Carbon-nanofiber electrodes directly grown on a nickel foam current collector for electrochemical energy storage devices

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Abstract

Supercapacitors are gaining interest in the energy storage sector and are working their way to replace batteries or to provide a high-power supplement to the battery energy. Despite their high-power density and long cycle life, their energy density is low presently. Even with the use of high surface area materials like graphene, activated carbon, and metal oxides, there has not been a considerable increase in the energy density, mostly due to the electrode preparation methods. This thesis has focused on preparing carbon nano fibers (CNF) that are directly grown on nickel foam current collectors, resulting in electrodes that are not only mechanically stable but also have an extended micro-porous structure on the macro-porous nickel foam. This leads to a electrochemical active surface area ca. 400 m²/g and thus provides a good architecture for enhanced performance of surface-limited electrochemical reactions. The electrode production process does not require an additional catalyst coating step, like other processes for production of carbon nano tubes (CNT) and CNF. Also, the CNF growth process yielding the dense CNF forest is performed at a very low temperature of 400 °C when compared to typical CNT growth processes. This largely simplifies fabrication of the overall structure.

The unique structure of the CNF with diameter ca. 50 nm on nickel foam was amalgamated with hydrous ruthenium oxide to achieve higher specific energy and power. Ruthenium oxide was coated on the directly grown CNF on nickel foam using a thermal decomposition technique. The underlying enhanced surface area allowed the coated ruthenium oxide to have a higher surface area, which in turn resulted in large pseudocapacitance. It was also observed that the preparation temperature greatly affected the capacitance. The prepared materials were characterized using a Scanning electron microscope (SEM), X-ray photon spectroscopy (XPS) and Energy-dispersive X-ray spectroscopy (EDS) to investigate the surface morphology and elemental composition. A thorough electrochemical characterization using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy was done to investigate the material performance as a supercapacitor electrode.

The as-grown CNF on nickel foam showed steady retention of capacitance of ca. $140 \pm 7 \text{ mF/cm}^2$ even when current density increased from 3 to 20 mA/cm². This is unique to this material as for most electrodes, capacitance significantly drops with increasing current. These electrodes also showed a 100 % retention in capacitance even after 10000 cycles at 10 mA/cm².

For the hydrous ruthenium oxide coated electrodes, a capacitance of 822 ± 4 mF/cm² at a current density 20 mA/cm² was achieved, which makes them among the bestperforming electrodes reported in the literature. These electrodes also exhibited excellent cycle life with 94 % initial capacitance retention after 5000 charge-discharge cycles. A unique capacitance trend with oxide formation temperature was observed for the ruthenium oxide-CNF electrodes when compared to the trend for ruthenium oxide alone.

Overall, this PhD project clearly shows that the hierarchical structures of CNF directly grown on nickel foam provide excellent electrode materials for high specific power supercapacitors, and it also acts as a good support material to form metal-oxide coating to yield high supercapacitor performance metrics. The overall electrochemical behavior of these materials also makes them an ideal candidate for other applications which require high surface area, like hydrogen production.

Résumé

Les supercondensateurs suscitent un intérêt de plus en plus important dans le secteur du stockage de l'énergie électrique et offrent une possibilité d'éventuellement remplacer les batteries ou du moins générer un apport de puissance important en complément des batteries. En dépit d'une densité depuissance élevée, les supercondensateurs montrent une densité d'énergie relativement faible. Malgré l'utilisation de matériaux tels que le graphene, les particules de carbone activé, et les oxides métalliques générant tous des valeurs de surface spécifique très élevées, l'accroissement en densité d'énergie est restée faible. Ces résultats sont en grande partie liés aux méthodes de préparation des électrodes. Cette thèse se concentre sur la réparation de nano-fibres de carbonne (CNF) fabriqués en "croissance directe" sur les collecteurs de courants formés de mousses métalliques de nickel. Il en résulte des électrodes qui sont non seulement stables du point de vue méchanique, mais qui montrent également une structure étendue de micro-porosité sur une mousse de nickel macro-poreuse. Cette structure génère une surface active électrochimique de l'ordre de 400 m²/g, et une architecture qui permet d'augmenter les performances des réactions électrochmiques contrôlées par des effets de surface. Le procédé de génération des électrodes par "croissance directe" ne nécessite aucune addition de catalyseur pour la croissance des CNF, contrairement aux procédés classiques de production des nanotubes de carbone (CNT) et des CNF. Le procédé de croissance générant des forêts denses de CNF est de plus fait à une température très basse de 400 °C en comparaison à la croissance typique des CNT. Cet aspect simplifie grandement le procédé de fabrication de la structure globale des électrodes.

La structure unique des forêts de CNF sur la mousse de nickel, chaque CNF ayant un diamètre de l'ordre de 50 nm, est fusionnée dans cette thèse avec du ruthenium hydrique afin d'obtenir une puissance et une énergie spécifique plus élevée. Un revêtement d'oxyde de ruthénium sur chaque CNF formant la forêt de nanostructures est ajouté par une technique de décomposition thermique. La valeur élevée de la surface spécifique du support permet donc également au revêtement d'oxide de ruthénium d'avoir une grande surface spécifique avec un accès facile pour les ions. Il en résulte une très grande pseudocapacitance. Nous avons également observé que la température de préparation des électrodes avait un effet important sur la capacitance obtenue.

La charactérisation des matériaux générés a été faite par microscopie électronique à balayage (SEM), la spectroscopie des photo-électrons X (XPS), et la spectroscopie au rayons X par dispersion d'énergie (EDS), ces techniques étant utilisées pour évaluer la morphologie et la composition des structures. Une analyse électrochimique poussée est faite pour évaluer les performances des structures en tant qu'électrodes de supercondensateurs. Ces techniques correspondent à la voltamétrie cyclique (CV), la charge-décharge galvanostatique (GCD), et la spectroscopie d'impédance électrochimique (EIS).

Les forêts de CNF sans revêtement sur mousse de nickel ont montré un maintien de la capacitance de l'ordre de 140 \pm 7 mF/cm² même lorsque la densité de courant augmentait de 3 à 20 mA/cm². Ce résultat est unique puisque généralement, la capacitance décroit de façon significative avec une augmentation du courant. Les électrodes dans cette étude ont également montrés une rétention de la capacitance de 100% même après 10,000 cycles à une densité de courant de 10 mA/cm².

Dans le cas des électrodes revêtues d'oxyde de ruthénium hydrique, une capacitance de $822 \pm 4 \text{ mF/cm}^2$ à une densité de courant de 20 mA/cm^2 a été obtenue, une telle valeur étant parmi les meilleures performances obtenues dans la litérature liée aux supercondensateurs. Ces électrodes ont également montré un cycle de vie excellent avec

94% de la capacitance initiale maintenue après 5,000 cycles de charge-décharge. De plus en comparant avec les tendances de l'oxyde de ruthénium comme seul constituant délectrode, une tendance unique de l'évolution de la capacitance obtenue pour les structures hybrides d'oxyde de ruthenium/CNF formés à différentes températures a été observée.

De façon générale, ce projet de doctorat montre clairement que la structure hiérarchique de forêts de CNF à l'échelle nanométrique, formés par croissance directe sur des mousses de nickel, génère des structures d'électrodes excellentes pour des supercondensateurs à puissance spécifique élevées. Ces structures agissent également comme un support très efficace pour la formation d'un revêtement d'oxyde métallique permettant des performances élevées de supercondensateurs. Le comportement électrochimique général de ces structures fait en sorte qu'ils constituent également des structure idéales pour d'autres applications requérant de grandes surface spécifiques, par exemple pour la production d'hydrogène.

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Abbreviations commonly used

CV	Cyclic voltammetry
GCD	Galvanostatic charge discharge
ΔV	voltage window (volts)
C ₂ H ₂	Acetylene
AC	Activated carbon
A	Amperes
С	Capacitance (Farads, F)
CNF	Carbon nano fibers
cm	centi-meter
CVD	Chemical vapor deposition
i	Current (A)
j	Current density (A/cm ²)
°C	Degree Celsius
EDLC	Electric double layer capacitor
EIS	Electrochemical impedance spectroscopy

EDX	Energy dispersive X-ray spectroscopy
F	farads
Cs	Gravimetric specific capacitance
HR-TEM	High resolution Transmission electron microscope
HR-XPS	High resolution X-ray Photoelectron Spectrometer system
μ	Micro
m	milli / meter
М	molar
nm	nano- meter
Ni-f	Nickel foam
КОН	Potassium Hydroxide
Ru	Ruthenium
RuO ₂	Ruthenium oxide
SEM	Scanning electron microscopy
Ε	Specific energy (wh/m ²)
SFigure	Supplementary figure
TEM	transmission electron microscopy
W	watt
XPS	X-ray Photoelectron Spectrometer system

Chapter 1 Introduction

1.1 Brief overview

Storing energy has been a massive concern in the present world, especially in the renewable energy sector. Currently, batteries are often being used for storing energy. However, they are usually made of toxic materials, take a long time to charge, have low power density, low energy density compared to traditional fuels, possess fire/explosion risk at higher temperatures, have limited lifetime (i.e. number of charging/discharging cycles), and are expensive. In order to overcome some of the abovementioned drawbacks of batteries, supercapacitors have been increasingly looked upon as alternative and complementary energy storage devices. Figure 1.1 shows the growth in interest in supercapacitor research in the recent past. Supercapacitors are energy storage devices like batteries, but can charge and discharge quickly, have higher power density, and usually store energy at the electrode-electrolyte interface. Although supercapacitors offer high power density and large cycle life, their poor energy density and cost have prevented them from being used as sole battery-replacement devices. The bottleneck of supercapacitors is their electrodes materials. Currently, carbon in various forms including graphene, activated carbon, and different metal oxides are being used. However, these come with significant limitations in terms of their performance due to the preparation methods of the electrodes, usage of additives like binders and some of the intrinsic properties of the materials, including their mechanical and chemical stability and ineffective range of pore sizes. Cost is also a vital consideration to be kept in mind for commercial success and to give a real competition to the existing technologies like secondary batteries and fuel cells. This Ph.D. thesis focuses on the production of new carbon-based binderless supercapacitors electrodes using facile techniques, and their material, electrochemical and performance characterization. These devices have plenty of applications, which include electric vehicles to achieve higher per charge mileage and faster acceleration, portable electronics, on-chip microdevices, and medical implants. This research may furthermore lead to materials that can be used for numerous applications such as water treatment (e.g. capacitive desalination), hydrogen storage, and electrochemical sensors.



Figure 1.1. The number of publications including articles, books, and other authentic open literature (2000–2018 (predicted)) from a search using supercapacitor as a keyword in Google scholar [1]. Reprinted with permission from Nano energy 2018, Vol. 52, pages 441-473. Copyright Elsevier (2018).

1.2 Thesis objectives and organization

The current commercial technology mostly uses carbon-based electrodes for supercapacitor manufacturing. Among carbon, activated carbon is the most-sought-after material due to its high surface area and low cost. In spite of high surface area, its energy and power density are still low in order to replace batteries, and it also suffers from lower conductivity. They also have a non-effective pore sizes, which add to the surface area but do not contribute to the charge storage . The requirement of a binder is essential to cast these carbons as a slurry on the current collectors which; (*a*) adds to the manufacturing

cost, (*b*) binders are non-conductive, which leads to an increased resistance, and (*c*) they reduce the overall specific electrochemically-active surface area of the electrode. As an overall objective, this PhD project has focused on developing binderless electrodes to make better supercapacitor electrodes that can provide higher power and energy density, also taking cost, availability, ease of synthesis, mechanical and chemical stability, and cycle life into account. The specific objectives included:

- a) Inspired by the direct-growth of CNT structures on stainless-steel, the first specific objective was to develop a novel and a facile procedure to make supercapacitor electrodes by growing carbon nanofibers (CNF) directly on a current collector material having good electrical conductivity and high specific surface area.
- b) To investigate the electrochemical and surface/bulk characteristics of such electrodes in order to evaluate and explain their performance as potential supercapacitor electrode materials, and to improve them to achieve higher performance metrics.
- c) To further improve the performance of these CNF binderless electrodes by engineering the nanoarchitecture of the electrode surface and /or by introducing redox capacitance. Further, use similar electrodes for applications like hydrogen and oxygen evolution.

This thesis is manuscript-based and follows the guidelines stipulated by McGill University. It consists of six chapters. Chapter 1 give a brief introduction to the topic, and outlines the project objectives. Chapter 2 is a literature survey section that includes an overview of supercapacitor types, the associated components and some main electrochemical methods to test them. This is followed by three published/submitted peer-reviewed articles, from Chapter 3 to Chapter 5. Chapter 3 focuses on the preparation of CNF and its relevant characterization, and Chapter 4 presents results on the use/performance of CNFs as supercapacitor electrodes. Chapter 5 presents results on the incorporation of ruthenium-oxide along with the CNF as supercapacitor electrodes with the aim of achieving better performance metrics. Chapter 6 summarizes all the discussed articles in this thesis and Chapter 7 addresses scientific knowledge contribution and future work.

Appendix A lists out my "side" projects and all-conference works during my doctoral studies. These works are closely related to my thesis work and have also spurred ideas for many of the ideas written in this thesis. The detailed work has not been appended as they digress from the main thesis topic. This is followed by a short note on the catalyst size effect in Appendix B, which is more relevant to Chapter 3 on CNF growth studies. Finally, in Appendix C, an article (submitted) on nickel oxide-CNF based electrodes are appended. Along with the effective use of these electrodes as supercapacitor electrodes, this article also demonstrates the ability of these electrodes for electrochemical hydrogen production by water splitting.

Chapter 2 Literature survey

2.1 Background

In the past few decades, there has been an urge to develop technologies that could subdue the use of fossil fuels and greenhouse gas emissions. Increasing the handy and efficient harnessing of non-conventional energy could be the best solution for this problem. However, harnessing renewable energy sources like wind and solar requires efficient electrical energy storage devices, due to the intermittent nature of these sources. Ragone plot in Figure 2.1 compares the specific energy and specific power of the mainly used energy devices.

Among electrochemical devices, batteries are playing a major role in the energy storage application. Almost all renewable energy sources currently use batteries to store energy [2]. Further, dependency on various battery sources ranging from small button cells to big and heavy lead-acid batteries has become inevitable in our daily life, ranging from powering flashlight, laptops, and phones to the transportation sector and general industries. Although batteries are the current default choice for energy-storage systems, they have modest life-times and specific power densities. They are often made of toxic materials leading to disposal problems, while some are made of rare and expensive materials (ex. Li-ion batteries) and cannot practically be used for all purposes. These devices are potentially dangerous when over-heated (e.g. Li-ion batteries) and might be heavy in weight (Lead-Sulphur batteries). One of the major problems of batteries is their limited cycle life (modern Li-ion batteries could be charged/discharged only up to 1000 times while keeping 80% of their initial charge storage capacity).

Even though batteries have better specific energy density than supercapacitors (Figure 2.1), they still have lower specific energy than the internal-combustion engine. Gasoline provides an energy density of ca. 12 kWh/kg and battery packs used in some modern electric vehicles have ca. 0.250 kWh/kg. This means we need about 48 kg of battery to provide the same energy 1 kg of gasoline (for example, a Tesla S' battery pack weights ca. 540 kg, while a comparable-size internal-combustion-engine car's fuel tank contains ca. 60L of gasoline, which is ca. 49 kg, less than 1/10th of the battery-pack weight). Apart from energy density, it is also easy to refuel a car, unlike battery vehicles that need some time to charge. Other questions like the cost associated with the battery material,

procurement of materials for making batteries and the socio-political factors for procuring, frequently arise with the use of battery-powered devices.

Supercapacitors, which are also called electrochemical capacitors or ultracapacitors, promise to compete with batteries as good energy storage candidates. They have received special attention due to their large power density and possible large energy densities, fast charging/discharging, long cycle life, low weight, wide thermal operating range, simple construction mechanism, and use of less toxic materials when compared to batteries [3–7]. Utilization of supercapacitors to store the harnessed wind energy [8], solar energy [9] and other renewable energies [8,10–12] have increased the prospects of non-conventional energy resources to be more promising. Their robustness, long cycle lifetime, and large power-density have attracted them for a variety of uses, such as electric/hybrid vehicles, low power devices, portable devices, day-night storage, power tools, storage of renewable energy sources and many more [13].



Figure 2.1. Simplified Ragone plot of mainly used energy storage devices. (note: correct units of specific energy and specific power are Wh kg⁻¹ *and W kg*⁻¹) *Reprinted with permission from Chem. Rev. 2004, 104, 10, 4245-4270. Copyright (2004) American Chemical Society. Note: Y axis is W Kg*⁻¹, *not Wh Kg*⁻¹.

According to the Zion market research (Figure 2.2), the supercapacitor market is expected to reach USD 2.1 billion by 2022, which is still small when compared to an estimated USD 81.65 billion and USD 65 billion for lithium and lead-acid batteries, respectively [15] which are currently the ubiquitously-used batteries. This scenario could change in the coming years with improvement in the energy density of supercapacitors, especially considering their environmental friendliness.



Figure 2.2. Global supercapacitor market revenue from 2014 to 2022 in USD. (Source: Zion market research 2017) [14].

2.2 Supercapacitors overview

Supercapacitors are electrochemical energy storage devices that store energy in the double layer at the electrode-electrolyte interface. Even though at this point, supercapacitors have intermediate specific energy storage ability, lying between that of dielectric capacitors and the batteries (Figure 2.1), research is being swiftly carried out to improve the energy density of supercapacitors [16–23]. Supercapacitors consist of electrodes, a separator between the electrodes and an electrolyte. They are also known to be quite eco-friendly, mostly due to the long-life cycles, which minimize recycling expenses, and also due to the nature of the electrode material itself, which is often a carbon allotrope, to a large extent.

An electrical double layer is formed when a potential is applied at the electrodes of the supercapacitor (Figure 2.3). The two layers of charge formed are :(1) the electric

charge layer at the surface of the polarized electrode, and (2) the layer of solvated ions in the electrolyte of the opposite polarity (forms the outer Helmholtz layer). The monolayer of the solvent (inner Helmholtz layer) separates these charges and it, hence, acts as a molecular dielectric. This formed double layer is similar to a conventional two plate capacitor, hence the equation

$$C = \frac{A\varepsilon}{d}$$
 Equation 2.1

can be used to calculate the capacitance. In this equation, C (in farads, F) is the capacitance, A (in m^2) is the surface area of the plates, ε (in Fm⁻¹) is the dielectric permittivity and d (in m) is the distance between the plates. In electrochemical capacitors, electrodes are often made with materials like activated carbon, which have a surface area ranging from 1000-3000 m²/g.

Therefore a strong emphasis is given on the preparation of nano-particle electrode materials to increase the surface area [24–26]. Further, the separation distance, *d*, which is the Helmoltz layer thickness is often in the range ca. 5-10 Å; thus, the resulting capacitance is much higher than that of a simple two-plate capacitor. Apart from the surface area of the electrode, its wettability, accessibility of its pores for the electrolyte ions and conductivity also play a crucial role in attaining large capacitance. As this double-layer is formed at each of the two electrodes in a cell, there will be two capacitors in series in a single electrochemical cell (see Figure 2.4 later in the thesis).



Figure 2.3. Schematics of an ideal double-layer of an electrochemical capacitor.

2.3 Brief history and current applications

The electrolytic capacitor using porous carbon electrodes was patented by General Electric corp. in 1957 [27]. In 1966, Standard Oil company (SOHIO), Cleveland, Ohio patented an electric double-layer capacitor (EDLC) which consisted of carbon electrodes, a separator of 0.001 inch and sulfuric acid as the electrolyte. In this setup, a positive electrode with a thin coat of lead oxide and a negative electrode with a thin coat of hydroquinone were used. Even today, a similar setup is used commercially. Later in 1970, SOHIO developed an electrolytic capacitor having carbon paste electrodes [28]. IBM patented an EDLC in 1972, which was fabricated using a high surface area activated

carbon, and a thin inert porous separator, to achieve low resistance and high capacitance [29]. Later in 1975, SOHIO licensed their patent to Nippon electric company, who went on to produce the first EDLC, and they termed it "SuperCapacitor" [30]. Even though these devices had low voltage and high internal resistance, they were found to be a useful part in the manufacturing of many consumer appliances. A capacitor with electrodes consisting of metal oxide and carbon was patented by Motorolla in 1992 [31]. In the past two decades, there has been strong growth in research on supercapacitors and plenty of patents are being filed every year. Commercial supercapacitors are produced by numerous companies, which include Maxwell technologies, Cooper industries, Nesscap, Skeleton technologies, Cap-XX and many more.

Supercapacitors are being used in a variety of applications ranging from handheld devices to transportation. However, currently due to their limitations due to low energy density, they are often used as a back-up for battery systems or for short duration high-power applications, like screw drilling. Automobile manufacturers have effectively started using supercapacitors to store energy during braking and use the stored energy for start-stop systems, thus increasing the overall fuel efficiency of the automobile. Supercapacitors are also used for grid-stabilization, to provide burst power for lifting operation, and for emergency doors in airplanes. With the advent of more research on materials, the applications are also expanding to wearable electronics, flexible and portable devices [32,33].

2.4 Classification of supercapacitors

2.4.1 Based on the electrode assembly

2.4.1.1 Symmetric supercapacitors

These supercapacitors have the same positive and negative electrodes. They have ideally the same mass loading of the active material, same composition, same design and subsequently, the working principle of both of the electrodes are ideally the same. Most commercial supercapacitors currently are symmetric types. Using the same electrode as a positive and negative electrode results in a narrow operating potential. For example, supercapacitors utilizing carbon-based symmetric electrodes with aqueous electrolytes have an operating voltage of only ca. 1V, and usually, the positive carbon electrode has a smaller operating potential window than the negative electrode. For the same reason, almost every commercial symmetric supercapacitor uses organic electrolytes, which could offer an operating potential window of ca. 2.5 to 3.0 V. However, organic electrolytes are expensive, not environmentally friendly and suffer safety issues (e.g. flammability). They also offer lesser specific capacitance, mostly due to their large-sized ions.

2.4.1.2 Asymmetric supercapacitors

These supercapacitors have two distinct electrodes made of different materials. The two electrodes could have the same or different charging-discharging mechanisms. If they have different charging mechanisms it is often addressed as hybrid cells as they have both EDLC mechanism and also pseudo-capacitance/battery like behavior involved. The individual electrodes often operate at a different potential, and when assembled into a full cell they provide an advantage of a larger voltage window even when they use
aqueous electrolytes, and hence they will have larger energy densities. Usually, the positive electrode is made of metal oxide or a conductive polymer while the negative electrode is made of carbonaceous material [34]. Different cells like activated carbon/manganese dioxide (MnO₂) [35], nickel hydroxide (Ni(OH)₂)/graphite foam [36], MnO₂ nanowires/ iron(III)oxide (Fe₂O₃) nanotubes [37], transition-metal-oxide nanowire/single-walled carbon nanotube hybrid [38] have been used, and graphitic carbon has also been used as a positive electrode to store anions [39].

2.4.2 Based on the charge/discharge chemistry

2.4.2.1 Non-Faradaic supercapacitors

The charge stored at the electrode-electrolyte interface in the electrochemical double-layer is purely physical (Figure 2.3). The rate of ion migration to/from the electrode-electrolyte interface as a result of capacitor charging/discharging is fast, hence these devices are highly reversible, giving a large power density. They are also simply called *Electric double-layer capacitors* (EDLC). As there is no chemical reaction at the surface of the electrodes, the cycle life of these devices is very long. As previously explained, a double layer is formed at the electrode-electrolyte interface (Figure 2.3), where the polarized water molecules act like the dielectric separator with the ion (of the electrolyte) and the real electrode surface acting as oppositely-charged electrodes. Since the hydration layer, which is acting like the dielectric layer, is small and the surface area of the electrode is large, the resulting capacitance is high (Equation 2.1). Thus, the working principle is similar to a simple two-plate capacitor, but with a small dielectric distance and higher plate area. High surface area materials such as activated carbon [40],

graphene [41], reduced graphene oxide [42], carbon aerogel [43], graphene aerogel [44] and carbon nanotubes [45] have been extensively used.

2.4.2.2 Faradaic supercapacitors

These can be classified as pseudo-capacitors and battery-type materials. Here a large part of charge transfer and storage is due to the redox reactions at the electrode surface and/or in the outer-most layer of the electrode solid phase. Transition metal oxides like ruthenium dioxide (RuO₂) [46], manganese dioxide (MnO₂) [35,47], nickel oxide (NiO)[48], and vanadium dioxide (VO₂)[49] in certain physical forms, and conducting polymers such as, polyaniline (PANI) [50], polythiophene (PThs) [51], polypyrole (PPy) [52], fall under pseudocapacitor materials.

Charge storage in pseudocapacitors happens because either (1) ions intercalate into the crystal lattice of the metal oxide electrode, and during the intercalation, the valence of the metal changes to maintain electrical neutrality, or (2) ions are electrochemically adsorbed onto the surface of the electrode material which causes a change in the metal valence state. In these processes, there is charge transfer across the double layer at the electrode-electrolyte interface, unlike the simple electrostatic attraction that occurs in EDLC supercapacitors. However, there is a linear relationship of charge stored with potential, and the current at the anodic/cathodic peak of the cyclic voltammogram (peak current) is directly proportional to the scan rate.

For example, with RuO² electrodes, the following reaction takes place in an acidic medium,

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x$$
, $0 \le x \le 2$ [53]

During the charging and the discharging of the supercapacitor, protons (H⁺) are intercalated and de-intercalated from the crystal lattice of the electrode (RuO₂) along with a change in the oxidation states of Ru at a specific potential within the working potential window [53]. During this, a charge of "xe-" will be stored during the charging process and the "xe-" charge will be removed during the discharging process. Similar to EDLC, the surface area is very important as the pseudocapacitance reaction occurs at the surface and a large area will result in a large number of reaction sites and thus higher capacitance. Apart from this, crystallinity, hydration, electrode architecture and electrolyte also play a vital role in the performance of faradaic supercapacitors (also called pseudocapacitors). Usually, metal oxides are less conductive, and the cycle life of these cells is rather short since these active materials react in the process of charging and discharging of the cell.

In the case of conducting polymers, they change their doping states (p/n) during charging and discharging, while ions go in and out of the polymer chains in the entire bulk of the electrode. This leads to a larger capacitance and makes conducting polymers an attractive material for electrochemical energy storage applications.

The main issue with these pseudocapacitor electrodes is poor cycle life. Preparation methods have been constantly evolving and composites with carbon are prepared in order to increase the surface area, prevent agglomeration among the metaloxide nanoparticles, and also to increase the conductivity and cycle-life.

Electrode materials like oxides of nickel, iron, and cobalt-based electrode materials, often can be classified as battery-type electrodes, and not as pseudocapacitance materials [54]. However, some battery type materials are found to behave like a pseudo-capacitor when the electrode architecture is engineered in a certain way. This is often expressed as "extrinsic" type pseudocapacitance [55].

2.5 Vital parts of a supercapacitor

Figure 2.4 shows the cross-section of a typical supercapacitor, with current collectors coated with an electrode material which forms the major thrust of this thesis., The electrodes are separated by a separator, and the whole system is impregnated with an electrolyte. The electrodes are often composites, either a mix of different active materials or just one type of active material, usually with a binder. The basic principle is to accumulate charge at the electrode-electrolyte interface and prevent the electrodes from electric shorting.



Figure 2.4 Schematics showing vital parts of a supercapacitor. (Note: grey and red altogether represent electrode materials; blue- electrolyte).

2.5.1 Electrolytes

The types of electrolytes typically used in supercapacitors are aqueous, organic electrolytes and room temperature ionic liquids [56]. Electrolytes that have higher

conductivity will help increase the power density, and the electrolytes which have larger potential working window will enable higher energy density. This is because energy is proportional to the square of the operating potential window (E=1/2CV²). Other considerations include cost, easiness to handle and environmental friendliness.

Aqueous electrolytes can be classified into acidic, basic and neutral types. The most common electrolytes reported in the literature are KOH (basic), H₂SO₄ (acidic) and Na₂SO₄ (neutral). The conductivity of these electrolytes at concentrations used in supercapacitors is high (~1 S cm⁻¹), which results in a low electrochemical series resistance and higher power density. Their ion sizes are small, which eases the access of the ions into the pores of the electrode, increasing the specific capacitance. The electrolyte used in this thesis work is 6 M KOH having a conductivity of 0.63 S cm⁻¹ [57]. This is the most widely used electrolyte. Neutral electrolytes offer a low corrosion environment for the cell components, but they have lower ionic conductivity than the acidic and basic electrolytes. The main drawback of aqueous electrolytes is their low operating potential window, which is usually around ~1 V for full cells (thermodynamically, water splits at a cell voltage of ca. ~1.23 V under standard conditions). This issue can be addressed by using asymmetric cells [58] with electrodes tailored to the specific electrolyte, or by using electroles that offer higher overpotential for the hydrogen and oxygen reactions [59].

Organic electrolytes have salts dissolved in solvents like acetonitrile, propylene carbonate or ethylene carbonate. Commonly used salts are tetraethyl ammonium tetra-fluoroborate (TEA BF4) [60], tetraethylammonium tetrafluoroborate (TEMA BF4) [61], 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF4)[62], and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF4) [63]. These electrolytes have a working potential window in the range of 2.5- 3.0 V, which increases the energy density of the cell. For this reason, most commercial cells use organic electrolytes. However, due

to the large ion size, their accessibility to small pores is limited and their capacitance is less when compared to the aqueous electrolyte. Acetonitrile has better conductivity than propylene carbonate, but it is toxic. These electrolytes are expensive, inflammable and care should be taken to keep them moisture-free, which adds extra to the capital cost of manufacturing.

Room-temperature ionic liquids (RTIL) have low vapor pressure and are chemically and thermally stable with low flammability, which makes them ideal for temperature-sensitive applications. Commonly reported RTILs are based on imidazolium [64], and pyrrolidinium [65]. They enable a wide operating potential window (2-6 V), which boosts the energy density [66]. However, the main drawback is their low ionic conductivity (10 mScm⁻¹) and high viscosity, which leads to poor energy and power density [67].

New classes of electrolytes include polymer and ceramic based electrolytes. These are particularly helpful in making solid-state devices and wearable electronics, which often require flexible devices and no leakage problems [68]. Some popular electrolytes in this class include some poly-vinyl alcohol (PVA) compounds such as PVA-H₃PO₄ [69], PVA-H₂SO₄ [70], PVA-KOH [71], as well as poly(urethane)-LiClO₄ [72], and Li₂S-P₂S₅ glass-ceramic electrolyte [73].

2.5.2 Binders

The binder is used to aggregate and hold the active material (nanoparticles) of an electrode over the current collector. It does play an important role in the mechanical integrity of the active electrode material and also the cell's cycle life. The binder helps to have good adhesion between the current collector and the electrode material, this being essential to reduce the electrochemical series resistance (ESR) and to maintain mechanical

stability. Polyvinylidene fluoride (PVDF) [74], Nafion [75], polytetra-fluoroethylene (PTFE) [76] are the most commonly used binders. They do add some disadvantages like (a) it is an inactive electrode material and hence its weight will reduce the gravimetric capacitance, energy, and power density; they also cover the pores of the active material resulting in a lower electrochemically-accessible area. (b) The ESR is increased as most binders are insulating polymers [77]. For these reasons, binders should be used in minimum quantity (typically 5-15wt.% of the electrode, excluding the current collector). In the recent past, many researchers have been trying to make binder-free electrodes [44,78] and have also used carbon nanotubes (CNT) [79] providing high conductivity and large specific surface area as binders. Carboxymethylcellulose (CMC) [80] and polyvinyl alcohol (PVA) [81] are also used at times as binders. Nafion is found to give mechanical stability to the electrodes and also reduces the charge transfer resistance [82]. The work presented in this thesis is, as already mentioned earlier, based on the development of binderless CNF-based supercapacitor electrodes.

2.5.3 Electrically-conductive additives

Some electrode materials, like activated carbon, are not electrically very conductive, which leads to an increase in the ESR of the cell. To minimize the ESR, these active electrode materials are mixed with electrically-conductive materials. Carbon blacks are the most used conductive additive [83,84]. This includes its subtypes such as acetylene black and ketjen black. Other additives used include carbon fibers [85], carbon nanotubes [86], etc. Even metallic additives have been tried by some researchers, but these may contribute to the pseudocapacitance and might have a limited life [87]. Carbon nanotubes should be an effective additive as they are conductive and also have high surface areas, however, their high cost is a drawback. The CNF-based electrodes developed in this PhD work do not incorporate electrically-conductive additives.

2.5.4 Separators

The main use of the separator is to prevent any direct electrical contact between the two electrodes. Properties like inertness to electrolytes, mechanical stability, high porosity are usually expected for a separator [77]. Cellulosic [88], polypropylene [89], glass-fiber [90], PTFE [76], polyethylene [91] are most-commonly used separators by researchers.

2.5.5 Current collectors

The main purpose of the current collector is to conduct current from/to the electrodes [92]. Electrodes are stuck/rolled over these current collectors. Materials which have low electrical resistivity, high mechanical strength, flexibility (in case of flexible electrodes), and chemical stability to the electrolyte are often chosen as current collectors. The conductivity and the contact of these collectors with the electrode plays a vital role in the performance of the supercapacitor.

Usually, metals like aluminum, copper or nickel [93] are used, as they have relatively low cost and have high electrical conductance [94]. However, materials like stainless steel [95], indium tin-oxide (ITO) [96], gold [97], titanium [98], and many other metals have also been used as current collectors. Among these, the most popular one among researchers is nickel foam (Ni-f) due to their inherent porous structure, lower cost when compared to most metal foams and their stability in aqueous solution.

Xing et al. (2011), have well explained the fact that the use of Ni foam (Ni-f) as a current collector for the electrochemical analysis may overestimate the performance of the electrode when the active material is used in small quantities [99]. Therefore, care should be taken to have a sufficient amount of active material on the Ni-f current

collectors in order to minimize the capacitance of the high-area Ni-f when interested in the evaluation of the capacitance of the active electrode material only. In fact, this negligence has resulted in a large number of overestimated capacitance values in the literature, especially when reported in gravimetric capacitance (F/g).

Even though the weight of the current collector is often not considered while calculating the specific capacitance, having a light-weight current collector is advantageous as it reduces the overall mass of the cell. This can be very useful when supercapacitors are constructed for small devices and automotive purposes. Zhou et al. [100] have demonstrated the use of CNT-based current collectors for oxide-based active electrode materials. These potentially provide higher power performance due to the high conductivity of the CNT and they are also lightweight.

Metal current collectors need to be rinsed with acid or dilute etchant in order to remove oxides on their surface, which might cause additional resistance to the performance of the system. Usually, the electrode material with a binder is pasted onto the current collector [101]. Techniques like electrophoretic deposition [102] and spray deposition [103] are also stated in the literature. There has also been a quest to modify the current collector in order to increase the contact with the electrode active material by using either different fabrication methods, chemical modifications, physical modifications, or growth of conductive nanoparticles [47,104–108]. In the current PhD project, the base active electrode material (CNF) is grown directly on nickel foam, thus minimizing the active material / current collector resistance.

2.5.6 Electrode materials

2.5.6.1 Activated carbon

Activated carbon (AC) is the most common electrode material in commercial supercapacitors, due to its large availability, low price, large specific surface area, and good chemical stability [109–112]. However, unevenly distributed pore sizes, especially if they are too small for the access of the electrolyte, and their low conductivity often leads to reduced performance of the supercapacitor. It is widely estimated that electrochemical double-layer capacitance of carbon is between 5 and 20 μ F/cm² (the basis is 'true' surface area of the electrode, not geometric) [113]. Commercial AC has a surface area ranging from 1000-3000 m²/g. Let us consider activated carbon with 3000 m²/g and take 20 μ F/cm² as the theoretical capacitance; this translates into 600 F/g. In reality, only ca. 200 F/g is effectively achieved, at most. Clearly, the surface area of the electrode material most often does not correlate directly with the capacitance, especially with materials having variable porosity like AC. In order to improve the conductivity, additives like carbon black could be useful, but this would reduce the surface area of the electrode [114–116].

The most common method of making AC is by pyrolysis of a precursor, which is usually fossil fuels like coal and bio-resources like wood and coconut shells [117], followed by an activation process. An activation step can be (a) physical; steam or CO₂ or a combination of these two used at temperatures ranging 600-1200 °C [118,119], or (b) chemical; the precursor is treated with chemicals (eg, KOH, ZnCl₂) and then pyrolyzed [120,121]. During this step, the surface area of the carbon material is increased. Numerous research has been made using a series of other precursors, including nutshells [122], rice husks [123], sugarcane bagasse [124] and many other materials [125–128].

Researchers have also tried to come out with composites of AC with other carbon allotropes like graphene and nanotubes, to incorporate diversified pore sizes and increase the conductivity of the electrode matrix to achieve higher capacitance [6,114,129–135]. For example, Chen et al [6] achieved capacitance of about 94 F/g when they used a graphene-AC composite with KOH as the electrolyte. CNT and AC (1400 m²/g) electrodes (AC:CNT= ~0.8:1) have shown a specific capacitance of 170 F/g from the CV curve at 1 mV/s [136]. Jia et al [137] have reported a capacitance of 136 F/g at 1 A/g for a fullerenegraphene composite. However, the percentage of fullerene used was high and also this article did not focus on any controlled formation of electrode architecture (GO: C60 = 0.2: 0.02 g).

