# Consolidated Nanomaterials Synthesized using Nickel micro-wires and Carbon Nanotubes

By

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Submitted in fulfillment of the requirements for the degree of MSc in Chemistry in the
Department of Chemistry, University of the Western Cape

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November 2007

# DECLARATION BY CANDIDATE

I declare that *Consolidated Composite Carbon Materials Produced by Template Synthesis: Synthesis, Structure and Properties* is my own work, that it has not been submitted before for any degree or examination in any other university, that all the sources I have quoted have been indicated and acknowledged as complete references.

**Wafeeq Davids** **November 2007**

**Signed: ……………..**

# ACKNOWLEDGEMENTS

My heartfelt gratitude goes first to the Almighty God in Heaven, without whom this work would have been a futile exercise.

I would like to express my deepest appreciation to Prof. Vladimir Linkov for affording me a chance to be a member of the SAIAMC and to the NRF and SANERI for financial support.

I would like to express the most profound and sincere gratitude to my co-supervisors, Dr. Alexander Nechaev and Dr. Patrick Ndungu for their constant encouragement, guidance, patience and invaluable instruction that contributed to the fulfillment of this work and my academic life throughout my research programme.

Thanks to all the members of the South African Institute of Advanced Materials Chemistry (SAIAMC) and Department of Chemistry for their friendly support and help all round.

I am extremely grateful to Adrian Joseph and Basil Julies for the extensive help with SEM and TEM measurements.

Grateful thanks are also due to Barbara Rogers and Sherine Adams for their role in keeping the laboratory organized and always being helpful.

I want to express my deepest gratitude to my family, whose support has been invaluable to me. To my parents Abedah and Magedien, I am grateful for your love, understanding and patience with me always.

Finally, I would like to thank my wife Fathiyah, for always being there for me. Thank you for your constant and endless love, support, understanding, patience and encouragement.

# ABSTRACT

Nano-devices are the next step in the application of nanomaterials in modern technology. One area of research that is receiving an increased amount of attention globally is the fabrication of new nano-devices for applications in hydrogen energy technologies. The current work focuses on the synthesis and characterization of nano-devices with potential application in alkaline electrolysis and secondary polymer lithium ion batteries.

Previous work with Nickel micro-wires demonstrated the potential to use these nanomaterials as electrodes in alkaline electrolysis. Carbon nanotubes have been shown to posse excellent electrochemical properties. A new direction in research is explored by combining nickel micro-wires with CNT, a new consolidated composite carbon nanocomposite can be realized and the characterization of such a novel composite was the focus of this thesis.

Novel composite carbon nanomaterials were synthesized using an electrochemical template technique and a hydrocarbon pyrolysis step. The first step involved the deposition of nickel within the pores of ion track etched Polyethylene terephthalate (PET) membrane; with pore diameters of 1μ, 0.4μ and 0.2 μ. Electrochemical deposition of nickel was carried out galvanostatically in a nickel hard bath between 35-40°C, and using a deposition current density of 75 $mAcm^2$. Carbon nanotubes were then deposited directly onto the surface of the nickel micro-wires via a chemical vapour deposition (CVD) technique using liquid petroleum gas (LPG) as the carbon source. CVD was done at a temperature of 800°C and the deposition time was 5 minutes.

The morphology and structural studies of these novel composite nanomaterials were studied by scanning electron microscopy (SEM), transmission electron microscopy

(TEM) and X-ray diffraction (XRD). Electrochemical investigations were done using Cyclic Voltammetry (CV), Chronoamperometry (CA) and Electrochemical Impedance Spectroscopy (EIS).

After removal of the template, before CNT CVD growth, SEM images revealed free standing arrays of nickel micro-wires, and after CNT growth via CVD the SEM micrographs showed that the morphology of the Ni micro-wires was moderately altered by the CVD process. From the XRD results it was shown that the crystallinity of the Ni micro-wires was persevered after the CVD process. The XRD of the nickel micro-wires with CNT grown directly on the surface revealed the characteristic CNT peak at $2\theta = 24.6^0$.

