm. Growth solution: 1.25 M NaOH-0.1 M APS. Growth time: 30 min.

Figure 21 shows cross-sectional images of Cu(OH)$_2$ NGCuNiPN-19.1 grown in 1.25 M NaOH-0.1 M APS solution for 30 min. A dense forest of Cu(OH)$_2$ nanorods were observed on the top and bottom faces of the Cu(OH)$_2$ NGCuNiPN sheet (Figure 21a). Some NiPN inside the sheet appeared to have an outer solid layer of material surrounding it (Figure 21e). A dense collection of Cu(OH)$_2$ nanorods were also observed in the cross-section the sheet (Figure 21f).
Figure 21. Cross-sectional SEM images of Cu(OH)$_2$ NGCuNiPN at varying locations: (a) Entire cross section. Scale bar = 20 µm. (b) Surface. Scale bar = 5 µm. (c) Near top surface. Scale bar = 4 µm. (d) Near bottom surface. Scale bar = 4 µm. (e) Near top surface. Scale bar = 1 µm. (f) Near bottom surface. Scale bar = 500 nm. Cu plating mass: 19.1 mg. Growth solution: 1.25 M NaOH-0.1 M APS. Growth time: 30 min.
3.6.2 Cu(OH)$_2$ nanorod growth with varying growth solution concentration

Figure 22 shows SEM images of Cu(OH)$_2$ NGCuNiPN grown for 30 min and 2 mg of plated Cu with varying NaOH-APS concentrations. The amount of Cu(OH)$_2$ nanorods decreases with increasing NaOH-APS concentration. Fewer and thinner nanorods were observed as concentration increased. The physical appearance of all these samples appear grey(top left of SEM images in Figure 22).

![Figure 22 SEM images of Cu(OH)$_2$ NGCuNiPN grown with varying growth solution concentrations (M NaOH/M APS): (a) 0.625/0.05, (b) 1.25/0.1, (c) 2.5/0.2, (d) 3.75/0.3 (Scale bar in magnified image = 400nm). Scale bar = 4µm. Plated Cu mass: approximately 2 mg. Growth time: 30 min.](image)
Figure 23. shows SEM images NiPN without any Cu plating submerged in 3.75 M NaOH-0.3 M APS for 180 min. No changes in the morphology of the plated Ni layer was observed. However, during submersion bubbles (Figure 24) were observed indicating a possible chemical reaction was taking place. The products of the reaction are examined in Section 3.9.2.

Figure 23. SEM of NiPN submerged in 3.75 M NaOH-0.3 M APS for 180 min. Scale bar = (a) 4 µm, (b) 500 nm.

Figure 24. Formation of bubbles during submersion of NiPN in 3.75 M NaOH-0.3 M APS.
Figure 25 shows cross-sectional SEM images of Cu(OH)$_2$ NGCuNiPN grown in 0.625 M NaOH-0.05 M APS. The length and number of Cu(OH)$_2$ nanorods are higher near the surface (Figure 25a and c) of the Cu(OH)$_2$ NGCuNiPN sheet compared to the core (Figure 25d and e), which can be attributed to more plated Cu at the surface of NiPN sheet compared to the core (Figure 19).
Figure 25. Cross-sectional SEM image of Cu(OH)$_2$ NGCuNiPN grown in 0.625 M NaOH-0.05 M APS: (a) entire cross section, scale bar = 40 µm, (b) near the surface of nanofibre sheet, scale bar = 4 µm, (c) near surface of nanofibre sheet, scale bar = 1 µm, (d) core of nanofibre sheet, scale bar = 4 µm, (e) core of nanofibre sheet, scale bar = 1 µm. Cu plating mass: approximately 2 mg. Growth time: 30 min.
Figure 26 shows cross-sectional SEM images of Cu(OH)$_2$ NGCuNiPN in 3.75 M NaOH-0.3 M APS growth solution for 30 min. Cu(OH)$_2$ nanorods are distributed evenly in cross section of the nanofibre sheet (Figure 26b). The amount of nanorods in the cross section and the surface (Figure 22d) appears be similar, which is different compared to nanorods growth at a lower concentration of NaOH-APS (Figure 25) where more Cu(OH)$_2$ nanorods appear on the surface compared to the core of the nanofibre sheet.
Figure 26. Cross section SEM image of Cu(OH)$_2$ NGCuNiPN grown in 3.75 M NaOH-0.3 M APS: (a) scale bar = 20 µm, (b) scale bar = 4 µm, (c) scale bar = 400 nm. Cu plating mass: approximately 2 mg. Growth time: 30 min.
3.6.3 Cu(OH)$_2$ nanorod growth with varying growth time

