TUNGSTEN MODIFIED

NICKEL OXIDES AND CARBIDES

FOR POTENTIAL USE

IN ELECTROCHEMICAL CAPACITORS

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Chemical Engineering with Distinction.

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ABSTRACT

Capacitors are electrochemical devices that store charge and energy. Capacitors compliment other power storage devices, such as fuel cells and batteries, in that they have advantages in power density and rapid discharge and recharge rates. Two main pathways are followed to obtain this capacitance; pseudocapacitance and double layer capacitance. Pseudocapacitance is required to obtain the high specific power per specific energy that normal double layer capacitance is unable to attain. Current materials for pseudocapacitance, such as ruthenium oxide, are expensive and economically unviable. The goal of this research is to combine a cheap, nickel oxide capacitor that provides relatively high capacitance over a small range of voltages with a more stable tungsten capacitor that might increase the overall performance. This thesis investigates capacitance from both carbon-carbon capacitance and pseudocapacitance from transition metal oxides in nickel oxide and tungsten modified nickel oxides. The addition of carbon substrate is incorporated to investigate a possible enhancement of overall capacitance by including both double layer capacitance and pseudocapacitance. Individual and bimetallic oxides are investigated as well as tungsten carbide supported on Ketjen carbon black for a more comprehensive understanding of the system in question. Samples are analyzed for bulk composition using XRD and phase purity is determined for all samples. Cyclic voltommetry is used to test capacitive behavior, and results are analyzed

using standard equations from literature. Due to the nature of the synthesis of most samples, low capacitance is observed with little to no pseudocapacitance in addition to trivial double layer capacitance.

Chapter 1

INTRODUCTION

1.1   Motivation

Capacitors are electrochemical devices that store charge and energy. They do so through two mechanisms, pseudocapacitance and double layer capacitance. Capacitors compliment other power storage devices in that they have strengths in power density and rapid discharge and recharge time. Materials used for these capacitors fall into three main categories: carbon-carbon capacitance[1,2] ,transition metal oxides[3,4] , and conductive polymeric materials [5-7]. As electrochemical devices, they bridge an important gap between batteries and traditional capacitors. They allow for the energy storage capability of a battery while enabling the power storage of normal capacitors [8,9]. This correlation can be better noted by studying the Ragone plot in Figure 1[9].
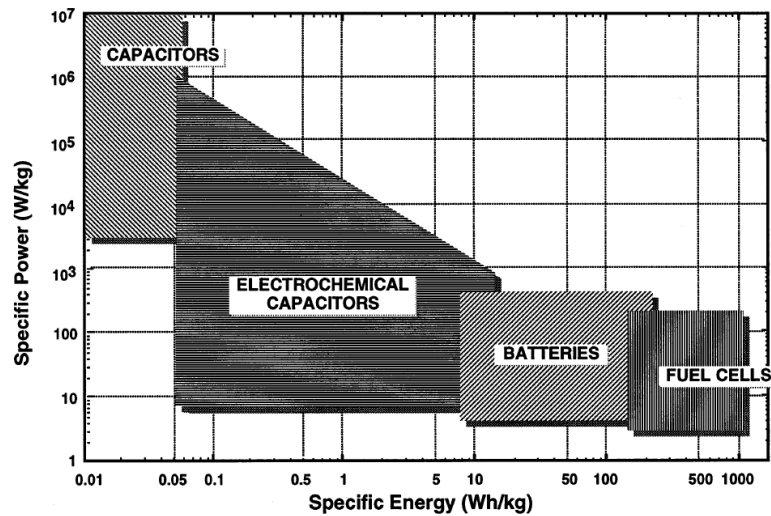
Figure 1: Ragone Plot

Capacitors are used in conjunction with, or to replace other power storage devices in applications where a larger specific power is advantageous. They are also preferred when short charge/discharge times are design constraints. These qualities are amplified by the addition of pseudocapacitors that incorporate materials that provide sites for fast, reversible Faradic reactions to occur at the surface[10]. In a successful capacitor, both the high surface area of traditional capacitors and pseudocapacitance are utilized to create a synergistic effect, optimizing overall performance.

Applications for electrochemical capacitors include automobiles, where they enhance acceleration in electric cars and allow for braking energy to be recovered[5,11]. They can also be used in series with batteries and fuel cells as they provide the short, high specific power bursts whereas batteries and fuel cells generally provide low specific powers over long periods. The capacitors have the ability to charge and discharge multiple times, and they could be recharged and reused rapidly by batteries that operate the devices [12].