Cyclic Voltammetry (CV) was performed on the consolidated composite nanomaterial in an alkaline solution. The CV revealed that the novel composite carbon nanomaterial was the most active for hydrogen evolution when compared to unmodified Ni micro-wires and a flat nickel electrode. This was attributed to the increase in electrochemical accessible surface area.

Electrochemical impedance spectroscopy (EIS) showed that the novel composite carbon nanomaterial had a much higher capacitance than the nickel micro-wires, a flat nickel electrode, a flat nickel substrate modified with CNT, and a graphite electrode. When a similar comparison was done using a commercially available anode for lithium ion battery applications, the novel consolidated composite carbon nanomaterial had double the capacitance of the commercial anode.

The consolidated composite carbon nanomaterial was modified by depositing Pt on to the surface of the CNT via electroless deposition. The presence of Pt was determined by

Energy dispersive spectrometry and the electrocatalytic activity of the Pt modified consolidated composite carbon nanomaterial was significantly improved.

The work presented in this thesis provides a new and unique direction in the synthesis and application of novel consolidated carbon nanomaterials through true synergistic effect between nickel micro-wires and CNT. The exploration of the characteristics of the system and the ability to functionalize the CNT with different moieties allows for a wide range of application in energy conversion devices.

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# Chapter 1: Introduction

Nanotechnology is considered to be the technology of the future; it is perhaps today's most advanced manufacturing technology, because it reaches the theoretical limit of accuracy which is the size of a molecule or atom. Nanotechnology deals with materials and systems having the following key properties. [1].

- They have at least one dimension of about 1 – 100 nm
- They are designed through processes that exhibit fundamental control over the physical and chemical attributes of molecular scale structures
- They can be combined to form large structures

Nanomaterials are materials that are expected to exhibit novel and significant improved physical, chemical and other properties for manifestation of new phenomena and processes which, owing to the nanoscale dimensions, are not observed at the macroscopic level. There are basically four focal research areas in nanomaterials. The first is the synthesis of nanomaterials via different techniques, the second, the study of the properties and structure of nanomaterials, the third, the development of new methods of obtaining nanomaterials and the fourth is where the nanomaterials are used as the basis for consolidated structures i.e. nano-composites or isolated forms for various purposes such as nano devices. [2].

Nanomaterials can be made of carbon, ceramics, chemical precursors, ferrites, metals, minerals, polymers, semi-conductors and silica or silicates. Nanotechnology products are devices that utilize nanostructures. There are many types of nanomaterials and nanotechnology products. A material that has generated a sustainable amount of interest in nanotechnology is carbon, due to the fact that it occurs in many different forms. Fullerenes or buckyballs are carbon (C60) molecules with a cage-like structure of 60 or more atoms. Nanotubes are cylindrically-shaped Fullerene molecules or strings of stacked C60 carbon molecules.

A new direction in synthesis, characterization and application of nanomaterials is consolidated nanomaterials. This is a new form of nanomaterial or nano device. Consolidated nanomaterials are synthesized by utilizing various techniques to obtain the nanomaterial or nano device. Consolidated nanomaterials are basically synthesized by merging two or more nanostructured materials together. In this study the consolidated nanomaterial was synthesized by combining Ni micro-wires and carbon nanotubes. Consolidated nanomaterials consist of a matrix and a dispersed second phase. This second phase may alter the consolidated nanomaterials electrical, thermal or magnetic properties; enhance its wear or erosion resistance; or serve as a strengthening or stiffening agent. Consequently the surface of consolidated nanomaterials can be tailored to specific requirements by selecting a suitable template and secondary phase. Consolidated nanomaterials have advantages over nanoparticles due to the fact that, when one studies the properties of nanoparticles you have to make the nanoparticle in some form of secondary phase, these are inks, pastes or pellets. Consolidated nanomaterials can be studied directly due to the fact that the material is in a solid form. In this study consolidated nanomaterials were synthesized by depositing nickel within the pores of a porous template to form nickel wires (matrix) and then modifying their surface by deposition of carbon nanotubes (second phase) on the nickel wire arrays. The large interest in consolidated nanomaterials results from their numerous potential application in various areas such as materials and biomedical science, electronics, optics, magnetism, energy storage and electrochemistry.