Figure 27 shows SEM images of Cu(OH)$_2$ NGCuNiPN with approximately 2 mg of Cu plated grown in 2.5 M NaOH-0.2 M APS growth solution for varying growth times of 30, 60, and 180 min. Varying growth times does not appear to change the morphology of the Cu(OH)$_2$ nanorods, which was the not expected result, since CuO nanosheets forms at time longer than 30 min when submerged in Cu foil [57]. The reason for the lack of CuO nanoflake formation could be due to the significantly lower amount of Cu; however, CuO peaks were observed by XRD (Section 3.7).
Figure 27. SEM images of Cu(OH)$_2$ NGCuNiPN with varying growth times: (a) 30 min, (b) 60 min, (c) 180 min (scale bar in magnified image = 400nm). Scale bar = 4µm. Growth solution: 2.5 M NaOH-0.2 M APS. Cu plating mass: approximately 2 mg.

3.7 X-ray diffraction

Figure 28 shows the XRD patterns of nanofibre sheets at each step of the fabrication process. XRD patterns of activated PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibres matched with stabilized PAN nanofibres (Figure 28a) [28]. Palladium or palladium oxide patterns were not detected due to the small amount in the nanofibres. XRD patterns of NiPN shows the addition of Ni (Figure 28b, JCPDS Card no. [04-0850]) [62]. XRD patterns of CuNiPN shows Cu and Ni peaks (Figure 28c, JCPDS Card no. [04-0836]) [63], and stabilized PAN nanofibres peaks disappeared, possibly due to the metals completely covering the nanofibre. Cu(OH)$_2$ NGCuNiPN
XRD patterns (Figure 28d) shows the presence of Cu(OH)$_2$ (JCPDS Card no. [80-0656]), CuO (JCPDS Card no. [48-1548]) [49], Ni, and stabilized PAN-co-MA. The lack of Cu shows all Cu was converted to Cu(OH)$_2$ and CuO. The presence of CuO was not found in literature for similar growth conditions and time on Cu foil. CuO XRD peaks were found at longer growth times or higher NaOH-APS concentrations [57].
3.8 Thermogravimetric analysis

Figure 29 shows thermograms of PAN-co-MA nanofibres and PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres. The main difference between the PAN-co-MA nanofibres and PAN-co-
MA/Pd(C₅H₇O₂)₂ nanofibres is the decrease in mass between 120°C and 210°C due to the conversion of Pd(C₅H₇O₂)₂ into Pd and PdO (confirmed in section 3.9.1). Starting at 296°C, the mass loss in the PAN-co-MA occurs [29,30]. This finding reinforces that heat-treatment at 250°C in argon is suitable for the activation of PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres.

Figure 29. Thermograms of PAN-co-MA nanofibres and PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres. Nitrogen atmosphere.

3.9 X-ray photoelectron spectroscopy

XPS was required to detect relatively smaller amounts of compounds that XRD cannot detect. The black bars above some of the XPS narrow scan spectrums indicate the range of binding energy that belongs to a compound from National Institute of Standards and Technology X-ray Photoelectron Spectroscopy Database.
3.9.1 Activated PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres

Figure 30a, b, and c show XPS spectra of activated PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres. The C1s orbital narrow scan indicates the presence of the bonds in the PAN-co-MA [64]. Pd 3d narrow scan shows the presence of metallic Pd and PdO [65], which confirms the generation of catalyst for electroless plating.

Figure 30. XPS spectra of activated PAN-co-MA/Pd(C₅H₇O₂)₂ nanofibres: (a) survey scan, (b) C 1s narrow scan, (c) Pd 3d narrow scan.
3.9.2 Effect of NaOH-APS solution on plated Ni

To determine the effect of the NaOH-APS solution on Ni, XPS spectrums were compared between NiPN and NiPN submerged in 3.75 M NaOH-0.3 M APS solution for 180 min (NiPN-180). Figure 31b shows Ni 2p narrow scan, which shows the presence of Ni, NiO, Ni(OH)$_2$, and NiOOH. The major differences between NiPN and NiPN-180 were the peaks at 853.3 eV and 854.1 eV, which indicated a higher presence of metallic Ni in NiPN. Submersion in NaOH-APS solution appears to promote the formation of Ni compounds. In addition, Seghiouer et al. shown Ni forms Ni(OH)$_2$ under alkaline solution [66]. Even though Ni compound were detected majority of NiPN is metallic Ni as these compounds were not detected in XRD.
Figure 31. XPS spectra comparing NiPN and NiPN submerged in 3.75 M NaOH-0.3 M APS solution for 180 min: (a) survey scan, (b) Ni 2p narrow scan, (c) O 1s narrow scan.
3.10 Electrical conductivity