2.2   Double layer capacitors

Traditional electrochemical double layer capacitors (EDLC) charge and discharge rapidly and allow for power storage on high surface area materials. Double layer capacitors store a charge on the surface of the material when a potential is applied to the material. Ions from the chosen electrolyte are then stored as charge carriers at the electrolyte/electrode interface[13]. As the surface area of the capacitor increases, the specific capacitance, or the ability to hold this charge increases with a linear correlation. A pictorial representation of an EDLC can be seen below in   Figure 2[14].
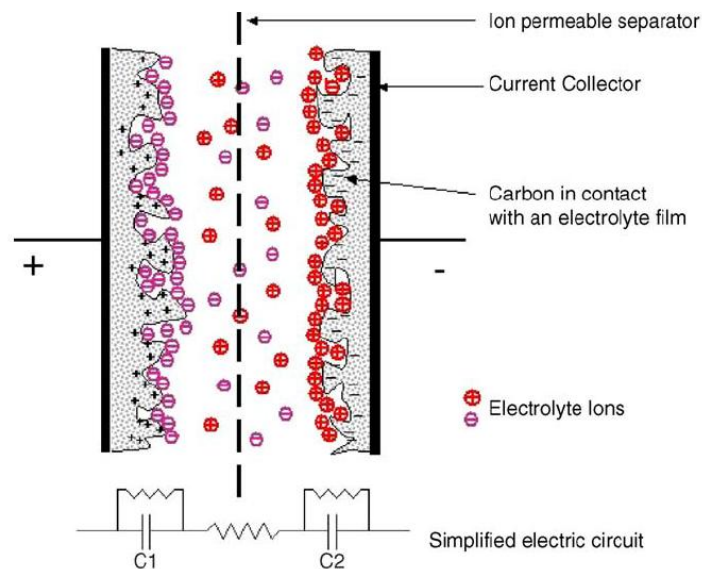

Figure 2: Electrochemical double layer capacitor

Typical electrochemical double layer capacitors include activated carbon, carbon fiber cloth, and carbon aerogels. The specific capacitance for these devices has been shown to be between 100-150 F/g [15,16]. Double layer

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capacitors do not completely utilize their surface area, however. Micropores less than 2 nm in diameter cannot be penetrated by the electrolyte and so a significant fraction of potential surface area is lost, limiting overall capacitance [17].

As standalone capacitors, EDLC's show small promise for commercial application as the overall capacitance and specific powers are rather low for industrial and everyday usage.

2.3   Pseudocapacitors

As the use of high power density energy storage devices increases, greater interest is lent to the pseudocapacitance of electrochemical capacitors. Pseudocapacitance (false capacitance) is similar to capacitance, but stores charge through a completely different mechanism. Reversible oxidation and reduction of metal ions on the surface of a capacitor permit charge to be stored for a period of time. This aspect of capacitors allows for a higher specific power density than conventional batteries in conjunction with higher energy density than traditional electrostatic capacitors[10]. In some studies, this power was shown to be ten times that of traditional batteries [18]. Since ELDCs do not provide enough specific capacitance to be used in many applications, additional capacitance is necessary.

Pseudocapacitance stores charge through Faradic oxidation and reduction reactions at the surface of the material being used [5,19,20]. Three main effects are observed at the surface of these materials. Firstly, different

compositions and phases can be formed from cations that react with the electrolyte [21,22]. Secondly, cations can intercalate into Van der Waals gaps of tunneled materials[23]. Finally, a charge-transfer process can result in cations electrochemically adsorbing onto the surface[24].

The capacitance documented for these materials can be as high as 760 F/g [25]. In addition, the energy density of pseudocapacitors is documented to be at least one order of magnitude greater than that of ELDLC's[18]. Typical examples of materials that show strong pseudocapacitance are RuO_2, IrO_2, and other transition metal oxides. These materials are extremely expensive and limit the widespread use of supercapacitors.. For these applications certain requirements must be met. Firstly, the materials of use must be able to sustain extended periods of charge and discharge with long cycle life over the potentials required[24,9]. Secondly, the material must be cheap and readily attainable for practical commercial viability. Other transition metal oxides, such as nickel oxide, have shown promising capacitance reaching up to 240 F/g [26] and are of critical importance to the future of supercapacitors.