Nanotubes belong to a promising group of nanostructured materials. Although other nanotubes based on boron nitride and molybdenum have been reported [3], currently carbon nanotubes are by far the most studied group. Carbon nanotubes are one of the most commonly used building blocks of nanotechnology with one hundred times the tensile strength of steel, a thermal conductivity better than all but the purest diamond and electrical conductivity similar to copper, but with the ability to carry much higher current, therefore they seem to be very interesting class of material [4].

The main objectives of this study are to synthesize consolidated composite carbon nanomaterial and to look at its physical and electrochemical properties.

Nanowire synthesis in pores of a polymeric template can be accomplished using electroless or electrochemical means. Chemical deposition methods have the advantage of filling or partially filling i.e. nanowires or nanotubes with pre-determined amounts by varying the deposition time. [5, 6]. With electrochemical deposition, the pores are continuously filled with control over the length of the resulting wire being achieved by varying the time of the applied potential [5, 6, 7]. However, it is the variation of the wire diameter which ultimately leads to the change and control of the resulting nano-wire or micro-wire properties. By synthesizing the nickel wires, the wires can then be used directly as a catalyst for carbon nanotube synthesis.

Carbon nanotubes have excellent electrical, mechanical and thermal properties. [8, 9]. The unique arrangement of the carbon atoms, allows for the modification of the outer wall of the nanotube with specific chemical functionalities that may or may not alter the general properties of the nanotube. [10]. By combining metal micro-wires and carbon nanotubes a new composite material can be realized which may have properties that differ from the individual components. In this study the synthesis of Ni wires within the pores of nuclear track-etched membrane is presented. The Ni wires were modified by CVD growth of carbon nanotubes and extensively characterized.

## Research area

The main research areas of the investigation were: Investigation of the synthesis of the consolidated composite carbon nanomaterials, its characterization and study of the physico-chemical properties influencing its electro-activity.

## Research frame work and design

Assumptions on which this study is based are given as follows:

- Carbon nanotubes exhibit unusual strength, excellent mechanical, electrical, thermal and magnetic properties.
- Nickel wires exhibit enhanced electrocatalytic activities compared to the corresponding bulk materials.
- Nickel is an excellent catalyst for the synthesis of carbon nanotubes via chemical vapour deposition.

The consolidated carbon nanomaterial will be characterized to determine its physico-chemical properties using a range of characterization techniques. The consolidated carbon nanomaterial was investigated on the basis of its electrocatalytic activities and capacitances.

## Range or Scope of the investigation

In this study the following research areas ***will be*** investigated

- The synthesis of novel consolidated carbon nanomaterial via template synthesis of nickel micro-wires and CVD growth of carbon nanotubes.
- Electrochemical deposition of nickel wires in porous track-etched membranes.
- Pyrolysis of (Liquid Petroleum Gas) LPG via chemical vapour deposition on nickel wires.
- The structural characterization of the consolidated composite carbon nanomaterial.
- The electrochemical characterization of the consolidated carbon nanomaterial.

## Investigation outline

Chapter 2: ***Literature Review: Synthesis of novel consolidated composite carbon material.***

The literature review focuses on the discussion of carbon nanotubes, their structure, synthesis and application. This is then followed by a discussion of template synthesis of nickel wires. This chapter is then concluded by the application of novel consolidated carbon nanomaterial in a number of fields.

Chapter 3: ***Materials and Method***

Chapter 3 fundamentally serves as a continuation of the literature review, but with more emphasis placed on the characterization techniques employed in the study. It also gives and outline of the different materials that were used in the study.

Chapter 4: ***Results and Discussion***

Chapter 4 gives insight into the synthesis of novel consolidated composite carbon materials. It first starts with the synthesis of the nickel wires via template synthesis and then the deposition of carbon nanotubes directly onto the surface of the nickel wires via chemical vapour deposition. This is then followed by the morphological study of the material by scanning electron microscopy, transmission electron microscopy and X – ray diffraction. Electrochemical characterization of the consolidated composite material was studied via cyclic voltammetry, chronoamperometry and electrochemical-impedance spectroscopy are also elaborated on.