Figure 32 shows the electrical conductivity of NiPN, CuNiPN (approximately 2 mg plated Cu), Cu(OH)₂ NGCuNiPN (approximately 2 mg plated Cu, 3.75 M NaOH-0.3 M APS growth solution, 30 min growth time), and NiPN submerged in 3.75 M NaOH-0.3 M APS growth solution for 30 and 180 min (NiPN-3.75/0.3-30, NiPN-3.75/0.3-180). Electrical conductivity decreased along the fabrication process from 2379±108 S/cm for NiPN to 1270±108 S/cm for Cu(OH)₂ NGCuNiPN. The electrical conductivity of NiPN-3.75/0.3-30 is lower than the electrical conductivity of NiPN. Longer submersion times does not alter electrical conductivity due to no significant difference in conductivity between NiPN-3.75/0.3-30 and NiPN-3.75/0.3-180.

![Figure 32. Electrical conductivity of nanofibre sheets.](image-url)
3.11 Conclusions

In this chapter, Cu(OH)$_2$ NGCuNiPN was successfully fabricated. The PAN-co-MA/Pd(C$_5$H$_7$O$_2$)$_2$ nanofibre substrates were fabricated using the electrospinning process. The activation process converted Pd(C$_5$H$_7$O$_2$)$_2$ into Pd and PdO catalyst for electroless plating, which was confirmed by XPS. Ni electroless plating coated the activated nanofibres with Ni uniformly and through the thickness of the substrate. Electroless Cu plating was performed afterwards and Cu was converted into Cu(OH)$_2$ nanorods with a NaOH-APS solution. Nanorod growth with more Cu increased the number of Cu(OH)$_2$ nanorods, while increase in NaOH-APS solution concentration reduced the number and length of Cu(OH)$_2$ nanorods. Increase in Cu(OH)$_2$ nanorod growth time does not appear to change the morphology of the Cu(OH)$_2$ nanorods, even though CuO nanosheets formed at growth times longer than 30 min in literature. No changes in morphology were observed when NiPN was submerged in NaOH-APS solution, even though XPS peaks found Ni was converted into Ni compounds (NiO, Ni(OH)$_2$, NiOOH) nevertheless majority of NiPN is metallic Ni as the compounds were not detected by XRD. Electrical conductivity of the nanofibre sheets decreased along the fabrication process from 2379 ± 108 S/cm for NiPN to 1270 ± 108 S/cm for Cu(OH)$_2$ NGCuNiPN. Submersion of NiPN in NaOH-APS solution reduced electrical conductivity, but longer submersion times did not alter electrical conductivity.
Chapter 4: Electrochemical Characterization of Cu(OH)$_2$ Nanorods Grown on Cu-Ni Plated Nanofibres

4.1 Introduction

In Chapter 4, the performance of NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN were characterized for the supercapacitor application. Investigations were separated into 3 sections. First, the performance of NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN with varying masses of Cu(OH)$_2$ nanorods were investigated to determine if the nanorods made a positive contribution to performance and the optimum amount of nanorods. Second, the performance of NiPN submerged in the nanorod growth solution and Cu(OH)$_2$ NGCuNiPN in varying growth solution concentrations were investigated with the purpose to identify whether the improved performance was from Ni compounds that formed during nanorod growth or the Cu(OH)$_2$ nanorods itself. These tests also identified the effect of growth solution concentration on performance. Third, addition electrochemical tests were conducted on the best performing electrode to identify more electrochemical characteristics, such as performance at higher current densities and capacitance retention over 1000 cycles.

4.2 Effect of the amount of Cu(OH)$_2$ nanorods

Capacitive behavior of NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN with varying masses of nanorods are characterized in the section. The mass of materials in NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN with varying masses of Cu(OH)$_2$ nanorods are displayed in Table 7. Cu(OH)$_2$ nanorod growth was performed in 1.25 M NaOH-0.1 M APS solution for 30 min. The mass of Cu(OH)$_2$ nanorods on each Cu(OH)$_2$ NGCuNiPN electrode is represented at the end of
the abbreviation; for example, Cu(OH)$_2$ NGCuNiPN-0.5 represents 0.5 mg of Cu(OH)$_2$ nanorods were grown on the NiPN. Cu(OH)$_2$ NGCuNiPN-1.9 had Cu(OH)$_2$ nanorods clustered at their tips (Figure 20d), while Cu(OH)$_2$ NGCuNiPN-1.8 does not even though their masses were similar.