2.4   Thesis Motivation

The motivation for this work is to investigate ways to augment nickel oxide capacitors so that they may be viable for commercial use. Although other cheap transition metal oxide scould possibly be investigated for capacitive behavior, this study focuses mainly on nickel oxides due to work within the group showing specific promise for this species. It is known that

nickel oxides are capable of charging high currents to a potential of 0.5 V versus normal hydrogen electrode (NHE) such that they obtain supercapacitive behavior. The hope is that by augmenting the NiO with other materials, a larger range of potentials could be obtained, providing an overall increase in specific capacitance. One such material that is stable over higher potentials is tungsten monocarbide (WC). In Chen research group, it has been shown that WC is stable over 0.8 V versus NHE. The hope is that by forming either nickel-tungsten bimetallic oxide, or simple WC modified nickel oxides, the overall capacitance can be increased to achieve commercial viability. Additionally, the pseudocapacitance from NiO is investigated with addition of high surface area carbon to couple the two major forms of capacitance in an attempt to create a more efficient overall material.

The investigation begins with studying the capacitance of WC supported on Ketjen carbon black at different loadings. Then, the bimetallic and monometallic non-supported oxides are investigated. Each sample was synthesized, characterized, and tested for capacitance. Finally, conclusions and recommendations are made for future investigation of these species.

Chapter 2

SYNTHESIS AND EVALUATION

2.1   Synthesis

The tungsten carbide samples were synthesized using slurry impregnation methods. The loadings of WC on Ketjen black carbon support were 30% and 60% by weight. A slurry was prepared by adding ammonium metatungstate to a beaker, and mixing with 30 mL of deionized water until complete dissolution. Ketjen black was added to provide the carbon support. A sonicator was utilized to impregnate the mixture for an hour. Afterwards, the beaker was placed in an oven to dry over 24 hours. Then the sample was calcined in an oven being ramped to 450°C in 2 hours and 20 minutes, then held at 450°C for 4 hours, and then ramped down to room temperature in 2 hours and 20 minutes. After ramping down to room temperature, the powder was further granulized in a crucible and placed in a quartz tube for carburization in a furnace reactor. This furnace was held under 10% hydrogen gas and 30% Methane gas for half an hour before being heated to 100°C over 1 hour. This was followed by an increase to 450°C over 1 hour and 30 minutes. It proceeded to ramp to 975°C over 8 hours and 45 minutes. It was held to react at 975°C for an hour, and then allowed to cool to room temperature. Finally, the sample was run under 6.0% of 1% O_2 99% N_2 for 1 hour.

Previous work in literature[26] and in Chen group has focused on nickel oxides (and other transition metal oxides) synthesized either by electrodeposition or sol-gel techniques. This paper focuses on powders synthesized ex-situ with slurry impregnation methods and simple calcinations. Metal oxide samples were generally synthesized using calcinations to create bulk phase pure oxides. For nickel oxide, nickel nitrate hexahydrate was utilized as precursor. Nickel nitrate hexahydrate was added to deionized water until complete dissolution. The resulting solution was placed in an oven at 120°C and left overnight. Afterwards, the resulting powder was ground with pestle and mortar for 15 minutes. The sample was placed in a calcining oven and calcined at 650°C for 24 hours.

Tungsten trioxide was available commercially, and no synthesis was required.

For Ni-W bimetallic oxide synthesis, a procedure from Xiao et. al [27] was used. Nickel tungsten oxide was prepared at a weight ratio of .5 Ni/(Ni+W). Nickel nitrate hexahydrate and ammonium metatungstate were utilized as precursors. Nickel nitrate hexahydrate was mechanically ground with tungsten trioxide for an hour using pestle and mortar until the powders were indistinguishable from one another. The resulting mixture was placed in an oven at 120°C and left overnight. Afterwards, the resulting powder was ground with pestle and mortar again for 2 hours. After mixing was complete, the sample was placed in a calcining oven and calcined at 650°C for 4 hours. Although a phase diagram was desired to determine different Ni-W-O phases present at these temperatures, none were readily available. After calcining, the

sample was pulverized and made into pellets to increase dispersion. The pellets were calcined at 650°C for 24 hours to complete the synthesis.

2.2   Evaluation

X-ray diffraction was used to characterize the bulk structure of each sample. An X'pert X-ray source and diffractometer were utilized. X'pert software was used to collect the data, and samples were compared to literature to determine structure. Samples were mounted on a metal sample holder and placed in the diffractometer. Diffraction angle varied over range $10° \leq 2\theta \leq 90°$.

For the powders to be used as electrodes, binder was added and the samples were pressed. To press powder samples into electrodes, N-methyl-2-pyrrolidone (NMP) and polyvinyidine fluoride (PVDF) were utilized as binders. PVDF was mixed with NMP until a clear, viscous liquid was obtained. Samples were mixed in at varying ratios depending on the surface area. This mixture was stirred until a uniform sample was obtained. This was spread over a glass microscope slide and formed to a rectangular prismic shape. The slide was placed in an oven at 120°C for 24 hours until dry. The electrode was pressed using a mechanical press and held at 360 psi for one minute. Excess sample was removed from the corners with a razor blade to allow for square samples in the electrochemical measurements.