2.5.6.2 Graphene

Graphene, which has a great conductivity, exhibits a high surface area (theoretical surface area: 2675 m²/g) with high mechanical [138], electronic [139], electrochemical [140], chemical and thermal abilities [139,141–145]. These properties could be ideally used to make supercapacitor electrodes which can give high power and high energy density, with low series resistance. The most common method of production of graphene oxide (GO) and reduced graphene oxide (r-GO) is *via* chemical exfoliation using Hummer's process [146]. GO and r-GO can be used as precursors to form a few-layer or single-layer graphene nanosheets. The other well-accepted approach is by chemical-vapor-deposition (CVD) [147]. It is a bottom-up approach, often yielding a high-quality monolayer as well as a multilayer, depending on the substrate. Another recent bottom-up approach for generating graphene nanostructures is through high temperature dissociation of a carbon precursor in the plasma phase followed by a controlled

homogeneous nucleation of the 2-dimensional structure [148–150]. Such process generating pure and highly crystalline graphene powders was developed at McGill University, but has not been tested in supercapacitor applications yet. Zhang et al. [146], Chen et al. [141], Huang et al. [151] have reviewed many other techniques for producing graphene.

Graphene is also mixed with other materials like CNT, MnO₂, RuO₂, polypropylene and many other compounds to form efficient electrode materials [115,152–154]. Despite all the good qualities of graphene, the capacitance exhibited is still low due to agglomeration and restacking of sheets during the synthesis and making of electrodes. Low-defect graphene is expensive to manufacture and current methods for large-scale manufacture often introduce large defects, which also results in poor capacitance. Xinming et al. could achieve only up to 42 mF/cm² using graphene fibers and MnO₂ nanoparticle composite, using a gel electrolyte [155], despite MnO₂ is known to exhibit high capacitance.

2.5.6.3 Fullerene

Although not widely used in the preparation of supercapacitors, there have been few articles that have demonstrated their ability as supercapacitor electrode material [137,156–158]. These works have mostly used fullerene as an additive along with other materials like AC and GO, and have observed an increase in the performance of the capacitance due to its addition. The ability to create precise self-assemblies has made this allotrope interesting [159], especially when incorporated with other large surface-area materials for designing the electrode architecture.

2.5.6.4 Carbon aerogels and xerogels

Organic aerogels and xerogels are produced by the sol-gel procedure from the polycondensation of different organic monomers [160]. These resorcinol-formaldehyde (RF) organic aerogels and their carbonized derivatives were first prepared and studied by Pekala [161]. Carbon aerogels and xerogels are usually derived from the pyrolysis of resorcinol-formaldehyde (RF) aerogels and xerogels. It is to be noted that the method of drying of RF determines whether aerogel or xerogels is formed. Aerogels are formed when the aqueous gel is dried supercritically. When aqueous gels are evaporatively dried, xerogels are formed [162]. Reagents like KOH, H₃PO₄, ZnCl₂, etc are also used for chemical activation of carbon aerogels and xerogels [162]. For physical activation, CO₂, steam or a combination of both is typically used [163,164]. These materials exhibit a specific surface area in the range 500-3000 m²/g [43,165,166] and capacitance in the range 150-250 F/g [43,165–168], which is almost close to the performance of activated carbon.

2.5.6.5 Carbon nanotubes (CNT) and carbon nanofibers (CNF)

CNT is a rolled-up stack of the graphene structure, has and shows a hollow inside. CNT includes single wall (SWCNT), double wall (DWCNT) and multi-wall (MWCNT) carbon nanotubes . Methods used for producing CNTs include (a) the plasma-based methods for bulk powder production using, for example, the carbon arc discharge, pulsed laser ablation, and thermal plasma reactors, and (b) chemical vapor deposition (CVD) as surface-based methods [169]. Growth of the CNT requires a catalyst nanoparticle acting both as a template for initiating the CNT structure and as a phase transformation material enabling the separation of carbon for example through an eutectic-like transformation[170–173]. Examples of catalysts are ferrocene [174], Fe [175], Ni [176] which are either coated on the substrate or injected as vapor along with the carbon precursor into the reactor. The growth conditions depend on the catalyst, carbon precursor and the conditions of the CVD. CNT often show lower capacitance due to lower specific surface area when compared to AC or graphene. CNT based electrode often shows capacitance less than 50 F/g, whereas activated carbon-based electrode show capacitances are often in the range 200-300 F/g [112,177]. However, due to the uniform formation of the pores and tubes, most of the surface area can be made accessible using an ideal electrolyte [178–180]. Most often, CNT is procured in the powder form and tends to agglomerate in the prepared supercapacitor electrodes, further reducing the surface area accessible to the electrolyte. CNT has also been used with other electrode materials to make composite electrodes [179,181–183]. Besides electrode materials, CNT has also been used as a binding material instead of the conventional PTFE or PVDF; in this case, the CNT structures also act as conductive additives and add additional surface area to the electrode [132,184–186].

Carbon nanofibers (CNF) are similar to CNT, but unlike the hollow CNT structures, CNF are entirely filled fibers with a mixture of crystalline and amorphous carbon structures. While the CNT structures are limited in size to typical maximum diameters in the order of 30-50 nm, CNF generally have larger diameters going from the CNT maximum range to a few hundreds of nanometers, in contrast to carbon fibers which have diameters well into the micrometer ranges. Major production methods are using electrospinning of organic polymers precursor and later thermally treating it to form a carbonaceous fiber. However, this method often produces fibers with a diameter more than 100 nm [187,188]. More discussion on CNF and the specific method used in this project will be given in the later sections.

2.5.6.6 Redox-based materials

Redox materials can be broadly classified into conducting polymers and metal oxides and hydroxides. The mechanism of energy storage by these materials has been discussed in the previous sections. The main factors considered for the selection of the material are its (a) proton and electron conductivity, (b) stability in the electrolyte across the working potential window, (c) rate capability, and (d) surface area. It is also widely reported that the water content within the oxide also influences the capacitance. For example, Sugimoto et al. have reported that the capacitance dropped from 342 F/g to 124 F/g, and to 24 F/g for RuO₂×0.5 H₂O, RuO₂×0.3 H₂O, and RuO₂, respectively, at a scan rate of 2 mV/s in 0.5 M H₂SO₄ [190]. Oxides of manganese are also known to exhibit pseudocapacitance behavior [191].

Among several other metal oxides reported in the literature, the most common ones are iron, cobalt, and nickel oxides [192]. They often exhibit a battery-like behavior, with prominent redox peaks in the CV plot, with peak currents being proportional to the square root of the scan rate. They are used in symmetric cells, and also as anode materials in asymmetric cells in combination with a carbon negative electrode, achieving higher energy density due to the widened operational voltage window, in comparison to the symmetric cell [193].

Conducting polymers like polyaniline and polypyrrole often offer a high rate capacity and have a relatively low cost and low environmental impact. However, these polymers often mechanically degrade over the cycles and lose their capacitance retention. To address this issue, these materials are often composited with carbon allotropes with capacitance in the range 80-500 F/g being achieved [193,194].

2.6 Electrochemical Characterization techniques

Capacitance, which is the most important metric for a supercapacitor, can be evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), or even by electrochemical impedance spectroscopy (EIS). However, GCD is the most commonly used technique. Both two and three-electrode cells have been used for electrochemical analysis. However, the two electrode cell measurement is more reliable as it resembles the commercial cells more closely. This configuration assumes the use of two electrodes and a separator between them, soaked with an electrolyte (Figure 2.4). A three-electrode cell consists of a reference electrode, a counter electrode and a working electrode, which is the supercapacitor electrode. Due to the widespread practice of reporting capacitances of the supercapacitors on a per one-electrode basis, all the capacitance values reported in this thesis are also stated per one electrode, for easier comparison of the data published in the literature. However, industrially speaking, supercapacitors are rated for the whole cell or a module pack of individual cells. Figure 2.5 shows a schematic of a two-electrode test cell used in this work.



Figure 2.5. Schematics of a two-electrode supercapacitor setup.

Typical CV and GCD plots of a supercapacitor are shown Figure 2.6 and Figure 2.7, respectively. Figure 2.6 shows the CV dependence on the scan rate for a 3.3 F supercapacitor. The CV tends to be rectangular with no occurrences of redox peaks, and GCD usually appears as an asymmetric triangular profile. The iR drop is often generated by the low conductivity of the electrode which causes series resistances. Conductive carbon black or any conductive additive can be added to minimize this.



Figure 2.6. A set of CV curves of a 3.3 F supercapacitor recorded at different scan rates. The scan rate increases in the direction of arrows [195].

Specific capacitance can be calculated by measuring the area under the CV curve (Figure 2.6) and using the following equation [153,196]:

$$C_{s} = \frac{4 \int IdV}{m \times \Delta V \times S}$$
 Equation 2.2

It can be also calculated by measuring the slope of the discharge curve from the GCD (Figure 2.7) and using the following equation [76,78,109]:

$$C_{s} = \frac{4I}{m\frac{dV}{dt}}$$
 Equation 2.3

In these equations, C_s is the gravimetric specific capacitance (in F/g), $\int IdV$ is the area under the CV curve, S is the scan rate (in V/s), ΔV is the voltage window (about 1V for aqueous electrolytes; if using discharge curve then ΔV is the effective voltage after the potential drop (IR drop), i.e. ΔV is the cell voltage), m is the mass of both electrodes (inclusive of conductive additive and binder), I is the discharge current (in amperes, A) and dV/dt is the slope of the discharge curve (in V/s). For experiments that involve low active electrode mass, reporting capacitance value per geometric area in F/cm² would be ideal as a small variation in the mass could result in a large deviation in the capacitance. For the same reason, there is a large amount of literature that has claimed to achieve huge capacitances using various active material, which is actually questionable.



Figure 2.7. Schematic representation of a GCD plot for a supercapacitor measured at a given current density.

A factor of 4 in Equation 2.3 and Equation 2.3 is employed because these equations are formulated to calculate the gravimetric specific capacitance of a full cell, not only that of one electrode. As stated previously, most researchers tend to report the specific capacitance per electrode. In a two-electrode cell, there are basically two capacitors in series, C_1 and C_2 , and the total cell capacitance, C_T is then:

$$\frac{1}{c_T} = \frac{1}{c_1} + \frac{1}{c_2}$$
 Equation 2.4

As we are dealing with a symmetric two-electrode cell, C_1 is equal to C_2 , and therefore C_1 , C_2 in series would be equal to $2C_T$:

$$\frac{1}{c_T} = \frac{2}{c_1}$$
 Equation 2.5

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If the gravimetric specific capacitance is desired, this capacitance must be multiplied by a factor of 2. This is because both the electrodes would have identical electrode mass (m), and therefore the mass of both electrodes would be 2m.

Energy density (E, Wh/kg), and power density (P, W/kg) can be calculated using the following two equations, respectively[198] [112, 147, 185, 126]:

$$E = \frac{1}{8}C_s \Delta V^2 \qquad \qquad Equation \ 2.6$$

$$P = \frac{E}{t}$$
 Equation 2.7

while the Coulombic efficiency (η) is given as [201–203]:

$$\eta = \frac{t_D}{t_C} 100 \qquad \qquad Equation 2.8$$

where tc and tb is the time taken for galvanostatic charging and discharging, respectively. The efficiency η is basically the ratio of charge drawn out to the charge stored in the cell.

In case of a slight deviation from the triangular behavior of the GCD for some pseudo-capacitive material, which is often the case in hybrid and battery-like capacitors, Equation 2.9 and Equation 2.10 may be used to avoid bigger miscalculation of the capacitance. If the deviation from the charge-discharge curve linearity is considerably large and if the CV has obvious peaks, it is more appropriate to calculate capacity (Q = it, Ampere hour) instead of capacitance.

$$C = \frac{2E_{\rm d}}{\Delta V^2} \qquad \qquad Equation \ 2.9$$

where ΔV represents the discharge potential window (V), and E_d stands for the discharge energy (J) which is calculated as:

$$E_{\rm d} = \int_{E_{min}}^{E_{max}} E(t) dt \qquad \qquad Equation \ 2.10$$

where E_{min} and E_{max} are the minimum and maximum potential of the operating window.



Figure 2.8. Nyquist plot of a 3.3 *F* supercapacitor recorded with an applied dc voltage 2.2 *V* (data retrieved from the Metroohm Nova database) [195].

Electrochemical impedance spectroscopy (EIS) is a useful tool to understand the physical picture of the electrode and its behavior, which can be represented as the electrical circuit. This technique basically exhibits a capacitive response to an applied AC signal. A typical Nyquist plot derived from an EIS measurement is shown in Figure 2.8. The starting point of the plot in the high-frequency region (left-hand extreme) can be assigned to the electrochemical series resistance (ESR), usually followed by a semicircle and a vertical response in the low-frequency region, which is a typical behavior of supercapacitor depicting capacitance behavior or a formation of EDLC. The semi-circle is often attributed to the charge-transfer phenomena. This semi-circle could be depressed mostly due to the physical nature of the electrodes, like porosity. Capacitance can be calculated using the EIS response, and a numerical fitting of the experimental data with an appropriate circuit is required. However, for an EDLC, a simple RC series circuit can be used for estimating the capacitance in the double layer using Equation 2.11. Here, Z is the imaginary part of the impedance, and f is the frequency (Hz).

$$c = \frac{-1}{2\pi f Z_{img}}$$

Equation 2.11

Chapter 3

Direct growth of carbon nanofiber forest on nickel foam without any external catalyst

3.1 Preface

This chapter presents a published in the journal Diamond and Related Materials and the complete citation is:

Deepak Sridhar, Sasha Omanovic, Jean-Luc Meunier. Direct growth of carbon nanofiber forest on nickel foam without any external catalyst, Diamond and Related Materials, Volume 81, 2018, Pages 70-76.

D. Sridhar (Ph.D. candidate) conceived the idea, planned the experiments, carried out both material preparation and characterizations, all electrochemical experiments and analysis of the results, and wrote the article. S. Omanovic and J-L. Meunier supervised the work, gave funding support for the experiments, and reviewed the manuscript.

This work was the first step towards the objective of making binderless electrodes. Several experiments with ideas including the deposition of the catalyst by using physical vapor deposition, and reduction of metal salts to form active growth sites were tried (results not included in this thesis). Finally, the method reported in this article was perceived to be more realistic for scale-up as well as suitable for supercapacitor applications. This article focuses on growing CNF directly on Ni-f without using any external catalyst. Best growth conditions to obtain a dense CNF forest on Ni-f along with the role of substrate etching, and growth temperature was studied. It was found that dense CNF forests could be achieved at a relatively low temperature of 400 °C and etching was crucial to growing CNF at a temperature of 500 °C. A similar growth process was adapted to grow a CNF forest on Ni-f for the works discussed in the subsequent Chapters 4 & 5.

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Highlights

- Carbon nano fibers (CNF) are grown directly on nickel foam without using any external catalyst
- The process temperature to grow densely covered CNF forest is as low as 400 °C
- Etching of nickel foam is essential for the dense CNF coverage, especially at the higher growth temperatures
- The diameter of the CNF can be tuned by changing the growth temperature

Abstract

Interest in the direct growth of carbon nanostructures on metal substrates is growing, especially in the field of supercapacitors, fuel cells, batteries and sensors. This paper presents results on the growth of carbon nanofibers (CNF) without the requirement of an external catalyst directly on nickel foam (Ni-foam) at a relatively low temperature of 400 °C. Etching of Ni-foam leads to the growth of CNF forests covering entirely the internal surfaces of the Ni-foam, with CNF diameters that can be tuned between 78 ± 32 nm and 375 ± 35 nm through a change in the growth temperature between 400 and 700 °C. The etching was found to be important to obtain a uniform surface CNF coverage and growth, particularly at higher temperatures. These CNF/Ni-foam composites yield 3D nano-scale internal forest structures in good contact with the micro-scale porosity of the metallic foam electrode. This work provides a foundation to use binderless CNF composite electrodes to obtain higher capacitance.

3.2 Introduction

Carbon nanostructures are used in a large number of applications, particularly in electrochemical devices such as sensors, batteries, fuel cells and supercapacitors. Onedimensional (1D) structures such as carbon nanotubes (CNT) and carbon nanofibers (CNF) form interesting wire-like structures having the potential for a strong enhancement of the surface area for current-collecting devices and/or better and wider distribution of active sites for electrochemical reactions. The main differences between CNT and CNF relate to their typical diameters and the level of crystallinity or rolled graphene-like organization. The CNF fibers, that are discussed in the present paper, typically have diameters roughly above the 50 nm range, with randomized or amorphous carbon structures that do not show the hollow cylindrical structure of rolled graphene sheets seen for CNT [204,205]. The most common methods for producing CNF are by chemical vapor deposition (CVD) or by electrospinning of the precursor material. Formation of CNF by CVD is often a single-step process unlike electrospinning which requires a carbonization step in addition to the forming step of fibers [206]. The CVD process for both CNT and CNF also has the characteristic of growing the fibers directly from the substrate surface, making in this way a potential nanoscale extension of the substrate surface. CNF are known to have relatively better electrical conductivity and surface area, along with good mechanical and structural properties, making them interesting for nano-composite structures and filler additives [207–209]. The CVD process for growing the CNF structures typically uses catalyst nanostructures that are immobilized either directly on the substrate, introduced with the feed gases, or follow from the heat treatment of a thin film coating [210-212]. This adds complexity and additional costs to the fabrication process, and generates some limitations in terms of the structural design of the base substrate. Providing the catalyst nanostructures necessary for enabling a forest-like growth of CNF within the highly porous metallic foam structures poses severe challenges. Metal dusting process is also used to grow carbon tubes mostly on metal alloys [213,214]. But these processes are complex, use relatively higher temperatures, have long process time and the morphology and the growth of carbon structures are not uniform. Lately, Bauman et al. have developed much simpler techniques using metal dusting to grow carbon fibers using halogenated hydrocarbon as feed gas on various metal alloys [215–217]. Nevertheless, harsh process conditions and corrosive environment caused by the chlorinated gasses is detrimental to the reactor and the control over the morphology of the carbon structures is difficult.

The fabrication processes of electrodes containing carbon nanomaterials are typically based on painting or other deposition processes onto the current collector, most often using an ink dispersion of the nanomaterial [218–220]. The possibility to directly grow the carbon nanostructures from the electrode surface can eliminate this step, therefore making their integration easier for various applications. Two additional advantages of a direct growth technique on the electrode metallic surface is minimization of the carbon/substrate contact electrical resistance and elimination of the need for adding an inert binder, both providing better accessibility to the electrolyte ions. For electrochemical devices such as supercapacitors, these effects help in achieving a higher capacitance and minimize the agglomeration phenomena of the active material which is directly linked to the ink-based dispersion process. An additional advantage of using 1D carbon nanostructures is their higher electrical conductivity compared to the commonly used activated carbon [157,207], eliminating in this way the need for addition of a conductive agent. Provided good wetting properties are achieved, strongly increased available surface area of the electrode could be achieved from 3-D architectures formed by forestlike CNF growth structures on the substrate. Ni-foams are now often used as current collectors in battery and supercapacitor research, these offering large surface areas for the deposition of the active material and non-corrosive behavior in alkali medium. A few research teams have tried to grow CNF or CNT directly on metal substrates. Zamri et al. for example have grown CNF directly on Cu and Mo TEM grids using ion irradiation technique [221], while Mata et al. have grown CNF on nickel and copper foils using hot filament-CVD [222,223]. The direct growth process is now well developed and provides means to grow CNT forests directly on stainless-steel(SS) structures without the step of adding an external catalyst [224–226]. A few authors have tried growing CNT on nickel without the use of an external catalyst [227,228], while some have used surface preparation techniques such as mechanical polishing [229]. One can observe from these

results that the coverage of nickel substrates with CNT or CNF is low and contains a large amount of amorphous carbon. This poor coverage and low density of carbon growth is often expected if the bulk metal is not modified with an external catalyst [230]. It is to be noted that most researchers used hydrogen gas in their processes and relatively high temperatures, in the range of 650 °C to 900 °C, either for growth or for pretreatment [231– 234].

In the present paper, we show the development of a novel one-step, simple method for growing dense CNF forests on Ni-foams without any external catalyst. Nifoams are etched and then used as substrates for growing CNF. Optimum growth conditions, effects of temperature on the growth, structural and material analysis of CNF have been reported.

3.3 Experiment

3.3.1 Growth of CNF

Ni-foam substrates (MTI corp.) of 99.99% purity having a thickness of 0.08mm are cut into small squares of 0.5 cm² and then rinsed with 0.1 M acetic acid for 2 minutes to remove surface oxides. These substrates are then sonicated in ethanol for 15 minutes. The cleaned samples are etched in an acid solution mixture of acetic acid (glacial), nitric acid (68-70 wt.%), sulphuric acid (95-98 wt%) and phosphoric acid (85 wt%) in the ratio 5:3:1:1. The Ni-foams are etched for 60 seconds and then thoroughly washed with Milli-Q water; the surface water is finally wicked using wipes. These etched Ni-foams are placed on a ceramic boat and inserted into the quartz tube (internal diameter 5.5 cm; length 1.22 m) of a split furnace (Linderg-Blue HTF5500; 120V/30A). This is followed by a "preheating step" for 30 minutes at various temperatures ranging from 300°C to 950°C. After 30 minutes, 50 sccm of acetylene (C₂H₂) is injected in the furnace tube for 5 minutes. Following the C₂H₂ step, the samples are maintained at the same temperature for 30 more minutes in what constitutes the "growth step". The preheating and the growth step are done at the same temperature. The system is then cooled down slowly to room temperature before removing the Ni-foams from the quartz tube. An argon flow of 500 sccm is used in the tube furnace throughout the experiment. Similar growth procedures are also followed with non-etched Ni-foams. The Ni-foams are weighed before and after the CNF growth in order to track the carbon mass accumulation.

3.3.2 Material characterization

For surface morphology, optical microscopy, scanning electron microscopy (SEM) (FEI Inspect F-50 FE-SEM) and transmission electron microscopy (TEM) (Tecnai G2F20-200 kV) are used; these electron microscopes also provide energy dispersive X-ray spectroscopy (EDS) analysis. For TEM imaging, the CNF are simply scraped off the Ni-foam surface and placed on the copper grid. The Ni-foams are cut using scissors for imaging the cross section. Raman (Renishaw micro Raman) with a green LASER (wavelength 514.5nm) as excitation source is used to analyze the quality and nature of the CNF.

3.4 Results and Discussion

CNF growth experiments are conducted in the temperature range from 300°C to 950°C. Considering a balance between the mechanical strength of the Ni-foam structure after etching and the growth of the CNF, we find a time frame of sixty seconds etching of the Ni-foam to be optimal. We determine that etching is a crucial step for the synthesis of CNF, as it creates finer and more uniform surface roughness patterns (Figure 3.1) which in turn provide the active growth sites. We clearly observe that almost no growth of CNF

on the non-etched Ni-foam under similar conditions for temperatures of 500 °C and above (SFigure 3.1). Almost no growth is observed when the preheating step or the growth step were skipped (SFigure 3.2). Prolonging the acetylene injection step without the growth step simply increases the carbon mass accumulation with very little CNF growth.

In a vision similar to the direct growth of CNTs where structural surface transformations are generated using recrystallization and/or diffusion followed by phase transformations [235–237], we believe that preheating of the Ni-foam also creates active growth sites by creating surface roughness scales in the nanometer range. Such sites may enable further diffusion of carbon together with modifying the local melting temperature. One may speculate that some limited amount of oxygen contamination may enable a local loading of nickel with carbon through a nickel carbonate phase pathway, therefore modifying the local melting point; this, however, still needs to be evaluated and confirmed. What is experimentally observed is that no CNF growth is occurring at temperatures below 350 °C or above 750 °C (SFigure 3.1). At both 350 °C and 750 °C transition points, we observe a sporadic formation of CNF. Figure 3.2 shows the SEM images of CNF grown at four temperatures. At 400 °C, there is a complete coverage of the Ni-foam by CNF, the extent of the coverage decreases with an increase in temperature (SFigure 3.1). CNF is grown in the holes, ridges, and troughs, completely covering of the nickel foam at 400 °C (SFigure 3.3). We also observe that moving to higher temperatures (particularly from 650 °C and above), a layer of carbon is seen to be formed on the inner walls of the CVD quartz tube. This indicates that some nickel nanostructures vaporized during the heating process and get deposited on the inner surface of the tube, acting as a catalyst source for carbon precipitation. Figure 3.3 shows the carbon mass accumulation on Ni-foam at various temperatures. Carbon absorption is higher on the etched Ni-foams when compared to non-etched structures at temperatures ranging from 400 °C to 850 °C.

There is no significant carbon deposition at temperatures below 300 °C and above 900 °C on the etched Ni-foam. On the other hand, for non-etched Ni-foams, there is no significant carbon deposition above 500 °C. Even though the growth temperature of 450 °C shows the highest carbon accumulation (Figure 3.3), 400 °C is enough to form uniform and dense coverage of CNF on Ni-foam.



Figure 3.1. a) Non-etched and b) Ni-foam etched for 60s.

Both the etched and the non-etched Ni-foams show complete coverage at 400 °C; however, the etched Ni-foam is mostly covered with CNF while the non-etched Ni-foam is covered with amorphous carbon and few CNF (SFigure 3.4). This suggests etching enhances the quantity of the CNF growth sites uniformly across Ni-foam. This also suggests that non-etched samples do have some sites where CNF growth can be initiated, but these sites are not uniformly distributed across the Ni-foam substrate surface. At these sites on the non-etched Ni-foam, the carbon diffuses and then precipitates during the growth phase, forming sparse CNF. This growth on non-etched Ni-foam is found only till the temperature 450 °C. The diameter of the CNF increase from 78 ± 32 nm to 376 ± 35 nm with the increase in the growth temperature from 400 °C to 700 °C, as shown in Figure 3.4 (average values and standard deviations based on 30 measurements for each estimation). The region near the tip of the CNF where the nanoparticle is located is slightly wider than these values, possibly because of more carbon precipitation sideways before the nickel nanoparticle separates from the Ni-foam surface. The increase in diameter with temperature could possibly be due to enhanced diffusion of carbon into the metal substrate.

TEM images (Figure 3.5) confirm the tip growth method [238] of these CNF, and EDS performed on the tip of the fibers confirms the presence of nickel along with carbon. SFigure 3.5 shows a cross section image of the CNF grown at 400 °C on etched Ni-foam and SFigure 3.6 shows elemental analysis and different points of this sample. The copper peaks observed is from the copper TEM grid being used. Almost no CNF growth is observed on non-etched Ni-foam at temperatures of 500 °C and above (Figure 3.1, SFigure 3.1 and SFigure 3.7).



Figure 3.2. SEM images of CNF grown at a) 400 °C, b) 550 °C, c) 650 °C, d) 700 °C. At 400 °C there is a complete coverage of Ni-f by CNF, while the other images were taken at locations of the Ni-f where CNF patches were formed.



Figure 3.3. Carbon mass accumulation on a Ni-foam at different process temperatures; a) on etched Ni-foam b) on non-etched Ni-foam.



Figure 3.4. variation in the diameter of the CNF with temperature (Error bars indicate standard deviations).



Figure 3.5. (a) and (b) are TEM images of 400 °C etched Ni-foam CNFs, and (c) is the EDX spectrum of the CNF head incorporating a Ni particle indicated by the arrow in (a).

Most CNF do show the presence of Ni nanoparticles at the tip (Ni-catalyst head). The number of nickel nanoparticles per 1 μ m² was about 20 and 11 after the growth of the CNF at 400 °C and 650 °C, respectively. The ferret diameter of the nanoparticle head remained almost the same at 58 ± 49 nm and 58 ± 48 nm at 400 °C and 650 °C, respectively (Figure 3.6). This confirms that similar size active sites are formed after etching. Because of the increased temperature, less weakly adhered nano sites stay on the Ni-foam and the
remaining is vaporized. The nickel nanoparticle on top of the CNF has a circularity of 0.80 ± 0.25 .



Figure 3.6. BSE image of CNF and nickel particle head ferret diameter count for CNFs formed at (a) 400 °C and (b) 650 °C.

The micro-Raman spectra were evaluated for all the samples. The D peak observed was recorded in the range of 1344-1353 cm⁻¹, the G peak in the range of 1585-1594 cm⁻¹ and the G' peak in the range of 2688-2702 cm⁻¹ (Figure 3.7). We also found peaks in the range 2930-2936 cm⁻¹, which are a combination scattering peak of D and G [239], while the peak around 3200 cm⁻¹ is an overtone of G band [240]. The latter two peaks were often small and are not used in the analysis. Lorentzian functions are used to fit the Raman

spectra and evaluate the full width at half maxima (FWHM) of the bands. The defect ratio, which is the ratio of the intensity of D peak (I_D) to G peak (I_G) is proportional to the disorder present in the carbon, while the L_a length parameter is an estimation of in planar graphitic crystallite size calculated using the equation, $L_a(nm)=4.4/(I_D/I_G)$ [241]. Often, it can be approximated that the graphitized (ordered) carbon mole fraction (X_G) is equal to I_G/(I_G+I_D) [242].

Raman spectra are found to be similar for CNF grown at 400 °C on etched and non-etched Ni-foam samples at various points, depicting the carbon to be of uniform nature (Figure 3.7). However, the I_D/I_G ratio for non-etched Ni-foam is lower than that one for the CNFs on the etched Ni-foam samples (Table 3.1). This suggests that these CNF have structural defects and are amorphous in nature. Surprisingly, carbon on the nonetched sample, which appears to be more amorphous, also appears to be slightly more graphitized, as evidenced from the Raman spectra. These differences, however, stay within a very close margin particularly in view of the approximation nature of these parameters. TEM images (Figure 3.5) also showed disordered orientation of the crystallite, with very little graphitized structure, confirming these fibrous to be more amorphous. Such low graphitized carbon formation could be due to the low growth temperature.

Smaller FWHM for the G' band and slight upshift of the peak was noticed for CNF on non-etched samples when compared with the CNF on etched Ni-foam, at 400 °C. Kastner et al. reported similar observation when they compared graphite crystallites to nanotubes [243]. One can note that the present CNF samples have lesser defect ratio than some of the other reported CNFs in the literature [242,244].

Sample	CNF on etched Ni-foam	CNF on non-etched Ni-	
		foam	
FWHM (G band), cm ⁻¹	75 ± 1	76 ± 2	
FWHM (G' band), cm ⁻¹	115 ± 31	92 ± 3	
G peak, cm ⁻¹	~1585	~1592	
G' peak, cm-1	~2688	~2709	
Id/Ig	1.08 ± 0.06	0.95 ± 0.01	
La(nm)= 4.4/ (ID/IG)	~4.07	~4.63	
$X_G = I_G / (I_G + I_D)$	0.48	0.51	

Table 3.1. Some key info on CNF grown at 400 °C on etched and non-etched Ni-foam.

Further, we observed that the FWHM for the G' decreased with increase in the synthesis temperature, indicating the improvement in graphitization of the CNFs (STable 3.1). It is also interesting to note that bald spots on etched Ni-foam with CNF grown at 450 °C had wider G' and higher ID/IG values (SFigure 3.8). It is clear that the orderliness in the carbon structures is not uniform and they do have spots with both high and low defects within the foam structure (SFigure 3.9 & SFigure 3.10). This explains in part that the CNF got well graphitized at higher temperatures. The spots where there was an absence of loosely held nickel particle (growth site) developed an amorphous layer, which had a higher defect ratio.



Figure 3.7. Raman spectra of the CNF grown at 400 °C on non-etched (above) and etched Ni-foam (below).

From the above observations, the CNF growth mechanism on Ni-foam could be in the following steps as illustrated in Figure 3.8: 1. Etching of the Ni-foam creates numerous nanostructured topographies acting as potential catalytic sites; etching also increases the overall surface area of the substrate; 2. Decomposition of the acetylene on the Ni-foam; 3. Diffusion of carbon into the Ni-foam substrate either by surface diffusion and/or by the possible formation of a new phase. Although not evaluated here, one possibility for such new phase could be nickel carbonate structures; 4. Growth phase where the carbon precipitates from the nickel nanostructures having size range in the order of 70 nm to 400 nm, and the CNF elongating through the commonly explained tip-growth model [231,245]. The loosely held nickel nanoparticles aids the growth of CNF. As suggested by Jarrah et al. there could also be formation and decomposition of Ni-carbide that would lead to free nickel particles just before the growth/elongation phase [232]. However, as nickel nano-particles are seen at the tip of the CNF, this seems to highlight local melting of nickel nano-sites followed by their separation from the substrate. Such melting starting to occur at a low temperature of 400 °C points out at a low melting temperature phase being generated.

Non-etched Ni-foam plausibly has almost no growth sites available at temperatures 500 °C and above. However, at a temperature of 400 °C, existing surface defects during the manufacturing process of the foam seem to act as growth sites. This is similar to the CNT direct growth process on stainless steel where etching is required on flat surfaces and on particles to generate active growth sites, but is not required on fine grids (400 mesh size for example) where the strain-forming process has generated the very fine grain structure [246,247].



Figure 3.8. Illustration of CNF growth on etched Ni-foam.

3.5 Conclusion

We have presented a facile technique for growing CNF directly on Ni-foam, at a relatively low temperature of 400 °C and at atmospheric pressure. Etching was found to be essential for a good growth of CNF throughout the nickel foam including the micrometer pores. We believe that etching creates more nano growth sites that are uniformly distributed and lead to formation of a dense and complete coverage of CNF layer. The diameter of these fibers was about 78 ± 32 nm, and could be tuned to a wider diameter upto 376 ± 35 nm with increase in the growth temperature The growth process seems to follow the well-known tip growth model. The present method does not use hydrogen and could be easily scaled up. This direct growth method yielding uniform CNF coverage is expected to enhance the performance of electrochemical devices such as supercapacitors, batteries, fuel cells and sensors through a decrease of the contact resistance, increase in surface area and better electrical conductance.

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3.6 Supplementary information



SFigure 3.1. Optical images of Ni-foam showing carbon deposition at various process. Top row(rectangles) represent etched samples and the bottom row (triangles) shows non-etched samples. With increase in temperature from 300 °C, we find that the carbon coverage increased until 450 °C and later tends to decrease. Beyond 700 °C we don't observe almost no carbon deposition at all. In the case of non-etched nickel foam (triangles) we don't see much carbon deposition from 500 °C onwards. Dark black areas correspond to dense CNF structures, while metal-like area show low density CNF.



SFigure 3.2. Optical images of etched samples (Squares) and non-etched samples (triangles) after growth a) with no pre-heat treatment b) with no growth phase and 30 min C_2H_2 injection. We can visually see that the foam has expanded, but there is no much growth of carbon.



SFigure 3.3. (a) and (b). SEM images showing CNF growth in the porous region (holes) of the nickel foam substrate. i.e. we see CNF on both the ridges and troughs of the foam. Similar observation on various locations indicate the growth of CNF on etched nickel foam seems to be present everywhere within the porous substrate at 400 °C.



SFigure 3.4. Images of CNF grown on non-etched Ni-foam at 400 $^{\circ}$ C a) SEM and b) TEM (however, the etched Ni-foam is mostly covered with CNF while the non-etched Ni-foam is covered with amorphous carbon and few CNF).



SFigure 3.5. Cross section SEM image of Ni-foam with CNF grown at non-etched 400 °C A. Secondary electron image B. Back scattered image.



SFigure 3.6. EDS analysis of a) CNF head on the Nickel nanoparticle b) Bulk nickel in the middle of the cross section image (refer to previous SEM image).



SFigure 3.7. Carbon deposition on non-etched Ni-foam at 650°C [note: there is almost no CNF on the surface].



SFigure 3.8. Raman spectra of CNF grown on etched Ni-foam at 450 °C.



SFigure 3.9. Raman spectra of CNF grown on etched Ni-foam grown at 550 °C at two different spots which displays different carbon quality.

STable 3.1. Some stats on CNF grown on etched Ni-foam at different temperatures

Temperature	450 °C	550 °C	650 °C
FWHM (G band), cm ⁻¹	70.1 ± 3.2	58.4 ± 7.5	52.6 ± 5.5
FWHM (G' band), cm ⁻¹	93.9 ± 12.0	90.2 ± 4.9	78.1 ± 0.3
G peak, cm ⁻¹	1591.4 ± 4.4	1583.5 ± 4.9	1574.6 ± 8.0
G' peak, cm ⁻¹	2700.6 ± 3.6	2706.99 ± 7.0	2696.5 ± 12.0
Id/Ig	1.12 ± 0.20	0.86 ± 0.58	1.05 ± 0.28



SFigure 3.10. Raman spectra of CNF grown on etched Ni-foam grown at 650 °C at two different spots which displays different carbon quality.

Small decrease in G' band, with increase in temperature indicates better crystallinity with increase in temperature. It is also worth noting that CNF grown at higher temperatures has a fairly intense G' peak at some points, indicating ordered carbon. Similar observations have been made with graphitization of MWCNT [248].

Chapter 4

Directly grown carbon nano-fibers on nickel foam as binder-free long-lasting supercapacitor electrodes

4.1 Preface

This chapter presents an article published in the journal, Materials Chemistry and Physics, and the complete citation is:

Deepak Sridhar, Jean-Luc Meunier, Sasha Omanovic. Directly grown carbon nano-fibers on nickel foam as binder-free long-lasting supercapacitor electrodes, Materials Chemistry and Physics, Volume 223, 2019, Pages 434-440.

D. Sridhar (Ph.D. candidate) conceived the idea, planned the experiments, carried out both material preparation, characterization and electrochemical experiments, did analysis of the results, and wrote the article. J-L. Meunier and S. Omanovic gave insightful comments on the results, provided funding support for the experiments, and reviewed the manuscript.

The previous chapter reports results on the successful preparation of a porous carbon electrode directly on a current collector (nickel foam), achieving the initial objective. However, the main objective of this thesis is to make viable supercapacitor electrodes. This article presents the use of the CNF directly grown on a nickel foam, discussed in Chapter 3, as supercapacitor electrodes. The process was slightly modified to best suit the application and the CNF on nickel foam was used as an electrode. A thorough electrochemical analysis was done on these electrodes. The results showed that

the electrode acted uniquely by showing stable capacitance with variation in current density. An areal capacitance of ca.142 mF/cm² was achieved, which is among the best results for CNT and CNF based materials reported in the literature. This electrode also formed the basis for preparing the ruthenium oxide-based supercapacitor electrode presented in the subsequent Chapter 5, and also for nickel oxide-based electrodes presented in Appendix C.