Table 7. Mass of materials in nanofibre electrodes. Unit in milligrams.

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<th>Electrode</th>
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</tbody>
</table>

Figure 33 shows CV curves of the various electrodes. These CV curves represent capacitance characteristics of faradaic redox reactions, since peaks and troughs are present and EDLC CV curves appear nearly rectangular. All anodic and cathodic peaks are symmetric, suggesting reversibility of charge-discharge cycles. Two strong redox peaks is present in each curve. Possible faradaic reactions for Ni, NiO, NiOOH, Ni(OH)$_2$, Cu, and Cu(OH)$_2$ are [15,66–69]:

\[
Ni + 2OH^- \leftrightarrow Ni(OH)_2 + 2e^-
\]

\[
NiO + OH^- \leftrightarrow NiOOH + e^-
\]

\[
Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-
\]

\[
2Cu + 2OH^- \leftrightarrow Cu_2O + H_2O + 2e^-
\]

\[
2Cu(OH)_2 + 2e^- \leftrightarrow Cu_2O + 2OH^- + H_2O
\]
Oxidation peaks shift further away from the NIPN oxidation peak at 0.367 V in the positive potential direction with the inclusion of Cu(OH)$_2$ nanorods. The mass of the nanorods did not shift the peaks except for Cu(OH)$_2$ NGCuNiPN-1.9, which shifted more in the positive direction possibly due to its clustered nanorod morphology. The oxidation peak of CuNiPN is on 0.406 V, which shifted more in the positive potential direction than any of the Cu(OH)$_2$ NGCuNiPN electrodes. Cu(OH)$_2$ NGCuNiPN-0.5 had the highest oxidation peak, suggesting a higher amount of energy is stored on this electrode compared to the other electrodes (confirmed by GDC in the next paragraph).

![CV curves of NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN with varying mass of Cu(OH)$_2$ nanorods](image)

Figure 33. CV curves of NiPN, CuNiPN, and Cu(OH)$_2$ NGCuNiPN with varying mass of Cu(OH)$_2$ nanorods (growth time: 30 min, growth solution: 1.25 M NaOH-0.1 M APS). Scan rate = 5 mV s$^{-1}$. 2 M KOH electrolyte.
GCD curves of the various electrodes are shown in Figure 34. The shape of the charge-discharge curves displays nonlinearities, which are representative of faradaic redox reactions, in agreement with CV curves. The specific capacitances calculated from discharge curves of NiPN and CuNiPN are 57 F g\(^{-1}\) and 51 F g\(^{-1}\). The specific capacitances of Cu(OH)\(_2\) NGCuNiPN-0.5,1.3,1.8, and 1.9 are 133, 78, 61, and 58 F g\(^{-1}\) respectively (Figure 35b). NiPN and CuNiPN electrodes have lower capacitances compared to Cu(OH)\(_2\) NGCuNiPN electrodes. For Cu(OH)\(_2\) NGCuNiPN electrodes, capacitance decreases with increasing Cu(OH)\(_2\) nanorod mass, which puts into question whether the increase in capacitance is due the presence of Cu(OH)\(_2\) nanorods or Ni compounds (NiO, NiOOH, Ni(OH)\(_2\)) created from the growth solution (investigated in section 3.6.2). If Cu(OH)\(_2\) nanorods does not improve capacitance, then increasing mass and amount of nanorods blocks reactive surface area of the Ni compound active material, which reduces capacitance. This would support the findings of the decrease in capacitance as the mass of Cu(OH)\(_2\) nanorods increases. Energy densities of the various electrodes are displayed in Figure 35c, which is in direct relationship to specific capacitance. The discharge times of NiPN and CuNiPN are 10 s and 14 s respectively. The discharge times of Cu(OH)\(_2\) NGCuNiPN-0.5,1.3,1.8, and 1.9 are 18, 16, 14, and 14 seconds respectively (Figure 35a), which indicates a longer discharge time for fewer Cu(OH)\(_2\) nanorods. The power densities of NiPN and CuNiPN are 1185 and 529 W kg\(^{-1}\) respectively. The low power density of CuNiPN is due to the high active material mass, even though Cu is the 2\(^{nd}\) most electrically conductive metal, which in theory should increase power density (refer to maximum instantaneous power equation in Section 1.2.1). The power density of Cu(OH)\(_2\) NGCuNiPN-0.5,1.3,1.8, and 1.9 are 1081, 841, 699, 548 W kg\(^{-1}\) respectively (Figure 35d), which indicates power density increases with fewer Cu(OH)\(_2\) nanorods.
Figure 34. GCD curves of NiPN, CuNiPN, Cu(OH)$_2$ NGCuNiPN with varying mass of Cu(OH)$_2$ nanorods (growth time: 30 min, growth solution: 1.25 M NaOH-0.1 M APS). Current = 0.1 A. Electrolyte: 2 M KOH.
Figure 35. (a) Discharge times, (b) specific capacitance, (c) energy density vs power density. Calculated from GCD curves of NiPN, CuNiPN, Cu(OH)$_2$ NGCuNiPN with varying mass of Cu(OH)$_2$ nanorods (growth time: 30 min, growth solution: 1.25 M NaOH-0.1 M APS). Current = 0.1 A. Electrolyte: 2 M KOH.
4.3 Effect of growth solution