Cyclic voltammetry was employed to test the capacitance of all samples. The experimental cell consisted a working, reference, and counter

electrode. A 4x4 cm piece of platinum mesh was used for the counter electrode. The reference electrode was a saturated calomel electrode (SCE). The working electrode consisted of glassy carbon backing with the sample of interest attached with a Teflon holding piece to ensure good connection. The setup can be seen below.
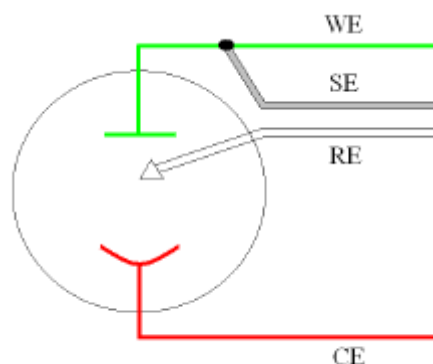

Figure 3: CV Cell [28]

A VersaSTAT 4 Potentiostat/Galvanostat was used to collect the data. The scanning rate used was 10 mV s^{-1}. Cyclic voltammetry was performed in the stability range of tungsten oxides, 0.0 V-8.0 V versus NHE in 1M sulfuric acid solution. 0.5 M Sulfuric acid was utilized as the electrolyte.

Calculations were performed on the resulting CV data to obtain relevant information. Capacitance was calculated using I, the current change at a certain potential and the scan rate, v using the equation $C = I/v$. The cycle used for these calculations was cycle 100 because capacitors should have the longest lifetime possible, and only 100 cycles were obtained. The specific capacitance was found by massing the electrode after measurements were performed, and dividing the overall capacitance by weight of active sample

(without binder or support). Energy was calculated by the equation $E = \frac{1}{2}CV^2$

where C is the specific capacitance, calculated earlier and V is the average voltage across the scan (0.4 V). Power was calculated from the equation $P = \frac{V^2}{4R}$

where R is calculated form Ohm's law, $V = IR$.

Chapter 3

OXIDES

3.1   Bulk characterization

Oxides of nickel, tungsten and bimetallic nickel tungstate were synthesized from powders. They were characterized for bulk composition using X-ray diffraction and all were found to show phase purity. For the nickel oxide sample, characteristic peaks were observed at $2\theta = 43.3, 37.3,$ and 62.9 [29]. The XRD results can be seen in Figure 4 with corresponding Miller indicies. FCC NiO was observed.
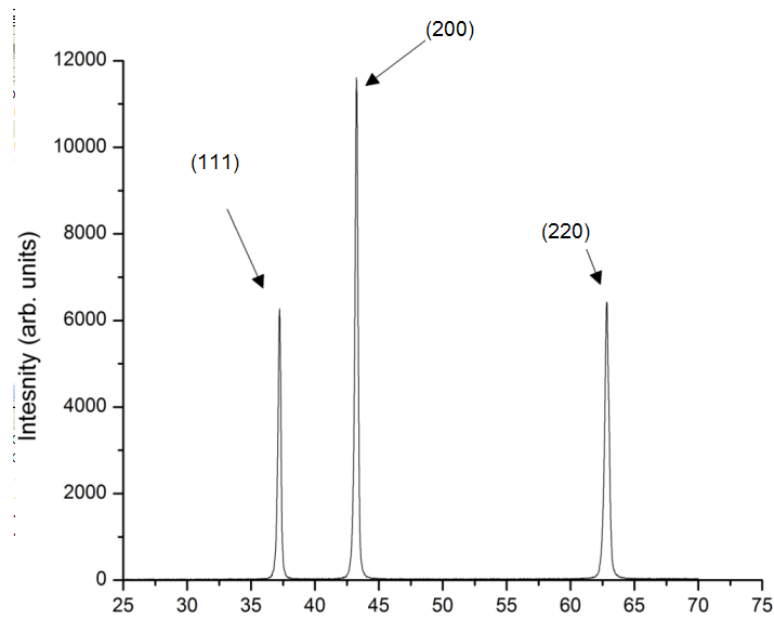