Chapter 5: ***Conclusion and Recommendations***

The study is concluded with a concise discussion of the objectives achieved pertaining to the study of novel consolidated carbon material. Recommendations are made, anomalies noted, and the greater relevance and implications of the study are discussed

# Chapter 2: Literature review

## 2. New forms of nanostructured carbon materials

There are a number of different forms of carbon materials which include graphite, diamond and the more recently discovered Fullerenes and carbon nanotubes. All these forms of carbon have different properties. The most interesting form of carbon which most researchers are interested in at present are carbon nanotubes, due to their unique properties.

### 2.1.1. Fullerenes - Carbon allotropes with closed shell arrangement

The chemical element Carbon was only known to exist in two forms - diamond and graphite until 1985 when Kroto and co-workers discovered an entirely new form of carbon, which became known as $C_{60}$ or the Fullerene molecule. The discovery of Fullerenes lead to the finding of carbon nanotubes. Fullerenes are large, closed-cage carbon clusters and have a number of unique properties that were not found in any other compound before. Fullerenes were discovered in 1985 by Kroto and Smalley [11]; they found strange results in mass spectra of evaporated carbon samples. Before the synthesis of the smaller Fullerenes C60 and C70, it was generally accepted that these large spherical molecules were unstable. However D.A. Bochvar and co-workers [12] had calculated that C60 in the gas phase was stable and had a relatively large band gap. Therefore with the discovery of Fullerenes and with their stability in the gas phase proven the search for other Fullerenes commenced.

### 2.1.2. Carbon Nanotubes – Carbon with graphene sheets arranged to form tubes.

In 1991 Iijima and co-workers [13] discovered carbon nanotubes. Carbon nanotubes have been investigated by many researchers all over the world. Their large length (up to several microns) and small diameter (a few nanometers) results in large aspect ratio. Carbon nanotubes can be seen as the nearly one dimensional form of Fullerene. Therefore carbon nanotubes are expected to have interesting electronic, mechanical and molecular properties.

Many exotic structures of Fullerenes exist: regular spheres, cones, tubes and also more complicated and strange shapes. In what follows we describe some of the most important and better-known structures. There are basically two forms of carbon nanotubes: multi-walled nanotubes (MWNT) and single-walled nanotubes (SWNT).

Carbon nanotubes are built from $sp^2$ carbon units and consist of honeycomb lattices of seamless structure. They are tubular having a diameter of a few nanometers but a length of many microns.

SWNTs are made of single seamlessly rolled graphite sheet with a typical diameter of about 1.4 nm which is similar to a buckyball (C60). [14]. SWNTs have a number of different structures which include armchair, zigzag or chiral shapes, and all depend on how the graphene walls of the nanotubes are rolled together see **Figure 2.1**.

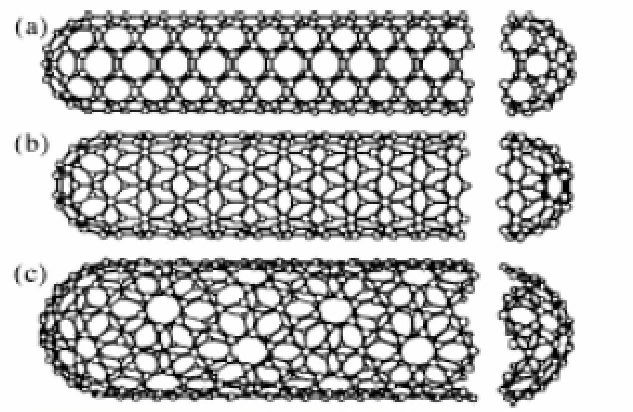


**Figure 2.1:** *Some SWNTs with different chiralities. The difference in structure is easily seen at the open end of the tubes a) armchair structure b) zigzag structure and c) chiral structure.*

The different shapes of the carbon nanotubes are distinguished by their unit cells which are determined by the chiral vector see **Figure 2.2** where $\hat{a}_1$ and $\hat{a}_2$ are unit vectors in the two-dimensional hexagonal lattice and n and m are integers. Another important parameter is the chiral angle, which is the angle between $C_h$ and $\hat{a}$.