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Highlights

- One step binder-free carbon nanofiber (CNF) electrodes prepared at 410 °C
- Electrode shows a good aerial capacitance of ca. 142 ± 7 mF/cm² at 10 mA/cm²
- Capacitance remains almost constant with increase in current from 3 to 20 mA/cm²
- 100 % retention in capacitance observed even after 10000 cycles at 10 mA/cm²

Abstract

Binder-free carbon nanofiber (CNF) electrodes are prepared using a facile one-step process on nickel foam (Ni-f). The amalgamation of the innate Ni-f pores and nanostructure caused by the growth of the CNF is found to show a good aerial capacitance. Cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy are used to electrochemically characterize these CNF/Ni-f supercapacitor electrodes. In a two-electrode cell using 6M KOH as an electrolyte, these electrodes show a good aerial capacitance of ca. 142 ± 7 mF/cm² at 10 mA/cm² and specific energy of 62 mWh/m² at a high-specific power of 82 W/m². The electrodes also show a 100% retention in capacitance even after 10000 cycles at 10 mA/cm². Simple one-step electrode preparation process with no external catalyst, reasonable aerial capacitance, excellent stability, and ideal retention of specific energy with an increase in specific power, makes this an interesting material for thin energy storage devices.

Keywords: carbon nano-fiber; nickel foam; supercapacitor; energy storage; non-Faradaic

4.2 Introduction

Research on supercapacitors has gained immense interest in recent years due to their wide advantages over batteries, such as higher specific power, simplicity in their construction, and their extensive applications [87,249]. The major drawback of supercapacitors is their low specific energy when compared to batteries. Many carbonaceous materials like graphene, activated carbon and fullerenes have been used to increase the double layer-specific capacitance and specific energy, which is due to their large specific surface area [157,250]. Among these, activated carbon is commonly used due to its very high specific surface area, but this often leads to a lower specific power due to poor electrical conductivity and intricate porosity of the material [156,251].

In most cases, these carbon materials are coated onto the current collector along with an electrically-insulating binder as a slurry mix and dried. This not only prolongs the preparation of the electrode and adds extra cost to the process, but also leads to diminished energy and specific power due to the addition of resistances at the coating interfaces, as well as resistance within the electrode material itself. Thus, binderless electrodes which have good contact with the current collector would be an ideal solution.

The use of carbon nanotubes (CNT) and carbon nanofibers (CNF) in supercapacitors has also been reported in the literature. Among these, some authors have tried to grow CNT separately and later coat them onto the current collector [252–254], which again leads to the problems mentioned in the previous paragraph. Nevertheless, some authors have directly grown these carbonaceous materials on the current collector/substrate [245,255–257]. This makes the use of CNT/CNF more interesting as the electrodes are now binder-free and the contact with the current collector is good, which results in a decrease in resistance. However, an extra material coat or a catalyst is used

on the current collector in order to grow these fibers [258,259] which makes the electrode preparation longer and more complicated.

Considering these challenges, we demonstrate in this article the use of directly grown CNF on nickel foam (Ni-f) as supercapacitor electrodes, this growth being made without any external catalyst. The fiber structure and the porosity of the electrodes also provide better ion diffusion paths for the intercalation of the ions and leads to higher energy and specific power. Apart from being binder-free with good adherence to the surface of the current collector, the CNF is also slightly hydrophilic, contributing to an increase in capacitance and a decrease in resistance. This electrode material provides specific energy of 63 mWh/m² at a specific power of 82 W/m² and, retained 100% capacitance even after 10000 cycles at 10 mA/cm².

4.3 Experimental

4.3.1 Electrode preparation

Square 80 μ m thick Ni-f (MTI corp.) of sides 1 cm is used as the substrate/current collector. The procedure to grow the carbon nanofibers on this substrate is very similar to the one we have recently published [260]. SFigure 4.1 shows the schematic of the steps to prepare CNF-Ni-f electrodes. In brief, Ni-f substrates are washed with 0.1 M acetic acid and then sonicated in ethanol for 10 min to remove surface impurities. Then, these substrates are placed in a horizontal quartz tube (internal diameter 5.5 cm; length 1.22 m) in a split furnace (Lindberg-Blue HTF5500; 120V/30A) using a ceramic boat. Argon (500 sccm) is flown throughout the process. The substrates are preheated at 410 °C for 30 minutes and then 50 sccm acetylene (C₂H₂) is introduced for 5 minutes as a carbon source. This is followed by 30 minutes of growth time, the furnace is later cooled down to room

temperature. The samples are weighed before and after the process using an ultramicro balance (Sartorius S4) to measure the amount of carbon deposited on Ni-f.

4.3.2 Material characterization

Scanning electron microscopy (SEM, FEI Inspect F-50 FE-SEM) is used to observe the surface morphology, while energy dispersive X-ray spectroscopy (EDX) enables elemental composition evaluations using the same device. K-Alpha X-ray Photoelectron Spectrometer system (XPS) from Thermo Fisher Scientific with an aluminum X-ray source is used to find the elemental surface composition. An X-ray spot size of 400 µm and pass energy of 50 eV are used for high-resolution HR-XPS curves. The Avantage v5.932 software is used for curve fitting. The background of each spectrum is corrected using Shirley type background subtraction and mixed Gaussian-Lorentzian line shape functions are used to fit all HR-XPS.

4.3.3 Electrochemical characterization

The as-grown CNF on Ni-f are used as electrodes in a sandwich-type of 2 electrode assembly in a "two-electrode coin cell", as shown in SFigure 4.2. This assembly is housed in a stainless-steel split cell to determine the metrics of the supercapacitor. P8 filter paper (Fisher scientific) is used as a separator, and KOH (6 M) is used as the electrolyte. The electrodes and the separator are soaked in the electrolyte for three days before testing to ensure their complete and uniform wetting. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) are performed using Autolab PGSTAT30 (Metrohm, Netherlands), which was controlled using NOVA 2.1.2 software. All values in this article are presented at a 95% confidence interval.

4.4 Results and Discussion

4.4.1 Surface morphology

SEM image of a bare Ni-f before the CNF growth is shown in Figure 4.1a. Dense, uniform and complete coverage of carbon is found after the CVD process (SFigure 4.3). Carbon mass accumulation after the growth is 3.5 ± 0.3 mg/cm² on the Ni-f substrate. It is to be noted that, there is a probability of a small mass contribution form the formed nickel oxide of ca. 1.6 % (SNote 1), but it is negligible when compared to carbon accumulation. SEM images clearly show dense growth of a CNF forest as can be seen in Figure 4.1b,c for growth temperature of 410 °C. At the growth temperature, the dense CNF formation is indistinguishable from that formed on the etched Ni-f samples (SFigure 4.4, SNote 4.1) and the thickness of the CNF on every section of the foam is ca. $2.5 \mu m$ (SFigure 4.5). Apart from the long straight fibers, we also see few helical fibers, which could be due to inhomogeneous catalytic activity [261] or unequal growth of carbon in a single direction due to the growth conditions, or enhanced crystallinity [262]. The size of these fibers is found to be much smaller in diameter and longer when compared to our previously grown CNF at 400 °C [260]. The average diameter of the CNF is 50.6 ± 1.8 nm and the diameter size distribution is shown in Figure 4.1d. As discussed in our previous article [260], the nanostructures and surface defects on the nickel foam are expected to act as growth sites where the metastable carbon-nickel phase is formed. On top of providing conductive paths along the fibers, the thick and open structure of the fiber forest enhances the specific surface area together with enabling good access for the movement of ions during charging and discharging of the electrode when assembled into a capacitor. These open stranded structures also help for better electrolyte penetration and wetting of the electrode. It should be noted that the growth of CNF is not only on the external surface

of the Ni-f but also inside the pores (Figure 4.1b). These formed nanostructures on the innate macroporosity of Ni-f give a multi-structure architecture which is ideal for the use of a capacitor electrode at both high and low current densities.



Figure 4.1. a) Ni-f before the CNF growth. b,c) SEM images showing the dense formation of CNF on Ni-f (non-etched) at lower, and higher magnification, respectively grown at 410 °C. (d) *Histogram showing the diameter size distribution of the CNF.*

Two additional benefits result from the CNF being directly grown from the nickel substrate: (a) the agglomeration of these fibers is minimized as their roots are anchored to the Ni-f surface in the direct growth process, and (b) there is a perfect contact between the current collector and the electrode material leading to a significant decrease in contact resistance.

4.4.2 Surface chemical composition

The XPS survey spectra recorded over a wide energy range (Figure 4.2a) shows an intense carbon peak while traces of oxygen and nickel are also detected. The presence of oxygen is observed because the experiment is done at atmospheric pressure. We have also observed that even after long purging times (>30 min) there is some presence of oxygen inside the furnace. And in our case argon is mostly a carrier gas than an authoritative protective gas. Figure 4.2b, c, d, show the high-resolution (HR) peaks and curve-fitting corresponding to carbon, oxygen, and nickel HR-XPS. The atomic percentages (at.%) of carbon, oxygen, nickel on the surface of the electrodes are $98.36 \pm$ 0.27, 1.33 ± 0.16 , 0.32 ± 0.12 at.% respectively. As XPS is highly surface sensitive, it might have not picked up strong signals from the underlying nickel foam. Thus, the detected nickel signal is probably from the nickel nano-heads on the tip of the CNF, which are covered by carbon. However, the possibility of signals from the Ni-f substrate can't be denied. The carbon HR-XPS in Figure 4.2b is fitted using three contributions centered around 284.3 eV, 285.7 eV, and 290.2 eV. These can be attributed to the sp² hybridized carbon structures of C=C, C=O, and O-C=O respectively [84,263,264]. However, the 285.7 eV and 290.2 eV may be also assigned to C-C (sp³ carbons) and π - π * transitions in C respectively [84,265]. The 529.4 eV, 531.5 eV and 533.2 eV peaks of the oxygen HR-XPS fitted curves can be assigned to NiO, C=O and O-C=O [266-268]. These various C-O structures are likely rendering the CNF surface polar moments, thus exhibiting

hydrophilic behavior. The 531. 5 eV peak could also be due to Ni₂O₃ [269,270], while the spectral peak at 533.2 eV can also signify surface moisture [271]. The HR-XPS of the Ni



Figure 4.2. (a) XPS survey scan of the Ni-f-CNF electrode. (b,c,d) HR-XPS of carbon, oxygen and nickel, respectively, including the deconvoluted contributions. Black dots and orange lines represent the experimental data and the fit line respectively.

2p electrons shows two spectral portions corresponding to spin-orbit doublets $2p_{3/2}$ and $2p_{1/2}$. Ni $2p_{3/2}$ can be fitted with three contributions; a doublet with peaks at 853.5 eV and 855.4 eV corresponding to NiO, and a satellite peak at 860.9 eV (870.7 eV, 873.2 eV, and 878.9 eV respectively in $2p_{1/2}$ region) [272,273]. Nevertheless, the co-existence of Ni₂O₃ cannot be dismissed, as the peak at 855.4 eV could also be assigned to Ni³⁺ state [274,275].

The EDX survey through electron microscopy also confirms the presence of the same three elements (SFigure 4.6).

4.4.3 Electrochemical characterization

In order to characterize the capacitive behavior of the Ni-f/CNF electrodes, cyclic voltammetry (CV) measurements were performed in a wide scan rate region, employing a two-electrode cell (Figure 4.3a). The rectangular shape of the CV curves, even at higher scan rates, and the absence of redox peaks suggest high charging/discharging rate capability of the electrode and a pure electric double layer capacitance (EDLC) behavior.

To extract quantitative capacitance values and more realistic characterization of the capacitive behavior of the electrodes during the charging and discharging process, galvanostatic charging/discharging (GCD) measurements were made at different current densities. The resulting curves (Figure 4.3b) show a triangular shape with symmetric charging and discharging slopes at all current densities, confirming that the electrodes behave as a pure EDLC capacitor.

Capacitance values are calculated using the discharge slope (dV/dt) of the GCDs in Figure 4.3b, knowing that the capacitance (C) is equal to I/(dv/dt), where I is the current density in A/cm² [92,276]. The corresponding variation of specific capacitance with current density is also shown in Figure 4.3b. Two interesting and rather unique behaviors can be observed. First, unlike commonly seen in the literature, at current densities above 3 mA/cm^2 the capacitance remains constant with an increase in current density up to 20 mA/cm², yielding a value 140.8 ± 7.9 mF/cm². This unusual behavior is possible most likely due to the 3-D nano-architecture of the electrode of varying porosity (macroporosity due to the Ni-f and micro- and meso-porosity due to CNF) enabling fast migration of ions during the charging/discharging process, even at high current densities.

Second, the capacitance is lower at the lowest current density (GCD rate), which is opposite to the literature. We speculate that this is due to the probable structural collapsing of the nanofibers, which would open to provide more electrochemical surface area at higher GCD rates (higher current densities). The gravimetric capacitance is about 40 F/g, which is on par with the values on CNTs reported in the literature [277,278]. However, the aerial capacitance is much higher than that reported on several CNT- and CNF-based electrodes [279,280], graphene-based electrodes [281,282], activated carbon-based electrode [283], and a few redox-based electrodes [284,285]. This paradox arises due to the fact that many reported values could have been based on a thin coating of electrode material, or by specific approximation of the weight of the active material leading to low mass loading, or simply an electrode with very small mass loading which would tend to show overestimated gravimetric capacitance [92]. On the other hand, higher aerial capacitance is more important in applications like wearable electronics, and sleek gadgets. For the same reason, our opinion is that the aerial capacitance is a more suitable quantity for relative comparison.

It is well known from the literature that not all surface area would actively contribute to the capacitance [286]. In order to achieve good supercapacitor performance, carbon electrodes should be tailored to provide a higher surface area, which can provide good accessibility to electrolyte ions. They should also have good conductivity (intra- and inter-structures) along with a suitable surface condition [287]. In order to estimate the electrochemical surface area (EASA) we consider a double layer capacitance value of 10 μ F/cm², as carbon materials are known to have a double layer capacitance in the range 5 to 20 μ F/cm² in liquid electrolytes [113]. Assuming that all the estimated capacitance from our electrode is purely from the double layer, an EASA value of 14080 cm² is obtained (per 1cm² of the geometric area) or a gravimetric EASA of 402 m²/g. This value is larger than those reported for CNTs and CNFs [288–290].

Figure 4.4 shows the Ragone plot for the system studied here. Specific energy and specific power are respectively calculated using the formulae E= 0.5 CV2 and P=E/t, where C is the specific capacitance of the cell, and t is the discharge time at various applied current density [291]. The specific energy varied from 62.6 mW/m2 to 58.18 mW/m2 with the change in specific power from 81.95 W/m2 to 3.97 W/m2. It is clear that the favorable 3D architecture of the electrode yielding macro/micro/meso-pores and high surface area of the CNF forest (Figure 4.1) enables the retention of specific energy even at high specific power. The rooted contact of the CNF to the Ni-f current collector and enhanced ion transport paths formed within the CNF forest also play a vital role.

In order to investigate the structure of the solid/electrolyte interface and chargerelated processes occurring at the interface, electrochemical impedance spectroscopy (EIS) measurements are made in the frequency range 10mHz to 100kHz, with an AC perturbation of 10 mV (rms). Figure 4.5a shows the corresponding Nyquist and phaseangle Bode plots. The Nyquist spectra (main plot) evidences the predominant capacitive behavior of the system, characterized by an almost vertical trend in impedance. The same is evidenced by the phase-angle trend in the Bode plot (Figure 4.5b). However, the inset plot, which is a zoomed-in part of the spectra recorded at high frequencies, evidences the presence of a *RC* behavior (additional time constant) characterized by a depressed semicircle, specifically pronounced on the freshly-prepared (non-cycled) electrode (0th cycle). The same is visible on the Bode plot at high frequencies (see the 'peak' visible between 1 and 10 kHz, 0th cycle). The presence of this high-frequency time constant can be related to the fast charge-transfer processes, most likely to the migration of charged species (ions) through the pores during the charging/discharging process.



Figure 4.3. Plot showing a) cyclic voltammetry of Ni-f-CNF electrode in a two-electrode supercapacitor set up recorded at scan rates of 1, 5, 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mV/s, following the direction of the arrows. b) Variation in the specific capacitance with the current density. Inset: Galvanostatic charge-discharge at 1, 3, 5, 10, 15, 20 mA/cm², in the direction of the arrow.



Figure 4.4. Ragone plot for the Ni-f-CNF with 6M KOH electrolyte, supercapacitor.

However, with cycling (charging/discharging) of the electrode, the pronounced high-frequency semicircle gets distorted (less pronounced) indicating rearrangement of the electrode structure to enable faster migration of ions, yielding higher capacitance; indeed, this could clearly be seen in Figure 4.6 (discussed below). Similar frequency responses have been observed in other carbon-based supercapacitors when there is very low contact resistance at the electrode interface [292,293].

The intersection of the high-frequency spectrum with the real impedance axis represents the equivalent-series-resistance (ESR) of the system. The value only slightly increases with an increase in cycling in the order of 0.56, 0.61, 0.64 and 0.66 Ω from the 0th cycle to 10000th cycle, respectively (Figure 4.5a). These values are much lower than most of those for directly-grown carbon materials reported in the literature [284,285,294,295]. The small amount of surface oxygen makes CNF electrodes used in the current work hydrophilic, contributing to a decrease in series resistance. The absence of binder in the

electrodes also helped to accomplish low ESR, as no extra resistance is added to the existing intrinsic resistance of the electrode. Further, since CNF are directly grown on the Ni-f current collector, the interfacial contact resistance at the electrode/current collector interface is small, which also contributes to the low ESR.

To quantify the impedance behavior of the capacitor, the EIS data were modelled employing an equivalent electrical circuit (EEC) shown in SFigure 4.7. In this EEC, ESR represents the equivalent-series-resistance, R_P is the polarization resistance (mainly related to the 'pore resistance') and CPE_P is the corresponding pseudo-capacitance expressed by a constant phase element (CPE), while CPE_d represents the electrochemical double layer capacitance, while W is the Warburg element accounting for the masstransport processes.

SFigure 4.8 shows the comparison of the experimental (symbols) and the fitted data (lines) as a Nyquist plot and the corresponding ECC component values are tabulated in STable 4.1. The power values of the CPE_{dl} element (N, CPE_{dl}) are close to one, indicating that the constant phase element indeed represents capacitance. A small deviation from unity (ideal capacitive behavior) is due to the electrode surface heterogeneity in terms of charge distribution, which is expected for CNF. Nevertheless, the CPE_{dl} values are close to the values obtained from GCD measurements. Further, with cycling, the pore resistance, R_P, decreases, indicating re-arrangement of the electrode structure yielding increased access of the electrolyte to the CNF surface ('widening' of the pores).

A characteristic frequency (f_0) corresponding to the frequency at a -45° phase angle is determined from the Bode plot (Figure 4.5b), together with the corresponding characteristic time constant ($t_0=1/f_0$): 3.83 Hz (0.26s), 2.85 Hz (0.35s), 2.69 Hz (0.37s), 2.47 Hz (0.40s) for the 0, 2000, 5000, 10000 cycles, respectively. Such small-time constants suggest quick reversible charge and discharge, which is due to high accessibility of the



Figure 4.5. (a) Nyquist (inset: zoomed part of the Nyquist in the high frequency region) and (b) *Phase angle Bode plot of the CNF-Ni-f supercapacitor recorded after the number of charging/discharging cycles indicated in the plot.*

entire CNF surface to the electrolyte, enabling fast ion transport, ultimately yielding high specific power [296,297]. The EIS spectra in Figure 4.5a do not show the presence of the Warburg impedance, unlike many carbon-based electrodes [298]; this further supports our claim on efficient (low-resistance) migration of ions into the electrode pores, i.e. excellent pore-configuration of the electrode [299].



Figure 4.6. *The specific capacitance of the Ni-f-CNF electrodes at different number of charging/discharging cycles recorded at a current density of 10 mA/cm².*

One of the major requirements of supercapacitors is the longevity in terms of maintaining/providing the required energy over many charging/discharging cycles. In order to test the performance of the capacitor investigated here, the system is subjected to constant charging/discharging at 10 mA/cm², over 10000 cycles. As Figure 4.6 shows, the CNF electrodes are found to be extremely stable, with a coulombic efficiency of ca. 92% after 10000 cycles (Equation 4.1). The capacitance increases during the initial cycling period, probably due to the re-arrangement of CNF to offer a more open structure enabling better access of electrolyte to the surface and faster migration of ions.

Surprisingly, even after 10000 cycles, the capacitor maintains its charge at ca. 100 % of the peak capacitance. This evidences excellent chemical and structural stability of the electrode, the capability of maintaining its open structure (macro/micro/meso-pores) over a large number of charging/discharging cycles. This, in turn makes the system studied here an excellent candidate for commercial long-life supercapacitors.

4.5 Conclusion

CNF having typically 50 nm diameter are grown directly on nickel foam substrates at a relatively low process temperature of 410 °C and without using any additional surface preparation step or an external catalyst. This process is not only simple but also adds an advantage of having the functional electrode material (CNF) grown directly on the current collector. This resulted in very low ESR of the supercapacitor and highspecific power. The conjunction of the innate porosity of the nickel foam, and the additional porous architecture caused by the CNF growth, lead to a specific aerial capacitance of 142 ± 7 mF/cm². This electrode material shows better aerial capacitance than several other reported carbon-based electrodes. These electrodes are showing high stability and can retain 100 % of their initial capacitance even after 10000 charge-discharge cycles. Even though the gravimetric capacitance is comparable to those reported in the literature, the application of this electrode material in supercapacitors is interesting considering the simplicity of its preparation.

Acknowledgment

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4.6 Supplementary



SFigure 4.1. Schematic showing the preparation steps of CNF on Ni-f.



SFigure 4.2. Schematic showing the supercapacitor CNF-Ni-f electrode assembly.



SFigure 4.3. Optical image showing dense CNF coverage of a Ni-f substrate after the CNF growth

SNote 4.1

During the CNF growth, metal oxide growth is also possible. Oxide formation is estimated to be $5.63 * 10^{-5} \pm 2.39 * 10^{-5}$ g. This was estimated by performing controlled set of experiments under the same conditions as mentioned in the section 2.1, without the carbon source.


SFigure 4.4. SEM image showing the CNF forest on etched Ni-f. Note that there is no significant difference between the CNF grown on the non-etched Ni-f substrates (Fig. 1) and the etched Ni-f substrates at this growth temperature

SNote 4.2 We found that carbon mass accumulation on the etched Ni-f is slightly higher than that on non-etched Ni-f, grown in the same batch. For this reason, we find that the capacitance of the CNF-on etched Ni-f gives slightly higher specific capacitance. However, the increase in capacitance is not statistically significant. Therefore, we employed the non-etched Ni-f substrate in our study.



SFigure 4.5. Cut cross section BSE image of the electrode showing the thickness of the grown CNF forest. It is to be noted that the nickel metal section in the middle (bright region) is only a small layer section of the foam. The dense growth of CNF on Ni-f makes it difficult to determine the exact thickness of the CNF forest.



SFigure 4.6. (a) and (b), EDX intensity peaks and inset figures show SEM image and the arrows point the EDX spot.

EDX on the fiber shows strong peaks of nickel and carbon. We also see oxygen on the surface, which could be from nickel oxide as well as the surface oxygen groups on carbon. EDX on nickel nanoparticle head, show relatively strong nickel peaks along with oxygen peak signifying the oxide state of nickel.



SFigure 4.7. Equivalent electrical circuit used for the experimental data fitting.



SFigure 4.8. EIS spectra recorded on the CNF-Ni-f supercapacitor at various numbers of charging/discharging cycles. The symbols represent the experimental and the line represents the data modelled using the EEC in SFigure 4.7.

cycle	ESR,	R _p ,	CPE _p ,	Ν,	W,	CPEdil,	N,
	mΩ	mΩ	$m\;\Omega^{\text{-1}}s^{\scriptscriptstyle N}$	CPE _p	$m\Omega^{-1}s^{0.5}$	$m\Omega^{-1} s^N/cm^2$	CPEdil
0	565	451	0.40	0.85	607	85.6	0.98
2000	590	296	304	0.40	930	154.0	0.97
5000	632	229	218	0.46	870	161.0	0.97
10000	658	180	106	0.52	824	167.8	0.78

STable 4.1. Fitted data obtained using the equivalent circuit.

$$\eta = \frac{t_D}{t_C} 100 \qquad \qquad Equation \ 4.1$$

Where; η *is coulombic efficiency,* t_D is galvanostatic discharge time, t_C is galvanostatic charge time).



SFigure 4.9. XRD comparison of plane of Ni-F and Ni-F with CNF.

The faint peak at 2θ =26 can attributed to the carbon fibers, and the remaining peaks are mostly from nickel foam [300]. However, it is hard to distinguish any other exact feature of the carbon fiber alone due to the under lying nickel foam.

Chapter 5

Carbon nano-fiber forest foundation for ruthenium oxide coated pseudo-electrochemical capacitors

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5.1 Preface

This chapter presents an article that has been submitted to a peer-reviewed journal in January 2020, and can be cited as:

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Author specific contributions:

D. Sridhar (Ph.D. candidate) conceived the idea, planned the experiments, carried out both material preparation and characterization experiments, and also all the electrochemical experiments and analysis of the results, and wrote the article. H. Yu, prepared ruthenium oxide coatings and reviewed the article. J-L. Meunier and S. Omanovic provided insightful comments on the results, provided funding support for the experiments, and reviewed the manuscripts. This work focuses on the improvement of the capacitance and energy density of the CNF electrodes discussed in the previous chapter. Psuedocapacitance was introduced, by forming a ruthenium oxide coating on the CNF electrodes. The idea was to use the high-porosity and high-surface-area CNF grown directly on a nickel foam as a template (substrate) for deposition of a ruthenium oxide coating. This would create enhanced specific charge transfer due to the large specific active surface area provided by CNF accompanied by fast reversible redox reactions in the Ru-oxide, leading to a higher capacitance and energy density. This research not only yielded a high areal capacitance of ca. 822 ± 4 mF/cm² which places this material among the high capacitance yielding ruthenium-based electrodes, but also led to many other interesting results related to the behavior of ruthenium oxide. It was found that the high capacitance trend is achieved at lower coating temperature, than those reported in literature, which is expected to result from the presence of the underlying CNF template. A comparison of the electrode behaviour in a two-electrode cell (which is similar to a commercial cell) and in a three-electrode cell is also discussed in this article.

Highlights

- Ruthenium oxide was coated on directly grown carbon nano-fibers using an easy to scale-up procedure.
- The effect of different oxide coating temperatures on the electrochemical performance of the pseudo-capacitor was studied. The trend is unique when compared to other ruthenium-based electrodes.
- Only a 10 % drop in specific capacitance when the current density changed from 3 to 100 mA/cm².
- A complete comparison of electrochemical results obtained from two-electrode and three-electrode cell measurements is reported.
- 822 ± 4 mF/cm² at a current density of 20 mA/cm² and retained 94 % of its initial capacitance after 5000 charge-discharge cycles were achieved.

Abstract

Ruthenium oxide was coated on directly grown carbon nano-fibers (CNF) on nickel foam current collectors at different coating temperatures. The extended surface area and the porous nature of the CNF forest along with the pseudo-capacitance nature of ruthenium oxide enhanced the performance of the electrodes. As the ruthenium oxide coating temperature played a vital role in the charge storage process, an ideal temperature for the oxide formation was determined to optimize the capacitance and stability. Using 6M KOH as the electrolyte, these samples showed a high aerial capacitance of $822 \pm 4 \text{ mF/cm}^2$ at a current density of 20 mA/cm² and retained 94 % of its initial capacitance after 5000 charge-discharge cycles. The maximum energy and power density measured were 362 mWh/m² and 957 kW/m² respectively. Considering the facileness and the high-performance metrics, this process is easy to scale-up and the electrodes are promising for high-power supercapacitors.

Keywords: Ruthenium oxide; carbon nano-fiber; CNF; CNT; pseudocapacitor; Ruthenium oxide-carbon nanofiber; supercapacitor

5.2 Introduction

Due to the rapid depletion of fossil fuels and the increasing severity of environmental pollution, innovation and research towards harnessing alternative energy resources have gained considerable attention [301]. One of the key challenges here is the storage and conversion of harnessed energy in an efficient manner. Among the energy storage devices currently available, batteries are favored by the market because of their high energy density. Supercapacitors, on the other hand, have a relatively lower energy density, but

they offer a fast charge/discharge rate, good stability, very long life-cycles, and have a high power density [32,302,303]. These unique advantages of supercapacitors make them desirable as power sources either individually or combined with other energy storage devices to build a hybrid power supply system. Lower energy densities are the biggest downside of these devices when compared to batteries. Developing economically viable high energy density materials for supercapacitor electrodes would be the potential solution for this problem.

Currently, various carbon-based materials have been intensively studied and proved to be excellent electrode materials for supercapacitors, which include carbon nanotubes (CNT), carbon aerogels, activated carbon, fullerene, graphene and carbon nano-fibers (CNF) [157,304–306]. The carbon materials have special advantages such as a high specific surface area, an excellent thermal and electrochemical stability, a wide operating temperature range, as well as good compatibility with metals oxides [307].

However, one common problem among most carbon-based materials is their inherent difficulty to be used directly as an electrode on the current collector as most carbon materials are in powder or flake forms. Therefore, binders are needed to produce a slurry mixture of the materials to manufacture mechanically intact electrodes. Inevitably, the binders are electrically non-conductive which will result in higher electric resistance and undesired coverage of the electrode material surface area, which will further reduce the overall performance of a supercapacitor [308,309]. Besides, the specific capacitance of carbon-based materials is still low because of their charge storage mechanism, which is based on the electrostatic charging/discharging of the electrochemical double-layer.

Another category of supercapacitors is called pseudocapacitors, which are mostly based on pseudocapacitive metal oxide/hydroxide materials such as RuO₂ , MnO₂, V₂O₅, ZnO, IrO₂, etc. [310–312]. Transition metal oxides/hydroxides can provide much higher

capacitance than carbon-based materials because of the contribution of very fast reversible redox reactions during the charge storage process on the surface and within the thin sub-surface region [313,314]. Among the transition metal oxides mentioned above, RuO₂ is believed to be one of the best candidates for its record-high capacitance, excellent electrical conductivity, and superior electrochemical reversibility and stability [193,315]. However, the major drawbacks that prevent using ruthenium oxide for commercial production include its high costs and loss of power density when operating at high charge/discharge rates. A promising solution to solve the problems mentioned above is to fabricate composite materials that utilize the porous structure and larger surface area of carbon materials together with transition metal oxides [316,317]. The hybrid materials show strength in improving energy and power density, as well as enhancing the cyclic stability of the electrodes operating in various electrolytes.

In this work, we introduce for the first time, RuO₂ loaded on CNF directly grown on nickel foam (Ni-f) substrates via a thermal decomposition method. The highly active redox nature of RuO₂ was fully realized by enhanced surface area from the underlying CNF, which further provided exceptional specific energy and specific power. The novel and facile technique to produce binder-less electrodes are easy to scale up for commercial production due to minimal preparation steps and minimal use of RuO₂. The effect of electrode preparation temperature on the capacitance was carefully investigated utilizing both surface characterization techniques and electrochemical measurements. This high-performance material with superior cycling stability makes it an outstanding candidate as pseudocapacitor electrodes for practical applications. Compared with ruthenium oxides produced by other methods, the capacitance of our electrodes is amongst the highest level of state of the art pseudocapacitors.

5.3 Materials and methods

5.3.1 Electrode preparation

CNF were grown on Ni-f (80 μ M thick, MTI corp.) using the method described in our previous article [305]. Briefly, Ni-f was cut into 1x1 cm squares and cleaned in 0.1 M acetic acid and then sonicated in ethanol for 10 minutes. Further, these pieces were dried and weighed (ultramicro balance Sartorius S4). Then, these cleaned foam pieces were placed on a ceramic boat and positioned at the center of a horizontal split furnace (Lindberg-Blue HTF5500; 120V/30A). Argon at a flow rate of 500 sccm was flown throughout the process. The Ni-f structure was preheated at 410 °C for 30 min and then 50 sccm of acetylene was passed for 5 min (injection phase), followed by a 30 min growth phase, and later the furnace was cooled down to the room temperature. The Ni-f was weighed before and after the growth of CNF to determine the carbon mass accumulation. The carbon accumulation was found to be 3.88 ± 0.07 mg/cm².

The ruthenium oxide layer was coated on the CNF by the thermal decomposition method. The precursor solution of 0.15 M RuCl₃. X H₂O (Sigma Aldrich 206229) was carefully applied on the CNF substrate using a pipet. A total of 3 drops (22.5 uL in total) of the precursor solution were deposited on the surface of CNF substrate to ensure the surface was fully covered. After applying the first coat, the CNF substrate was placed into the furnace in air and was annealed for 15 min at different temperatures (200 °C, 250 °C, 300 °C, 350 °C, 400 °C – experimental parameter). Then, the CNF substrate was removed from the furnace and placed at room temperature for cooling during 10 min before another layer was applied. Three (3) layers of RuCl₃. X H₂O precursor solution were applied in total and the last layer was annealed in the furnace for 1h in order to fully oxidize the precursor. This method was determined as being optimal, following several

experiments using variations in coating layers (results not discussed in this article). A schematic of the electrode preparation is shown in Figure 5.1. Error bars in the graphs or the measure of variability reported in this work represent standard deviation with n=3, unless specified with a different n value.



*Figure 5.1. Schematic of the electrode preparation from Ni-f to RuO*₂-CNF.

5.3.2 Material characterization

Hitachi Cold FE SU-8000 SEM (Scanning electron microscope) along with energydispersive X-ray spectroscopy (EDX) was used to evaluate the surface topography and elemental composition. Transmission electron microscope (TEM) images were captured using Talos-F200X from Thermo Fisher scientific. S160 carbon film- 200 mesh copper grids from Agar Scientific were used to mount the sample. The RuO₂-CNF electrode was simply scraped off the Ni-f, and then acetone (optima, Fischer chemical) was added onto the scraped power and pipetted onto the grid. This method was adopted to ensure the presence of RuO₂ on the grid. For imaging uncoated CNF, the whole CNF forest (including Ni-f) was sonicated in acetone for two minutes and drop casted on the grid. K-Alpha X-ray Photoelectron Spectrometer system (XPS) from Thermo Fisher Scientific was used with an aluminum X-ray source to find the elemental surface composition. An X-ray spot size of 400 µm and a pass energy of 50 eV (high pass) and 20 eV (low pass) were used for high-resolution HR-XPS curves and the dwell time was set at 50 ms with energy step size 0.10 eV. A dwell time of 10 ms and pass energy of 200 eV with an energy step size of 1.00 eV was used to acquire the survey spectrum. Avantage v5.932 software was used for curve fitting. The background of each spectrum was corrected using the Shirley-type background subtraction and the mixed Gaussian-Lorentzian line shape functions were used to fit all HR-XPS. Raman spectroscopy measurements were obtained using a DXR3 Raman (Thermo Fisher Scientific) with a laser wavelength of 532 nm, and a laser power of 5 mW.

5.3.3 Electrochemical characterization

The electrodes were assembled into a 2-electrode symmetric setup using a stainlesssteel split cell, and the electrodes were separated using a filter paper (P8 Fisher scientific) soaked in 6M KOH (electrolyte). Autolab PGSTAT30 (Metrohm, Netherlands) with NOVA software (v. 2.3; Metrohm, the Netherlands) was used to perform cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis. Experiments were also repeated using a threeelectrode setup for the best performing sample in 6M KOH, using Hg/HgO (1M KOH, -129 mV vs. saturated calomel electrode) reference electrode and a graphite rod as the counter electrode. The working electrode was housed in a PTFE holder (WonATech Co., ltd., South Korea) with a working area of 1 cm² exposed to the electrolyte, and the graphite rod was placed in a glass frit to separate it from the working electrode (Ace glass, Inc., USA).

5.4 Results and Discussion

5.4.1 Surface and material composition analysis

Figure 5.2a & b show the SEM images of Ni-f prior to CNF growth and RuO₂ coatings. The Ni-f shows a 3D architecture with different sizes and shapes of pores. When examined under higher magnification (Figure 5.2b), we can notice that the surface of pure Ni-f is rather smooth and no special micro/nano-structures can be observed apart from the grain boundaries. Figure 5.2c-e show the surface of the Ni-f after the CNF growth and ruthenium oxide coatings at different magnifications. Uncoated CNF is shown in Figure 5.2c, and the bright dots are nickel particles, which are formed during the CNF growth process. Such, spots do not show up on the subsequent images which are coated with RuO₂. Figure 5.2d indicates the CNF-forest coverage with RuO₂ coat is quite uniform over the Ni-f including inside the foam open structure. Figure 5.2e shows the dense structure of the CNF-forest providing a high surface area and porosity scales in the order of μ m and below. Figure 5.2f shows the RuO₂ coating having a smooth and uniform coverage on the CNF structures, with the highly porous and ultrafine 3D network being preserved. The tubular-shaped CNFs coated with ruthenium oxide are observed to have an average diameter of 66 ± 8 nm. Clusters of RuO₂ coating on CNF can be observed in the backscattered-electron image in Figure 5.2g, and the corresponding secondary-electron image is shown in Figure 5.2h. EDX spectra on these regions confirming the carbon and RuO₂ composition is shown in SFigure 5.1 in the supplemental section of the paper.



Figure 5.2. SEM images of (a, b) Ni-f before the growth of CNF, (c, d, e) RuO₂ coated on CNF, (f) uncoated CNF (g, h) back scattered-electron and secondary electron image of RuO₂ coat.