Figure 4: XRD of NiO

Tungsten oxide showed tungsten oxide peaks at $2\theta = 34.1$ and 28.8. This sample was taken directly from manufacture, and so it was assumed to be phase pure WO_3. The XRD for tungsten oxide can be seen below in Figure 5, with corresponding Miller indices.
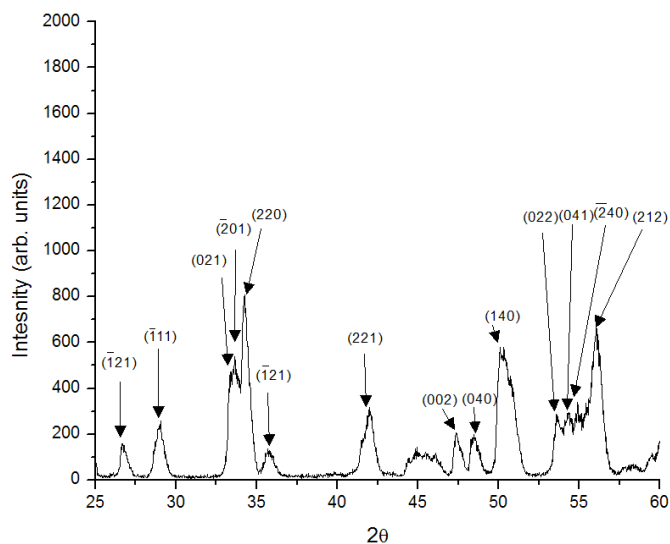

Figure 5: XRD of WO$_3$[33]

Bimetallic nickel-tungsten oxide showed bimetallic oxide peaks at $2\theta = 15.4$, 19.1, 25.0, 30.9, and 54.8. This sample still retained several nickel oxide and tungsten oxide peaks as well, indicating that not all metallic oxides in the bulk formed bimetallic bonds. It can be seen, however, from Figure 6 that the relative intensities of the $NiWO_4$ peaks dominate the plot. It is also possible that other forms of oxide are present in the bulk at different stoichiometric ratios of Ni-W-O.
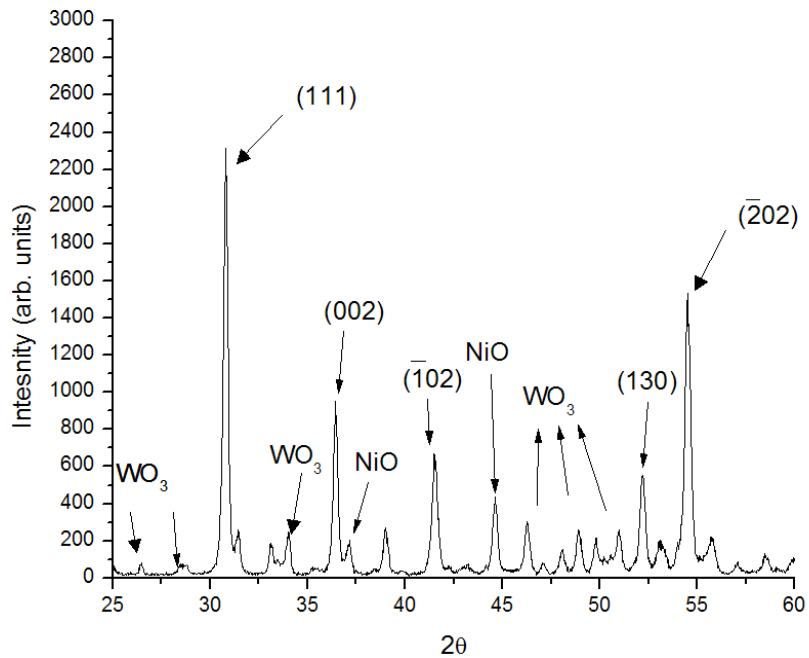
Figure 6: XRD of bimetallic oxide[34]

We then assume that the bulk is composed mostly phase pure

$NiWO_4$ with NiO and WO_3 contributions [30]. For Miller indicies of the WO_3 and

NiO samples labeled above, see previous XRD's of each sample.

3. 2 Electrochemical characterization

Electrodes synthesized from calcination were placed into the

sulfuric acid solution as the working electrode. Pulses were taken and data were

generated as cyclic voltammograms to test the capacitive capabilities of the

respective samples.

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Figure 7 represents the CV results for NiO, WO_3, and $NiWO_4$. Surprisingly, they all showed similar shape and capacitive behavior, contrary to what literature suggests.
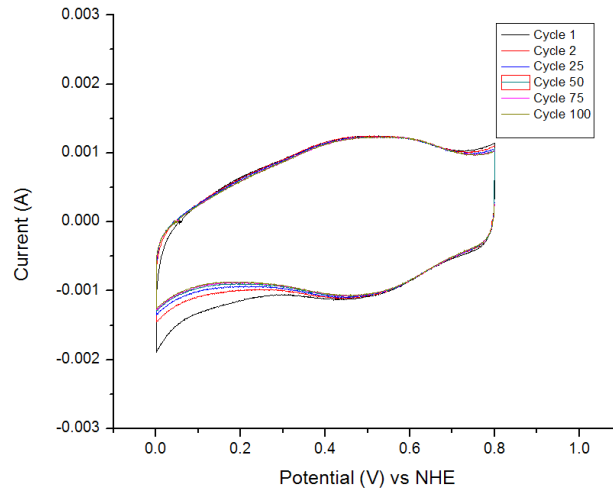