Electrochemical characteristics were compared between NiPN, NiPN submerged in the nanorod growth solution, and Cu(OH)$_2$ NGCuNiPN electrodes to determine whether the increase in capacitance was due to Cu(OH)$_2$ nanorods or Ni compounds. NiPN was submerged in 3.75 M NaOH-0.3 M APS for 30 min (NiPN-3.75/0.3-30) and 180 min (NiPN-3.75/0.3-180) were analyzed. In addition, Cu(OH)$_2$ NGCuNiPN grown at varying concentrations between 0.625 M NaOH-0.05 M APS to 3.75 M NaOH-0.3 M APS were analyzed. In this section, the numbers after the abbreviation Cu(OH)$_2$ NGCuNiPN represents the concentration of the growth solution; for example, Cu(OH)$_2$ NGCuNiPN-3.75/0.3 represents Cu(OH)$_2$ NGCuNiPN grown with 3.75 M NaOH-0.3 M APS solution. All Cu(OH)$_2$ NGCuNiPN were grown for 30 min with approximately 2 mg of plated Cu. The mass of the electrodes is displayed in Table 8. For NiPN-3.75/0.3-30 and NiPN-3.75/0.3-180 no noticeable changes in mass were detected from NiPN, likely due to the actual change in mass being very small (below 1 mg). For Cu(OH)$_2$ NGCuNiPN-3.75/0.3, the mass of Cu(OH)$_2$ nanorods were undetectable by the scale, even though they were observed in SEM (Figure 22d and Figure 26).
Table 8. Mass of total active material and their respective components in 12 mm x 6 mm electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Concentration (M NaOH-M APS)</th>
<th>Active (mg)</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPN-3.75/0.3-30</td>
<td>3.75-0.3</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>NiPN-3.75/0.3-180</td>
<td>3.75-0.3</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Cu(OH)2 GCuNiPN-0.625/0.05</td>
<td>0.625-0.05</td>
<td>3.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Cu(OH)2 GCuNiPN-1.25/0.1</td>
<td>1.25-0.1</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>Cu(OH)2 GCuNiPN-2.5/0.2</td>
<td>2.5-0.2</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu(OH)2 GCuNiPN-3.75/0.3</td>
<td>3.75-0.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 36 shows CV curves of the various electrodes. Similar to electrodes in section 4.1, large redox current peaks are detected meaning capacitance characteristics are faradaic redox reactions. The anodic and cathodic peaks are also symmetric, suggesting reversibility of the faradaic redox reactions. The oxidation peaks are higher and reduction troughs are lower with increasing NaOH-APS concentration, suggesting electrodes submerged at higher concentrations stores more energy. For Cu(OH)2 GCuNiPN oxidation peaks shifts to lower potentials as concentration increases. SEM images show the number of nanorods decrease and more Ni being exposed (Figure 22) as NaOH-APS concentration increases could be a reason for the shift towards the NiPN oxidation peak (0.406 V). NiPN-3.75/0.3-30 and NiPN-3.75/0.3-30 shifts away from the NiPN peak possibly due to larger amounts of Ni compounds.
Figure 36. CV curves of NiPN submerged in 3.75 M NaOH-0.3 M APS for 30 min and 180 min, Cu(OH)$_2$ NGCuNiPN with growth solution concentration (Cu mass: 2 mg, growth time: 30 min). Scan rate = 5 mV s$^{-1}$. 2 M KOH electrolyte.

Figure 37 shows GDC curves of the various electrodes charged and discharged at a current of 0.1 A. Similar to the electrodes in section 4.1, the shape of the discharge curves displays nonlinearities, which are representative of Faradaic redox reactions. For Cu(OH)$_2$ NGCuNiPN (Figure 37 and Figure 38a), discharge times increases from 18 s to 39 s as growth solution concentration increases from 0.625 M NaOH/0.05 M APS to 3.75 M NaOH/0.3 M APS. For NiPN-3.75/0.3-30 and NiPN-3.75/0.3-180 discharge times are 33 s and 51 s respectively. Discharge times increase with higher concentration and longer submersion times.
Figure 37. GCD curves of NiPN submerged in 3.75 M NaOH-0.3 M APS for 30 min and 180 min, Cu(OH)$_2$ NGCuNiPN with varying growth solution concentration (Cu mass: 2 mg, growth time: 30 min). Current: 0.1 A. Electrolyte: 2 M KOH.