HR-TEM of the CNF (uncoated) in Figure 5.3a shows a mixture of graphitized and amorphous regions. We also see a narrow hollow core in this image, however not all CNF have shown such tubular structure (SFigure 5.2). A small region in Figure 5.3b indicated in the white square is digitally magnified and shown Figure 5.3b. These graphitized pockets are disorganized in orientation amidst the amorphous region. The spacing between the graphitic lattice is about 0.34 nm. Graphitic layers here are wavy, discontinuous and the crystallite size appears to be small. The crystallite size (La) calculated from Raman spectra (SFigure 5.3) using a formula proposed by Mallet-Ladeira et al. [318], and was calculated to be 2.21 ± 0.80 nm. Raman spectra showed only a faint peak center around 640 cm⁻¹ in the case of RuO₂-CNF in addition to standard D (~1344), G(~1586), G' (~2681) and a peak at ~2390 which is a combination scattering peak of D and G' [239,260]. It is reported in the literature that Ru crystallites show peaks centered at ~520 cm⁻¹ and ~640 cm⁻¹ [319]. However, in the present work, we could not clearly decipher a peak at 520 cm⁻¹. The defect ratio (I_D/I_G) of the as-grown CNF is found to be 2.28 ± 0.08, indicating a relatively high disorder in the structure [320]. The curve fitting parameters of the D and G peaks are shown in STable 5.1. A TEM image of the prepared RuO₂-CNF sample shows sheet-like RuO₂ formation (Figure 5.3c). It is to be noted that samples prepared for the TEM imaging were scrapped off the electrode. Thus, it does not really represent the topography of the actual electrode structure. It can be observed that these RuO₂ sheets are randomly present on top of the CNF. An HR-TEM and the associated EDX spectra confirming the presence of RuO₂ are shown in SFigure 5.4.



Figure 5.3. a) HR-TEM image of uncoated CNF showing a large number of zones having graphitic layer structures when viewed in high resolution, b) enlarged image of the white-box in Figure 3b, showing one example of such zone. The white lines and the arrow depict the spacing between the graphitic layers which is found to be ~0.34 nm characteristic of graphite. c) TEM image of RuO₂ coated CNF. Arrows show some RuO₂ sheets (dark regions).



Figure 5.4. a) XPS survey scan of the RuO₂-CNF electrode. b) The elemental composition of the Ru O₂-CNF electrode determined using EDX and XPS.

An XPS-survey spectrum confirms the presence of ruthenium, carbon, oxygen, and chloride on the electrode surface (Figure 5.4a). The elemental composition determined from the EDX (SFigure 5.1) and the XPS is shown in Figure 5.4b. Figure 5.5

a,b,c show the HR-XPS for Cl2p, Ru3p and O1s, respectively. Ru 3p core-level spectra are analyzed instead of Ru3d to avoid peak overlapping with C1s core level spectra, which could deter the identification of Ru species appropriately. NIST database was used to assign the majority of the fitted peaks [321] and the fitted peak values of all the elements are shown in STable 5.2.

In Figure 5.5a, the peaks at 198.29 ± 0.02 and 199.99 ± 0.02 eV correspond to the Cl $2p_{3/2}$ and Cl $2p_{1/2}$, respectively, due to the presence of chlorides remained from the hydrous RuCl₃ precursor after the thermal decomposition (0.95 ± 0.05 atm % of Cl in the coating, Figure 5.4b).

Figure 5.5b shows Ru 3p spectra with a doublet fitted with curves assigned to the same chemical states as in Ru 3d spectra. In the Ru $3p_{3/2}$ part of the spectra, the curves with peaks at 462.87 ± 0.22, and 466.02 ± 0.30 eV were assigned to RuO₂, and RuCl₃ respectively. Spin-orbit splitting (SOS) between Ru $3p_{3/2}$ and Ru $3p_{1/2}$ is found to be ~22 eV. In the O1s core spectra shown in Figure 5.5c, RuO₂ is assigned to the curves with a peak centered at 530.35 ± 0.09 eV. Additionally, the peak at 532.43 ± 0.15 eV can be assigned to C=O [322]. Determined binding energies and fit parameters are shown in STable 5.2.



Figure 5.5. Fitted HR-XPS of a) Cl2p b) Ru3p and d) O1s. Black dots, olive and orange line represents, experimental data, background and fitted data respectively.

5.5 Electrochemical analysis

5.5.1 Cyclic voltammetry measurements

Cyclic voltammetry (CV) experiments were carried out for RuO₂-CNF electrodes prepared at different temperatures (Figure 5.6a). In order to reach a stable response, the two-electrode cell was initially cycled for 20 cycles at 100 mV/s, followed by five cycles at a given scan rate and the 5th cycle was then recorded and displayed in Figure 5.6a. This stabilization was done in order to open the pores in the electrode and remove the plausible effect of irreversible surface functionalities which would lead to irreversible redox peaks. Only the electrode prepared at 200 °C showed visible reversible broad peaks on the CV. SFigure 5.5 shows CV of the electrode prepared at 200 °C at different scan rates. The broad anodic peak centered at around 0.5 V and the corresponding cathodic peak centered at around 0.45 V (Figure 5.6a), can be deconvoluted into multiple peaks, which could be associated with the following simplified reaction [323]:

$$RuO_{x}(OH)_{y} + zH_{2}O + ze^{-} \rightarrow RuO_{x-z}(OH)_{y+z} + zOH^{-} \qquad Equation 5.1$$

All other electrodes exhibit almost a perfect rectangular pattern, similar to the EDLC behavior. However, the underlying charging/discharging reactions are both of the electrostatic and redox nature (Equation 5.1) and are well documented in the literature [324].



Figure 5.6. a) CV measurements of RuO₂-CNF electrodes prepared at different temperatures in a two-electrode set-up at 20 mV/s. b) corresponding specific capacitances measured.

The capacitance of the material was calculated from the CVs in Figure 5.6a using Equation 5.2, where a factor of 2 is used to calculate the capacitance of only one electrode [305,325].

$$C = 2 \frac{Q_{avg}}{\Delta V}$$
 Equation 5.2

where Q_{avg} (As = C) is the average cathodic and anodic charge, and ΔV (V) is the voltage window.

Samples of RuO₂-CNF prepared at 200 °C showed the highest capacitance, 944 ± 17 mF/cm², and the capacitance is shown to decrease with the increase in the electrode preparation temperature (Figure 5.6b). The presence of water in the lattice of the RuO₂ is the plausible reason for the increased capacitance at lower temperatures due to enhanced protonic and electronic conduction [326]. At higher temperatures (> 300 °C), RuO₂ is known to become more crystalline and loses water content, which leads to proton diffusion limitation causing reduced capacitance [193,327–329].

Figure 5.7a shows CV recorded at different scan rates for the electrodes prepared at 250 °C. The shape of the CV remains semi-rectangular even at higher scan rates, signifying the easy access of ions into the porous structure of the electrode to rapidly form a double layer along with lower series resistance. The linear dependence of the anodic current recorded at 0.5 V with varying scan rates (Figure 5.7b) suggests a surfacecontrolled behavior rather than a diffusion-controlled behavior. This is due to the easy accessibility of the ions into the pores followed by the occurrence of the pseudocapacitance redox reaction (Equation 5.1), as previously mentioned.



Figure 5.7. a) CV of RuO_2 -CNF electrodes prepared at 250 °C at scan rates of 5, 10, 20, 50, 80, 100, 200 mV/s following the direction of the arrows. b) Anodic current at a potential of 0.5 V vs scan rate for RuO_2 -CNF electrodes prepared at 250 °C.

5.5.2 Galvanostatic charge-discharge measurements

Although CV can be used to determine the capacitance of an electrode, a more suitable way of doing this is by employing the galvanostatic charge/discharge method, which more closely reflects the real use of a supercapacitor. The galvanostatic charge-discharge curves of CNF-RuO₂ electrodes produced at different temperatures were recorded at a current density of 20 mA/cm² and are shown in Figure 5.8a. These curves show symmetric triangular behavior, like most of EDLC/pseudo-capacitor materials [330] and affirm the extraordinary reversibility of the redox reaction. Contrary to CV measurement for 200 °C sample (Figure 5.6a) which showed broad peaks, the GCD for the same samples does not show any obvious deviation from linearity. This example alone clearly suggests the best method for evaluating capacitance would be GCD for obtaining more realistic capacitance.

Capacitance was calculated from the discharge curve using the following equation:

$$C = 2 \frac{j}{(dV/dt)}$$
 Equation 5.3

where C is the specific capacitance (F/cm²), j is the applied current density (A/cm²) and dV/dt is the slope of the discharge curve after the initial IR drop portion. A factor of 2 is used to estimate the capacitance for only one electrode. The capacitance values obtained at 20 mA/cm² for various electrodes with an operating voltage window from 0 to 0.8 V are summarized in Figure 5.8b.



Figure 5.8. a) GCD plots recorded at 20 mA/cm² for Ni-f + RuO₂ (red), Ni-f + CNF (black), and CNF-Ru electrodes prepared at 400, 350, 300, 250, and 200 °C - the temperature decreases in the direction of the arrow. b) corresponding specific capacitances measured.

As control electrodes, CNF on Ni-f and RuO₂ deposited directly on the Ni-f, are shown. The CNF electrode gave a capacitance of $142 \pm 7 \text{ mF/cm}^2$, which is in agreement with previous studies [331]. When RuO₂ was deposited on the Ni-f, the resulting capacitance decreased to $53 \pm 8 \text{ mF/cm}^2$. This shows that, despite the fact that RuO₂ is an

excellent pseudo-capacitor material whose capacitance is based on the occurrence of fast reversible redox reactions in the solid phase (Equation 5.1), applying it directly on the Ni-f current collector is not desirable. However, when the two configurations are combined together, the resulting capacitance increased tremendously, which is due to the combination of the high surface area template provided by the CNF and the pseudo-capacitive behavior of RuO₂. The capacitance reached a maximum value for the electrodes produced at 200 °C and 250 °C ($835 \pm 40 \text{ mF/cm}^2$ and $822 \pm 4 \text{ mF/cm}^2$, respectively). These values are significantly higher than those recorded on RuO₂-CNT and RuO₂-CNF based electrodes [332–337], RuO₂ graphene-based [338] and other ruthenium-based electrodes [339–342]. Some of the recent results reported in the literature are shown in Table 5.1.

Figure 5.8b shows that with an increase in electrode preparation temperature, the resulting capacitance decreases. This trend in capacitance behavior shows higher capacitance at lower oxide preparation temperatures when compared to previously studied RuO₂ electrodes [326,332,343–346]. The method of preparation employed in this work along with the underlying evenly distributed CNF has enabled higher capacitance values. Studies have reported that the protonic and electronic conduction pathway in the RuO₂. x H₂O varies with the water content within the rutile structure, thus influencing the achievable capacitance [347–349].

Electrode	Specific capacitance (mF/cm²)	Scan rate (mV/s)	Electrolyte	Reference
RuO ² electrodes deposited on to TiO ² nanofibers	Ca. 275	10	0.5 M H ₂ SO ₄	[350]
RuO ² deposited on the surface- roughened Ti plate	4.4	10	0.5 M H ₂ SO ₄	[350]
RuO ₂ deposited on TiO ₂ nanorods	74.8	10	0.5 M H ₂ SO ₄	[350]
RuO ₂ /CNT films	272	5	0.1 M Na2SO4	[333]
Ruthenium oxide nano string clusters anchored Graphene oxide	Ca. 584 (859 F/g)	5	1 M H ₂ SO ₄	[351]
Ruthenium oxide-carbon nanotube Composites	208.5	10	0.1 M Na2SO4	[352]
Pt nanotubes and ruthenium dioxide composite	320	2	0.5 M H ₂ SO ₄	[353]
Tubular ruthenium oxide on silicon 3D microstructures	99.3	5	0.1 M Na2SO4	[354]
graphene nano wall-ruthenium oxides	113	2	0.1 M Na2SO4	[355]
RuO2 thin films	53.82	5	H2SO4-PVA	[356]
RuO ₂ on CNT forest	37.7	100	0.5 M H2SO4	[357]
Ru nanoparticle with reduced graphene oxide	238.5	5	1 M NaNO3	[338]
RuO ₂ on CNF	777 ± 11 (822 ± 04)	20 (20 mA/cm ²)	6М КОН	Present work

Table 5.1. Capacitance summary of some recent ruthenium-based electrodes.

In order to investigate the influence of current density on the charging/discharging rate and the resulting capacitance, GCD curves for the electrode prepared at 250 °C were recorded (Figure 5.9a), and the variation of capacitance with current density is shown in Figure 5.9b. As it can be seen from Figure 5.9a, the shape of the GCD curves is not dependant on the current density; all the curves show symmetrical/triangular behavior. With an increase in current density, the charging/discharging rate increases, as evidenced by the increase in the corresponding slopes of the curves. To evaluate if this is at the expense of a decreased capacitance, the corresponding values were calculated; as it can be seen in Figure 5.9b, the capacitance shows a general decrease with the increase in current density, which is to be expected. Capacitance values change from roughly 830 mF/cm² at 3 mA/cm² to 760 mF/cm² at 100 mA/cm².

Most ruthenium-based capacitors have the disadvantage of lower capacitance (and thus also lower energy density) at higher charge/discharge currents [338,358–360]. However, for the RuO₂-CNF electrodes (Figure 5.9b), only a 10 % decrease in the capacitance is observed at a high current density of 100 mA/cm² when compared to the capacitance at 5 mA/cm². This is because the high surface area and the well-connected CNF support provide a template for the distribution of the RuO₂ leading to faster proton diffusion, less series resistance and the larger double layer area formation at the electrode surface, leading to these enhanced supercapacitor qualities.



Figure 5.9. a) GCD measurements for RuO₂-CNF electrodes at 3, 5, 10, 20, 50, 100 mA/cm² in the direction of the arrow. b) Variation in the specific capacitance with current density calculated from the corresponding GCD measurements.

5.5.3 Electrochemical impedance spectroscopy measurements

To elucidate the electrochemical characteristics of various components within the electrochemical cell, EIS measurements were performed (Figure 5.10a). Analyses are

carried out at a *dc* cell voltage of 0 V, and with a sinusoidal *ac* voltage amplitude of ± 10mV in the frequency range 10 mHz to 100 MHz. A semicircle in the higher frequency region (inset to Figure 5.10a) is attributed to the parallel combination of the charge transfer resistance (R_{ct}) and the corresponding pseudocapacitance. Only samples prepared at 200 °C show a clear semicircle at a higher frequency region. Remaining electrodes formed at the higher temperatures show an inclined line instead of the semicircle in the higher frequency region. Disappearance of semi-circle may be due to better conductivity of the coating and better accessibility of the porous region on the electrode [305,361].

All electrodes show a vertical trend in the lower frequency region, almost parallel to the imaginary impedance axis, indicating good capacitive behavior. Therefore, a series RC-model was adapted to interpret the data and the capacitances at a low frequency (0.01 Hz) were calculated for various samples using Equation 5.4 [362,363].

$$C = -\frac{1}{(2\pi f Z'')}$$
 Equation 5.4

where f (Hz) is the frequency, and Z'' (Ω cm²) is the imaginary part of the impedance. The calculated capacitance values are shown in Figure 5.10b, and they are comparable to the values obtained from CV (Figure 5.7b) and GCD (Figure 5.8b) measurements.



Figure 5.10. a) Nyquist plots for various RuO₂-CNF electrodes prepared at different temperatures (inset: zoomed-in the high-frequency region). b) Capacitances obtained using EIS measurements for electrodes prepared at different temperatures.

5.5.4 Energy and power density calculations

Figure 5.11 shows the Ragone plots of the RuO₂-CNF electrode produced at 250 °C, together with nickel oxide-CNF structures (unpublished work) and with CNF fibers

only [331]. Specific energy and specific power of the cell were calculated using Equation Equation 5.5 and Equation Equation 5.6 respectively. For the RuO₂-CNF electrode, a specific energy value varied from 362 mWh/m² to 336 mWh/m² when the power density was increased from 12 W/m² to 957 W/m². This translates roughly into a maximum energy density of 13.51 Wh/kg and a max power density of 35.71 kW/kg (estimated based on mass loading of RuO₂ only, and the mass loading is shown in SFigure 5.6). This performance is significantly higher than just that of CNF electrodes, and the ability to deliver higher specific power at higher specific energy is enhanced when compared to nickel-oxide CNF electrodes (Appendix C). The present specific energy results are comparable to other high specific capacitance yielding electrodes, such as RuO₂-CNT/CNF-based electrodes [50, 70–72], RuO₂-graphene oxide-based electrodes [54, 73] and other RuO₂-composite based electrodes [49, 74].

$$E = \frac{1}{8}C\Delta V^{2}$$
Equation 5.5
$$P = \frac{E}{t}$$
Equation 5.6



*Figure 5.11. Ragone plot comparing the performance of RuO*₂-*CNF (present work), CNF* [305] *and Nickel oxide-CNF.*

5.5.5 Three and two electrode measurement comparison

As shown in Figure 5.9b, capacitance decreases with an increase in current density. This could be related to the decrease in utilization of surface area of the electrode, i.e. to the accessibility of the electrode area to electrolyte ions. For pseudo-capacitors, it can also be related to a decrease in the depth of intercalation of protons below the metal-oxide surface area. In order to examine this in more detail, CV measurements in a three-electrode cells were recorded at various scan rates. A comparison with the two-electrode cell at a scan rate of 20 mV/s is presented in Figure 5.12a & b. The three-electrode configuration was used here because the potential of the reference electrode is fixed, thus enabling monitoring the behavior of only one electrode in a well-defined potential region, as a function of scan rate.


*Figure 5.12. CV of RuO*₂-CNF electrodes prepared at 250 °C in 6 M KOH electrolyte recorded at 20 mV/s *a*) using three-electrode set-up *b*) using two-electrode cell.

The CV curves with varying scan rates are shown in Figure 5.13a. These tend to slant at higher scan rates, suggesting higher series resistance. A comparison with EIS confirms higher series resistance in the three-electrode supporting this trend (SFigure 5.7). This effect diminishes in the two-electrode cell, as the electrodes are pressed against each other tightly, which then compresses the CNF and form a conducive network for



Figure 5.13. a) CV measurements of RuO₂-CNF prepared at 250 °C in a three-electrode system at scan rates of 5, 10, 20, 50, 80, 100, 200 mV/s following the direction of the arrows. b) change in capacitances with scan-rate (capacitances are reported per electrode).

better conductivity. Using the CV in Figure 5.13a, the corresponding capacitance values were calculated from the average cathodic and anodic charge (Figure 5.13b). A comparison of GCD measurements for RuO₂-CNF prepared at 250 °C electrodes at 5

mA/cm² is shown in SFigure 5.8. Variation of capacitances calculated using two and threeelectrode cell with applied frequency during EIS measurements is shown in SFigure 5.9.

To evaluate the contribution of the inner and outer layer of the electrode to the capacitance, Trisatti's method was used (Figure 5.14) using the results from the threeelectrode measurements [343]. At an infinitely high scan rate it is assumed that only the easily-accessible outer surface area of the electrode participates in the formation of the capacitance (C_{outer}), while at an infinitely low scan rate, a maximum (total) possible capacitance (C_{T}) is achieved. The intercept of the linear portion of the trend in Figure 5.14a with the ordinate yields a value of 60 mF/cm², which represents the contribution of an outer surface area of the electrode (C_{outer}) to the total capacitance. On the other hand, the intercept of the linear trend in Figure 5.14b yields a value of 1062 mF/cm², which includes both inner and outer surface capacitance (C_{inner}) to the total capacitance (C_{T}). The contribution of the inner surface capacitance (C_{inner}) to the total capacitance can then be calculated by subtracting C_{outer} from C_T , which yields a value of 1002 mF/cm².



Figure 5.14. a) Capacitance as a function of the inverse of scan rate. b) The inverse of capacitance as a function of scan rate. Red lines indicate linear fit.

5.5.6 Cycling stability

In order to evaluate the stability of the prepared RuO₂-CNF electrodes, long-term cycling (5000 cycles) GCD experiments were performed at a current density of 200 mA/cm² (Figure 5.15) in a full cell (i.e. 2 cell electrode). Electrodes prepared at 200 °C,

showed a steep linear decrease in capacitance until 3000 cycles and mostly remained stable during the later cycles. The electrodes were also observed to have poor physical stability when assembled into a cell with electrolyte, and the overall capacitance retention was ca. 60 % after 5000 cycles. Electrodes prepared at 250 °C, 300 °C, 350 °C, 400 °C showed a capacitance retention of 94 %, 95 %, 93 % and 81 % respectively after 5000 cycles. This also suggests that oxide forming temperatures of 250 °C and above provide stable coatings. All these electrodes showed a minor gradual decrease in capacitance. Even though electrodes prepared at 400 °C seemed to be mechanically stable after the cycling test, the increased dropped in capacitance retention could be mostly attributed to the architecture of the electrode. As deduced from TGA curves (SFig. 6), these electrodes barely have any hydrous protonic/hydroxyl ion conduction path, and the capacitance is solely depended on the electrochemically active surface area. The capacitance would have dropped due to the mechanical degradation of micro and meso porous area of the electrode with cycling. It was also found that the stability of the capacitance for the Ni-f / RuO₂-CNF structure generated at 250 °C is much better than other high capacitance ruthenium-based electrodes reported in the literature [332,368–372].



*Figure 5.15. specific capacitances at different GCD cycle numbers for various RuO*₂*-CNF electrodes measured at 200 mA/cm*²*.*

5.6 Conclusion

In this article, RuO₂ was coated directly on CNF forests grown on Ni-f. The influence of different preparation conditions on the electrochemical performance for supercapacitor applications was studied. The deposition of RuO2 shows to significantly increase the specific capacitance when compared to CNF only or RuO₂ only electrodes. This increase is due to the pseudocapacitance offered by RuO₂ along with the surface area of the CNF template, and the preparation conditions of the electrode. RuO₂ coated at 250 °C showed 94 % capacitance retention after 5000 cycles, and maximum specific energy and maximum specific power of 362 mWh/m² and 957 W/m². High specific capacitance, cycling stability and the facileness of the electrode preparation that easily enables scaled up, make this a promising material in applications where the charge per area is essential. This methodology can be used to prepare other metal oxide and conductive polymer coats for similar applications.

Acknowledgment

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5.7 Supplementary



SFigure 5.1. Energy dispersive spectra (EDX) spectrum of the hydrous RuO₂ coated CNF electrodes.



SFigure 5.2. TEM image of uncoated CNF. No hollow core can be observed in these CNF.



SFigure 5.3. Raman spectra of the un-coated CNF (in black) and RuO₂ coated CNF (in red). Peak positions were determined by fitting the curves with Lorentzian functions, after background subtraction and data normalization.

Fit parameters for D and G bands using Lorentzian function		
D Peak, cm ⁻¹	1344.43 ± 0.86	
G peak, cm ⁻¹	1586.34 ± 0.92	
D band FWHM, cm ⁻¹	151.52 ± 6.90	
G band FWHM, cm ⁻¹	79.56 ± 0.92	
Id/Ig	2.28 ± 0.08	
La (nm)	2.21 ± 0.80	

STable 5.1. Raman characterisation of CNF forest to calculate the crystallite size (La) and the defect density (I_D/I_G).

 L_a is calculated using SEquation 5.1 [318]. Where L_a in nm and E_L is the excitation energy in eV In this study EL is 2.33 eV corresponding to the 532 nm laser.

$$L_a = \frac{4 \cdot 4}{\frac{I_D}{I_G}} \left(\frac{2.41}{E_L}\right)^4$$
 SEquation 5.1



SFigure 5.4. a) HR-TEM of a RuO₂ coated CNF. b) EDX spectra performed in the region shown in a white square in Figure 5.4a.

Compound	Peak BE (eV)	FWHM (eV)
O1s (RuO ₂)	530.35 ± 0.09	2.20 ± 0.08
O1s (C=O)	532.43 ± 0.15	3.35 ± 0.18
Ru ₃ p ₃ (RuO ₂)	462.87 ± 0.22	3.49 ± 0.01
Ru ₃ p ₁ (RuO ₂)	484.96 ± 0.15	3.49 ± 0.01
Ru ₃ p ₃ (RuCl ₃)	466.02 ± 0.30	3.48 ± 0.02
Ru ₃ p ₁ (RuCl ₃)	488.07 ± 0.20	3.48 ± 0.02
Cl ₂ p ₃ (RuCl ₃)	198.29 ± 0.02	2.35 ± 0.24
Cl ₂ p ₁ (RuCl ₃)	199.99 ± 0.02	2.35 ± 0.24

STable 5.2 Fitted peak values for all the HR-XPS discussed in the main article



SFigure 5.5. a) CV at different scan rates for the RuO₂-CNF electrodes prepared at 200 °C. b) Peak potential at different scan rates for RuO₂-CNF-electrodes prepared at 200 °C. The anodic peak shift rightwards and the cathodic peaks shift leftwards with increase in the scan rate.



SFigure 5.6. Mass accumulation of RuO₂ on CNF directly grown on Ni-f.



SFigure 5.7. Comparison of Nyquist plots for RuO₂-CNF electrodes prepared at 250 °C measured using three-electrode and two-electrode cell. Three-electrode measurements show higher series resistance than the two electrode measurements.



SFigure 5.8. Comparison of GCD measurements for RuO₂-CNF prepared at 250 °C electrodes at 5 mA/cm² a) using three-electrode cell b) using two electrode cell.

With a series RC model to fit the EIS data, the real C'(ω) and imaginary C"(ω) parts of capacitances were calculated using SEquation 5.2 and SEquation 5.3 [276].

$$C'(\omega) = \frac{-Z''}{\omega |Z(\omega)|^2}$$
 SEquation 5.2

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$$C''(\omega) = \frac{Z'}{\omega |Z(\omega)|^2}$$
 SEquation 5.3

Where, -Z" and Z' are imaginary and real components of the impedance (Z, ohms), $\omega = 2\pi f$, and f is the frequency (Hz).

The relationship of the capacitance with frequency is shown in SFigure 5.9 (a and b) for the two and three-electrode measurements respectively. This demonstrates the decrease in C'(w) with an increase in frequency as observed previously in the Nyquist plot. C''(w) indicates the energy dissipation and this increases with the increase in frequency (note: capacitances are reported per electrode). As the peak C'' shifts to the higher frequency in the two-electrode cell than the three-electrode cell (SFigure 5.9), it is evident that the delivery of stored energy is slightly faster (i.e. delivers energy in less time) in the later cell setup at higher power.



SFigure 5.9. Variation of real and imaginary part of the capacitances with frequency measured using a) three-electrode and b) two-electrode cell.



SFigure 5.10. X-ray diffraction pattern of RuO₂-CNF electrode surface.

The strong occurrence of nickel peaks makes it hard to observe peaks of hydrous RuO₂. However, a small peak at $2\theta = 26$ can be ascribed to the carbon fibers [373]. The peaks at 2θ ; 44.45, 52.05, 76.62, 92.62, 98.16 all correspond to nickel.

Chapter 6 Conclusions

This thesis work focused primarily on producing electrodes for supercapacitors. For this purpose, it is desired to make electrodes that are binderless, have high specific capacitance and that can have good cycling stabilities. In order to achieve this, we introduced a novel technique to grow CNF directly on a Ni-f current collector. Most of the procedures published in the literature often require a catalyst deposition before the initiation of the CNF growth, and the growth temperatures are usually 650 °C or above. The method introduced in this thesis did not incorporate any external catalyst to initiate CNF growth and could grow dense CNF forest at a relatively low temperature of 400 °C. A thorough investigation of the preparation methods and the growth conditions was done and it was concluded that the dense CNF forests could be grown at temperatures as low as 400 °C, while the growth at higher temperatures, up to 750 °C, required etching of the Ni-f.

Later, with a slightly modified growth process, dense CNF forests were reproduced and used as electrodes in a EDLC type supercapacitor. This method not only provided binder-free electrodes, but also a uniform forest of CNF forming a 3-D architecture with its coverage within the foam structure, involving a wide range of pore sizes. These CNF ensured almost constant specific capacitance even when operated at higher currents. This was possible due to the mixed macro and mesoporosity created by the Ni-f substrate and the CNF forest along with the nanosized diameters of the long CNF structures. Additionally, the CNF were also hydrophilic due to the surface functionalities. This enabled good wetting of the electrodes and helped in lowering the ESR, enabling the electrodes to provide high specific power. This was possible as the entire CNF growth process was done at an atmospheric pressure, which also makes the process more economical. Added to its capacitance of $142 \pm 7 \text{ mF/cm}^2$ at 10 mA/cm^2 , which is on par with CNT-based electrodes reported in the literature, our electrodes also exhibited almost constant specific energy (ca. 60 mW/m²) across a varying specific power (81.95 W/m² to 3.97 W/m²). The ECSA was estimated to be 402 m²/g.

Further, this multi-porosity architecture was utilized as a template to form NiO₂ (Appendix B) and RuO₂ coatings on CNFs to enhance the performance metrics of supercapacitors by introducing pseudocapacitance. Finally, with the combination of RuO₂ and directly-grown CNF a specific capacitance of $822 \pm 4 \text{ mF/cm}^2$ was achieved at a current density of 20 mA/cm², which is among the highest specific capacitance values reported in the literature.

Similar preparation techniques can be applied with the CNF as templates along with other metal oxides or mixed metal oxides and can be used for applications like supercapacitors, electrochemical production of hydrogen and oxygen, batteries, capacitive deionization, sensors, and other electrochemical cells. These electrodes make interesting material particularly for thin energy storage devices, where higher energy per geometrical area is critical. Such devices include wearable devices, electronic panels, and small handheld devices.

Chapter 7

Original contribution and recommendations for future work

7.1 Original contributions

This thesis work has led to several original contributions in the field of carbon nanofibers and particularly with their use as supercapacitor electrodes. The following points outline the major original contributions of this work:

- For the first time, CNF were grown directly on nickel foam without using any external catalyst at a process temperature as low as 400 °C to achieve dense coverage. The process conditions were also engineered to change the CNF diameter, which makes this process attractive to produce CNF of a desired diamter as per the application requirements.
- This technique not only made the growth process simple but also created a well adhered, mechanically stable multi-porosity carbon structure on macroporous Nif which is hydrophilic, making it ideal for supercapacitor electrode application. The unique trend of constant capacitance with increasing current density was observed, which is a rare observance. This finding proved that electrode architecture can, in fact, change the specific energy dependence trend with a specific power.
- Ruthenium oxide was coated on directly-grown CNF using an easy-to-scale-up procedure for the first time and the effect of different oxide coating formation

temperatures on the electrochemical performance of the pseudo-capacitor was studied. Additionally, these electrodes had a minimal drop in their specific capacitance when the operating current density was increased. Such finding is a large improvement from other published results, which have often reported a significant drop in capacitance at higher currents. The achieved capacitance, along with its cyclic stability and capacitance retention, ranks these CNF-Ru-oxide electrodes amongst the best electrodes used for making supercapacitors.

7.2 Recommendation for future work

This thesis has proved the potential use of directly grown CNF and its subsequent modifications for its use as supercapacitor electrodes. The process can be made much more viable for commercial manufacturing by increasing the production speed. There are also many fundamental aspects regarding the electrode architecture and the material science aspects of the electrode that can be studied and fine-tuned to enhance the electrochemical performance of these electrodes. Some of the specific recommendations for future work are:

- 1. To switch the current batch growth of directly grown CNF to a roll to roll process which would significantly reduce the production time and cost.
- 2. The substitution of nickel foam with an even cheaper substrate in the form of a foam would make these cells even more economical. In this step, alloys (especially bimetallic-catalysts proven to enhanced carbon growth like Fe-Co, Fe-Mo) can be studied. This can be accompanied with detailed studies related to the growth kinetics

and including modeling related to the fluid dynamics of the feed gases in the reactor and the growth kinetics on the catalyst.

- 3. The mechanism behind the growth of CNF on nickel foam is not fully understood and a definite answer for what intermediate phase is formed during the growth phase is to be determined. Even though these are not directly related to the supercapacitor application, fundamental research on this could potentially describe several CNF, CNT and graphene growth mechanisms.
- 4. Having well graphitized CNF would enhance its conductivity and widen its potential applications. In order to achieve well graphitized CNF, more studies with the growth process are to be done. One method that could be tested based on the findings in this thesis, is annealing the CNF forest at higher temperatures after the growth step. From the experimental experience, a catalyst that has lower carbon solubility could probably reduce the wavy formation of graphitic layers and could form larger crystallites.
- 5. Energy density is a major metric that needs the utmost focus for improvement in order to commercialize the existing material to compete with batteries. Asymmetric electrode set-up with CNF or other carbon-based materials as the negative electrode, and metal oxide-CNF based electrodes as a positive electrode are worth investigating in order to operate over a wider potential window.
- 6. Even though there are few studies, including this thesis, which have investigated the effect of water content in ruthenium oxide, the actual mechanism for the enhancement of capacitance is still not well understood. Water content in the structure and solid morphology are the most probable factors. Evaluating the effect of electrolyte type (aqueous, organic, gel-polymer type) on the capacitance obtained for the hydrous ruthenium oxide would also be interesting.

- 7. Dip and drop coating methods used in this work for forming the metal oxide is a very convenient method for very large-scale production. A method to form ideal metal oxide integrated along with the CNF growth in the horizontal CVD furnace would be an interesting innovation towards commercial success.
- 8. CNF studied in this work can be used for other applications including capacitive deionization, water purification, Li-batteries, and other material composites. It can be also used as a catalyst bed for various known transition metal catalysts for the purpose of fuel cell and electrochemical production of hydrogen and oxygen.

Appendix A

Projects and conference articles that have resulted from this Ph.D. work have been listed below, classified as student projects, conference articles, unpublished work.

Student projects co-supervised during my doctoral work:

- 1. Layered carbon nanofiber and activated carbon electrodes for high energy supercapacitors by Lalita Bharatula.
- Effect of various carbon blacks on activated carbon-based supercapacitors by Wadah Rafie.

Conferences:

- Ruthenium oxide- CNF electrodes for high energy density binderless supercapacitors D. Sridhar et al. 30th International Conference on Diamond and Carbon Materials, Sep 08-12, 2019, Seville, Spain.
- Ruthenium oxide- CNF electrodes for high energy density binderless supercapacitors D. Sridhar et al. Polytechnique /McGill /Laval University Spring Research Day, March 19, 2019, Montreal, Quebec.
- 3. Layered carbon nanofiber and activated carbon electrodes for high energy supercapacitors L. Bharatula, D. Sridhar (as supervisor) et al. Nov 20, 2018. Chemical eng. research day McGill University, Montreal, Quebec.

- Binderless carbon nanofiber electrodes as long-lasting supercapacitor electrodes D. Sridhar et al. 8th ECS Montreal student symposium. March 27, 2018. Montreal, Quebec.
- Binderless carbon nanofiber electrodes as long-lasting supercapacitor electrodes D. Sridhar et al. Polytechnique -McGill University Research Day. April 17, 2018. Montreal, Quebec.
- Direct growth of carbon nanofibers on nickel foam and its application as electrochemical supercapacitor electrodes D. Sridhar et al. 231st ECS Meeting. May 28
 June 2, 2017. New Orleans, Louisiana.
- Electrochemical and surface analysis of modified nickel foam used for direct growth of carbon nanofibers D. Sridhar et al. 7th ECS Montreal student symposium. May 26, 2017. Montreal, Quebec.
- Study on the effect of current collector etching on the contact resistance of supercapacitors D. Sridhar et al. 6th ECS Montreal Student Symposium. 10 June 2016. Montreal, Quebec.

Unpublished works:

- Electrochemical studies of modified nickel foam used for carbon nanofiber growth D. Sridhar, J.L. Meunier, S. Omanovic.
- Carbon nanowalls on copper foam and its applications for supercapacitors D.Sridhar, S.Omanovic, J.L. Meunier.

Appendix B

Binary phase diagram of nickel/ Nature of catalyst and nickel

Often catalysts are chosen based on the carbon solubility and the nature to form graphite precipitation. Metals like Cu and Zn have extremely low solubility of carbon and hence cannot be used as a catalyst for carbon growth. Metals like nickel, iron, and cobalt have C solubility ranging from ca. 0.5–1.0 wt.% with the temperature ranging between 800–900 °C. Once saturation of carbon in these metal catalysts is reached, the graphite precipitation as tubes (single, double or multi-wall) or fibers begin. In between, there could be the formation of intermediate carbides which are often meta-stable [374]. The relationship between melting point and carbon solubility as a function of particle diameter for a few materials is shown in Figure B. 1. For a nickel, it is very apparent that the melting point significantly reduces when the particle diameter is reduced below 60 nm. Similarly, the solubility of carbon for nickel increases steeply as the diameter reduces below 20 nm.



Figure B. 1. a) melting temperatures of few metals as a variation with particle diameter b) solubility of carbon as a function of particle diameter. Reprinted With permission IOP Publishing: Journal of Physics: Condensed Matter [375].



Figure B. 2. Ni-C phase system. Reprinted with permission from Springer Nature: Bulletin of Alloy Phase Diagrams [376].

Figure B. 2 shows the Ni-C phase diagram. It can be observed that there is almost no carbon solubility in the bulk nickel below 800 °C. However, this scenario drastically changes in the presence of nanostructures and the solubility of carbon will occur at lower temperatures. For the same reason, we could grow CNF at a relatively lower temperature of 400 °C.

Appendix C

Nickel oxide on directly grown carbon nanofibers for energy storage applications

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C.1 Preface

This chapter presents an article that have been submitted to a peer-reviewed journal in January 2020, and can be cited as:

Abraham G. Vidales, Deepak Sridhar, Jean-Luc Meunier, Sasha Omanovic. Nickel oxide on directly grown carbon nanofibers for energy storage applications, Journal Energy Technology. submitted. January 2020

Author specific contributions:

D. Sridhar (Ph.D. candidate) conceived the idea, planned the experiments, prepared CNF forest and performed XPS, performed electrochemical tests, and supercapacitor analysis section. A. Gomez contributed to the introduction, coating of CNF with nickel oxide and analysis of H production section. J-L. Meunier and S. Omanovic provided insightful comments on the results, provided funding support for the experiments, and reviewed the manuscripts.