Figure 7: CV of WO_3

Small, broad reduction peaks were observed at ~0.5 V. Small and broad oxidation peaks were observed at around ~0.5 V as well. Because each of the oxide samples tested show these broad peaks, it can be assumed that they represent oxidation and reduction of oxide species in the bulk, rather than the surface. Pseudocapacitance is expected where sharper peaks are observed; the sharper the peak, the more activity due to oxidation and reduction at the interface, and therefore the more pseudocapacitance. To be oxidized or reduced on the surface would indicate that pseudocapacitance is relevant here. However, very small ranges of current were noticed for each sample, resulting from low to no pseudocapacitance.

3.3 Conclusions and recommendations

Relevant values were calculated and tabulated pure data points, and are analyzed below. The specific capacitances, specific energies, and specific powers are reported in Table 1 .

	Tungsten Oxide	Nickel Oxide	Nickel-Tungsten Bimetallic Oxide
Specific Capacitance (f/g)	2.27	3.27	4.03
Specific Energy (Wh/kg)	0.079	0.114	0.14
Specific Power (W/kg)	0.212	0.204	0.201

Table 3: Capacitor comparison of oxides

All oxide samples have low values for specific capacitance, energy, and power, indicating contradictions to previous work. There were two primary purposes for investigating the pure oxide samples. Firstly, previous work of capacitors using nickel oxides was to be attempted using novel powder samples. Secondly, a synergistic effect was to be analyzed for the bimetallic system of nickel-tungsten as a novel capacitor. This also might be due to interferences from overly oxidized nickel at the interface. It is well documented that stoichiometric NiO forms a green powder, whereas our samples formed a grayish powder. Further investigation into the selectivity of our synthesis methods would be required in order to obtain better results.

Although literature reports NiO[26] in the form of thin films and in other materials, no literature currently exists on NiO powder formed in this way being used as a capacitor. There may be several forces acting against NiO in this form. Bulk characterization shows phase pure NiO for the samples tested, but no surface sensitive techniques were employed to test the dispersion of particles at the surface. Perhaps there is very limited NiO on the surface, which would also explain why the three samples show similar values of capacitance and like-shaped voltammograms. The small capacitance shown is mostly due to double layer- capacitance at the surface of the electrodes.

The results of the NiO cyclic voltammetry are further suspect due to the lack of instability over a large number of cycles. In Figure 12 of the Appendix, the nickel oxide voltammogram shows stability in sulfuric acid solution. Nickel oxide, however, is only stable in alkaline solutions at the voltages investigated . This shows that there is most likely no interaction between the metal oxide and the electrolyte, indicating that pseudocapacitance would be unachievable at the current conditions.

There is promising data that show a possible synergistic effect of using the nickel-tungsten bimetallic oxide as opposed to traditional monometallic oxide. The data presented are suspect due to the complete lack of pseudocapacitance, however, so this conclusion can only be speculated.

To further investigate why these results diverge from expected behavior, several techniques could be implemented. The characterization of both the surface composition and surface area must be determined to successfully pinpoint the issue. These could be investigated by XPS and BET

respectively. Before any of these could be implemented, however, a more selective synthesis procedure would need to be developed in order to obtain surface metal oxides without mixed phases.