The specific capacitances and energy densities of the electrodes are displayed in Figure 38b and c. For Cu(OH)$_2$ NGCuNiPN, specific capacitance and energy density increases with increasing growth solution concentration that also decreases the number of Cu(OH)$_2$ nanorods (Figure 22). The comparison between NiPN-3.75/0.3-30 and Cu(OH)$_2$ NGCuNiPN-3.75-0.3 shows the addition of Cu(OH)$_2$ nanorods did not improve energy density; therefore, the improvement was from the conversion of Ni to the Ni compounds. Specific capacitance (227 Fg$^{-1}$ to 233 Fg$^{-1}$) and energy density (8.94 Wh kg$^{-1}$ to 9.09 Wh kg$^{-1}$) were nearly identical. The nearly identical specific capacitance and energy density could be due to poor interfaces between the Cu(OH)$_2$ nanorods and NiPN current collector. Discharge times increased (33 s to 39 s) and
power density decreased (968 W kg\(^{-1}\) to 848 W kg\(^{-1}\)) due to the addition of Cu(OH)\(_2\) nanorods. 

The reason for reduced power density could be due to the poor electrical properties of Cu(OH)\(_2\).

NiPN-3.75/0.3-180 performed the best overall in terms of specific capacitance (348 Fg\(^{-1}\)) and energy density (13.3 Wh kg\(^{-1}\)) relative to the other electrodes. NiPN-3.75/0.3-180 has the longest discharge time of 51 s due to the increased energy storage capacity. The difference in power densities between NiPN-3.75/0.3-30 and NiPN-3.75/0.3-180 are 968 W kg\(^{-1}\) and 944 W kg\(^{-1}\) respectively, which are nearly identical (Figure 38d).
Figure 38. (a) Discharge times, (b) specific capacitance, (c) energy density vs power density. Calculated from GCD curves of NiPN submerged in 3.75 M NaOH-0.3 APS for 30 min and 180 min, Cu(OH)$_2$ NGCuNiPN with varying growth solution concentration (Cu mass: 2 mg, growth time: 30 min). Current: 0.1 A. 2 M KOH electrolyte.
4.4 Further electrochemical characterization on NiPN-3.75/0.3-180

Further electrochemical tests were performed on NiPN-3.75/0.3-180, since it had the best overall energy and power density compared to the other tested electrodes. Figure 39 shows CV curves of Ni-3.75/0.3-180 at varying scan rates from 2 mVs$^{-1}$ to 50 mVs$^{-1}$. The minimal change in shape of the anodic and cathodic peaks suggests excellent electron conduction from 2 mVs$^{-1}$ to 30 mVs$^{-1}$; however, at a high scan rate of 50 mVs$^{-1}$ asymmetrical peaks were spotted. The shift of the CV curves with increasing scan rate are due to the internal resistance of the electrode.

![Figure 39](image)

**Figure 39.** CV curves of NiPN-3.75/0.3-180 at varying scan rates. 2 M KOH electrolyte.

Figure 40 shows GCD curves of Ni-3.75/0.3-180 at varying current densities, which shows charge/discharge time decrease with increasing current densities. Figure 41a shows the discharge time, active material mass specific capacitance, and total material mass specific
capacitance (mass of active material + nanofibre substrate). Discharge time decreased with increased current density from 56 s to 6 s at 3.6 A g\(^{-1}\) to 28.8 A g\(^{-1}\) respectively. Specific capacitance decreased 11%, 5%, and 5% each time current density was doubled starting at 3.6 A g\(^{-1}\) until 28.8 A g\(^{-1}\). This illustrates excellent rate capability, as only 20% of capacitance is loss at 28.8 A g\(^{-1}\), which differs from most Ni based electrodes that showed a decrease in capacitance of above 40% at higher current densities (Figure 42) [70–72]. The reason for the excellent rate capability could be excellent interface between the Ni compounds and Ni current collector and the high conductivity of the electrode to reduce electron loss. All the electrodes referenced in Figure 42 except for this work used a polymer binder to attach the active material to the substrate.