Abstract

Nickel oxide on directly grown carbon nanofibers (CNF-NiO) electrodes were fabricated and used as cathodes for hydrogen production by water electrolysis and as electrode materials for supercapacitors. Tafel polarization from the CNF-NiO electrodes showed an improvement of the hydrogen evolution reaction. This was attributed to the increment of the electrochemically active surface area, conductivity, and to the synergy effects between the nickel oxide, carbon nanofibers and nickel foam substrate. When used for supercapacitor applications, these electrodes showed a specific capacitance of ca. 776.20 ± 26 mF cm-2 at a current density 3 mA cm-2. These electrodes prepared using a facile method also exhibited a capacitance retention of 89.00 % even after 3000 cycles with a coulombic efficiency of 89.00 % when cycled at 20 mA cm-2. Considering the simplistic approach of the electrode preparation, the stability and the capacitance, this method opens avenue to try various metal oxide deposit on the directly grown CNF template.

Keywords: Carbon nanofibers, Hydrogen; Metal oxides, Supercapacitors; Water electrolysis.

C.2 Introduction

According to the Intergovernmental Panel on Climate Change (IPCC), since the industrial revolution, global warming is rapidly increasing and the record set of temperatures reached in the last 25 years is a tangible proof of this [377]. The dependence on fossil energies results in emissions of greenhouse gases, with carbon dioxide (CO₂) (80% of the contribution) as the product of combustion. As global energy demand continues to grow, CO₂ emissions are expected to rise by 1.3% annually; consequently, the use of fossil fuels for energy needs will increase resulting in critical environmental problems in the world.

In the same context, fossil fuels are rapidly being depleted. The most optimistic estimates show that there are oil reserves for another 100 years [378,379]. Therefore, new energy resources are quickly being designed to reduce the amount of unbalanced anthropogenic CO₂ and avoid possible detriments from our current standard of living. With this regard, the society is seeking ways to decrease the reliance on fossil fuels by trying to find alternative energy production and storage devices. In this research work, the use of nickel oxide (NiO) on directly grown carbon nanofibers (CNF) as electrodes is considered for application in hydrogen generators (water electrolyzers) and electrochemical supercapacitors (ES), as ways of storing (surplus) green electricity (e.g., produced by wind turbines or solar panels).

Hydrogen (H₂) is considered to be the best alternative to the current fossil fuel energy economy [380–382]. Besides, H₂ has the highest specific energy density (per mass), its chemical energy can be converted directly into electrical energy using fuel cells, or it can also be burned, in both cases producing just pure water [383]. However, renewable

avenues (mostly by water electrolysis) currently provide only 4% of H₂, and the other 96% comes from hydrocarbon reforming [384,385]. As such, environmental savings/benefits to produce H₂ gas are minimal considering plenty of fossil fuels required and amount of CO₂ produced by their reformation. Hence, renewable techniques for H₂ production must be employed instead [386]. Water electrolysis can be the proper technology to address these issues [384]. Moreover, when used in combination with solar/wind/hydroelectricity-producing systems, water electrolysis provides a clean route to H₂, without the consumption of fossil fuels or the emission of CO₂ [383]. Unfortunately, among the industrial methods of H₂ production, water electrolysis is not yet costcompetitive due to its high operating costs.

A significant portion of these costs is associated with the poor performance, fouling susceptibility, and insufficient durability of current electrocatalyst materials (cathodes) on which the hydrogen evolution reaction (HER) takes place [387]. Moreover, currently, the best-performing HER electrocatalyst is platinum (Pt). To overcome these significant barriers without significantly sacrificing catalytic performance, numerous research efforts have been devoted to reducing the Pt usage or to replacing it with other materials [388–391].

With this in mind, specific metal oxide electrodes have demonstrated excellent performances in the cathodic evolution of H₂ [392–395]. Two aspects make metal oxides interesting for applications as a HER cathode material: their better corrosion stability and fouling resistance, in comparison to pure metals. As a consequence of the different surface chemistry of oxides, compared to the respective pure metals, oxides are more resistant to deactivation caused by the (electro)deposition of ions (impurities) dissolved in the electrolyte [394]. Additionally, some research studies claim that the oxidative

treatment of the cathode material could lead to a relative improvement of its performance [392–395].

Furthermore, metal oxides can be used as electrodes in electrochemical supercapacitors. Electrochemical supercapacitors store potential energy in an electric field. They are considered to be the bridge gap between capacitors and batteries. Their main advantage is that they can store much more energy per unit mass than conventional capacitors and can accept and deliver charge much faster and with a much greater number of cycles than standard batteries. There are two main types of supercapacitors based on the mechanism of energy storage: electrochemical double-layer capacitors and pseudocapacitors. The first one uses mostly carbon-based electrodes, which exhibit much higher electrostatic double-layer capacitance due to a larger accessible surface area. The second one uses metal oxide or conducting polymer electrodes with a high electrochemical pseudocapacitance, which is achieved by reversible faradaic electron charge-transfer with redox reactions in the solid phase. The second type of supercapacitor can yield higher energy density than the carbon-based supercapacitors. This research work aimed to develop nickel oxide (NiO) and carbon nanofibers (CNF) electrodes to be used as both cathodes for H₂ production by water electrolysis and as electrochemical supercapacitor electrode materials, in an alkaline electrolyte.

C.3 Experimental Procedure

C.3.1 Electrode synthesis

A nickel foam (Nif) structure in the shape of a disc having 16 mm in diameter and 80 μm in thickness were punched from a foam sheet (MTI Corp., USA), cleaned using 0.1

M acetic acid (Fisher Scientific, USA), and then sonicated in ethanol (Fisher Scientific, USA) for 10 minutes to remove surface impurities. This disc of Nif was first used as a substrate for the growth of carbon nanofiber (CNF). The CNF forest-like growth on the inside and outside surfaces of the Nif structure was described previously [305]. Cleaned Nif are placed on a ceramic boat inside a quartz tube (internal diameter 55 mm; length 1220 mm) within a horizontal furnace (Lindberg-Blue HTF5500; USA, 120V/30A). A flow of 500 SCCM of argon (MEGS Specialty Gases Inc., 99.999 wt.% pure, Canada) was supplied in the furnace throughout the process. After 30 minutes of preheating at 683 K, 50 SCCM of acetylene (MEGS specialty Gases Inc., Canada, dissolved, 99.999 wt.% pure) were passed through the quartz tube as a carbon source for 5 minutes, followed by a 30 minutes growth time at the same temperature. Then the samples were cooled down to room temperature. The diameter of these CNF was typically ca. 50 nm. These nanometersized CNF forest-like structure covering the micron-sized porosity of the foam makes it a nano-structured surface inside micro-structured cavity. Afterward, nickel oxide (NiO) was deposited by dipping the CNF structure using using a dip coater (MTI, TL0-01 Desktop Dip Coater, USA) with an immersion time of 1 minute into the precursor solution and withdrawal speed of 1 cm s⁻¹. The precursor solution used was 0.2 M NiCl₂.6H₂O (purity 99.9%, Sigma-Aldrich, Canada), dissolved in deionized water (resistivity 18.2 M Ω cm). After the CNF structures were dipped and removed from the metal-precursor solution, the samples were dried in an oven at 373 K for five minutes to evaporate the solvent and subsequently transferred into a furnace at 573 K for fifteen minutes. The samples were then removed and allowed to cool at room temperature for ten minutes. In total, three layers were deposited by dip coating, and final thermal treatment/calcination was effectuated at 573 K for one hour to decompose the metal salts into the desired metal oxides. Finally, the resulting samples (referred to as CNF-NiO) were rinsed several times in deionized water to remove excess salts that may still be on

the surface, dried in argon, and then weighed again (using an ultramicro balance Sartorius S4, USA) to determine the electrocatalyst loading before electrochemical testing. For comparison purposes, a flat Ni foil (purity: 99.9%; hereafter referred to as Ni-s) was used as a control cathode. The bare Nif (diameter 16 mm) weighed 74.94 ± 1.49 mg cm⁻², while CNF accumulation and NiO coating accumulation were 3.79 ± 0.37 mg cm⁻² and 7.06 ± 0.85 mg cm⁻² per side, respectively.

C.3.2 Material characterization

Scanning Electron Microscope (SEM) was used to investigate the surface morphology, topography, and structure of the deposited NiO on CNFs (CNF-NiO), while Energy Dispersive Spectroscopy (EDS) was conducted to quantify their elemental bulk composition. Both measurements were performed using a Hitachi SU-3500 variable Pressure with SEM/EDS detectors (Hitachi, Japan). Furthermore, High-Resolution X-ray Photoelectron Spectroscopy (HR-XPS) examined the surface elemental composition and oxidative states of the samples employing a Thermo Scientific K-alpha X-ray Photoelectron Spectrometer (Thermo Fisher Scientific, USA).

C.3.3 Electrochemical analysis

The electrocatalytic activity of the electrodes toward hydrogen evolution and their capacitive behavior were investigated using Linear Tafel Polarization (LTP), Chronoamperometry (CA), Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), and Galvanostatic Charge/Discharge (GCD). These measurements were performed in a standard three-electrode electrochemical cell in 1 M KOH (prepared
using 96 wt.% KOH, Fisher Scientific, USA) at room temperature and atmospheric pressure. The working electrode (WE) was housed in a Teflon holder (WonATech CO. Ltd.) exposing a geometric surface area of the electrode to the electrolyte of 1 cm² (11.28 mm diameter). A saturated calomel electrode (SCE) (Accumet electrode, Fisher Scientific, USA) was used as the reference electrode and a graphite rod as the counter electrode (CE). During the measurements, the CE was separated from the cell by a glass frit (Ace Glass, Inc., USA) to prevent oxygen formed on the CE to migrate towards the WE and interfere with the HER. To maintain an oxygen-free electrolyte, the electrolyte solution was purged with argon prior electrochemical measurements for 30 minutes and continued to be purged during the measurements. The electrochemical measurements were carried out in a computer-controlled potentiostat/galvanostat (Autolab PGSTAT30, Metrohm, the Netherlands) using NOVA software (v. 2.3; Metrohm, the Netherlands).

C.4 Results and discussion

C.4.1 Surface characterization of the electrodes

Figure C. 1 shows the SEM images of the nickel foam (Nif, substrate), carbon nanofiber (CNF) forest, and CNF forest with a NiO coating (CNF-NiO). It is to be noted that nickel is not only present as nickel oxide, but also as nickel chloride as discussed below in the XPS analysis. These images confirm a dense growth of a CNF forest and indicate that the deposition of the NiO coatings on the CNF did not affect their structure. As seen, the underneath structure of the fiber forest is thick and open, which increases the available surface area and enables a better contact of the electrolyte and electrode. This potentially results in a higher number of surface reaction sites for the HER, and thus



Figure C. 1. SEM micrographs of the a) Nif, b) CNF forest on Nif (CNF), c) NiO on CNF forest (CNF-NiO).

in enhanced apparent HER kinetics when the electrode is used as a cathode in the water electrolyzer. In the case of use of the material as a supercapacitor electrode, the structure in Figure C. 1c enables facilitated mass transport of ions during the charging and discharging of the electrode (open structure) and also higher charge storage (large specific surface area).

As illustrated in Figure C. 1a and 1b, the growth of CNF is dense and covers the entire Nif surface area, including the pores. These nanostructures seen in Figure C. 1c consist of multiple structural fibers, which give a multi-structure architecture, increasing the electrochemically active surface area. EDS spectra and the determined atomic percentages are shown in SFigure C 1 and STable C 1 respectively.

Figure C. 2a shows the XPS survey spectrum of the CNF-NiO electrode, confirming the presence of nickel in oxide states, nickel chloride salts, and chloride. The atomic percentages of nickel, oxygen, chloride, and carbon (surface composition) are 27.65 ± 1.40 , 40.24 ± 1.41 , 20.34 ± 1.89 , 11.77 ± 0.79 , respectively. Figure C. 2b-e show the HR-XPS of carbon, oxygen, nickel, and chloride, respectively. The NIST database is used to assign the fitted peaks [321], a Shirley type background subtraction is used to correct the background, and a mixed Laurentia-Gaussian line shape function is used to fit the HR-XPS. STable C 2 shows deconvolution peak energy values.

The three deconvoluted curves in Figure C. 2b with peaks at 284.8, 286.1 \pm 0.2 eV, 289.2 \pm 0.1 for carbon HR-XPS can be assigned to C-C (adventitious carbon), C-O, and C=O. This indicates the presence of oxygen-containing surface species that functionalized the underlaying CNF. Given that the penetration of the beam is up to 8-10 nm, the detection of carbon suggests that not the whole CNF surface area was covered by NiO and/or that the thickness of the NiO layer is smaller than the beam penetration depth.

However, these peaks could be simply due to surface contamination while handling samples in the ambient atmosphere [396].

In Figure C. 2*c*, the peaks at 531.2 ± 0.1 eV, 531.9 ± 0.1 eV and 532.6 ± 0.1 eV for the oxygen HR-XPS fitted curves correspond to oxygen in Ni(OH)², C-O and in C=O. It should be noted that the response at 531.9 eV could also be associated with NiO or Ni₂O₃ or Ni(OH)². Ni 2p_{3/2} portion of the Ni2P HR-XPS is shown in Figure C. 2*d*, and the corresponding sensitivity factor is used for the quantification of the fitted curves. Peaks of the fitted curves at 855.6 eV ± 0.01 and 861.7 ± 0.1 eV can be assigned to Ni in Ni(OH)² and to its satellite peak (Figure C. 2d). Nevertheless, these binding energies overlap with the vibrations of Ni₂O₃ / Ni₂O₃·*x*H₂O and NiO. Therefore, the existence of these species cannot be dismissed. NiCl₂ and its satellite peak can be attributed to the deconvoluted curves with vibrations at 856.6 ± 0.03 eV and 865.4 ± 0.2 eV [397]. In the prepared electrode samples, 16.1 ± 1.3 at.%. is associated with Ni(OH)², and 11.1 ± 1.0 at.% is associated with NiCl₂, which accounts to a total nickel content of ca. 27 at.%.

HR-XPS of Cl₂ 2p (Figure C. 2e) is fitted with two curves with peaks separated by a spin-orbit splitting \approx 1.6 eV at 198.8 ± 0.03 eV (2p_{3/2}) and 200.4 ± 0.03 eV (2p_{1/2}) which is assigned to NiCl₂ and quantifies to 20.9 ± 3.7 at.%. This quantity is twice of the Ni component associated with NiCl₂ as every Ni is bonded with two Cl atoms and hence justifies the fitted curves.



Figure C. 2. XPS spectra of the CNF-NiO electrode: a) survey spectrum; HR-XPS of b) C 1s, c) O 1s, d) Ni 2p3/2, and e) Cl 2p regions. Black dots, red lines and olive lines are experimental data, fitted data and background respectively.

C.4.2 Hydrogen evolution reaction

A HER electrocatalyst should exhibit a few characteristics, such as to enable large cathodic current density at low overpotentials, but also to be durable (mechanically and electrocatalytically) [398,399]. To investigate the HER performance of the CNF-NiO electrode and to compare its behavior to that of pure Ni-s plate (current state-of-the-art in alkaline water electrolysis cells, and control electrocatalyst in this work), Nif, and CNF electrochemical measurements were conducted in 1 M KOH at room temperature by linear sweep voltammetry (LSV) and chronoamperometry (CA). Figure C. 3 presents the results, where all polarization curves were corrected for iR-drop. As it is seen, the results obtained from LSV (Figure C. 3a) and CA (Figure C. 3b) are in agreement (it is noted that for the CA graph, current density values were obtained when the steady state was reached). The Tafel curve recorded on the control cathode (Ni-s) shows a classical Tafelian behavior, with a long linear region. This control surface yielded the lowest electrocatalytic activity in the HER among the investigated electrodes. As expected, the Nif cathode yielded a higher HER current than the control surface (by ca. 1.2 orders of magnitude), which could be prescribed to its larger surface area (see Figure C. 1c). The Tafel curve of the CNF electrode yielded a higher HER current than that of the Nif cathode; given that carbon is a very poor HER catalyst, this could be prescribed to the substantial increase in cathode surface area (Figure C. 1). However, the presence of Ni nanoparticles imbedded at the tip of the CNF can potentially play a role in the catalytic activity (these nanoparticles were being generated through the tip-growth pattern during the CNF synthesis).



Figure C. 3. Linear Tafel polarization curves for the electrodes investigate in this study, recorded in 1 M KOH using a) linear sweep voltammetry at a scan rate of 1 mVs-1, and b) chronoamperometry (galvanostatic polarization).

Figure C. 3 also shows that the HER current increased significantly when a layer of NiO was added on top of CNF, indicating the excellent electrocatalytic performance of NiO. From the linear part of Tafel curves in Figure C. 3 and employing Equation C.1 below, kinetic parameters related to the HER, the Tafel slope, (*bc*, mV dec⁻¹), the electron transfer

coefficient (α) and the exchange current density (j_0 , μ A cm⁻²) were determined. The corresponding values are presented in Table C.1[398,399].

$$\eta = a + b_c log(j)$$
 Equation C.1

Where,

$$a = \frac{2.3 RT}{\alpha nF} \log(j_0)$$

$$b_c = \frac{2.3 RT}{\alpha nF}$$

and η is the overpotential (V), *j* is the current density (A cm⁻²), *R* is the gas constant (8.314 J K⁻¹ mol⁻¹), *T* is the temperature (K), *n* is the number of electrons exchanged (-) and *F* is the Faraday constant (96485 J).

As shown in Table C.1, the electrodes yielded Tafel slopes ranging from 84 to 196 mV dec⁻¹. A small Tafel slope is highly desirable since it enables an increase in HER kinetics with a smaller overpotential change (energy input) [400,401]. According to the results in Figure C. 3, among all tested electrodes, the CNF-NiO exhibits the lowest Tafel slope (~84 mV dec⁻¹), indicating the superior electrocatalytic activity in comparison to the other electrodes [400]. Besides, our catalysts lead to a Tafel slope much lower than many previously reported inexpensive and efficient HER catalysts in the same electrolyte [398,402,403].

	6	<i>,</i>	0		
-	Sample	b_c (mV dec ⁻¹)	α	<i>j</i> ₀(µA cm ⁻²)	
-	Ni-s	196 ± 14	0.29 ± 0.04	3.1 ± 0.6	
	Nif	152 ± 12	0.39 ± 0.04	110 ± 26	
	CNF	103 ± 3	0.56 ± 0.09	190 ± 90	
	CNF-NiO	84 ± 6	0.67 ± 0.05	360 ± 60	

Table C.1: Tafel slope, transfer coefficient, and apparent exchange current density values for theinvestigated electrodes obtained from polarization curves in Figure 4.

In general, two elementary reaction steps are involved in the HER (in the alkaline medium), the Volmer step being the first and mandatory step:

$$H_2O + e^- \leftrightarrow M - H_{ads} + OH^-$$
 Equation C.2

followed by either the Heyrovsky step:

$$H_{2}O + M - H_{ads} + e^{-} \leftrightarrow H_{2} + M + OH^{-}$$
 Equation C.3

or the Tafel step:

$$M-H_{ads} + M-H_{ads} - \leftarrow \rightarrow H_2 + M \qquad Equation C.4$$

If the Volmer step associated with proton absorption is rate-determining, a Tafel slope of ~120 mV dec⁻¹ is expected, while the Heyrovsky and Tafel steps give ~40 and ~30 mV dec⁻¹, respectively [388,404]. The Tafel slope values presented in Table C.1 166

indicate that the Volmer step is the rate-determining step in the HER on Ni-s, Nif, and CNF electrodes. The deviation of the Tafel slope on the Ni-s electrode to higher values indicates a poorer electrocatalytic performance of this electrode in the HER. On the other hand, the CNF-NiO electrode yielded a value of 84 mV dec⁻¹, which is between the values that characterize the Heyrovsky and Volmer steps as the rate-determining step (*rds*).

Figure C. 4a summarizes the HER onset overpotential on the electrodes investigated in this work. The onset overpotential for CNF-NiO is around 20 mV, and it is considerably lower than that for the Ni-s control electrode, and it is very close to the thermodynamic potential of HER (i.e., 0 V) [388,405].

Apparent values of the exchange current densities (j_0) for the HER on the investigated electrodes were determined, and the values are presented in Table C.1 [406]. These values represent the 'starting point' for the electrocatalytic activity in the HER, and high values are desirable. Comparison of the cathode performance based on the published data is difficult, since operation conditions, such as the temperature, electrolyte type and concentration and the actual surface of electrodes often differ vastly; however, based on j_0 an indirect comparison can be made. Such comparison results in a value for Ni-s that is close to that one published on the HER Volcano curve [407], while the value for CNF-NiO is very close to the values of the best-performing noble-metal HER electrocatalysts (e.g., Pt/C, $j_0 = 0.6$ mA cm⁻² in 0.1 M KOH [408]). However, it should be noted that this is an apparent exchange current density value, which takes into account both the intrinsic (actual electrocatalytic activity of the material) and extrinsic (surface area of the electrode) effects. Nevertheless, it shows that by depositing NiO on CNF (CNF-NiO), the electrocatalytic activity (per geometric area) of the HER approaches that of the best-performing HER electrocatalysts(e.g., Ir, Ru), and is much higher than those

recorded on other Ni-based catalysts (Ni₁Co₉/C, $j_0 = 9.1 \times 10^{-3}$ mA cm⁻² [409], Ni₆₄W₃₆, $j_0 = 1.6 \times 10^{-6}$ mA cm⁻² in 0.1 M NaOH [410]) and Ni-oxide based catalysts (Ni_{0.6}Mo_{0.4}O_x, $j_0 = 23.9\mu$ A cm⁻² [398], Ni_{0.2}Co_{0.8}O_x 25.3, $j_0 = 25.3 \mu$ A cm⁻² in 1 M NaOH, [402]). Table C.1 also shows that the apparent exchange density values follow the same trend as the Tafel slope values.

The electron transfer coefficients (α) given in Table C.1 were similarly calculated from the Tafel curves presented in Figure C. 3. This parameter allows for the comparison of the electrocatalytic activity of electrodes, and larger values would indicate better HER performance. All three electrodes have a significantly higher α value than the control Nis. This trend is similar to the trend in electrocatalytic activity for the other parameters shown in Table C.1, again evidencing that the CNF-NiO electrode is the most active in the HER among the investigated materials.

Finally, another common way of quantifying the electrochemical activity of the electrodes for HER is comparing the resulting current densities at a fixed overpotential. Figure C. 4b illustrates the difference in electrocatalytic activity of all the electrodes at a fixed overpotential of -80 mV. CNF-NiO yields the highest extrinsic electrocatalytic activity with a value two orders of magnitude larger than control Ni-s. The trend in the electrocatalytic activity presented in Figure C. 4b is similar to the trends in values presented in Table C.1.

The HER catalytic activity of electrodes is related to a number of factors, among which the intrinsic electrocatalytic activity, the morphology, the electrochemical active surface area, and the electrical conductivity of the electrodes are the fundamental factors. The Nif and CNF as the supports for NiO provides a large surface area, allowing more active sites to be exposed for electrolyte access [411]. The internal gaps within the Nif increase the surface area accessible to the electrolyte, maximizing the number of active electrocatalytic sites for the HER [412]. Considering that the directly-grown CNF on Nif are well graphitized [305], it is expected an enhance of the HER performance due to the improved electrical conductivity of CNF-NiO when compared to NiO, which is a semiconductor [401]. Coating CNF by NiO would also improve the electrical contact between the catalyst and the electrode [401]. Namely, the outstanding HER activity for our electrode can be attributed to the synergistic effects from the good electrical conductivity, large surface area, and 3D porous structures of the Nif and CFN supports and NiO catalyst.



Figure C. 4. a) Onset HER overpotential and b) HER current density at -80 mV obtained from the polarization curves in Figure 4.

C.4.4 Electrochemical supercapacitors

The previous section demonstrated that the CNF-NiO electrode has a remarkable electrocatalytic activity in HER. In this section, the performance of this, and the other three electrodes investigated in this work, for charge storage applications as supercapacitor electrodes is discussed.

The initial evaluation of the charge storage/delivery capability of the CNF-NiO electrode was done by cyclic voltammetry (CV). Figure C. 5 shows the corresponding CV, together with the CVs of CNF and Nif. For the initial comparison of the charge storage/delivery capacitance, the area under the CVs can be considered. As expected, when the Nif is covered by CNF, the CV charge increased significantly. However, the deposition of the NiO layer on the CNF (CNF-NiO) resulted in two effects. First, the charge storage/delivery capacity of the electrode further increased, by a significant amount, and the contribution of faradaic reactions became evident, by the presence of a broad peak in the anodic sweep (around -0.3 V) and cathodic current at potentials more negative than -0.4 V. This indicates the deviation from a pure electrochemical-double layer (EDLC) capacitor, which yields a rectangular shape CV. Given that the surface of CNF and CNF-NiO exposed to the electrolyte is similar (Figure C. 1), it appears that the difference between the capacitance of CNF and CNF-NiO is due to the faradaic contribution of the NiO layer.



Figure C. 5. Cyclic voltammograms of bare nickel foam (Nif), CNF grown on nickel foam (CNF), and nickel oxide-coated CNF-nickel foam (CNF-NiO) recorded at a scan rate of 10 mV s⁻¹.

The capacitance (*C*, in F) of the three electrodes was calculated from the results in Figure C. 5 using the following equation:

$$C = \frac{Q}{\Delta E}$$
 Equation C.5

where Q is the average charge of the anodic and cathodic CV cycle (C), and ΔE is the working potential window (V); the values calculated for Nif, CNF, and CNF-NiO are 9.07 ± 0.57 mF cm⁻², 164.36 ± 34.43 mF cm⁻², and 640.20 ± 33.84 mF cm⁻², respectively at a scan rate of 10 mV s⁻¹. One can see that the deposition of the NiO layer on top of CNF resulted in four-fold increase in capacitance, which represents a rather significant improvement in the charge storage/delivery capability of the electrode. Nickel oxides are observed to show quite visible/defined CV current peaks when used for electrochemical storage [413,414]. However, in our experiments the CNF-NiO electrode did not exhibit this behavior, probably due to the architecture of the electrodes. This architecture could have led to the fast intercalation of the ions into the NiO subsurface structure in order to compensate the change in the oxidative state of nickel during the anodic/cathodic bias, thus rendering the electrode to behave predominately as a pseudocapacitor rather than as a Nernstian system [55,415]. Such kind of pseudocapacitive behavior has been reported for nickel-based electrodes in the past [413,416]. Moreover, in three-electrode measurements, the selected potential window also influences the shape of the CV, along with the chosen electrolyte.

In order to verify CV results in Figure C. 5 and further characterize the capacitive behavior of the three electrode, galvanostatic charge/discharge (GCD) measurements were performed and the results are presented in Figure C. 6. The shape of the CNF-NiO curve is in accordance with the CV curve shape, displaying a slight deviation from the pure double-layer capacitors. Namely, the GCD curve exhibits a minor non-linearity due to the occurrence of redox reactions related to the change in oxidative state of Ni in NiO, as already discussed above. It is interesting to note that even CNF electrodes showed slight non-linearity (Figure C. 6), mostly due to redox reactions caused by surface functionalities. Interestingly, such deviation from linearity of the same samples was completely absent in our previous findings when tested in a 2-electrode cell [245,305].

Since the behavior is of the pseudo-capacitive nature (non-linear and asymmetric), the corresponding capacitance values were calculated using the following equation:

$$C = \frac{2E_{\rm d}}{\Delta E^2} \qquad \qquad Equation \ C.6$$

where ΔE represents the discharge potential window (V), and E_d stands for the discharge energy (J) which is calculated as:

$$E_{\rm d} = \int_{E_{min}}^{E_{max}} E(t)dt \qquad \qquad Equation \ C.7$$

At higher currents, there is a significant iR-drop leading to a narrower operating potential window (Δ E); therefore, 0.8 V is considered as Δ E in all the calculations. The calculated specific capacitance values of Nif, CNF, and CNF-NiO are 1.83 ± 0.48 mF cm⁻², 154.33 ± 39.25 mF cm⁻², 776.20 ± 26.00 mF cm⁻² respectively. Similar to the CV results, the data in Figure C. 6 shows evidences that the presence of contribution of the NiO layer towards charge storage/delivery is rather significant. In fact, the capacitance of our CNF-NiO electrode seems to be sufficiently higher than that of electrodes reported in literature, such as NiO, MnO₂ [37,417] based electrodes , Co(OH)₂ [418], MoO₃ based [419] and WO₃ based [420], Fe₂O₃ [37] and many other electrodes [418,421,422].



Figure C. 6. GCD curves recorded at a current density of 3 mA cm⁻² *for the three electrodes used in this study.*

To investigate the charging-discharging behavior of the CNF-NiO electrode in more detail, GCD curves were recorded at various current densities, and the results are presented in Figure C. 7. With an increase in current, the charging/discharging time decreases, indicating a decrease in the electrode capacitance. Employing Equations (6) and (7), the resulting capacitance values were calculated and shown in Figure C. 8. It can be seen that with an increase in current density, the specific capacitance decreased from 776.20 \pm 26.00 mF cm⁻² to 338.81 \pm 85.06 mF cm⁻². This behavior is commonly reported in the literature [287,423,424], and can be related to the dependence of NiO layer utilization-depth for charge storage. Namely, at higher currents the redox zone in the NiO solid phase becomes "shallower", and this is because there is no sufficient time for the intercalating ions (mostly H⁺) to reach deeper under the oxide surface and compensate the nickel redox charge change [425,426]. In addition, the migration of counter-ions required to compensate the electrostatic double-layer charging in narrow pores in the



Figure C. 7. GCD for CNF-NiO recorded at 3, 5, 10, 20 mA cm⁻², in the direction of the arrow.



Figure C. 8. Variation of specific capacitance with current density (capacitance calculated using discharge curves) for the CNF-NiO electrode.

material is limited at higher currents, thus diminishing the utilization of the whole surface area of the electrode.

Figure C. 9 shows the Ragone plot for the CNF-NiO electrode. Although the data presented above was recorded in a 3-electrode cell, Equation 8 and Equation 9 were used to calculate the specific energy (Ecell, mWh m⁻²) and specific power (P, Wm⁻²) in order to approximate the results for a 2-cell configuration. The specific energy values varied from 150.9 ± 37.8 to 345.0 ± 11.6 mWh m⁻², with the decrease in specific power from 54.6 ± 2.2 to 5.7 ± 0.1 W m⁻². This energy density range is much higher than that obtained on other metal oxide-based and CNT-metal oxide-based electrodes [416,427].

$$E_{cell} = 2E$$
 Equation C.8

$$P = \frac{E_{cell}}{t_d} \qquad \qquad Equation \ C.9$$



Figure C. 9. Ragone plot for the CNF-NiO cell with 1M KOH.

Electrochemical impedance spectroscopy (EIS) measurements were made in the frequency range 10 mHz to 100 kHz, with an AC perturbation of 10 mV (RMS) to study the charge related process at the electrode-electrolyte interface. Figure C. 10a represents the EIS response of the Nif electrode. The spectrum is characterized by a linear trend in the mid and low-frequency region (denoted by CPE), with a slope of ca. 45-deg. This indicates that the behavior of the Nif electrode is controlled mostly by mass-transport, rather than its capacitive behavior. Namely, pure capacitance would yield a linear trend at ca. 90-deg. Further, the spectrum indicates the presence of one time constant at high frequencies (τ_1 , see the inset to the figure), which represents only the minor contribution to the impedance behavior of the system.

When CNF are anchored on the Nif (CNF), the EIS response changes (Figure C. 10b). In this case, the spectrum reveals the presence of two-time constants and a linear behavior at lower frequencies. The first time constant at high frequencies (τ_1 , inset to the Figure C. 10b) can be related to the response of the Nif (similar to Figure C. 10a), while

the EIS response of CNF could then be associated with the second time constant, τ₂, in the mid-frequency range. Unlike the 45-deg angle of the linear part of the EIS spectra of Nif in Figure C. 10a, the linear region of the CNF response in Figure C. 10b is significantly steeper, indicating a significant contribution of the capacitive behavior of the system. Thus, the linear response in Figure C. 10b, denoted by the constant phase element, CPE, can be related to the pseudo-capacitive behavior of CNF, i.e. to surface redox reactions occurring on CNF (oxidation/reduction of oxygen-containing functional groups).



Figure C. 10. Nyquist plot for a) Nif b) CNF and c) CNF-NiO electrodes recorded with an AC perturbation of 10 mV. The inset plots are zoomed-in portions of the higher frequency region.

When CNFs are covered by a NiO layer (CNF-NiO), the EIS behavior further changes and three-time constants could now be seen on the Nyquist plot (Figure C. 10c). The first time constant (τ_1 , inset to the Figure C. 10c) can be related to the response of Nif, the second time constant (τ_2 , inset to the Figure C. 10c) can be prescribed to the response of NiO-uncovered CNF, while the third time constant (τ_3 , main plot of Figure C. 10c) can then be related to the response of NiO, followed by the CPE behavior in the lowfrequency region.

An important parameter related to supercapacitors is their stability, i.e. retention of initial capacitance with cycling. In order to investigate this behavior of the CNF-NiO electrode, 3000 charging/discharging cycles were continuously made, at a current density of 20 mA cm⁻² (Figure C. 11). After 3000 cycles, 89.5% retention in capacitance, with a Coulombic efficiency of 89% (SEquation 1) can be observed. The shape of the discharge curve remained almost the same without any additional distortion (SFigure C 2), suggesting that no significant changes in the structure of the electrode occurred during the cycling. Further, the slight decrease in Coulombic efficiency after 3000 cycles evidences that only minor decrease in reversibility of the electrode occurred. This performance is comparable to similar electrodes which were prepared using complex synthesis process [428,429].



Figure C. 11. Capacitance retention of the CNF-NiO electrodes at various cycles, measured at 20 mA cm-2.

C.5 Conclusions

In this article, CNF-NiO electrodes were synthesized and tested as electrodes for hydrogen evolution and supercapacitors. For hydrogen production, they showed promising results. CNF-NiO showed a significant improvement in all the electrochemical parameters such as Tafel slope, transfer coefficient, and exchange current density as compared to metallic nickel (the state-of-the-art catalyst). It should be interesting to determine the use of these electrodes for PEM-type electrolyzers and to produce the mixed oxides in the form of nanoparticles, which could potentially increase the electrode electrical conductivity and their electrochemical activity. Furthermore, they could potentially be used as anodes for the oxygen evolution reaction (OER). These electrodes also showed capacitance of 776.20 \pm 26.00 mF cm⁻² at a specific current of 3 mA cm⁻², and capacitance retention of 89% after 3000 cycles. The specific energy varied from 150.58 \pm 37.80 to 344.97 \pm 11.56 mWh m⁻² with the change in specific power from 54.62 \pm 2.17 to 5.71 \pm 0.1 W m⁻². The facile synthesis of the electrodes and high capacitance makes these electrodes attractive for supercapacitor application provided there is a method to decrease the iR-drop at higher current density.

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C.6. Supplementary material

STable C 1:	Relative	atomic	percentage	of elements	present ir	the	coatings	obtained	by
EDS.									

Element	At. %
Ni	25.9 ± 3.15
Ο	9.6 ± 3.19
С	48.1 ± 5.31
Cl	16.3 ± 2.15



SFigure C 1. Energy-dispersive spectroscopy (EDS) spectra of CNF-NiO. Elemental identifiers are given above the respective peak

	Peak BE	FWHM	Area	Atomic
Compound	(eV)	(eV)	(N)	%
2P _{3/2} (NiCl ₂)	198.79 ± 0.03	1.51 ± 0.04	90.63 ± 0.81	14.69 ± 2.73
2P _{1/2} (NiCl ₂)	200.43 ± 0.03	1.35 ± 0.04	38.73 ± 1.37	6.25 ± 0.99
C1s (C-C)	284.79 ± 0.00	1.50 ± 0.11	28.16 ± 4.29	4.49 ± 0.65
C1s (C-O)	286.08 ± 0.16	2.24 ± 0.37	26.26 ± 8.26	4.00 ± 0.68
C1s (C=O)	289.17 ± 0.12	1.72 ± 0.29	19.76 ± 3.80	3.09 ± 0.20
O1s (Ni(OH)2)	531.17 ± 0.06	1.43 ± 0.02	217.12 ± 46.47	33.82 ± 1.77
O1s (C-O)	531.86 ± 0.05	0.91 ± 0.06	25.92 ± 11.04	3.99 ± 1.37
O1s (C=O)	532.62 ± 0.08	1.59 ± 0.16	15.95 ± 4.40	2.47 ± 0.40
Ni2p3 (Ni(OH)2)	855.64 ± 0.01	1.66 ± 0.11	37.81 ± 5.24	5.97 ± 0.32
Ni2p3 (NiCl ₂)	856.63 ± 0.04	2.70 ± 0.27	56.08 ± 14.76	8.68 ± 1.01
Ni 2P3 sat				
(Ni(OH)2, /NiO)	861.67 ± 0.07	3.41 ± 0.06	66.47 ± 20.44	10.16 ± 1.59
Ni (2p3 NiCl2)	865.41 ± 0.22	3.43 ± 0.01	14.76 ± 1.26	2.38 ± 0.41

STable C 2. Details of the XPS curve fit.



SFigure C 2. GCD of the CNF-NiO electrode recorded at a current density of 20 mA cm-2. This plot confirms the pseudocapacitance like behavior. The discharge curves maintain the same shape, and no real phase changes are seen.