Chapter 4

CARBIDES

4.1 Bulk characterization

Carbides were characterized for bulk composition using XRD in a similar manner to those done on oxides. Phase pure WC was found for both 30% WC on KJB and 60% WC on KJB. WC peaks occurring at $2\theta = 48.3$, 35.6, and 31.5 [31]. For 30% WC on KJB a small peak of W_2C at $2\theta = 39.6$ [32]. It was assumed that this small amount of W_2C would be rinsed away in the first few cleaning cycles of C.V. The XRD results for the WC characterization can be found below in Figure 8.
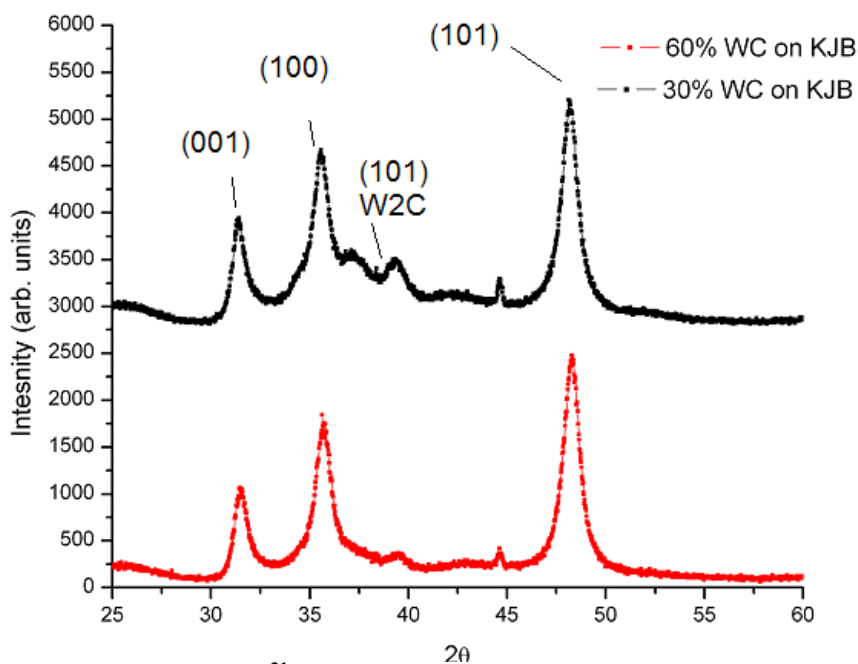

Figure 8: XRD of WC samples[31]

The relative intensities of the WC peaks to the W_2C peaks suggest that this assumption is valid, due to the low quantity of W_2C in the bulk.

4.2   Electrochemical characterization

Cyclic voltammetry was taken of both WC samples and of the simple carbon support as a control.
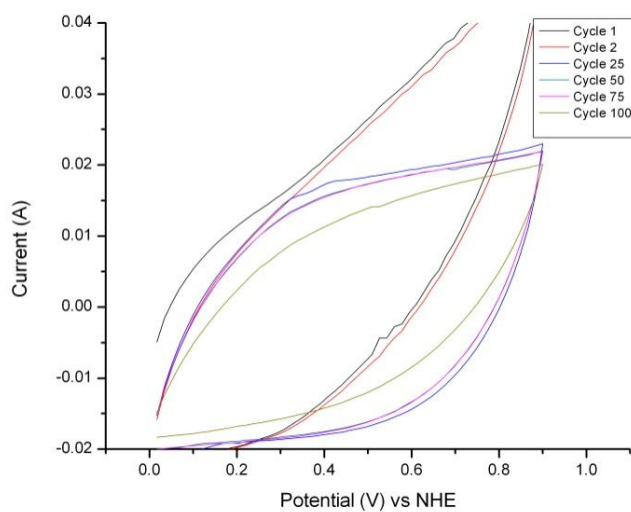

Figure 9: CV of KJB control

The cyclic voltammogram of the KJB electrode showed no irregularity in shape and no pseudocapacitance, which was expected. The overall shape of the curve resembles normal double layer electrochemical capacitors. The capacitance of this sample is consistently larger than those previously studied in this thesis due to the large surface area available.

The cyclic voltammogram of the 30% and 60% electrodes show significant interactions between the electrolyte and the bulk metal, but no pseudocapacitance. The voltammogram of 30% WC on KJB can be seen in Figure 10.
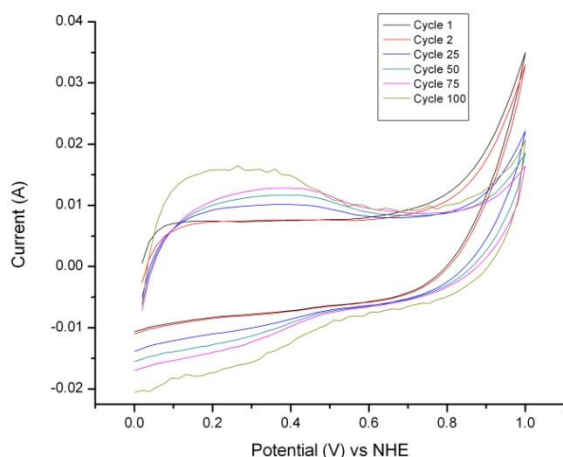

Figure 10: CV of 30% WC on KJB

Reversible oxidation of WC occurs after 0.8 V. Although the overall current range is larger than that for the oxide samples analyzed, this is probably due to the KJB carbon support that is utilized.