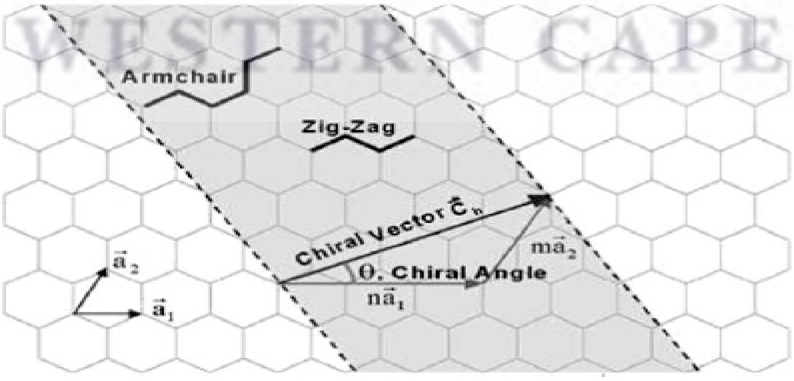


**Figure 2.2:** *Schematic diagram showing how a hexagonal sheet of graphite is'rolled' to form a carbon nanotube. [15].*

When n = m and the chiral angle is 30 degrees the shape is known as an armchair type. When m or n are zero and the chiral angle is equal to zero the nanotubes shape is known as zigzag. Chiral nanotubes occur when the chiral angle is between 0 degrees and 30 degrees. [15].

MWNTs can be considered as a collection of concentric SWNTs with different diameters see **Figure 2.3**. In a MWNT, the diameter usually ranges between 2 – 25 nm and the distance between the sheets is about 0.34 nm. [16, 17].

**Figure 2.3:** *Graphene sheets rolled up into concentric cylinders form MWNTs*

## 2.2. Physico-chemical synthesis methods of Carbon Nanotubes

Carbon nanotubes are generally produced by three main techniques namely, electric-arc discharge, laser ablation and chemical vapour deposition.

### 2.2.1. Synthesis of Carbon Nanotubes by electric-arc discharge

The arc-discharge method [18, 19] is one by which carbon nanotubes were first produced. This is the most widely used process for producing carbon nanotubes, and is also used in producing Fullerenes. It is based on an electric arc-discharge generated between two graphite electrodes (rods) under an inert atmosphere of helium (He) or argon (Ar) gas. [16, 20]. A high temperature occurs between the two electrodes during the process which then allows the sublimation of carbon nanotubes. Two kind of synthesis can be performed in the arc: evaporation of pure graphite or co-evaporation of graphite and metal. [21]. It has been shown [22] that the addition of small amounts of transition metal powders, like cobalt, nickel and iron, to the electrodes favours the growth of single walled nanotubes. The metal serves as a catalyst, preventing the growing tubular structures from wrapping around and closing into smaller Fullerene cage. [22]. The arc-discharge evaporation of pure graphite rods has been carried out not only in gases like helium (He) or argon (Ar) but also in methane ($CH_4$). [23]. It was found that methane is an excellent gas for the synthesis of MWCNTs. This is due to the thermal decomposition of methane producing hydrogen ($2CH_4 \longrightarrow C_2H_2 + 3H_2$) which is and exothermic reaction that achieves higher temperature and activity compared to inert gases such as He or Ar. [24]. The high activity is due to the formation of $H_2$ gas from the thermal decomposition of methane which is not observed when using inert gases. The main drawback of the electric-arc discharge method is the purification of carbon nanotubes.

Removal of non-nanotube carbon and metal catalyst materials is more expensive than production itself. [25].

### 2.2.2. Laser Ablation as a production method for Carbon Nanotubes

Laser ablation is the process of removing materials from a solid or occasionally liquid surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimes. Usually, laser ablation refers to removing materials with a pulsed laser, but it is possible to ablate material with a continous wave laser beam if the laser intensity is high enough.