 $\eta_c = \frac{t_d}{t_c}$

SEquation C.1

Where, η_c is Coulombic efficiency (%) t_d is discharge time (s) t_c is charging time (s)

References

- W. Raza, F. Ali, N. Raza, Y. Luo, K.H. Kim, J. Yang, S. Kumar, A. Mehmood, E.E. Kwon, Recent advancements in supercapacitor technology, Nano Energy. 52 (2018) 441–473. doi:10.1016/j.nanoen.2018.08.013.
- [2] D.C. Green, Renewable Energy Sources, in: Home Energy Inf. SE 7, Springer International Publishing, 2014: pp. 47–51. doi:10.1007/978-3-319-11349-4_7.
- [3] P. Sharma, T.S. Bhatti, A review on electrochemical double-layer capacitors, Energy Convers. Manag. 51 (2010) 2901–2912. doi:10.1016/j.enconman.2010.06.031.
- [4] M. Seredych, M. Koscinski, M. Sliwinska-Bartkowiak, T.J. Bandosz, Active pore space utilization in nanoporous carbon-based supercapacitors: Effects of conductivity and pore accessibility, J. Power Sources. 220 (2012) 243–252. doi:10.1016/j.jpowsour.2012.07.074.
- [5] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, Electrochim. Acta. 45 (2000) 2483–2498. doi:10.1016/S0013-4686(00)00354-6.
- [6] Y. Chen, X. Zhang, H. Zhang, X. Sun, D. Zhang, Y. Ma, High-performance supercapacitors based on a graphene–activated carbon composite prepared by chemical activation, RSC Adv. 2 (2012) 7747. doi:10.1039/c2ra20667f.
- [7] H.-J. Choi, S.-M. Jung, J.-M. Seo, D.W. Chang, L. Dai, J.-B. Baek, Graphene for energy conversion and storage in fuel cells and supercapacitors, Nano Energy. 1 (2012) 534–551. doi:10.1016/j.nanoen.2012.05.001.
- [8] C. Abbey, G. Joos, Supercapacitor energy storage for wind energy applications, IEEE Trans. Ind. Appl. 43 (2007) 769–776. doi:10.1109/TIA.2007.895768.
- [9] Y. Hou, R. Vidu, P. Stroeve, Solar Energy Storage Methods, Ind. Eng. Chem. Res. 50 (2011) 8954–8964. doi:10.1021/ie2003413.
- [10] Z. Zhou, M. Benbouzid, J. Frédéric Charpentier, F. Scuiller, T. Tang, A review of energy storage technologies for marine current energy systems, Renew. Sustain. Energy Rev. 18 (2013) 390–400. doi:10.1016/j.rser.2012.10.006.
- [11] G.L. Park, A.I. Schäfer, B.S. Richards, Renewable energy-powered membrane technology: Supercapacitors for buffering resource fluctuations in a wind-powered membrane system for brackish water desalination, Renew. Energy. 50 (2013) 126– 135. doi:10.1016/j.renene.2012.05.026.
- [12] D.B. Murray, J.G. Hayes, D.L. O'Sullivan, M.G. Egan, Supercapacitor Testing for Power Smoothing in a Variable Speed Offshore Wave Energy Converter, Ocean. Eng. IEEE J. 37 (2012) 301–308. doi:10.1109/JOE.2012.2188157.
- [13] J.R. Miller, A.F. Burke, Electrochemical capacitors: challenges and opportunities for real-world applications, Electrochem. Soc. Interface. 17 (2008) 53.
- [14] Global Supercapacitor Market worth USD 2,096.16 Million by 2022, (n.d.).

https://www.zionmarketresearch.com/news/super-capacitor-market (accessed November 23, 2019).

- [15] Battery Industry Analysis: Market Size, Growth, Forecast & Trends, (n.d.). https://analysis.technavio.com/battery-industry-research (accessed December 2, 2019).
- [16] A. Bello, F. Barzegar, D. Momodu, J. Dangbegnon, F. Taghizadeh, M. Fabiane, N. Manyala, Asymmetric supercapacitor based on nanostructured graphene foam/polyvinyl alcohol/formaldehyde and activated carbon electrodes, J. Power Sources. 273 (2015) 305–311. doi:10.1016/j.jpowsour.2014.09.094.
- [17] S. Zhong, C. Zhan, D. Cao, Zeolitic imidazolate framework-derived nitrogendoped porous carbons as high performance supercapacitor electrode materials, Carbon N. Y. 85 (2015) 51–59. doi:10.1016/j.carbon.2014.12.064.
- [18] A. Sahoo, Y. Sharma, Synthesis and characterization of nanostructured ternary zinc manganese oxide as novel supercapacitor material, Mater. Chem. Phys. 149–150 (2015) 721–727. doi:10.1016/j.matchemphys.2014.11.032.
- [19] W. Du, X. Xu, D. Zhang, Q. Lu, F. Gao, Green synthesis of MnO x nanostructures and studies of their supercapacitor performance, Sci. China Chem. (2015). doi:10.1007/s11426-014-5242-4.
- [20] T. Fan, S. Tong, W. Zeng, Q. Niu, Y. Liu, C.-Y. Kao, J. Liu, W. Huang, Y. Min, A.J. Epstein, Self-assembling sulfonated graphene/polyaniline nanocomposite paper for high performance supercapacitor, Synth. Met. 199 (2015) 79–86. doi:10.1016/j.synthmet.2014.11.017.
- [21] L. Li, X. Zhu, D. Yang, L. Gao, J. Liu, R.V. Kumar, J. Yang, Preparation and characterization of nano-structured lead oxide from spent lead acid battery paste., J. Hazard. Mater. 203–204 (2012) 274–82. doi:10.1016/j.jhazmat.2011.12.021.
- [22] W. Deng, Y. Zhang, L. Yang, Y. Tan, M. Ma, Q. Xie, Sulfur-doped porous carbon nanosheets as an advanced electrode material for supercapacitors, RSC Adv. 5 (2015) 13046–13051. doi:10.1039/C4RA14820G.
- [23] C. Yang, Y. Kim, J. Miyawaki, Y.A. Kim, M. Yudasaka, S. Iijima, K. Kaneko, E ff ect of the Size and Position of Ion-Accessible Nanoholes on the Speci fi c Capacitance of Single-Walled Carbon Nanohorns for Supercapacitor Applications, (2015). doi:10.1021/jp510630e.
- [24] S. Bose, T. Kuila, A.K. Mishra, R. Rajasekar, N.H. Kim, J.H. Lee, Carbon-based nanostructured materials and their composites as supercapacitor electrodes, J. Mater. Chem. 22 (2012) 767–784. doi:10.1039/C1JM14468E.
- [25] D.S. Su, R. Schlögl, Nanostructured carbon and carbon nanocomposites for electrochemical energy storage applications, ChemSusChem. 3 (2010) 136–168. doi:10.1002/cssc.200900182.
- [26] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical

supercapacitors, Chem. Soc. Rev. 41 (2012) 797. doi:10.1039/c1cs15060j.

- [27] H.I. Becker, Low voltage electrolytic capacitor, (1957). https://www.google.com/patents/US2800616.
- [28] D.L. Boos, Electrolytic capacitor having carbon paste electrodes, (1970). https://www.google.com/patents/US3536963.
- [29] B.E. Hart, R.M. Peekema, Electrochemical double layer capacitor, (1972). http://www.google.com/patents/US3652902.
- [30] M. Conte, Supercapacitors Technical Requirements for New Applications, Fuel Cells. 10 (2010) 806–818. doi:10.1002/fuce.201000087.
- [31] F.P. Malaspina, Supercapacitor electrode and method of fabrication thereof, (1992). https://www.google.com/patents/WO1992011649A1?cl=en.
- [32] L. Dong, C. Xu, Y. Li, Z.H. Huang, F. Kang, Q.H. Yang, X. Zhao, Flexible electrodes and supercapacitors for wearable energy storage: A review by category, J. Mater. Chem. A. 4 (2016) 4659–4685. doi:10.1039/c5ta10582j.
- [33] Flexible batteries power the future of wearable technology, (n.d.). https://www.manchester.ac.uk/discover/news/flexible-batteries-power-the-futureof-wearable-technology/ (accessed November 30, 2019).
- [34] S.M. Lipka, J.R. Miller, T.D. Xiao, J. Dai, Asymmetric electrochemical supercapacitor and method of manufacture thereof, (2009). https://www.google.com/patents/US7576971.
- [35] T. Brousse, P.-L. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y. Zhou, F. Favier, D. Bélanger, P. Simon, Long-term cycling behavior of asymmetric activated carbon/MnO2 aqueous electrochemical supercapacitor, J. Power Sources. 173 (2007) 633–641. doi:10.1016/j.jpowsour.2007.04.074.
- [36] J. Ji, L.L. Zhang, H. Ji, Y. Li, X. Zhao, X. Bai, X. Fan, F. Zhang, R.S. Ruoff, Nanoporous Ni(OH)2 Thin Film on 3D Ultrathin-Graphite Foam for Asymmetric Supercapacitor, ACS Nano. 7 (2013) 6237–6243. doi:10.1021/nn4021955.
- [37] P. Yang, Y. Ding, Z. Lin, Z. Chen, Y. Li, P. Qiang, M. Ebrahimi, W. Mai, C.P. Wong, Z.L. Wang, Low-Cost High-Performance Solid-State Asymmetric Supercapacitors Based on MnO2 Nanowires and Fe2O3 Nanotubes, Nano Lett. 14 (2014) 731–736. doi:10.1021/nl404008e.
- [38] P.-C. Chen, G. Shen, Y. Shi, H. Chen, C. Zhou, Preparation and Characterization of Flexible Asymmetric Supercapacitors Based on Transition-Metal-Oxide Nanowire/Single-Walled Carbon Nanotube Hybrid Thin-Film Electrodes, ACS Nano. 4 (2010) 4403–4411. doi:10.1021/nn100856y.
- [39] H. Wang, M. Yoshio, A.K. Thapa, H. Nakamura, From symmetric AC/AC to asymmetric AC/graphite, a progress in electrochemical capacitors, J. Power Sources. 169 (2007) 375–380. doi:10.1016/j.jpowsour.2007.02.088.
- [40] K.K. Denshchikov, M.Y. Izmaylova, A.Z. Zhuk, Y.S. Vygodskii, V.T. Novikov, A.F.

Gerasimov, 1-Methyl-3-butylimidazolium tetraflouroborate with activated carbon for electrochemical double layer supercapacitors, Electrochim. Acta. 55 (2010) 7506–7510. doi:10.1016/j.electacta.2010.03.065.

- [41] J. Yan, T. Wei, B. Shao, F. Ma, Z. Fan, M. Zhang, C. Zheng, Y. Shang, W. Qian, F. Wei, Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors, Carbon N. Y. 48 (2010) 1731–1737. doi:10.1016/j.carbon.2010.01.014.
- [42] K.H. Kim, M. Yang, K.M. Cho, Y.-S. Jun, S.B. Lee, H.-T. Jung, High quality reduced graphene oxide through repairing with multi-layered graphene ball nanostructures., Sci. Rep. 3 (2013) 3251. doi:10.1038/srep03251.
- [43] R. Saliger, U. Fischer, C. Herta, J. Fricke, High surface area carbon aerogels for supercapacitors, J. Non. Cryst. Solids. 225 (1998) 81–85. doi:10.1016/S0022-3093(98)00104-5.
- [44] S. Ye, J. Feng, P. Wu, Deposition of three-dimensional graphene aerogel on nickel foam as a binder-free supercapacitor electrode, ACS Appl. Mater. Interfaces. 5 (2013) 7122–7129. doi:10.1021/am401458x.
- [45] M.V. Kiamahalleh, S.H.S. Zein, G. Najafpour, S.A. Sata, S. Buniran, Multiwalled Carbon Nanotubes Based Nanocomposites for Supercapacitors: a Review of Electrode Materials, Nano. 07 (2012) 1230002. doi:10.1142/S1793292012300022.
- [46] H. Xia, S. Meng, G. Yuan, C. Cui, L. Lu, A Symmetric RuO 2 / RuO 2 Supercapacitor Operating at 1 . 6 V by Using a Neutral Aqueous Electrolyte, Electrochem. Solid-State Lett. 15 (2012) 62–65. doi:10.1149/2.023204esl.
- [47] T. Zhu, S.J. Zheng, Y.G. Chen, J. Luo, H.B. Guo, Y.E. Chen, Improvement of hydrothermally synthesized MnO2 electrodes on Ni foams via facile annealing for supercapacitor applications, J. Mater. Sci. 49 (2014) 6118–6126. doi:10.1007/s10853-014-8343-8.
- [48] A. Bello, K. Makgopa, M. Fabiane, D. Dodoo-Ahrin, K.I. Ozoemena, N. Manyala, Chemical adsorption of NiO nanostructures on nickel foam-graphene for supercapacitor applications, J. Mater. Sci. 48 (2013) 6707–6712. doi:10.1007/s10853-013-7471-x.
- [49] X. Xia, D. Chao, C.F. Ng, J. Lin, Z. Fan, H. Zhang, Z.X. Shen, H.J. Fan, VO2 nanoflake arrays for supercapacitor and Li-ion battery electrodes: performance enhancement by hydrogen molybdenum bronze as an efficient shell material, Mater. Horizons. 2 (2015) 237–244. doi:10.1039/C4MH00212A.
- [50] S.B. Kulkarni, U.M. Patil, I. Shackery, J.S. Sohn, S. Lee, B. Park, S. Jun, Highperformance supercapacitor electrode based on a polyaniline nanofibers/3D graphene framework as an efficient charge transporter, J. Mater. Chem. A. 2 (2014) 4989–4998. doi:10.1039/C3TA14959E.
- [51] H. Zhang, Z. Hu, M. Li, L. Hu, S. Jiao, A high-performance supercapacitor based

on a polythiophene/multiwalled carbon nanotube composite by electropolymerization in an ionic liquid microemulsion, J. Mater. Chem. A. 2 (2014) 17024–17030. doi:10.1039/C4TA03369H.

- [52] H.P. de Oliveira, S.A. Sydlik, T.M. Swager, Supercapacitors from Free-Standing Polypyrrole/Graphene Nanocomposites, J. Phys. Chem. C. 117 (2013) 10270–10276. doi:10.1021/jp400344u.
- [53] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nat Mater. 7 (2008) 845–854. http://dx.doi.org/10.1038/nmat2297.
- [54] Y. Gogotsi, R.M. Penner, Energy Storage in Nanomaterials Capacitive, Pseudocapacitive, or Battery-like?, ACS Nano. 12 (2018) 2081–2083. doi:10.1021/acsnano.8b01914.
- [55] P. Simon, Y. Gogotsi, B. Dunn, Where Do Batteries End and Supercapacitors Begin?, Science (80-.). 343 (2014) 1210–1211. doi:10.1126/science.1249625.
- [56] A. Balducci, R. Dugas, P.L. Taberna, P. Simon, D. Plée, M. Mastragostino, S. Passerini, High temperature carbon–carbon supercapacitor using ionic liquid as electrolyte, J. Power Sources. 165 (2007) 922–927. doi:10.1016/j.jpowsour.2006.12.048.
- [57] R.J. Gilliam, J.W. Graydon, D.W. Kirk, S.J. Thorpe, A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures, Int. J. Hydrogen Energy. 32 (2007) 359–364. doi:10.1016/J.IJHYDENE.2006.10.062.
- [58] W. Ma, H. Nan, Z. Gu, B. Geng, X. Zhang, Superior performance asymmetric supercapacitors based on ZnCo2O4@MnO2 core-shell electrode, J. Mater. Chem. A. 3 (2015) 5442–5448. doi:10.1039/C5TA00012B.
- [59] H. Xia, B. Li, L. Lu, 1.8 V symmetric supercapacitors developed using nanocrystalline Ru films as electrodes, RSC Adv. 4 (2014) 1111–11114. doi:10.1039/C3RA47396A.
- [60] B.W. Ricketts, C. Ton-That, Self-discharge of carbon-based supercapacitors with organic electrolytes, J. Power Sources. 89 (2000) 64–69. doi:10.1016/S0378-7753(00)00387-6.
- [61] K. CHIBA, T. UEDA, H. YAMAMOTO, Highly Conductive Electrolytic Solution for Electric Double-layer Capacitor Using Dimethylcarbonate and Spiro-type Quaternary Ammonium Salt, Electrochemistry. 75 (2007) 668–671. doi:10.5796/electrochemistry.75.668.
- [62] P. Kurzweil, M. Chwistek, Electrochemical stability of organic electrolytes in supercapacitors: Spectroscopy and gas analysis of decomposition products, J. Power Sources. 176 (2008) 555–567. doi:10.1016/j.jpowsour.2007.08.070.
- [63] W. Lu, L. Qu, L. Dai, K. Henry, Superior Capacitive Performance of Aligned Carbon Nanotubes in Ionic Liquids, ECS Trans. 6 (2008) 257–261. doi:10.1149/1.2943245.

- [64] A. Balducci, U. Bardi, S. Caporali, M. Mastragostino, F. Soavi, Ionic liquids for hybrid supercapacitors, Electrochem. Commun. 6 (2004) 566–570. doi:10.1016/j.elecom.2004.04.005.
- [65] M. Anouti, L. Timperman, A pyrrolidinium nitrate protic ionic liquid-based electrolyte for very low-temperature electrical double-layer capacitors, Phys. Chem. Chem. Phys. 15 (2013) 6539–6548. doi:10.1039/C3CP44680H.
- [66] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, Carbons and electrolytes for advanced supercapacitors, Adv. Mater. 26 (2014) 2219–2251. doi:10.1002/adma.201304137.
- [67] Y. Shao, M.F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R.B. Kaner, Design and Mechanisms of Asymmetric Supercapacitors, Chem. Rev. 118 (2018) 9233–9280. doi:10.1021/acs.chemrev.8b00252.
- [68] V. S. Bagotsky, A. M. Skundin, Y. M. Volfkovich, Electrochemical Supercapacitors with Carbon Electrodes, in: Electrochem. Power Sources, John Wiley & Sons, Inc., 2014: pp. 263–313. doi:10.1002/9781118942857.ch27.
- [69] S.A. Hashmi, R.J. Latham, R.G. Linford, W.S. Schlindwein, Conducting polymerbased electrochemical redox supercapacitors using proton and lithium ion conducting polymer electrolytes, Polym. Int. 47 (1998) 28–33. doi:10.1002/(SICI)1097-0126(199809)47:1<28::AID-PI3>3.0.CO;2-C.
- [70] H. Yu, J. Wu, L. Fan, Y. Lin, K. Xu, Z. Tang, C. Cheng, S. Tang, J. Lin, M. Huang, Z. Lan, A novel redox-mediated gel polymer electrolyte for high-performance supercapacitor, J. Power Sources. 198 (2012) 402–407. doi:10.1016/j.jpowsour.2011.09.110.
- [71] J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen, G. Shen, Flexible asymmetric supercapacitors based upon Co9S8 nanorod//Co3O4@ RuO2 nanosheet arrays on carbon cloth, ACS Nano. 7 (2013) 5453–5462. doi:10.1021/nn401450s.
- [72] R. Latham, Supercapacitors using polymer electrolytes based on poly(urethane), Solid State Ionics. 147 (2002) 243–248. doi:10.1016/S0167-2738(02)00023-1.
- [73] B.E. Francisco, C.M. Jones, S.H. Lee, C.R. Stoldt, Nanostructured all-solid-state supercapacitor based on Li 2S-P 2S 5 glass-ceramic electrolyte, Appl. Phys. Lett. 100 (2012). doi:10.1063/1.3693521.
- [74] V. Ruiz, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, Influence of electrode preparation on the electrochemical behaviour of carbon-based supercapacitors, J. Appl. Electrochem. 37 (2007) 717–721. doi:10.1007/s10800-007-9305-5.
- [75] F. Lufrano, P. Staiti, M. Minutoli, Influence of Nafion Content in Electrodes on Performance of Carbon Supercapacitors, J. Electrochem. Soc. 151 (2004) A64. doi:10.1149/1.1626670.
- [76] K.-C. Tsay, L. Zhang, J. Zhang, Effects of electrode layer composition/thickness and electrolyte concentration on both specific capacitance and energy density of

supercapacitor, Electrochim. Acta. 60 (2012) 428–436. doi:10.1016/j.electacta.2011.11.087.

- [77] P. Azaïs, Manufacturing of Industrial Supercapacitors, Supercapacitors Mater. Syst. Appl. (2013) 307–321. doi:10.1002/9783527646661.ch10.
- [78] D. Yu, K. Goh, H. Wang, L. Wei, W. Jiang, Q. Zhang, L. Dai, Y. Chen, Scalable synthesis of hierarchically structured carbon nanotube-graphene fibres for capacitive energy storage., Nat. Nanotechnol. 9 (2014) 555–62. doi:10.1038/nnano.2014.93.
- [79] F. Markoulidis, C. Lei, C. Lekakou, E. Figgemeier, D. Duff, S. Khalil, B. Martorana, I. Cannavaro, High-performance Supercapacitor cells with Activated Carbon/MWNT nanocomposite electrodes, IOP Conf. Ser. Mater. Sci. Eng. 40 (2012) 012021. doi:10.1088/1757-899X/40/1/012021.
- [80] S.R. Sivakkumar, W.J. Kim, J.-A. Choi, D.R. MacFarlane, M. Forsyth, D.-W. Kim, Electrochemical performance of polyaniline nanofibres and polyaniline/multiwalled carbon nanotube composite as an electrode material for aqueous redox supercapacitors, J. Power Sources. 171 (2007) 1062–1068. doi:10.1016/j.jpowsour.2007.05.103.
- [81] F. Markoulidis, C. Lei, C. Lekakou, D. Duff, S. Khalil, B. Martorana, I. Cannavaro, A method to increase the energy density of supercapacitor cells by the addition of multiwall carbon nanotubes into activated carbon electrodes, Carbon N. Y. 68 (2014) 58–66. doi:http://dx.doi.org/10.1016/j.carbon.2013.08.040.
- [82] B.C. Kim, J.S. Kwon, J.M. Ko, J.H. Park, C.O. Too, G.G. Wallace, Preparation and enhanced stability of flexible supercapacitor prepared from Nafion/polyaniline nanofiber, Synth. Met. 160 (2010) 94–98. doi:10.1016/j.synthmet.2009.10.011.
- [83] N. Jäckel, D. Weingarth, M. Zeiger, M. Aslan, I. Grobelsek, V. Presser, Comparison of carbon onions and carbon blacks as conductive additives for carbon supercapacitors in organic electrolytes, J. Power Sources. 272 (2014) 1122–1133. doi:10.1016/j.jpowsour.2014.08.090.
- [84] M. Zhu, C.J. Weber, Y. Yang, M. Konuma, U. Starke, K. Kern, A.M. Bittner, Chemical and electrochemical ageing of carbon materials used in supercapacitor electrodes, Carbon N. Y. 46 (2008) 1829–1840. doi:10.1016/j.carbon.2008.07.025.
- [85] G. Wang, Z. Shao, Z. Yu, Comparisons of different carbon conductive additives on the electrochemical performance of activated carbon, Nanotechnology. 18 (2007) 205705. doi:10.1088/0957-4484/18/20/205705.
- [86] Y.J. Kim, Y.A. Kim, T. Chino, H. Suezaki, M. Endo, M.S. Dresselhaus, Chemically Modified Multiwalled Carbon Nanotubes as an Additive for Supercapacitors, Small. 2 (2006) 339–345. doi:10.1002/smll.200500327.
- [87] M. Lu, F. Beguin, E. Frackowiak, Supercapacitors: materials, systems and applications, John Wiley & Sons, 2013.
- [88] H. Wei, S. Wei, W. Tian, D. Zhu, Y. Liu, L. Yuan, X. Li, Fabrication of thickness controllable free-standing sandwich-structured hybrid carbon film for high-rate and high-power supercapacitor, Sci. Rep. 4 (2014). http://dx.doi.org/10.1038/srep07050.
- [89] Y. Chen, X. Zhang, D. Zhang, Y. Ma, High power density of graphene-based supercapacitors in ionic liquid electrolytes, Mater. Lett. 68 (2012) 475–477. doi:10.1016/j.matlet.2011.11.008.
- [90] Y. Kibi, T. Saito, M. Kurata, J. Tabuchi, A. Ochi, Fabrication of high-power electric double-layer capacitors, J. Power Sources. 60 (1996) 219–224. doi:10.1016/S0378-7753(96)80014-0.
- [91] A. Rana, A. Chaudhary, P.B. Karandikar, Effect of carbon nanotubes on the capacitance of an ultra-capacitor, Glob. Humanit. Technol. Conf. South Asia Satell. (GHTC-SAS), 2013 IEEE. (2013) 124–127. doi:10.1109/GHTC-SAS.2013.6629901.
- [92] M.D. Stoller, R.S. Ruoff, Best practice methods for determining an electrode material's performance for ultracapacitors, Energy Environ. Sci. 3 (2010) 1294. doi:10.1039/c0ee00074d.
- [93] D. Liu, Q. Wang, L. Qiao, F. Li, D. Wang, Z. Yang, D. He, Preparation of nanonetworks of MnO2 shell/Ni current collector core for high-performance supercapacitor electrodes, J. Mater. Chem. 22 (2012) 483–487. doi:10.1039/C1JM13894D.
- [94] A. Yu, V. Chabot, J. Zhang, Electrochemical supercapacitors for energy storage and delivery: fundamentals and applications, CRC Press, 2013.
- [95] S.K. Mondal, N. Munichandraiah, Anodic deposition of porous RuO2 on stainless steel for supercapacitor studies at high current densities, J. Power Sources. 175 (2008) 657–663. doi:10.1016/j.jpowsour.2007.08.104.
- [96] A. Sumboja, X. Wang, J. Yan, P.S. Lee, Nanoarchitectured current collector for high rate capability of polyaniline based supercapacitor electrode, Electrochim. Acta. 65 (2012) 190–195. doi:10.1016/j.electacta.2012.01.046.
- [97] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon, Nat Nano. 5 (2010) 651–654. http://dx.doi.org/10.1038/nnano.2010.162.
- [98] Y. Wang, A. Yuan, X. Wang, Pseudocapacitive behaviors of nanostructured manganese dioxide/carbon nanotubes composite electrodes in mild aqueous electrolytes: effects of electrolytes and current collectors, J. Solid State Electrochem. 12 (2008) 1101–1107. doi:10.1007/s10008-007-0445-7.
- [99] W. Xing, S. Qiao, X. Wu, X. Gao, J. Zhou, S. Zhuo, S.B. Hartono, D. Hulicova-Jurcakova, Exaggerated capacitance using electrochemically active nickel foam as current collector in electrochemical measurement, J. Power Sources. 196 (2011) 4123–4127. doi:10.1016/j.jpowsour.2010.12.003.

- [100] R. Zhou, C. Meng, F. Zhu, Q. Li, C. Liu, S. Fan, K. Jiang, High-performance supercapacitors using a nanoporous current collector made from super-aligned carbon nanotubes., Nanotechnology. 21 (2010) 345701. doi:10.1088/0957-4484/21/34/345701.
- [101] S. ZHOU, X. LI, Z. WANG, H. GUO, W. PENG, Effect of activated carbon and electrolyte on properties of supercapacitor, Trans. Nonferrous Met. Soc. China. 17 (2007) 1328–1333. doi:10.1016/S1003-6326(07)60271-4.
- [102] R. Nandhini, P.A. Mini, B. Avinash, S.V. Nair, K.R.V. Subramanian, Supercapacitor electrodes using nanoscale activated carbon from graphite by ball milling, Mater. Lett. 87 (2012) 165–168. doi:10.1016/j.matlet.2012.07.092.
- [103] P.-L. Taberna, G. Chevallier, P. Simon, D. Plée, T. Aubert, Activated carbon–carbon nanotube composite porous film for supercapacitor applications, Mater. Res. Bull. 41 (2006) 478–484. doi:10.1016/j.materresbull.2005.09.029.
- [104] C.J. Farahmandi, J.M. Dispennette, Diffusion bond between aluminum foil current collector and aluminum, carbon composite electrode, (2000). https://www.google.com/patents/US6059847.
- [105] E. Taer, M. Deraman, I.A. Talib, S.A. Hashmi, A.A. Umar, Growth of platinum nanoparticles on stainless steel 316L current collectors to improve carbon-based supercapacitor performance, Electrochim. Acta. 56 (2011) 10217–10222. doi:10.1016/j.electacta.2011.09.007.
- [106] E.C. Jerabek, M. Mikkor, Ultracapacitor current collector, (2001). https://www.google.com/patents/US6201685.
- [107] K.H. An, W.S. Kim, Y.S. Park, J.-M. Moon, D.J. Bae, S.C. Lim, Y.S. Lee, Y.H. Lee, Electrochemical Properties of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes, Adv. Funct. Mater. 11 (2001) 387–392. doi:10.1002/1616-3028(200110)11:5<387::AID-ADFM387>3.0.CO;2-G.
- [108] C. Portet, P.. Taberna, P. Simon, C. Laberty-Robert, Modification of Al current collector surface by sol–gel deposit for carbon–carbon supercapacitor applications, Electrochim. Acta. 49 (2004) 905–912. doi:10.1016/j.electacta.2003.09.043.
- [109] Y. Huang, S.L. Candelaria, Y. Li, Z. Li, J. Tian, L. Zhang, G. Cao, Sulfurized activated carbon for high energy density supercapacitors, J. Power Sources. 252 (2014) 90–97. doi:10.1016/j.jpowsour.2013.12.004.
- [110] E. Frackowiak, Carbon materials for supercapacitor application, Phys. Chem. Chem. Phys. 9 (2007) 1774–1785. doi:10.1039/B618139M.
- [111] P. Liu, M. Verbrugge, S. Soukiazian, Influence of temperature and electrolyte on the performance of activated-carbon supercapacitors, J. Power Sources. 156 (2006) 712–718. doi:10.1016/j.jpowsour.2005.05.055.
- [112] M. Sevilla, R. Mokaya, Energy storage applications of activated carbons: supercapacitors and hydrogen storage, Energy Environ. Sci. 7 (2014) 1250–1280.

doi:10.1039/C3EE43525C.

- [113] P. Simon, A.F. Burke, Nanostructured carbons: double-layer capacitance and more, Electrochem. Soc. Interface. 17 (2008) 38.
- [114] F. Markoulidis, C. Lei, C. Lekakou, D. Duff, S. Khalil, B. Martorana, I. Cannavaro, A method to increase the energy density of supercapacitor cells by the addition of multiwall carbon nanotubes into activated carbon electrodes, Carbon N. Y. 68 (2014) 58–66. doi:10.1016/j.carbon.2013.08.040.
- [115] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya, L.-C. Qin, Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density., Phys. Chem. Chem. Phys. 13 (2011) 17615–24. doi:10.1039/c1cp21910c.
- [116] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Graphene-based ultracapacitors., Nano Lett. 8 (2008) 3498–502. doi:10.1021/nl802558y.
- T. Wigmans, Industrial aspects of production and use of activated carbons, Carbon N. Y. 27 (1989) 13–22. doi:10.1016/0008-6223(89)90152-8.
- [118] Y. Huang, C. Hou, H. Hsi, J. Wu, Optimization of highly microporous activated carbon preparation from Moso bamboo using central composite design approach, J. Taiwan Inst. Chem. Eng. 000 (2015) 1–10. doi:10.1016/j.jtice.2014.12.019.
- [119] Suhas, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Lignin--from natural adsorbent to activated carbon: a review., Bioresour. Technol. 98 (2007) 2301–12. doi:10.1016/j.biortech.2006.08.008.
- [120] O. Ioannidou, a. Zabaniotou, Agricultural residues as precursors for activated carbon production-A review, Renew. Sustain. Energy Rev. 11 (2007) 1966–2005. doi:10.1016/j.rser.2006.03.013.
- [121] Y. Ji, T. Li, L. Zhu, X. Wang, Q. Lin, Preparation of activated carbons by microwave heating KOH activation, Appl. Surf. Sci. 254 (2007) 506–512. doi:10.1016/j.apsusc.2007.06.034.
- [122] a. Aygün, S. Yenisoy-Karakaş, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Microporous Mesoporous Mater. 66 (2003) 189–195. doi:10.1016/j.micromeso.2003.08.028.
- [123] Y. Chen, Y. Zhu, Z. Wang, Y. Li, L. Wang, L. Ding, X. Gao, Y. Ma, Y. Guo, Application studies of activated carbon derived from rice husks produced by chemical-thermal process - A review, Adv. Colloid Interface Sci. 163 (2011) 39–52. doi:10.1016/j.cis.2011.01.006.
- [124] K.J. Cronje, K. Chetty, M. Carsky, J.N. Sahu, B.C. Meikap, Optimization of chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride, Desalination. 275 (2011) 276–284. doi:10.1016/j.desal.2011.03.019.
- [125] A. Demirbas, Agricultural based activated carbons for the removal of dyes from

aqueous solutions: A review, J. Hazard. Mater. 167 (2009) 1–9. doi:10.1016/j.jhazmat.2008.12.114.

- [126] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review, J. Environ. Manage. 85 (2007) 833–846. doi:10.1016/j.jenvman.2007.07.031.
- [127] G. Dobele, T. Dizhbite, M. V. Gil, a. Volperts, T. a. Centeno, Production of nanoporous carbons from wood processing wastes and their use in supercapacitors and CO 2 capture, Biomass and Bioenergy. 46 (2012) 145–154. doi:10.1016/j.biombioe.2012.09.010.
- [128] N. Isoda, R. Rodrigues, A. Silva, M. Gonçalves, D. Mandelli, F.C. a Figueiredo, W.A. Carvalho, Optimization of preparation conditions of activated carbon from agriculture waste utilizing factorial design, Powder Technol. 256 (2014) 175–181. doi:10.1016/j.powtec.2014.02.029.
- [129] C. Zheng, X. Zhou, H. Cao, G. Wang, Z. Liu, Synthesis of porous graphene/activated carbon composite with high packing density and large specific surface area for supercapacitor electrode material, J. Power Sources. 258 (2014) 290– 296. doi:10.1016/j.jpowsour.2014.01.056.
- [130] A. Davies, A. Yu, Material advancements in supercapacitors: From activated carbon to carbon nanotube and graphene, Can. J. Chem. Eng. 89 (2011) 1342–1357. doi:10.1002/cjce.20586.
- [131] B.N.M. Dolah, M. a R. Othman, M. Deraman, N.H. Basri, R. Farma, I. a Talib, M.M. Ishak, Supercapacitor Electrodes from Activated Carbon Monoliths and Carbon Nanotubes, J. Phys. Conf. Ser. 431 (2013) 012015. doi:10.1088/1742-6596/431/1/012015.
- [132] G. Xu, C. Zheng, Q. Zhang, J. Huang, M. Zhao, J. Nie, X. Wang, F. Wei, Binder-free activated carbon/carbon nanotube paper electrodes for use in supercapacitors, Nano Res. 4 (2011) 870–881. doi:10.1007/s12274-011-0143-8.
- [133] W. Lu, R. Hartman, L. Qu, L. Dai, Nanocomposite electrodes for high-performance supercapacitors, J. Phys. Chem. Lett. 2 (2011) 655–660. doi:10.1021/jz200104n.
- [134] L.L. Zhang, X. Zhao, M.D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, R.S. Ruoff, Highly conductive and porous activated reduced graphene oxide films for high-power supercapacitors., Nano Lett. 12 (2012) 1806–12. doi:10.1021/nl203903z.
- [135] K. Shi, M. Ren, I. Zhitomirsky, Activated Carbon-Coated Carbon Nanotubes for Energy Storage in Supercapacitors and Capacitive Water Purification, ACS Sustain. Chem. Eng. 2 (2014) 1289–1298. doi:10.1021/sc500118r.
- [136] A. Borenstien, M. Noked, S. Okashy, D. Aurbach, Composite Carbon Nano-Tubes (CNT)/Activated Carbon Electrodes for Non-Aqueous Super Capacitors Using

Organic Electrolyte Solutions, J. Electrochem. Soc. 160 (2013) A1282–A1285. doi:10.1149/2.103308jes.

- [137] J. Ma, Q. Guo, H.-L. Gao, X. Qin, Synthesis of C 60 /Graphene Composite as Electrode in Supercapacitors, Fullerenes, Nanotub. Carbon Nanostructures. 23 (2014) 477–482. doi:10.1080/1536383X.2013.865604.
- [138] C. Lee, X. Wei, J.W. Kysar, J. Hone, of Monolayer Graphene, Science (80-.). 321 (2008) 385–388.
- [139] a. H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, a. K. Geim, The electronic properties of graphene, Rev. Mod. Phys. 81 (2009) 109–162. doi:10.1103/RevModPhys.81.109.
- [140] D. Chen, L. Tang, J. Li, Graphene-based materials in electrochemistry., Chem. Soc. Rev. 39 (2010) 3157–80. doi:10.1039/b923596e.
- [141] J. Chen, C. Li, G. Shi, Graphene Materials for Electrochemical Capacitors, J. Phys. Chem. Lett. 4 (2013) 1244–1253. doi:10.1021/jz400160k.
- [142] W. Bao, Electrical and Mechanical Properties of Graphene, (2011). http://www.escholarship.org/uc/item/339425tf.
- [143] S. Ghosh, I. Calizo, D. Teweldebrhan, E.P. Pokatilov, D.L. Nika, a. a. Balandin, W. Bao, F. Miao, C.N. Lau, Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits, Appl. Phys. Lett. 92 (2008). doi:10.1063/1.2907977.
- [144] A. a Balandin, Thermal properties of graphene and nanostructured carbon materials., Nat. Mater. 10 (2011) 569–581. doi:10.1038/nmat3064.
- [145] C. Wang, D. Li, C.O. Too, G.G. Wallace, Electrochemical properties of graphene paper electrodes used in lithium batteries, Chem. Mater. 21 (2009) 2604–2606. doi:10.1021/cm900764n.
- [146] L.L. Zhang, R. Zhou, X.S. Zhao, Graphene-based materials as supercapacitor electrodes, J. Mater. Chem. 20 (2010) 5983. doi:10.1039/c000417k.
- [147] Y. Huang, J. Liang, Y. Chen, An overview of the applications of graphene-based materials in supercapacitors, Small. 8 (2012) 1805–1834. doi:10.1002/smll.201102635.
- [148] R. Pristavita, N.-Y. Mendoza-Gonzalez, J.-L. Meunier, D. Berk, Carbon nanoparticle production by inductively coupled thermal plasmas: controlling the thermal history of particle nucleation, Plasma Chem. Plasma Process. 31 (2011) 851–866.
- [149] R. Pristavita, J.L. Meunier, D. Berk, Carbon nano-flakes produced by an inductively coupled thermal plasma system for catalyst applications, Plasma Chem. Plasma Process. 31 (2011) 393–403. doi:10.1007/s11090-011-9289-0.
- [150] R. Pristavita, N.-Y. Mendoza-Gonzalez, J.-L. Meunier, D. Berk, Carbon blacks produced by thermal plasma: the influence of the reactor geometry on the product morphology, Plasma Chem. Plasma Process. 30 (2010) 267–279.
- [151] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, Graphene-Based Electrodes, Adv.