The double layer region of the 30% WC sample is smaller than that of pure KJB, and in the 60% sample it is even smaller. The simple explanation for this is that the WC sites on the KJB are inactive towards pseudocapactive behavior. For this reason the 60% sample may be oversaturated with WC active sites, disabling much of the double layer capacitance required for successful charge separation and storage. The low current ranges of 60% WC on KJB can be seen in Figure 11 below.
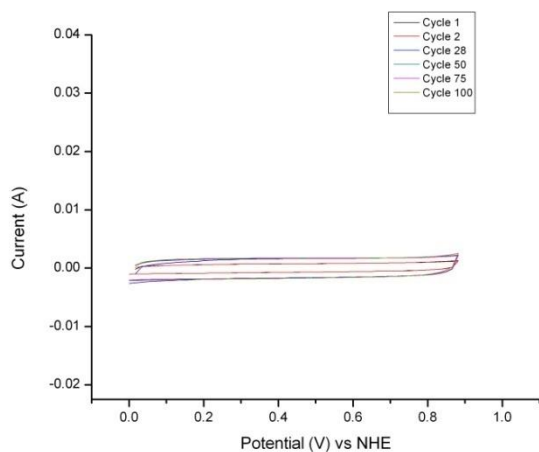
Figure 11: CV of 60% WC on KJB

4.3   Conclusions and recommendations

The results seen in the voltammogram of the WC and KJB electrode are shown in Table 2.

Table 4: Capacitance comparison for carbides and KJB control

	KJB Control	30%WC on KJB	60% WC on KJB
Specific Capacitance (f/g)	7.36	17.27	0.85
Specific Energy (Wh/kg)	0.828	2.4	0.12
Specific Power (W/kg)	16.56	43.16	0.43

Although these values are much lower than expected out of any capacitors, the fact that there is a carbon support allows these samples to show

better capacitive capabilities than that of the oxides analyzed. The fact that there is less capacitance for the 60% sample than the 30% sample, however, shows that there is a desired percentage of coverage to promote double layer capacitance when it is determined that WC is inactive as a pseudocapacitor.

At first glance it appears that the 30% WC on KJB is a better capacitor than the high surface area KJB. The value calculated of 17.27 for 30% WC on KJB is somewhat deceiving, due to the nature of the calculation method. The specific capacitance is based on the material of interest, in this case WC. If we take the mass of the entire sample, including the KJB support than this value become 3/10 of what 17.27, or 5.18 resulting in a value lower than that of standalone KJB. In this case it is evident that again, the presence of WC hinders rather than helps capacitive behavior for the samples.

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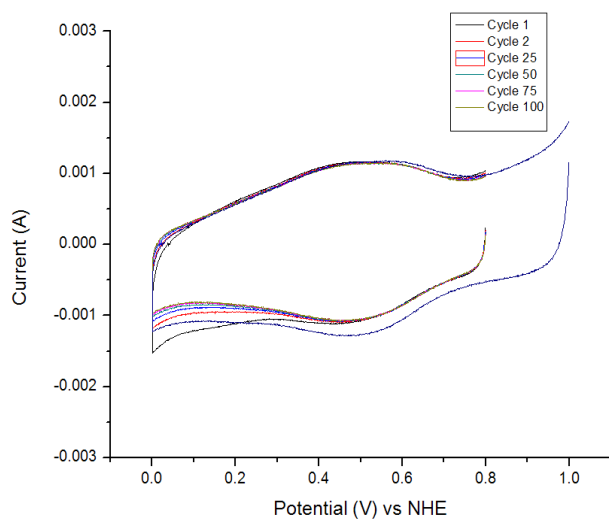34. Natl. Bur. Stand. (U.S.) Monogr. 25,2,27 (1963).

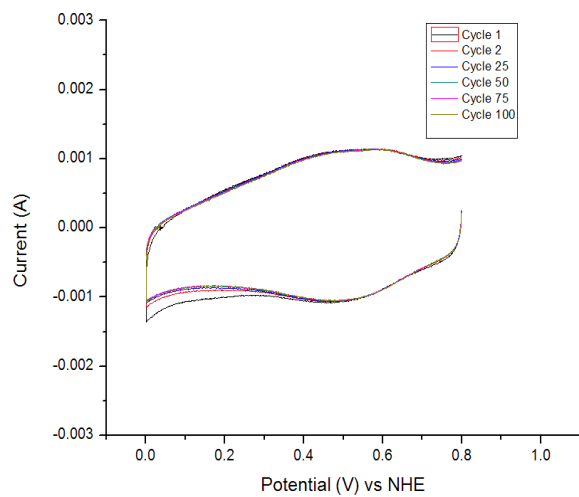# APPENDICIES

Figure 12: CV of NiO

Figure 13: CV of NiWO$_4$

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