![Graph of GCD curves of NiPN- 3.75/0.3-180 at varying currents densities. 2 M KOH electrolyte.](image)

**Figure 40.** GCD curves of NiPN- 3.75/0.3-180 at varying currents densities. 2 M KOH electrolyte.
Figure 41. (a) Discharge times and capacitances, (b) areal and volumetric capacitance, (c) energy densities vs power density. Calculated from GCD curves at varying current densities of NiPN-3.75/0.3-180. 2 M KOH electrolyte.
Figure 42. Capacitance retention at increasing current densities.
Areal capacitance of Ni-3.75/0.3-180 is comparable to some of the highest found in literature to the best of my knowledge (Figure 41a and b).

**Table 9. Areal density in comparison to other works.**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Areal Capacitance (F cm$^{-2}$)</th>
<th>Current Density (mA cm$^{-2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo$_2$O$_4$ microspheres</td>
<td>~0.425 [1]</td>
<td>1</td>
<td>[73]</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$-Ni(OH)$_2$ on carbon nanofibres</td>
<td>6.04 [5]</td>
<td>5</td>
<td>[74]</td>
</tr>
<tr>
<td>NiO/Ni(OH)$_2$ on contrawires</td>
<td>0.404 [4]</td>
<td>4</td>
<td>[69]</td>
</tr>
<tr>
<td>Ni$_3$Cu hydroxide on carbon paper</td>
<td>3.14 [2]</td>
<td>2</td>
<td>[75]</td>
</tr>
<tr>
<td>Ni(OH)$_2$/carbon nanotubes grown on Ni foam</td>
<td>16 [2.5]</td>
<td>2.5</td>
<td>[76]</td>
</tr>
<tr>
<td>NiPN-3.75/0.3-180</td>
<td>1.52 [13.9]</td>
<td>13.9</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 41c shows the energy and power density of Ni-3.75/0.3-180 at varying current densities normalized by active material mass and total mass (mass of active material + nanofibre substrate). When normalized with active material mass, energy and power densities were 13.2 Wh kg$^{-1}$ and 7893 W kg$^{-1}$ respectively at 28.8 A g$^{-1}$ active material mass current density, which is equivalent to 8.85 Wh kg$^{-1}$ and 5300 W kg$^{-1}$ at 19.3 A g$^{-1}$ total material mass current density.

Figure 43 shows the discharge time, capacitance retention, and power retention of Ni-3.75/0.3-180 derived from 1000 GCD cycles at an active material current density of 7.2 A g$^{-1}$. Specific capacitance increased by 44 % (330 F g$^{-1}$ to 476 F g$^{-1}$), power density decreased by 8 % (1165 W kg$^{-1}$ to 1075 W kg$^{-1}$), and discharge time increased by 9 s after 1000 cycles.
Interestingly, capacitance increased with increasing cycles, which normally decreases with increasing cycles. However, the increase in capacitance is found in other works [69,70,73] and likely due to the conversion of Ni to compounds in alkali 2 M KOH electrolyte, similar to how the Ni compounds were first produced in the NaOH-APS growth solution. The decrease in power density also supports this prediction, since the amount of electrically conductive Ni is reduced.

Figure 43. Discharge time, capacitance retention, and power retention of NiPN-3.75/0.3-180 for 1000 GCD cycles. Electrolyte: 2 M KOH. Specific active material current density: 7.2 A g⁻¹.

4.5 Conclusions

In this chapter, electrochemical behavior of the nanofibre electrodes was characterized. By comparing the performance of NiPN, NiPN submerged in the nanorod growth solution, and Cu(OH)₂ NGCuNiPN electrodes, it was found that Cu(OH)₂ nanorods did not improve energy
density and decreased power density. The conversion of Ni to Ni compounds by submersion in the nanorod growth solution was responsible for the increase in energy density. NiPN-3.75/0.3-180 had highest energy density compared to the other tested electrodes. GCD tests at a current density of 28.8 A g\(^{-1}\) showed NiPN-3.75/0.3-180 had a discharge time of 6s, specific power density of 7893 W kg\(^{-1}\), specific capacitance of 312 F g\(^{-1}\), and energy density of 13.2 Wh kg\(^{-1}\). The energy density surpassed the goal of 10 Wh kg\(^{-1}\), but not the power density of 20,000 W kg\(^{-1}\). Only 20% of capacitance is loss when current density was increased from 3.6 g\(^{-1}\) to 28.8 A g\(^{-1}\). Cyclic testing after 1000 cycles for NiPN-3.75/0.3-180 showed specific capacitance increased by 44%, but power density decreased by 8 %, and discharge time increased by 9 s. The increase in discharge time and capacitance is likely due to the formation of additional Ni to Ni compounds in alkali 2 M KOH electrolyte, similar to how the Ni compounds were originally produced in the NaOH-APS growth solution.
Chapter 5: Conclusions and Future Work

5.1 Conclusions

NiPN and Cu(OH)\(_2\) NGCuNiPN supercapacitor electrodes were successfully fabricated. Cu(OH)\(_2\) nanorods were found to reduce power density and did not improve energy density. However, the submersion of NiPN in NaOH-APS nanorod growth solution converted Ni to Ni compounds (NiO, Ni(OH)\(_2\), NiOOH), which significantly improved energy density.