Mater. 24 (2012) 5979-6004. doi:10.1002/adma.201201587.

- [152] D. Yu, L. Dai, Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors, J. Phys. Chem. Lett. 1 (2010) 467–470. doi:10.1021/jz9003137.
- [153] W. Wang, S. Guo, M. Penchev, I. Ruiz, K.N. Bozhilov, D. Yan, M. Ozkan, C.S. Ozkan, Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors, Nano Energy. 2 (2013) 294–303. doi:10.1016/j.nanoen.2012.10.001.
- [154] D.H. Lee, J.E. Kim, T.H. Han, J.W. Hwang, S. Jeon, S.-Y. Choi, S.H. Hong, W.J. Lee, R.S. Ruoff, S.O. Kim, Versatile carbon hybrid films composed of vertical carbon nanotubes grown on mechanically compliant graphene films., Adv. Mater. 22 (2010) 1247–52. doi:10.1002/adma.200903063.
- [155] X. Li, T. Zhao, Q. Chen, P. Li, K. Wang, M. Zhong, J. Wei, D. Wu, B. Wei, H. Zhu, Flexible all solid-state supercapacitors based on chemical vapor deposition derived graphene fibers, Phys. Chem. Chem. Phys. 15 (2013) 17752–17757. doi:10.1039/C3CP52908H.
- [156] D. Sridhar, K. Balakrishnan, S. Raghavan, K. Muralidharan, Performance Enhancement of Activated Carbon Based Supercapacitors By Incorporation of Fullerene Self-Assemblies, in: 228th ECS Meet., ECS, Phenoix, 2015. http://ma.ecsdl.org/content/MA2015-02/9/586.abstract.
- [157] D. Sridhar, K. Balakrishnan, T.J. Gnanaprakasa, S. Raghavan, K. Muralidharan, Self-assembled fullerene additives for boosting the capacity of activated carbon electrodes in supercapacitors, RSC Adv. 5 (2015) 63834–63838. doi:10.1039/C5RA10903E.
- [158] K. Okajima, A. Ikeda, K. Kamoshita, M. Sudoh, High rate performance of highly dispersed C60 on activated carbon capacitor, Electrochim. Acta. 51 (2005) 972–977. doi:10.1016/j.electacta.2005.04.055.
- [159] T.J. Gnanaprakasa, D. Sridhar, W.J. Beck, K. Runge, B.G. Potter, T.J. Zega, P.A. Deymier, S. Raghavan, K. Muralidharan, Graphene mediated self-assembly of fullerene nanorods, Chem. Commun. 51 (2015) 1858–1861. doi:10.1039/C4CC09362C.
- [160] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon aerogels for catalysis applications: An overview, Carbon N. Y. 43 (2005) 455–465. doi:10.1016/j.carbon.2004.10.022.
- [161] R.W. Pekala, Polymerization, crosslinking, carbonization to carbon foam, (1989). https://www.google.com/patents/US4873218.
- [162] M.S. Contreras, C.A. Páez, L. Zubizarreta, A. Léonard, S. Blacher, C.G. Olivera-Fuentes, A. Arenillas, J.-P. Pirard, N. Job, A comparison of physical activation of carbon xerogels with carbon dioxide with chemical activation using hydroxides, Carbon N. Y. 48 (2010) 3157–3168. doi:10.1016/j.carbon.2010.04.054.

- [163] C. Lin, J. a. Ritter, Carbonization and activation of sol-gel derived carbon xerogels, Carbon N. Y. 38 (2000) 849–861. doi:10.1016/S0008-6223(99)00189-X.
- [164] F.J. Maldonado-Hódar, M.A. Ferro-García, J. Rivera-Utrilla, C. Moreno-Castilla, Synthesis and textural characteristics of organic aerogels, transition-metalcontaining organic aerogels and their carbonized derivatives, Carbon N. Y. 37 (1999) 1199–1205. doi:10.1016/S0008-6223(98)00314-5.
- [165] N. Liu, J. Shen, D. Liu, Activated high specific surface area carbon aerogels for EDLCs, Microporous Mesoporous Mater. 167 (2013) 176–181. doi:10.1016/j.micromeso.2012.09.009.
- [166] F. Lufrano, P. Staiti, E.G. Calvo, E.J. Juárez-Pérez, J. a. Menéndez, a. Arenillas, Carbon xerogel and manganese oxide capacitive materials for advanced supercapacitors, Int. J. Electrochem. Sci. 6 (2011) 596–612.
- [167] Y.J. Lee, G.-P. Kim, Y. Bang, J. Yi, J.G. Seo, I.K. Song, Activated carbon aerogel containing graphene as electrode material for supercapacitor, Mater. Res. Bull. 50 (2014) 240–245. doi:10.1016/j.materresbull.2013.11.021.
- [168] E.G. Calvo, N. Ferrera-Lorenzo, J.A. Menéndez, A. Arenillas, Microwave synthesis of micro-mesoporous activated carbon xerogels for high performance supercapacitors, Microporous Mesoporous Mater. 168 (2013) 206–212. doi:10.1016/j.micromeso.2012.10.008.
- [169] K. Donaldson, R. Aitken, L. Tran, V. Stone, R. Duffin, G. Forrest, A. Alexander, Carbon Nanotubes: A Review of Their Properties in Relation to Pulmonary Toxicology and Workplace Safety, Toxicol. Sci. 92 (2006) 5–22. doi:10.1093/toxsci/kfj130.
- [170] D. Harbec, J.-L. Meunier, Growth of carbon nanotubes above the peritectic temperature of tungsten metal catalyst, Carbon N. Y. 49 (2011) 2206–2215.
- [171] H. Kataura, Y. Kumazawa, Y. Maniwa, Y. Ohtsuka, R. Sen, S. Suzuki, Y. Achiba, Diameter control of single-walled carbon nanotubes, Carbon N. Y. 38 (2000) 1691– 1697.
- [172] A.G. Nasibulin, P. V Pikhitsa, P. Queipo, M. Choi, E.I. Kauppinen, Investigations of mechanism of carbon nanotube growth, Phys. Status Solidi. 243 (2006) 3095– 3100.
- [173] R. Brukh, S. Mitra, Mechanism of carbon nanotube growth by CVD, Chem. Phys. Lett. 424 (2006) 126–132.
- [174] R. Shah, X. Zhang, S. Talapatra, Electrochemical double layer capacitor electrodes using aligned carbon nanotubes grown directly on metals., Nanotechnology. 20 (2009) 395202. doi:10.1088/0957-4484/20/39/395202.
- [175] Y. Zhou, H. Xu, N. Lachman, M. Ghaffari, S. Wu, Y. Liu, A. Ugur, K.K. Gleason, B.L. Wardle, Q.M. Zhang, Advanced asymmetric supercapacitor based on conducting polymer and aligned carbon nanotubes with controlled

nanomorphology, Nano Energy. 9 (2014) 176–185. doi:10.1016/j.nanoen.2014.07.007.

- [176] S. Wei, W.P. Kang, J.L. Davidson, J.H. Huang, Supercapacitive behavior of CVD carbon nanotubes grown on Ti coated Si wafer, Diam. Relat. Mater. 17 (2008) 906– 911. doi:10.1016/j.diamond.2007.12.063.
- [177] A. Yu, A. Davies, Z. Chen, Electrochemical Supercapacitors, in: Electrochem. Technol. Energy Storage Convers., Wiley-VCH Verlag GmbH & Co. KGaA, 2011: pp. 317–382. doi:10.1002/9783527639496.ch8.
- [178] J.H. Kim, K.-W. Nam, S.B. Ma, K.B. Kim, Fabrication and electrochemical properties of carbon nanotube film electrodes, Carbon N. Y. 44 (2006) 1963–1968. doi:10.1016/j.carbon.2006.02.002.
- [179] C. Du, N. Pan, Supercapacitors using carbon nanotubes films by electrophoretic deposition, J. Power Sources. 160 (2006) 1487–1494. doi:10.1016/j.jpowsour.2006.02.092.
- [180] Y.-K. Hsu, Y.-C. Chen, Y.-G. Lin, L.-C. Chen, K.-H. Chen, High-cell-voltage supercapacitor of carbon nanotube/carbon cloth operating in neutral aqueous solution, J. Mater. Chem. 22 (2012) 3383–3387. doi:10.1039/C1JM14716A.
- [181] Y.M. Chen, J.H. Cai, Y.S. Huang, K.Y. Lee, D.S. Tsai, Preparation and characterization of iridium dioxide-carbon nanotube nanocomposites for supercapacitors., Nanotechnology. 22 (2011) 115706. doi:10.1088/0957-4484/22/11/115706.
- [182] J. Yan, Z. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. Song, M. Zhang, Carbon nanotube/MnO2 composites synthesized by microwave-assisted method for supercapacitors with high power and energy densities, J. Power Sources. 194 (2009) 1202–1207. doi:10.1016/j.jpowsour.2009.06.006.
- [183] Y. Zhang, X. Sun, L. Pan, H. Li, Z. Sun, C. Sun, B.K. Tay, Carbon nanotube–ZnO nanocomposite electrodes for supercapacitors, Solid State Ionics. 180 (2009) 1525– 1528. doi:10.1016/j.ssi.2009.10.001.
- [184] S.D. Perera, B. Patel, N. Nijem, K. Roodenko, O. Seitz, J.P. Ferraris, Y.J. Chabal, K.J. Balkus, Vanadium Oxide Nanowire–Carbon Nanotube Binder-Free Flexible Electrodes for Supercapacitors, Adv. Energy Mater. 1 (2011) 936–945. doi:10.1002/aenm.201100221.
- [185] S. Boukhalfa, K. Evanoff, G. Yushin, Atomic layer deposition of vanadium oxide on carbon nanotubes for high-power supercapacitor electrodes, Energy Environ. Sci. 5 (2012) 6872–6879. doi:10.1039/C2EE21110F.
- [186] X. Xiao, X. Peng, H. Jin, T. Li, C. Zhang, B. Gao, B. Hu, K. Huo, J. Zhou, Freestanding Mesoporous VN/CNT Hybrid Electrodes for Flexible All-Solid-State Supercapacitors, Adv. Mater. 25 (2013) 5091–5097. doi:10.1002/adma.201301465.
- [187] Y. Liu, J. Zhou, L. Chen, P. Zhang, W. Fu, H. Zhao, Y. Ma, X. Pan, Z. Zhang, W.

Han, E. Xie, Highly Flexible Freestanding Porous Carbon Nanofibers for Electrodes Materials of High-Performance All-Carbon Supercapacitors, ACS Appl. Mater. Interfaces. 7 (2015) 23515–23520. doi:10.1021/acsami.5b06107.

- [188] M. Inagaki, Y. Yang, F. Kang, Carbon nanofibers prepared via electrospinning, Adv. Mater. 24 (2012) 2547–2566. doi:10.1002/adma.201104940.
- [189] N. Hiremath, J. Mays, G. Bhat, Recent Developments in Carbon Fibers and Carbon Nanotube-Based Fibers: A Review, Polym. Rev. 57 (2017) 339–368. doi:10.1080/15583724.2016.1169546.
- [190] W. Sugimoto, H. Iwata, K. Yokoshima, Y. Murakami, Y. Takasu, Proton and electron conductivity in hydrous ruthenium oxides evaluated by electrochemical impedance spectroscopy: The origin of large capacitance, J. Phys. Chem. B. 109 (2005) 7330–7338. doi:10.1021/jp0442520.
- [191] L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H.N. Alshareef, Y. Cui, Symmetrical MnO2–Carbon Nanotube–Textile Nanostructures for Wearable Pseudocapacitors with High Mass Loading, ACS Nano. 5 (2011) 8904– 8913. doi:10.1021/nn203085j.
- [192] R.S. Kate, S.A. Khalate, R.J. Deokate, Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: A review, J. Alloys Compd. 734 (2018) 89–111. doi:10.1016/J.JALLCOM.2017.10.262.
- [193] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, Chem. Soc. Rev. 41 (2012) 797–828. doi:10.1039/c1cs15060j.
- [194] V. Khomenko, E. Frackowiak, F. Beguin, Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations, Electrochim. Acta. 50 (2005) 2499–2506.
- [195] Metrohm Autolab, (n.d.). https://www.metrohm-autolab.com/ (accessed November 29, 2019).
- [196] B. Kim, H. Chung, W. Kim, High-performance supercapacitors based on vertically aligned carbon nanotubes and nonaqueous electrolytes, Nanotechnology. 23 (2012) 155401. doi:10.1088/0957-4484/23/15/155401.
- [197] Z. Lei, Z. Chen, X.S. Zhao, Growth of Polyaniline on Hollow Carbon Spheres for Enhancing Electrocapacitance, J. Phys. Chem. C. 114 (2010) 19867–19874. doi:10.1021/jp1084026.
- [198] X. Li, L. Yang, Y. Lei, L. Gu, D. Xiao, Microwave-Assisted Chemical-Vapor-Induced in Situ Polymerization of Polyaniline Nanofibers on Graphite Electrode for High-Performance Supercapacitor, ACS Appl. Mater. Interfaces. 6 (2014) 19978–19989. doi:10.1021/am505533c.
- [199] K.H. An, W.S. Kim, Y.S. Park, Y.C. Choi, S.M. Lee, D.C. Chung, D.J. Bae, S.C. Lim, Y.H. Lee, Supercapacitors Using Single-Walled Carbon Nanotube Electrodes, Adv. Mater. 13 (2001) 497–500. doi:10.1002/1521-4095(200104)13:7<497::AID-</p>

ADMA497>3.0.CO;2-H.

- [200] T.B. Schon, P.M. DiCarmine, D.S. Seferos, Polyfullerene Electrodes for High Power Supercapacitors, Adv. Energy Mater. 4: 1301509 (2014). doi:10.1002/aenm.201301509.
- [201] Z. Huang, H. Zhang, Y. Chen, W. Wang, Y. Chen, Y. Zhong, Microwave-assisted synthesis of functionalized graphene on Ni foam as electrodes for supercapacitor application, Electrochim. Acta. 108 (2013) 421–428. doi:10.1016/j.electacta.2013.06.080.
- [202] H.R. Ghenaatian, M.F. Mousavi, S.H. Kazemi, M. Shamsipur, Electrochemical investigations of self-doped polyaniline nanofibers as a new electroactive material for high performance redox supercapacitor, Synth. Met. 159 (2009) 1717–1722. doi:10.1016/j.synthmet.2009.05.014.
- [203] L. Demarconnay, E. Raymundo-Piñero, F. Béguin, Adjustment of electrodes potential window in an asymmetric carbon/MnO2 supercapacitor, J. Power Sources. 196 (2011) 580–586. doi:10.1016/j.jpowsour.2010.06.013.
- [204] P.M. Ajayan, Nanotubes from Carbon, Chem. Rev. 99 (1999) 1787–1800. doi:10.1021/cr970102g.
- [205] I. Kang, Y.Y. Heung, J.H. Kim, J.W. Lee, R. Gollapudi, S. Subramaniam, S. Narasimhadevara, D. Hurd, G.R. Kirikera, V. Shanov, M.J. Schulz, D. Shi, J. Boerio, S. Mall, M. Ruggles-Wren, Introduction to carbon nanotube and nanofiber smart materials, Compos. Part B Eng. 37 (2006) 382–394. doi:10.1016/j.compositesb.2006.02.011.
- [206] L. Feng, N. Xie, J. Zhong, Carbon nanofibers and their composites: A review of synthesizing, properties and applications, Materials (Basel). 7 (2014) 3919–3945. doi:10.3390/ma7053919.
- [207] M.H. Al-Saleh, U. Sundararaj, A review of vapor grown carbon nanofiber/polymer conductive composites, Carbon N. Y. 47 (2009) 2–22. doi:10.1016/j.carbon.2008.09.039.
- [208] E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder, P. Pötschke, Carbon nanofibers for composite applications, Carbon N. Y. 42 (2004) 1153–1158.
- [209] Y. Yang, M.C. Gupta, K.L. Dudley, R.W. Lawrence, Conductive carbon nanofiberpolymer foam structures, Adv. Mater. 17 (2005) 1999–2003. doi:10.1002/adma.200500615.
- [210] T. Iwasaki, Y. Makino, M. Fukukawa, H. Nakamura, S. Watano, Low-temperature growth of nitrogen-doped carbon nanofibers by acetonitrile catalytic CVD using Ni-based catalysts, Appl. Nanosci. 6 (2016) 1211–1218. doi:10.1007/s13204-016-0535-x.
- [211] W. Fan, Y. Wang, J. Chen, Y. Yuan, A. Li, Q. Wang, C. Wang, Controllable growth of uniform carbon nanotubes/carbon nanofibers on the surface of carbon fibers,

RSC Adv. 5 (2015) 75735-75745. doi:10.1039/C5RA15556H.

- [212] S.A. Moshkalyov, A.L.D. Moreau, H.R. Guttiérrez, M.A. Cotta, J.W. Swart, Carbon nanotubes growth by chemical vapor deposition using thin film nickel catalyst, Mater. Sci. Eng. B. 112 (2004) 147–153. doi:10.1016/j.mseb.2004.05.038.
- [213] J. Chang, H. Tsai, W. Tsai, J.P.C. C, A. Asap, J. Chang, H. Tsai, W. Tsai, Different Types of Nanosized Carbon Materials Produced by a Metal Dusting Process, (2008) 20143–20148.
- [214] H. Ghorbani, A.M. Rashidi, S. Rastegari, S. Mirdamadi, M. Alaei, Mass production of multi-wall carbon nanotubes by metal dusting process with high yield, Mater. Res. Bull. 46 (2011) 716–721. doi:10.1016/j.materresbull.2011.01.021.
- [215] Y.I. Bauman, A.S. Lysakova, A. V. Rudnev, I. V. Mishakov, Y. V. Shubin, A.A. Vedyagin, R.A. Buyanov, Synthesis of nanostructured carbon fibers from chlorohydrocarbons over Bulk Ni-Cr Alloys, Nanotechnologies Russ. 9 (2014) 380– 385. doi:10.1134/S1995078014040041.
- [216] Y.I. Bauman, N. V. Kutaev, P.E. Plyusnin, I. V. Mishakov, Y. V. Shubin, A.A. Vedyagin, R.A. Buyanov, Catalytic behavior of bimetallic Ni–Fe systems in the decomposition of 1,2-dichloroethane. Effect of iron doping and preparation route, React. Kinet. Mech. Catal. 121 (2017) 413–423. doi:10.1007/s11144-017-1180-4.
- [217] Y.I. Bauman, I. V. Mishakov, A.A. Vedyagin, S. Ramakrishna, Synthesis of bimodal carbon structures via metal dusting of Ni-based alloys, Mater. Lett. 201 (2017) 70– 73. doi:10.1016/j.matlet.2017.04.135.
- [218] D.-Y. Cho, K. Eun, S.-H. Choa, H.-K. Kim, Highly flexible and stretchable carbon nanotube network electrodes prepared by simple brush painting for cost-effective flexible organic solar cells, Carbon N. Y. 66 (2014) 530–538. doi:10.1016/j.carbon.2013.09.035.
- [219] F. Bonaccorso, A. Bartolotta, J.N. Coleman, C. Backes, 2D-Crystal-Based Functional Inks, Adv. Mater. 28 (2016) 6136–6166.
- [220] M. Romagnoli, M. Lassinantti Gualtieri, M. Cannio, F. Barbieri, R. Giovanardi, Preparation of an aqueous graphitic ink for thermal drop-on-demand inkjet printing, Mater. Chem. Phys. 182 (2016) 263–271. doi:10.1016/j.matchemphys.2016.07.031.
- [221] M. Zamri, P. Ghosh, W. Zhipeng, Y. Hayashi, M. Tanemura, Direct growth of carbon nanofibers on metal mesh substrates by ion irradiation method, Tech. Dig. 2009 22nd Int. Vac. Nanoelectron. Conf. IVNC 2009. 9 (2009) 43–44. doi:10.1109/IVNC.2009.5271843.
- [222] D. Mata, M. Ferro, A.J.S. Fernandes, M. Amaral, F.J. Oliveira, P.M.F.J. Costa, R.F. Silva, Wet-etched Ni foils as active catalysts towards carbon nanofiber growth, Carbon N. Y. 48 (2010) 2839–2854. doi:10.1016/j.carbon.2010.04.016.
- [223] D. Mata, M. Amaral, A.J.S. Fernandes, F.J. Oliveira, P.M.F.J. Costa, R.F. Silva, Self-

assembled cones of aligned carbon nanofibers grown on wet-etched Cu foils, Carbon N. Y. 49 (2011) 2181–2196. doi:10.1016/j.carbon.2011.01.035.

- [224] C.E. Baddour, F. Fadlallah, D. Nasuhoglu, R. Mitra, L. Vandsburger, J.L. Meunier, A simple thermal CVD method for carbon nanotube synthesis on stainless steel 304 without the addition of an external catalyst, Carbon N. Y. 47 (2009) 313–318. doi:10.1016/j.carbon.2008.10.038.
- [225] C.E. Baddour, D.C. Upham, J.L. Meunier, Direct and repetitive growth cycles of carbon nanotubes on stainless steel particles by chemical vapor deposition in a fluidized bed, Carbon N. Y. 48 (2010) 2652–2656. doi:10.1016/j.carbon.2010.03.031.
- [226] N. Hordy, N.Y. Mendoza-Gonzalez, S. Coulombe, J.L. Meunier, The effect of carbon input on the morphology and attachment of carbon nanotubes grown directly from stainless steel, Carbon N. Y. 63 (2013) 348–357. doi:10.1016/j.carbon.2013.06.089.
- [227] C. Du, N. Pan, CVD growth of carbon nanotubes directly on nickel substrate, Mater. Lett. 59 (2005) 1678–1682. doi:10.1016/j.matlet.2005.01.043.
- [228] R. Shi, A Single-Step Process for Preparing Supercapacitor Electrodes from Carbon Nanotubes, Soft Nanosci. Lett. 01 (2011) 11–15. doi:10.4236/snl.2011.11003.
- [229] N.K. Reddy, J.L. Meunier, S. Coulombe, Growth of carbon nanotubes directly on a nickel surface by thermal CVD, Mater. Lett. 60 (2006) 3761–3765. doi:10.1016/j.matlet.2006.03.109.
- [230] N. Zhao, J. Kang, Direct Growth of Carbon Nanotubes on Metal Supports by Chemical Vapor Deposition, in: S. Yellampalli (Ed.), Carbon Nanotub. - Synth. Charact. Appl., InTech, 2011: p. 514. doi:10.5772/19275.
- [231] N. Jeong, J. Lee, Growth of filamentous carbon by decomposition of ethanol on nickel foam: Influence of synthesis conditions and catalytic nanoparticles on growth yield and mechanism, J. Catal. 260 (2008) 217–226. doi:10.1016/j.jcat.2008.10.006.
- [232] N.A. Jarrah, J.G. van Ommen, L. Lefferts, Mechanistic aspects of the formation of carbon-nanofibers on the surface of Ni foam: A new microstructured catalyst support, J. Catal. 239 (2006) 460–469. doi:10.1016/j.jcat.2006.02.021.
- [233] J.K. Chinthaginjala, D.B. Thakur, K. Seshan, L. Lefferts, How Carbon-Nano-Fibers attach to Ni foam, Carbon N. Y. 46 (2008) 1638–1647. doi:10.1016/j.carbon.2008.07.002.
- [234] V. Martínez-Hansen, N. Latorre, C. Royo, E. Romeo, E. García-Bordejé, A. Monzón, Development of aligned carbon nanotubes layers over stainless steel mesh monoliths, Catal. Today. 147 (2009) S71–S75.
- [235] R.L. Vander Wal, L.J. Hall, Carbon nanotube synthesis upon stainless steel meshes, Carbon N. Y. 41 (2003) 659–672. doi:10.1016/S0008-6223(02)00369-X.
- [236] S. Esconjauregui, C.M. Whelan, K. Maex, The reasons why metals catalyze the nucleation and growth of carbon nanotubes and other carbon nanomorphologies,

Carbon N. Y. 47 (2009) 659-669. doi:10.1016/j.carbon.2008.10.047.

- [237] J. a Rodríguez-Manzo, M. Terrones, H. Terrones, H.W. Kroto, L. Sun, F. Banhart, In situ nucleation of carbon nanotubes by the injection of carbon atoms into metal particles., Nat. Nanotechnol. 2 (2007) 307–11. doi:10.1038/nnano.2007.107.
- [238] R.T.K. Baker, Catalytic growth of carbon filaments, Carbon N. Y. 27 (1989) 315–323. doi:10.1016/0008-6223(89)90062-6.
- [239] I. Childres, L.A. Jauregui, W. Park, H. Cao, Y.P. Chen, Raman spectroscopy of graphene and related materials, New Dev. Phot. Mater. Res. 1 (2013).
- [240] C. Fantini, M.A. Pimenta, M.S. Strano, Two-phonon combination Raman modes in covalently functionalized single-wall carbon nanotubes, J. Phys. Chem. C. 112 (2008) 13150–13155.
- [241] C. Fauteux, R. Longtin, J. Pegna, M. Boman, Raman characterization of laser grown carbon microfibers as a function of experimental parameters, Thin Solid Films. 453 (2004) 606–610.
- [242] Y. Wang, S. Serrano, J.J. Santiago-Avilés, Raman characterization of carbon nanofibers prepared using electrospinning, Synth. Met. 138 (2003) 423–427. doi:10.1016/S0379-6779(02)00472-1.
- [243] J. Kastner, T. Pichler, H. Kuzmany, S. Curran, W. Blau, D.N. Weldon, M. Delamesiere, S. Draper, H. Zandbergen, Resonance Raman and infrared spectroscopy of carbon nanotubes, Chem. Phys. Lett. 221 (1994) 53–58. doi:10.1016/0009-2614(94)87015-2.
- [244] Y. Liu, C. Pan, J. Wang, Raman spectra of carbon nanotubes and nanofibers prepared by ethanol flames, J. Mater. Sci. 39 (2004) 1091–1094. doi:10.1023/B:JMSC.0000012952.20840.09.
- [245] D. Sridhar, S. Omanovic, J.-L. Meunier, Direct Growth of Carbon Nanofibers on Nickel Foam and Its Application As Electrochemical Supercapacitor Electrodes, in: ECS Meet. Abstr., 2017: p. 604. http://ma.ecsdl.org/content/MA2017-01/7/604.abstract.
- [246] C.E. Baddour, F. Fadlallah, D. Nasuhoglu, R. Mitra, L. Vandsburger, J.-L. Meunier, A simple thermal CVD method for carbon nanotube synthesis on stainless steel 304 without the addition of an external catalyst, Carbon N. Y. 47 (2009) 313–318.
- [247] N. Hordy, N.-Y. Mendoza-Gonzalez, S. Coulombe, J.-L. Meunier, The effect of carbon input on the morphology and attachment of carbon nanotubes grown directly from stainless steel, Carbon N. Y. 63 (2013) 348–357.
- [248] R.A. DiLeo, B.J. Landi, R.P. Raffaelle, Purity assessment of multiwalled carbon nanotubes by Raman spectroscopy, J. Appl. Phys. 101 (2007). doi:10.1063/1.2712152.
- [249] Y. Wang, Y. Song, Y. Xia, Electrochemical capacitors: mechanism, materials, systems, characterization and applications, Chem. Soc. Rev. 45 (2016) 5925–5950. doi:10.1039/C5CS00580A.

- [250] F. Wang, X. Wu, X. Yuan, Z. Liu, Y. Zhang, L. Fu, Y. Zhu, Q. Zhou, Y. Wu, W. Huang, Latest advances in supercapacitors: from new electrode materials to novel device designs, Chem. Soc. Rev. 46 (2017) 6816–6854. doi:10.1039/C7CS00205J.
- [251] T. Chen, L. Dai, Carbon nanomaterials for high-performance supercapacitors, Mater. Today. 16 (2013) 272–280. doi:10.1016/j.mattod.2013.07.002.
- [252] C. Du, J. Yeh, N. Pan, High power density supercapacitors using locally aligned carbon nanotube electrodes, Nanotechnology. 16 (2005) 350–353. doi:10.1088/0957-4484/16/4/003.
- [253] C. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, High power electrochemical capacitors based on carbon nanotube electrodes, Appl. Phys. Lett. 70 (1997) 1480– 1482. doi:10.1063/1.118568.
- [254] T. Zhao, S. She, X. Ji, W. Jin, A. Dang, H. Li, T. Li, S. Shang, Z. Zhou, In-situ growth amorphous carbon nanotube on silicon particles as lithium-ion battery anode materials, J. Alloys Compd. 708 (2017) 500–507. doi:10.1016/J.JALLCOM.2017.03.019.
- [255] J.R. McDonough, J.W. Choi, Y. Yang, F. La Mantia, Y. Zhang, Y. Cui, Carbon nanofiber supercapacitors with large areal capacitances, Appl. Phys. Lett. 95 (2009) 1–3. doi:10.1063/1.3273864.
- [256] Y. Gao, G.G.P. Pandey, J. Turner, C.R. Westgate, B. Sammakia, Chemical vapordeposited carbon nanofibers on carbon fabric for supercapacitor electrode applications, Nanoscale Res. Lett. 7 (2012) 651. doi:10.1186/1556-276X-7-651.
- [257] A.M. Saleem, A. Boschin, D.H. Lim, V. Desmaris, P. Johansson, P. Enoksson, Coincell supercapacitors based on CVD grown and vertically aligned carbon nanofibers (VACNFs), Int. J. Electrochem. Sci. 12 (2017) 6653–6661. doi:10.20964/2017.07.46.
- [258] S.H. Yoon, S. Lim, Y. Song, Y. Ota, W. Qiao, A. Tanaka, I. Mochida, KOH activation of carbon nanofibers, Carbon N. Y. 42 (2004) 1723–1729. doi:10.1016/j.carbon.2004.03.006.
- [259] J.R. McDonough, J.W. Choi, Y. Yang, F. La Mantia, Y. Zhang, Y. Cui, Carbon nanofiber supercapacitors with large areal capacitances, Appl. Phys. Lett. 95 (2009) 2009–2011. doi:10.1063/1.3273864.
- [260] D. Sridhar, S. Omanovic, J.-L. Meunier, Direct growth of carbon nanofiber forest on nickel foam without any external catalyst, Diam. Relat. Mater. 81 (2018) 70–76.
- [261] M. Lu, H.-L. Li, K.-T. Lau, Formation and Growth Mechanism of Dissimilar Coiled Carbon Nanotubes by Reduced-Pressure Catalytic Chemical Vapor Deposition, J. Phys. Chem. B. 108 (2004) 6186–6192. doi:10.1021/jp0360265.
- [262] A. Shaikjee, N.J. Coville, The synthesis, properties and uses of carbon materials with helical morphology, J. Adv. Res. 3 (2012) 195–223. doi:10.1016/j.jare.2011.05.007.
- [263] X. Lu, N. Hiremath, K. Hong, M.C. Evora, V.H. Ranson, A.K. Naskar, G.S. Bhat, N.-

G. Kang, J.W. Mays, Improving mechanical properties of carbon nanotube fibers through simultaneous solid-state cycloaddition and crosslinking, Nanotechnology. 28 (2017). doi:10.1088/1361-6528/aa6223.

- [264] Q. Huang, D. Zeng, S. Tian, C. Xie, Synthesis of defect graphene and its application for room temperature humidity sensing, Mater. Lett. 83 (2012) 76–79. doi:10.1016/j.matlet.2012.05.074.
- [265] L.X. Su, Q. Lou, Z. Jiao, C.X. Shan, Plant Cell Imaging Based on Nanodiamonds with Excitation-Dependent Fluorescence, Nanoscale Res. Lett. 11 (2016). doi:10.1186/s11671-016-1641-0.
- [266] A.R. González-Elipe, R. Alvarez, J.P. Holgado, J.P. Espinos, G. Munuera, J.M. Sanz, An XPS study of the Ar+-induced reduction of Ni2+in NiO and Ni-Si oxide systems, Appl. Surf. Sci. 51 (1991) 19–26. doi:10.1016/0169-4332(91)90058-R.
- [267] V. Eshkenazi, E. Peled, L. Burstein, D. Golodnitsky, XPS analysis of the SEI formed on carbonaceous materials, Solid State Ionics. 170 (2004) 83–91. doi:10.1016/S0167-2738(03)00107-3.
- [268] Y. Wang, M. Zhang, D. Pan, Y. Li, T. Ma, J. Xie, Nitrogen/sulfur co-doped graphene networks uniformly coupled N-Fe2O3nanoparticles achieving enhanced supercapacitor performance, Electrochim. Acta. 266 (2018) 242–253. doi:10.1016/j.electacta.2018.02.040.
- [269] K.S. Kim, N. Winograd, X-ray photoelectron spectroscopic studies of nickel-oxygen surfaces using oxygen and argon ion-bombardment, Surf. Sci. 43 (1974) 625–643. doi:10.1016/0039-6028(74)90281-7.
- [270] S.D. Chavhan, R. Hansson, L.K.E. Ericsson, P. Beyer, A. Hofmann, W. Brütting, A. Opitz, E. Moons, Low temperature processed NiOxhole transport layers for efficient polymer solar cells, Org. Electron. Physics, Mater. Appl. 44 (2017) 59–66. doi:10.1016/j.orgel.2017.01.040.
- [271] C. Petit, M. Seredych, T.J. Bandosz, Revisiting the chemistry of graphite oxides and its effect on ammonia adsorption, J. Mater. Chem. 19 (2009) 9176. doi:10.1039/b916672f.
- [272] N. Kitakatsu, V. Maurice, C. Hinnen, P. Marcus, Surface hydroxylation and local structure of NiO thin films formed on Ni(111), Surf. Sci. 407 (1998) 36–58. doi:10.1016/S0039-6028(98)00089-2.
- [273] E. Heracleous, A.F. Lee, K. Wilson, A.A. Lemonidou, Investigation of Ni-based alumina-supported catalysts for the oxidative dehydrogenation of ethane to ethylene: structural characterization and reactivity studies, J. Catal. 231 (2005) 159– 171. doi:10.1016/J.JCAT.2005.01.015.
- [274] E.. Khawaja, M.. Salim, M.. Khan, F.. Al-Adel, G.. Khattak, Z. Hussain, XPS, auger, electrical and optical studies of vanadium phosphate glasses doped with nickel oxide, J. Non. Cryst. Solids. 110 (1989) 33–43. doi:10.1016/0022-3093(89)90179-8.

- [275] A. Davidson, J.F. Tempere, M. Che, H. Roulet, G. Dufour, Spectroscopic studies of nickel(II) and nickel(III) species generated upon thermal treatments of nickel/ceriasupported materials, J. Phys. Chem. 100 (1996) 4919–4929. doi:10.1021/jp952268w.
- [276] P.L. Taberna, P. Simon, J.F. Fauvarque, Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon-Carbon Supercapacitors, J. Electrochem. Soc. 150 (2003) A292. doi:10.1149/1.1543948.
- [277] L. Liu, Z. Niu, J. Chen, Flexible supercapacitors based on carbon nanotubes, Chinese Chem. Lett. 29 (2018) 571–581. doi:10.1016/j.cclet.2018.01.013.
- [278] S. Kumar, M. Nehra, D. Kedia, N. Dilbaghi, K. Tankeshwar, K.H. Kim, Carbon nanotubes: A potential material for energy conversion and storage, Prog. Energy Combust. Sci. 64 (2018) 219–253. doi:10.1016/j.pecs.2017.10.005.
- [279] C. Ma, Y. Song, J. Shi, D. Zhang, X. Zhai, M. Zhong, Q. Guo, L. Liu, Preparation and one-step activation of microporous carbon nanofibers for use as supercapacitor electrodes, Carbon N. Y. 51 (2013) 290–300. doi:10.1016/j.carbon.2012.08.056.
- [280] A.M. Saleem, S. Shafiee, T. Krasia-Christoforou, I. Savva, G. Göransson, V. Desmaris, P. Enoksson, Low temperature and cost-effective growth of vertically aligned carbon nanofibers using spin-coated polymer-stabilized palladium nanocatalysts, Sci. Technol. Adv. Mater. 16 (2015). doi:10.1088/1468-6996/16/1/015007.
- [281] X. Li, T. Zhao, K. Wang, Y. Yang, J. Wei, F. Kang, D. Wu, H. Zhu, Directly drawing self-assembled, porous, and monolithic graphene fiber from chemical vapor deposition grown graphene film and its electrochemical properties, Langmuir. 27 (2011) 12164–12171. doi:10.1021/la202380g.
- [282] Z. Weng, Y. Su, D.W. Wang, F. Li, J. Du, H.M. Cheng, Graphene-cellulose paper flexible supercapacitors, Adv. Energy Mater. 1 (2011) 917–922. doi:10.1002/aenm.201100312.
- [283] M. Cowell, R. Winslow, Q. Zhang, J. Ju, J. Evans, P. Wright, Composite carbonbased ionic liquid supercapacitor for high-current micro devices, J. Phys. Conf. Ser. 557 (2014). doi:10.1088/1742-6596/557/1/012061.
- [284] M.A. McArthur, N. Ullah, S. Coulombe, S. Omanovic, A binder-free Ir0.4Ru0.6oxide/functionalized multi-walled carbon nanotube electrode for possible applications in supercapacitors, Can. J. Chem. Eng. 96 (2018) 74–82. doi:10.1002/cjce.22837.
- [285] N. Ullah, M.A. McArthur, S. Omanovic, Iridium-ruthenium-oxide coatings for supercapacitors, Can. J. Chem. Eng. 93 (2015) 1941–1948. doi:10.1002/cjce.22318.
- [286] M. Zhi, F. Yang, F. Meng, M. Li, A. Manivannan, N. Wu, Effects of pore structure on performance of an activated-carbon supercapacitor electrode recycled from scrap waste tires, in: ACS Sustain. Chem. Eng., 2014: pp. 1592–1598. doi:10.1021/sc500336h.

- [287] B.E. Conway, Electrochemical supercapacitors: scientific fundamentals and technological applications, Springer Science & Business Media, 2013.
- [288] N.W.A. Wahab, S. Sufian, T.D.N. Van, M.S. Shaharun, Comparative Studies of Pristine and Functionalized CNFs Surface Properties and their Performance in Iron Distribution, Procedia Eng. 148 (2016) 136–145. doi:10.1016/J.PROENG.2016.06.546.
- [289] S.-H. Park, W.-J. Lee, Hierarchically mesoporous CuO/carbon nanofiber coaxial shell-core nanowires for lithium ion batteries, Sci. Rep. 5 (2015) 9754. http://dx.doi.org/10.1038/srep09754.
- [290] M.E. Birch, T.A. Ruda-Eberenz, M. Chai, R. Andrews, R.L. Hatfield, Properties that Influence the Specific Surface Areas of Carbon Nanotubes and Nanofibers, Ann. Occup. Hyg. 57 (2013) 1148–1166. doi:10.1093/annhyg/met042.
- [291] B.K. Kim, S. Serubbable, A. Yu, J. Zhang, Electrochemical supercapacitors for energy storage and conversion, in: Handb. Clean Energy Syst., John Wiley & Sons, Ltd., 2015. doi:10.1002/9781118991978.hces112.
- [292] D. Premathilake, R.A. Outlaw, S.G. Parler, S.M. Butler, J.R. Miller, Electric double layer capacitors for ac filtering made from vertically oriented graphene nanosheets on aluminum, Carbon N. Y. 111 (2017) 231–237. doi:10.1016/j.carbon.2016.09.080.
- [293] K.B. Li, D.W. Shi, Z.Y. Cai, G.L. Zhang, Q.A. Huang, D. Liu, C.P. Yang, Studies on the equivalent serial resistance of carbon supercapacitor, Electrochim. Acta. 174 (2015) 596–600. doi:10.1016/j.electacta.2015.06.008.
- [294] X. Zhang, X. Wang, L. Jiang, H. Wu, C. Wu, J. Su, Effect of aqueous electrolytes on the electrochemical behaviors of supercapacitors based on hierarchically porous carbons, J. Power Sources. 216 (2012) 290–296. doi:10.1016/j.jpowsour.2012.05.090.
- [295] S.M. Jung, D.L. Mafra, C.-T. Lin, H.Y. Jung, J. Kong, Controlled porous structures of graphene aerogels and their effect on supercapacitor performance, Nanoscale. 7 (2015) 4386–4393. doi:10.1039/C4NR07564A.
- [296] J.R. Miller, Pulse power performance of electrochemical capacitors: technical status of present commercial devices, in: Proc. 8th Int. Semin. Double Layer Capacit. Similar Energy Storage Devices, Deerf. Beach, Fla.(Dec. 7-9, 1998), 1998.
- [297] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, Laser scribing of high-performance and flexible graphene-based electrochemical capacitors, Science (80-.). 335 (2012) 1326–1330.
- [298] C. Kim, K.S. Yang, Electrochemical properties of carbon nanofiber web as an electrode for supercapacitor prepared by electrospinning, Appl. Phys. Lett. 83 (2003) 1216–1218. doi:10.1063/1.1599963.
- [299] X. Xia, Q. Hao, W. Lei, W. Wang, D. Sun, X. Wang, Nanostructured ternary composites of graphene/Fe2O3/polyaniline for high-performance supercapacitors, J. Mater. Chem. 22 (2012) 16844. doi:10.1039/c2jm33064d.
- [300] J. Dore, A. Burian, S. Tomita, STRUCTURAL STUDIES OF CARBON

NANOTUBES AND RELATED MATERIALS BY NEUTRON AND X-RAY DIFFRACTION, 2000.

- [301] P. Thounthong, V. Chunkag, P. Sethakul, S. Sikkabut, S. Pierfederici, B. Davat, Energy management of fuel cell/solar cell/supercapacitor hybrid power source, J. Power Sources. 196 (2011) 313–324. doi:10.1016/j.jpowsour.2010.01.051.
- [302] F. Ran, X. Yang, L. Shao, Recent progress in carbon-based nanoarchitectures for advanced supercapacitors, Adv. Compos. Hybrid Mater. 1 (2018) 32–55. doi:10.1007/s42114-017-0021-2.
- [303] Poonam, K. Sharma, A. Arora, S.K. Tripathi, Review of supercapacitors: Materials and devices, J. Energy Storage. 21 (2019) 801–825. doi:10.1016/j.est.2019.01.010.
- [304] E. Frackowiak, F. Béguin, Carbon materials for the electrochemical storage of energy in capacitors, Carbon N. Y. 39 (2001) 937–950. doi:10.1016/S0008-6223(00)00183-4.
- [305] D. Sridhar, J.L. Meunier, S. Omanovic, Directly grown carbon nano-fibers on nickel foam as binder-free long-lasting supercapacitor electrodes, Mater. Chem. Phys. 223 (2019) 434–440. doi:10.1016/j.matchemphys.2018.11.024.
- [306] X. Li, B. Wei, Supercapacitors based on nanostructured carbon, Nano Energy. 2 (2013) 159–173. doi:10.1016/j.nanoen.2012.09.008.
- [307] C.F. Liu, Y.C. Liu, T.Y. Yi, C.C. Hu, Carbon materials for high-voltage supercapacitors, Carbon N. Y. 145 (2019) 529–548. doi:10.1016/j.carbon.2018.12.009.
- [308] Z. Zhu, S. Tang, J. Yuan, X. Qin, Y. Deng, R. Qu, G.M. Haarberg, Effects of various binders on supercapacitor performances, Int. J. Electrochem. Sci. 11 (2016) 8270– 8279. doi:10.20964/2016.10.04.
- [309] Q. Abbas, D. Pajak, E. Frackowiak, F. Béguin, Effect of binder on the performance of carbon/carbon symmetric capacitors in salt aqueous electrolyte, Electrochim. Acta. 140 (2014) 132–138. doi:10.1016/j.electacta.2014.04.096.
- [310] C. qi YI, J. peng ZOU, H. zhi YANG, X. LENG, Recent advances in pseudocapacitor electrode materials: Transition metal oxides and nitrides, Trans. Nonferrous Met. Soc. China (English Ed. 28 (2018) 1980–2001. doi:10.1016/S1003-6326(18)64843-5.
- [311] A. Afif, S.M. Rahman, A. Tasfiah Azad, J. Zaini, M.A. Islan, A.K. Azad, Advanced materials and technologies for hybrid supercapacitors for energy storage – A review, J. Energy Storage. 25 (2019) 100852. doi:10.1016/j.est.2019.100852.
- [312] S. Najib, E. Erdem, Current progress achieved in novel materials for supercapacitor electrodes: mini review, Nanoscale Adv. 1 (2019) 2817–2827. doi:10.1039/c9na00345b.
- [313] V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage, Energy Environ. Sci. 7 (2014) 1597–1614. doi:10.1039/c3ee44164d.
- [314] B.E. Conway, Electrochemical Supercapacitors Scientific, n.d.

- [315] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, Progress of electrochemical capacitor electrode materials: A review, Int. J. Hydrogen Energy. 34 (2009) 4889–4899. doi:10.1016/j.ijhydene.2009.04.005.
- [316] Q. Li, S. Zheng, Y. Xu, H. Xue, H. Pang, Ruthenium based materials as electrode materials for supercapacitors, Chem. Eng. J. 333 (2018) 505–518. doi:10.1016/j.cej.2017.09.170.
- [317] M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, Nanostructured Carbon-Metal Oxide Composite Electrodes for Supercapacitors: Review, Nanoscale. (2012) 72–88. doi:10.1039/c2nr32040a.
- [318] P. Mallet-Ladeira, P. Puech, C. Toulouse, M. Cazayous, N. Ratel-Ramond, P. Weisbecker, G.L. Vignoles, M. Monthioux, A Raman study to obtain crystallite size of carbon materials: A better alternative to the Tuinstra-Koenig law, Carbon N. Y. 80 (2014) 629–639. doi:10.1016/j.carbon.2014.09.006.
- [319] A. V Korotcov, Y. Huang, K. Tiong, D. Tsai, Raman scattering characterization of well-aligned RuO2 and IrO2 nanocrystals, J. Raman Spectrosc. An Int. J. Orig. Work All Asp. Raman Spectrosc. Incl. High. Order Process. Also Brillouin Rayleigh Scatt. 38 (2007) 737–749.
- [320] M.S. Dresselhaus, A. Jorio, A.G. Souza Filho, R. Saito, Defect characterization in graphene and carbon nanotubes using Raman spectroscopy, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 368 (2010) 5355–5377. doi:10.1098/rsta.2010.0213.
- [321] A. V. Naumkin, A. Kraut-Vass, S.W. Gaarenstroom, C.J. Powell, NIST X-ray Photoelectron Spectroscopy (XPS) Database, Version 4.1, (2012). https://srdata.nist.gov/xps/ (accessed June 17, 2019).
- [322] D. Briggs, G. Beamson, XPS Studies of the Oxygen 1s and 2s Levels in a Wide Range of Functional Polymers, Anal. Chem. 65 (1993) 1517–1523. doi:10.1021/ac00059a006.
- [323] S. Trasatti, Physical electrochemistry of ceramic oxides, Electrochim. Acta. 36 (1991) 225–241. doi:10.1016/0013-4686(91)85244-2.
- [324] S. Trasatti, G. Buzzanca, Ruthenium dioxide: A new interesting electrode material. Solid state structure and electrochemical behaviour, J. Electroanal. Chem. 29 (1971)
 4–8. doi:10.1016/S0022-0728(71)80111-0.
- [325] S. Zhang, N. Pan, Supercapacitors Performance Evaluation, Adv. Energy Mater. 5 (2015) 1401401. doi:10.1002/aenm.201401401.
- [326] K.H. Chang, C.C. Hu, C.Y. Chou, Textural and capacitive characteristics of hydrothermally derived RuO 2·H2O nanocrystallites: Independent control of crystal size and water content, Chem. Mater. 19 (2007) 2112–2119. doi:10.1021/cm0629661.
- [327] G. Arabale, D. Wagh, M. Kulkarni, I.S. Mulla, S.P. Vernekar, K. Vijayamohanan, A.M. Rao, Enhanced supercapacitance of multiwalled carbon nanotubes functionalized with ruthenium oxide, Chem. Phys. Lett. 376 (2003) 207–213.

doi:10.1016/S0009-2614(03)00946-1.

- [328] I.H. Kim, K.B. Kim, Electrochemical characterization of hydrous ruthenium oxide thin-film electrodes for electrochemical capacitor applications, J. Electrochem. Soc. 153 (2006). doi:10.1149/1.2147406.
- [329] S. Chalupczok, P. Kurzweil, H. Hartmann, C. Schell, The Redox Chemistry of Ruthenium Dioxide: A Cyclic Voltammetry Study—Review and Revision, Int. J. Electrochem. 2018 (2018) 1–15. doi:10.1155/2018/1273768.
- [330] Q. Li, S. Zheng, Y. Xu, H. Xue, H. Pang, Ruthenium based materials as electrode materials for supercapacitors, Chem. Eng. J. 333 (2018) 505–518. doi:10.1016/j.cej.2017.09.170.
- [331] D. Sridhar, J.L. Meunier, S. Omanovic, Directly grown carbon nano-fibers on nickel foam as binder-free long-lasting supercapacitor electrodes, Mater. Chem. Phys. 223 (2019) 434–440. doi:10.1016/j.matchemphys.2018.11.024.
- [332] I.-H. Kim, J.-H. Kim, Y.-H. Lee, K.-B. Kim, Synthesis and characterization of electrochemically prepared ruthenium oxide on carbon nanotube film substrate for supercapacitor applications, J. Electrochem. Soc. 152 (2005) A2170–A2178.
- [333] X. Wang, Y. Yin, C. Hao, Z. You, A high-performance three-dimensional micro supercapacitor based on ripple-like ruthenium oxide-carbon nanotube composite films, Carbon N. Y. 82 (2015) 436–445. doi:10.1016/j.carbon.2014.10.087.
- [334] K.S. Yang, C.H. Kim, B.H. Kim, Preparation and electrochemical properties of RuO2-containing activated carbon nanofiber composites with hollow cores, Electrochim. Acta. 174 (2015) 290–296. doi:10.1016/j.electacta.2015.05.176.
- [335] A.L.M. Reddy, S. Ramaprabhu, Nanocrystalline metal oxides dispersed multiwalled carbon nanotubes as supercapacitor electrodes, J. Phys. Chem. C. 111 (2007) 7727–7734. doi:10.1021/jp069006m.
- [336] S. Yan, H. Wang, P. Qu, Y. Zhang, Z. Xiao, RuO2/carbon nanotubes composites synthesized by microwave-assisted method for electrochemical supercapacitor, Synth. Met. 159 (2009) 158–161. doi:10.1016/j.synthmet.2008.07.024.
- [337] Y.W. Ju, G.R. Choi, H.R. Jung, C. Kim, K.S. Yang, W.J. Lee, A hydrous ruthenium oxide-carbon nanofibers composite electrodes prepared by electrospinning, J. Electrochem. Soc. 154 (2007) 192–197. doi:10.1149/1.2426898.
- [338] H.K. Hassan, N.F. Atta, M.M. Hamed, A. Galal, T. Jacob, Ruthenium nanoparticlesmodified reduced graphene prepared by a green method for high-performance supercapacitor application in neutral electrolyte, RSC Adv. 7 (2017) 11286–11296. doi:10.1039/c6ra27415c.
- [339] C.C. Hu, H.Y. Guo, K.H. Chang, C.C. Huang, Anodic composite deposition of RuO2·xH2O-TiO2 for electrochemical supercapacitors, Electrochem. Commun. 11 (2009) 1631–1634. doi:10.1016/j.elecom.2009.06.014.
- [340] N. Kang, T. Yu, G.H. Lim, T. Koh, B. Lim, Facile synthesis of carbon-supported,

ultrasmall ruthenium oxide nanocrystals for supercapacitor electrode materials, Chem. Phys. Lett. 592 (2014) 192–195. doi:10.1016/j.cplett.2013.12.020.

- [341] V.D. Patake, C.D. Lokhande, Chemical synthesis of nano-porous ruthenium oxide (RuO 2) thin films for supercapacitor application, Appl. Surf. Sci. 254 (2008) 2820– 2824. doi:10.1016/j.apsusc.2007.10.044.
- [342] Y. Guo, W. Zhang, Y. Sun, M. Dai, Ruthenium nanoparticles stabilized by mercaptan and acetylene derivatives with supercapacitor application, MethodsX. 5 (2018) 795–796. doi:10.1016/j.mex.2018.07.004.
- [343] S. Ardizzone, G. Fregonara, S. Trasatti, "Inner" and "outer" active surface of RuO2 electrodes, Electrochim. Acta. 35 (1990) 263–267. doi:10.1016/0013-4686(90)85068-X.
- [344] M. Ramani, B.S. Haran, R.E. White, B.N. Popov, Synthesis and Characterization of Hydrous Ruthenium Oxide-Carbon Supercapacitors, J. Electrochem. Soc. 148 (2002) A374. doi:10.1149/1.1357172.
- [345] X. Hao, J. Zhao, Q. Zhang, Temperature-dependent textural and electrochemical properties of a ruthenium oxide capacitor prepared by exchange membrane controlled ion diffusion, Ceram. Int. 42 (2016) 9170–9177. doi:10.1016/j.ceramint.2016.03.009.
- [346] W. Sugimoto, Ruthenium Oxides as Supercapacitor Electrodes, in: G. Kreysa, K. Ota, R.F. Savinell (Eds.), Encycl. Appl. Electrochem., Springer New York, New York, NY, 2014: pp. 1813–1821. doi:10.1007/978-1-4419-6996-5_511.
- [347] I.-H. Kim, K.-B. Kim, Electrochemical Characterization of Hydrous Ruthenium Oxide Thin-Film Electrodes for Electrochemical Capacitor Applications, J. Electrochem. Soc. 153 (2006) A383. doi:10.1149/1.2147406.
- [348] W. Dmowski, T. Egami, K.E. Swider-Lyons, C.T. Love, D.R. Rolison, Local atomic structure and conduction mechanism of nanocrystalline hydrous RuO 2 from X-ray scattering, J. Phys. Chem. B. 106 (2002) 12677–12683. doi:10.1021/jp0262281.
- [349] C.C. Hu, W.C. Chen, K.H. Chang, How to Achieve Maximum Utilization of Hydrous Ruthenium Oxide for Supercapacitors, J. Electrochem. Soc. 151 (2004). doi:10.1149/1.1639020.
- [350] Y.R. Ahn, M.Y. Song, S.M. Jo, C.R. Park, D.Y. Kim, Electrochemical capacitors based on electrodeposited ruthenium oxide on nanofibre substrates, Nanotechnology. 17 (2006) 2865–2869. doi:10.1088/0957-4484/17/12/007.
- [351] K.Y. Kumar, S. Archana, R. Namitha, B.P. Prasanna, S.C. Sharma, M.S. Raghu, Ruthenium oxide nanostring clusters anchored Graphene oxide nanocomposites for high-performance supercapacitors application, Mater. Res. Bull. 107 (2018) 347– 354. doi:10.1016/j.materresbull.2018.08.011.
- [352] Y. Yin, X. Wang, Z. You, Integration of ruthenium oxide-carbon nanotube composites with three-dimensional interdigitated microelectrodes for the creation of on-chip supercapacitors, Int. J. Electrochem. Sci. 12 (2017) 3883–3906.

doi:10.20964/2017.05.39.

- [353] A. Ponrouch, S. Garbarino, E. Bertin, D. Guay, Ultra high capacitance values of Pt@RuO 2 core-shell nanotubular electrodes for microsupercapacitor applications, J. Power Sources. 221 (2013) 228–231. doi:10.1016/j.jpowsour.2012.08.033.
- [354] X. Wang, Y. Yin, X. Li, Z. You, Fabrication of a symmetric micro supercapacitor based on tubular ruthenium oxide on silicon 3D microstructures, J. Power Sources. 252 (2014) 64–72. doi:10.1016/j.jpowsour.2013.11.109.
- [355] J. Li, M. Zhu, Z. An, Z. Wang, M. Toda, T. Ono, Constructing in-chip microsupercapacitors of 3D graphene nanowall/ruthenium oxides electrode through silicon-based microfabrication technique, J. Power Sources. 401 (2018) 204–212. doi:10.1016/j.jpowsour.2018.08.099.
- [356] D.P. Dubal, G.S. Gund, R. Holze, H.S. Jadhav, C.D. Lokhande, C.J. Park, Solutionbased binder-free synthetic approach of RuO2 thin films for all solid state supercapacitors, Electrochim. Acta. 103 (2013) 103–109. doi:10.1016/j.electacta.2013.04.055.
- [357] R. Warren, F. Sammoura, F. Tounsi, M. Sanghadasa, L. Lin, Highly active ruthenium oxide coating via ALD and electrochemical activation in supercapacitor applications, J. Mater. Chem. A. 3 (2015) 15568–15575. doi:10.1039/c5ta03742e.
- [358] N. Lin, J. Tian, Z. Shan, K. Chen, W. Liao, Hydrothermal synthesis of hydrous ruthenium oxide/graphene sheets for high-performance supercapacitors, Electrochim. Acta. 99 (2013) 219–224. doi:10.1016/j.electacta.2013.03.115.
- [359] V.K.A. Muniraj, C.K. Kamaja, M. V. Shelke, RuO2·nH2O Nanoparticles Anchored on Carbon Nano-onions: An Efficient Electrode for Solid State Flexible Electrochemical Supercapacitor, ACS Sustain. Chem. Eng. 4 (2016) 2528–2534. doi:10.1021/acssuschemeng.5b01627.
- [360] K. Krishnamoorthy, P. Pazhamalai, S.J. Kim, Ruthenium sulfide nanoparticles as a new pseudocapacitive material for supercapacitor, Electrochim. Acta. 227 (2017) 85–94. doi:10.1016/j.electacta.2016.12.171.
- [361] D. Saha, Y. Li, Z. Bi, J. Chen, J.K. Keum, D.K. Hensley, H.A. Grappe, H.M. Meyer, S. Dai, M.P. Paranthaman, A.K. Naskar, Studies on Supercapacitor Electrode Material from Activated Lignin- Derived Mesoporous Carbon, (2014).
- [362] Q.L. Chen, K.H. Xue, W. Shen, F.F. Tao, S.Y. Yin, W. Xu, Fabrication and electrochemical properties of carbon nanotube array electrode for supercapacitors, Electrochim. Acta. (2004). doi:10.1016/j.electacta.2004.04.010.
- [363] J.R. Miller, R.A. Outlaw, B.C. Holloway, Graphene double-layer capacitor with ac line-filtering performance, Science (80-.). 329 (2010) 1637–1639. doi:10.1126/science.1194372.
- [364] W. Wang, S. Guo, I. Lee, K. Ahmed, J. Zhong, Z. Favors, F. Zaera, M. Ozkan, C.S. Ozkan, Hydrous ruthenium oxide nanoparticles anchored to graphene and carbon

nanotube hybrid foam for supercapacitors., Sci. Rep. 4 (2014) 4452. doi:10.1038/srep04452.

- [365] J.K. Lee, H.M. Pathan, K.D. Jung, O.S. Joo, Electrochemical capacitance of nanocomposite films formed by loading carbon nanotubes with ruthenium oxide, J. Power Sources. 159 (2006) 1527–1531. doi:10.1016/j.jpowsour.2005.11.063.
- [366] R. Wang, P. Jia, Y. Yang, N. An, Y. Zhang, H. Wu, Z. Hu, Ruthenium Oxide/Reduced Graphene Oxide Nanoribbon Composite and Its Excellent Rate Capability in Supercapacitor Application, Chinese J. Chem. 34 (2016) 114–122. doi:10.1002/cjoc.201500595.
- [367] J.H. Jang, K. Machida, Y. Kim, K. Naoi, Electrophoretic deposition (EPD) of hydrous ruthenium oxides with PTFE and their supercapacitor performances, Electrochim. Acta. 52 (2006) 1733–1741. doi:10.1016/j.electacta.2006.01.075.
- [368] Y. Meng, L. Wang, H. Xiao, Y. Ma, L. Chao, Q. Xie, Facile electrochemical preparation of a composite film of ruthenium dioxide and carboxylated graphene for a high performance supercapacitor, RSC Adv. 6 (2016) 33666–33675. doi:10.1039/c6ra03615e.
- [369] D. Zhao, X. Guo, Y. Gao, F. Gao, An electrochemical capacitor electrode based on porous carbon spheres hybrided with polyaniline and nanoscale ruthenium oxide, ACS Appl. Mater. Interfaces. 4 (2012) 5583–5589. doi:10.1021/am301484s.
- [370] P.R. Deshmukh, S. V. Patil, R.N. Bulakhe, S.D. Sartale, C.D. Lokhande, Inexpensive synthesis route of porous polyaniline-ruthenium oxide composite for supercapacitor application, Chem. Eng. J. 257 (2014) 82–89. doi:10.1016/j.cej.2014.06.038.
- [371] P. Wang, H. Liu, Y. Xu, Y. Chen, J. Yang, Q. Tan, Supported ultrafine ruthenium oxides with specific capacitance up to 1099 F g-1 for a supercapacitor, Electrochim. Acta. 194 (2016) 211–218. doi:10.1016/j.electacta.2016.02.089.
- [372] R.C. Ambare, S.R. Bharadwaj, B.J. Lokhande, Non-aqueous route spray pyrolyzed Ru:Co 3 O 4 thin electrodes for supercapacitor application, Appl. Surf. Sci. 349 (2015) 887–896. doi:10.1016/j.apsusc.2015.04.175.
- [373] A. El-Deen, N. Barakat, K. Khalild, H. Kim, Hollow carbon nanofibers as an effective electrode for brackish water desalination using the capacitive deionization process, New J Chem. 38 (2014). doi:10.1039/C3NJ00576C.
- [374] C.P. Deck, K. Vecchio, Prediction of carbon nanotube growth success by the analysis of carbon–catalyst binary phase diagrams, Carbon N. Y. 44 (2006) 267–275. doi:10.1016/j.carbon.2005.07.023.
- [375] A. Moisala, A.G. Nasibulin, E.I. Kauppinen, The role of metal nanoparticles in the catalytic production of single-walled carbon nanotubes—a review, J. Phys. Condens. Matter. 15 (2003) S3011–S3035. doi:10.1088/0953-8984/15/42/003.
- [376] M. Singleton, P. Nash, The C-Ni (Carbon-Nickel) system, Bull. Alloy Phase

Diagrams. 10 (1989) 121-126. doi:10.1007/BF02881419.

- [377] O. Edenhofer, Climate change 2014: mitigation of climate change, Cambridge University Press, 2015.
- [378] F. Mueller-Langer, E. Tzimas, M. Kaltschmitt, S. Peteves, Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term, Int. J. Hydrogen Energy. 32 (2007) 3797–3810.
- [379] J.A. Turner, A Realizable Renewable Energy Future, Science (80-.). 285 (1999) 687– 689.
- [380] T. Hijikata, Research and development of international clean energy network using hydrogen energy (WE-NET), Int. J. Hydrogen Energy. 27 (2002) 115–129.
- [381] P. Kruger, Electric power requirement for large-scale production of hydrogen fuel for the world vehicle fleet, Int. J. Hydrogen Energy. 26 (2001) 1137–1147.
- [382] C. Mitsugi, A. Harumi, F. Kenzo, WE-NET: Japanese hydrogen program, Int. J. Hydrogen Energy. 23 (1998) 159–165.
- [383] D. Pletcher, X. Li, S. Wang, A comparison of cathodes for zero gap alkaline water electrolysers for hydrogen production, Int. J. Hydrogen Energy. 37 (2012) 7429– 7435. doi:10.1016/j.ijhydene.2012.02.013.
- [384] R.F. De Souza, J.C. Padilha, R.S. Gonçalves, M.O. De Souza, J. Rault-Berthelot, Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: towards the best device, J. Power Sources. 164 (2007) 792–798.
- [385] M. Ni, M.K.H. Leung, D.Y.C. Leung, Energy and exergy analysis of hydrogen production by a proton exchange membrane (PEM) electrolyzer plant, Energy Convers. Manag. 49 (2008) 2748–2756.
- [386] L. Zhang, K. Xiong, S. Chen, L. Li, Z. Deng, Z. Wei, In situ growth of ruthenium oxide-nickel oxide nanorod arrays on nickel foam as a binder-free integrated cathode for hydrogen evolution, J. Power Sources. 274 (2015) 114–120.
- [387] R.L. LeRoy, Industrial water electrolysis: present and future, Int. J. Hydrogen Energy. 8 (1983) 401–417.
- [388] E. Navarro-Flores, Z. Chong, S. Omanovic, Characterization of Ni, NiMo, NiW and NiFe electroactive coatings as electrocatalysts for hydrogen evolution in an acidic medium, J. Mol. Catal. A Chem. 226 (2005) 179–197.
- [389] M.M. Jaksic, Hypo-hyper-d-electronic interactive nature of interionic synergism in catalysis and electrocatalysis for hydrogen reactions, Int. J. Hydrogen Energy. 26 (2001) 559–578.
- [390] D.W. Kirk, S.J. Thorpe, H. Suzuki, Ni-base amorphous alloys as electrocatalysts for alkaline water electrolysis, Int. J. Hydrogen Energy. 22 (1997) 493–500.
- [391] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, Prog. Energy Combust. Sci. 36 (2010) 307–326.
- [392] S.M.A. Shibli, J.N. Sebeelamol, Development of Fe2O3-TiO2 mixed oxide

incorporated Ni–P coating for electrocatalytic hydrogen evolution reaction, Int. J. Hydrogen Energy. 38 (2013) 2271–2282.

- [393] A.C. Tavares, S. Trasatti, Ni+ RuO2 co-deposited electrodes for hydrogen evolution, Electrochim. Acta. 45 (2000) 4195–4202.
- [394] S. Trasatti, Hydrogen evolution on oxide electrodes, in: Mod. Chlor-Alkali Technol., Springer, 1992: pp. 281–294.
- [395] E. Veggetti, I.M. Kodintsev, S. Trasatti, Hydrogen evolution on oxide electrodes: Co3O4 in alkaline solution, J. Electroanal. Chem. 339 (1992) 255–268.
- [396] J. Lomon, P. Chaiyabin, T. Saisopa, K. Seawsakul, N. Saowiang, K. Promsakha, P. Poolcharuansin, N. Pasaja, A. Chingsungnoen, R. Supruangnet, N. Chanlek, H. Nakajima, P. Songsiriritthigul, XPS and XAS preliminary studies of diamond-like carbon films prepared by HiPIMS technique, J. Phys. Conf. Ser. 1144 (2018). doi:10.1088/1742-6596/1144/1/012048.
- [397] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, The role of the Auger parameter in XPS studies of nickel metal, halides and oxides, Phys. Chem. Chem. Phys. 14 (2012) 2434–2442. doi:10.1039/c2cp22419d.
- [398] A.G. Vidales, S. Omanovic, Evaluation of nickel-molybdenum-oxides as cathodes for hydrogen evolution by water electrolysis in acidic, alkaline, and neutral media, Electrochim. Acta. 262 (2018) 115–123.
- [399] A.G. Vidales, L. Dam-Quang, A. Hong, S. Omanovic, The influence of addition of iridium-oxide to nickel-molybdenum-oxide cathodes on the electrocatalytic activity towards hydrogen evolution in acidic medium and on the cathode deactivation resistance, Electrochim. Acta. 302 (2019) 198–206.
- [400] J. Miao, F.-X. Xiao, H. Bin Yang, S.Y. Khoo, J. Chen, Z. Fan, Y.-Y. Hsu, H.M. Chen, H. Zhang, B. Liu, Hierarchical Ni-Mo-S nanosheets on carbon fiber cloth: A flexible electrode for efficient hydrogen generation in neutral electrolyte, Sci. Adv. 1 (2015) e1500259.
- [401] H. Zhou, Y. Wang, R. He, F. Yu, J. Sun, F. Wang, Y. Lan, Z. Ren, S. Chen, One-step synthesis of self-supported porous NiSe2/Ni hybrid foam: an efficient 3D electrode for hydrogen evolution reaction, Nano Energy. 20 (2016) 29–36.
- [402] A.G. Vidales, K. Choi, S. Omanovic, Nickel-cobalt-oxide cathodes for hydrogen production by water electrolysis in acidic and alkaline media, Int. J. Hydrogen Energy. 43 (2018) 12917–12928.
- [403] M.A. McArthur, L. Jorge, S. Coulombe, S. Omanovic, Synthesis and characterization of 3D Ni nanoparticle/carbon nanotube cathodes for hydrogen evolution in alkaline electrolyte, J. Power Sources. 266 (2014) 365–373.
- [404] D.J. Li, U.N. Maiti, J. Lim, D.S. Choi, W.J. Lee, Y. Oh, G.Y. Lee, S.O. Kim, Molybdenum sulfide/N-doped CNT forest hybrid catalysts for high-performance hydrogen evolution reaction, Nano Lett. 14 (2014) 1228–1233.

- [405] X. Zou, X. Huang, A. Goswami, R. Silva, B.R. Sathe, E. Mikmeková, T. Asefa, Cobalt-embedded nitrogen-rich carbon nanotubes efficiently catalyze hydrogen evolution reaction at all pH values, Angew. Chemie Int. Ed. 53 (2014) 4372–4376.
- [406] H. He, M. Li, Preparation of three-dimensional porous graphene/ruthenium oxide nano-composite for high performance supercapacitors by electrochemical method, Integr. Ferroelectr. 189 (2018) 147–157. doi:10.1080/10584587.2018.1456181.
- [407] S. Trasatti, Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions, J. Electroanal. Chem. Interfacial Electrochem. 39 (1972) 163–184.
- [408] W. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen oxidation and evolution reaction kinetics on platinum: acid vs alkaline electrolytes, J. Electrochem. Soc. 157 (2010) B1529–B1536.
- [409] S. Baranton, C. Coutanceau, Nickel cobalt hydroxide nanoflakes as catalysts for the hydrogen evolution reaction, Appl. Catal. B Environ. 136 (2013) 1–8.
- [410] M.A. Oliver-Tolentino, E.M. Arce-Estrada, C.A. Cortés-Escobedo, A.M. Bolarín-Miro, F. Sánchez-De Jesús, R. de G. González-Huerta, A. Manzo-Robledo, Electrochemical behavior of NixW1- x materials as catalyst for hydrogen evolution reaction in alkaline media, J. Alloys Compd. 536 (2012) S245–S249.
- [411] M. Yu, S. Zhao, H. Feng, L. Hu, X. Zhang, Y. Zeng, Y. Tong, X. Lu, Engineering thin MoS2 nanosheets on TiN nanorods: advanced electrochemical capacitor electrode and hydrogen evolution electrocatalyst, ACS Energy Lett. 2 (2017) 1862–1868.
- [412] J. Wang, H. Zhong, Z. Wang, F. Meng, X. Zhang, Integrated three-dimensional carbon paper/carbon tubes/cobalt-sulfide sheets as an efficient electrode for overall water splitting, ACS Nano. 10 (2016) 2342–2348.
- [413] L. Zhang, D. Shi, T. Liu, M. Jaroniec, J. Yu, Nickel-based materials for supercapacitors, Mater. Today. xxx (2018). doi:10.1016/j.mattod.2018.11.002.
- [414] Q. Liu, C. Lu, Y. Li, Controllable synthesis of ultrathin nickel oxide sheets on carbon cloth for high-performance supercapacitors, RSC Adv. 7 (2017) 23143–23148. doi:10.1039/c6ra27550h.
- [415] T. Brousse, D. Bélanger, J.W. Long, To Be or Not To Be Pseudocapacitive?, J. Electrochem. Soc. 162 (2015) A5185–A5189. doi:10.1149/2.0201505jes.
- [416] A.G. Vidales, J. Kim, S. Omanovic, Ni 0.6-x Mo 0.4-x Ir x-oxide as an electrode material for supercapacitors: investigation of the influence of iridium content on the charge storage/delivery, J. Solid State Electrochem. (2019) 1–11.
- [417] X. Liu, J. Wang, G. Yang, Amorphous nickel oxide and crystalline manganese oxide nanocomposite electrode for transparent and flexible supercapacitor, Chem. Eng. J. 347 (2018) 101–110. doi:10.1016/j.cej.2018.04.070.
- [418] N. Li, C.Y. Zhi, H. Zhang, High-performance Transparent and Flexible Asymmetric Supercapacitor based on Graphene-wrapped Amorphous FeOOH Nanowire and

Co(OH) 2 Nanosheet Transparent Films Produced at air-water interface, Electrochim. Acta. 220 (2016) 618–627. doi:10.1016/j.electacta.2016.10.068.

- [419] F. Zhou, Z. Ren, Y. Zhao, X. Shen, A. Wang, Y.Y. Li, C. Surya, Y. Chai, Perovskite photovoltachromic supercapacitor with all-transparent electrodes, ACS Nano. 10 (2016) 5900–5908.
- [420] Y. Zhong, Z. Chai, Z. Liang, P. Sun, W. Xie, C. Zhao, W. Mai, Electrochromic asymmetric supercapacitor windows enable direct determination of energy status by the naked eye, ACS Appl. Mater. Interfaces. 9 (2017) 34085–34092. doi:10.1021/acsami.7b10334.
- [421] M. Pasta, F. la Mantia, L. Hu, H.D. Deshazer, Y. Cui, Aqueous supercapacitors on conductive cotton, Nano Res. 3 (2010) 452–458. doi:10.1007/s12274-010-0006-8.
- [422] J. Bae, M.K. Song, Y.J. Park, J.M. Kim, M. Liu, Z.L. Wang, Fiber supercapacitors made of nanowire-fiber hybrid structures for wearable/flexible energy storage, Angew. Chemie Int. Ed. 50 (2011) 1683–1687.
- [423] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, Electrochim. Acta. 45 (2000) 2483–2498. doi:10.1016/S0013-4686(00)00354-6.
- [424] B.E. Conway, V. Birss, J. Wojtowicz, The role and utilization of pseudocapacitance for energy storage by supercapacitors, J. Power Sources. 66 (1997) 1–14. doi:10.1016/S0378-7753(96)02474-3.
- [425] X. Lang, A. Hirata, T. Fujita, M. Chen, Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors, Nat. Nanotechnol. 6 (2011) 232.
- [426] I. Shakir, M. Nadeem, M. Shahid, D.J. Kang, Ultra-thin solution-based coating of molybdenum oxide on multiwall carbon nanotubes for high-performance supercapacitor electrodes, Electrochim. Acta. 118 (2014) 138–142.
- [427] M.F. El-Kady, M. Ihns, M. Li, J.Y. Hwang, M.F. Mousavi, L. Chaney, A.T. Lech, R.B. Kaner, Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage, Proc. Natl. Acad. Sci. 112 (2015) 4233–4238.
- [428] S. Cheng, L. Yang, Y. Liu, W. Lin, L. Huang, D. Chen, C.P. Wong, M. Liu, Carbon fiber paper supported hybrid nanonet/nanoflower nickel oxide electrodes for highperformance pseudo-capacitors, J. Mater. Chem. A. 1 (2013) 7709–7716. doi:10.1039/c3ta10560a.
- [429] C. Wang, J. Xu, M.F. Yuen, J. Zhang, Y. Li, X. Chen, W. Zhang, Hierarchical composite electrodes of nickel oxide nanoflake 3D graphene for high-performance pseudocapacitors, Adv. Funct. Mater. 24 (2014) 6372–6380. doi:10.1002/adfm.201401216.