The fabrication of Cu(OH)\(_2\) NGCuNiPN consist of five steps. In first step, the substrate for the electrode, PAN-co-MA/Pd(C\(_5\)H\(_7\)O\(_2\))\(_2\) nanofibres were fabricated by electrospinning. In the second step, the nanofibres were heat treated to convert the Pd(C\(_5\)H\(_7\)O\(_2\))\(_2\) to metallic Pd and PdO. Metallic Pd was a catalyst for electroless Ni and Cu plating on the nanofibre substrate, which was the third and fourth step of the fabrication process. In the last step, Cu was converted into Cu(OH)\(_2\) nanorods by submersion of the metallic nanofibre sheet into a NaOH-APS growth solution. It was found that the mass of plated Cu had a direct relationship to the number of Cu(OH)\(_2\) nanorods grown on the NiPN. When Cu(OH)\(_2\) nanorods were grown with a constant mass of Cu, increasing the NaOH-APS nanorod growth solution concentration decreased the number and length of Cu(OH)\(_2\) nanorods grown.

Electrochemical characterization determined the conversion of Ni to Ni compounds improved energy density and the Cu(OH)\(_2\) nanorods only decreased power density. When comparing both NiPN submerged and Cu(OH)\(_2\) NGCuNiPN in the same 3.75 M NaOH-0.3 M APS solution for 30 min, the specific energy densities were nearly identical (8.94 Wh kg\(^{-1}\) and
9.09 Wh kg\(^{-1}\) respectively) and the power density decreased due to the presence of the nanorods (968 W kg\(^{-1}\) and 848 W kg\(^{-1}\) respectively).

Further electrochemical characterization was performed on NiPN submerged in 3.25 M NaOH-0.3 M APS solution for 180 min due to its superior combination of energy and power density compared to other tested electrodes. The discharge time, specific energy, and power densities were 6 s, 13.2 Wh kg\(^{-1}\) and 7892 W kg\(^{-1}\) respectively when a current density of 28.8 A g\(^{-1}\) was applied to NiPN-3.75/0.3-180. Only 20\% of capacitance is loss when current density was increased from 3.6 g\(^{-1}\) to 28.8 A g\(^{-1}\). The energy density surpassed the goal of 10 Wh kg\(^{-1}\), but the power density did not reach 20,000 W kg\(^{-1}\). Cyclic testing showed specific capacitance increased by 44\% to 476 F g\(^{-1}\), but power density decreased by 8\%, and discharge time increased by 9 s after 1000 cycles. The increase in capacitance and decrease in power was likely due to the formation of additional Ni compounds under alkali conditions similar to their formation in the NaOH-APS solution.

5.2 Future work

This study started foundations for future research. Suggestions of future research before implementation into regenerative braking systems are in the following:

1) Determine how much power density degrades and energy density improves by cyclic testing over 10,000 cycles. Also find faster methods to convert Ni to the Ni compounds.

2) Determine the relationship between power density and the amount of Ni plated on the nanofibre substrate. Power density in theory can be improved by plating more Ni.

3) A cost analysis is important to identify the cost comparison between NiPN supercapacitor electrodes to other supercapacitor electrodes already in the market.
4) Material cost can be lowered by replacing two materials, PAN-co-MA with lignin and Pd(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2} with Copper(II) acetate. Lignin is a low-cost material generated as a byproduct in the industrial pulping processes, which is usually burnt as a low energy fuel. Prior work shown lignin can be fabricated into nanofibres that undergo similar thermal stabilization processes to PAN-co-MA in this work [77]. Pd(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2} can also be replaced with copper(II) acetate, prior work had shown the conversion of copper(II) acetate into metallic Cu between 200°C to 300°C [78]. Cu is able to catalyze both electroless plating processes used in this thesis [34].

5) Lower diameter nanofibres can be electrospun by lowering the polymer concentration in the electrospinning solution. Smaller diameter nanofibres would, in theory, improve supercapacitor performance due to higher surface area. However, the gases generated from the electroless plating could be an issue, since the gases could be trapped inside the nanofibre sheet due to smaller pore sizes.
Bibliography