The laser ablation method had been originally used as a source of metal clusters and ultrafine particles. [26, 27]. It was then later developed for Fullerene and carbon nanotube production. The carbon nanotube method was developed by Richard Smalley and Co-workers at Rice University, who at that time of the discovery of carbon nanotubes, were blasting metals with the laser to produce various metal molecules. When they heard of the discovery, they substituted the metals with graphite to create multi-walled carbon nanotubes. [28]. Later that year the same team used a composite of graphite and metal catalyst particles (cobalt and nickel) to synthesize single-walled nanotubes. [29].

The basic principle of this method is as follows: In laser ablation carbon is vaporized from the surface of a solid disk of graphite into a high density helium or argon flow, using a focused pulsed laser. A graphite target is placed in a quartz tube mounted in a temperature controlled furnace. The temperature is then increased to 1200 $^0$C. The tube is then filled with a flowing inert gas and a scanning laser beam is focused on the target. Laser vaporization produces carbon species, which are swept by the flowing gas from the high temperature zone and then deposited on a conical water cooled-copper collector. [16, 18].

### 2.2.3. Chemical Vapour Deposition of Carbon Nanotubes by Hydrocarbon Pyrolysis

The first two methods, arc-discharge and laser ablation, have the drawback that they do not allow the location and alignment of the synthesized carbon nanotubes to be controlled. This can be avoided by the chemical vapour deposition (CVD) method. CVD is a popular method for producing CNTs in which a hydrocarbon vapour is thermally decomposed in the presence of a metal catalyst. The method is also known as thermal or catalytic CVD to distinguish it from the many other kinds of CVD used for various purposes. Compared with arc-discharge and laser ablation, CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure. CVD is a versatile technique in that it harnesses a variety of hydrocarbons in any state (solid, liquid and gas), enables the use of various substrates and allows CNT growth in a variety of forms, such as powders, thin or thick films, aligned or entangled, straight or coiled or even a desired architecture of nanotubes at predefined sites on a patterned substrate. [30]. In fact, CVD has been used for producing carbon filaments and fibers since 1959. [31, 32, 33]. The CVD process involves passing a hydrocarbon vapour through a tube furnace in which a catalyst material is present at sufficiently high temperature to decompose the hydrocarbon. CNTs grow over the catalyst and are collected upon cooling the system to room temperature. CNTs have been successfully synthesized also using organometallic catalyst precursors. [34]. The three main parameters for CNT growth in CVD are type of hydrocarbon, type of catalyst and growth temperature.

In this research chemical vapour deposition was chosen as the preferred method for the synthesis of carbon nanotubes. There are a number of different reasons why CVD was chosen.

Carbon nanotubes produced by arc-discharge are normally long and straight, with good crystallinity, but are difficult to purify because they contain carbon particles and even amorphous carbon. Carbon nanotubes made from Laser ablation are primarily SWNTs with good diameter control and few defects, but it is a cost intensive technique because it requires expensive lasers and high power requirements.

The Chemical Vapour Deposition method has drawn a lot of interest recently, an important advantage being that the diameter of the nanotubes can be easily controlled and adjusted through the pore shape and size when using suitable templates. Another advantage of CVD is that it is very easy to 'scale up' the method making it favourable for commercial production.

**LPG Pyrolysis:** In the chemical vapour deposition method the synthesis of carbon nanotubes occurs by using gaseous carbon-containing source gas. These source gases are typically pure $C_2H_2$ or a $CH_4$:$H_2$ mixture, which decompose under conditions that promote carbon nanotube growth. In the group at the South African Institute for Advanced Materials Chemistry (SAIAMC) LPG is chosen as the carbon source for carbon nanotube synthesis. [35]. The simplicity and versatility of the CVD technique developed at the institute for this purpose does not require complicated vacuum equipment and high-power equipment for initiating or maintaining an electric arc or a laser source. The carbon source used by the institute is liquid petroleum gas (LPG), and one of the advantages of the developed method is that it does not need hydrogen to pre-treat the catalysts or control the growth of the carbon nanotubes. LPG has already been employed to grow carbon nanotubes [36,37]; however in previous studies the use of different substrates or catalysts was not examined. In the SAIAMC, carbon nanotubes have been successfully synthesized on various substrates such Co foil, Ni foil and Ni porous membranes by CVD and by using LPG as the carbon source see **Figure 2.4**.

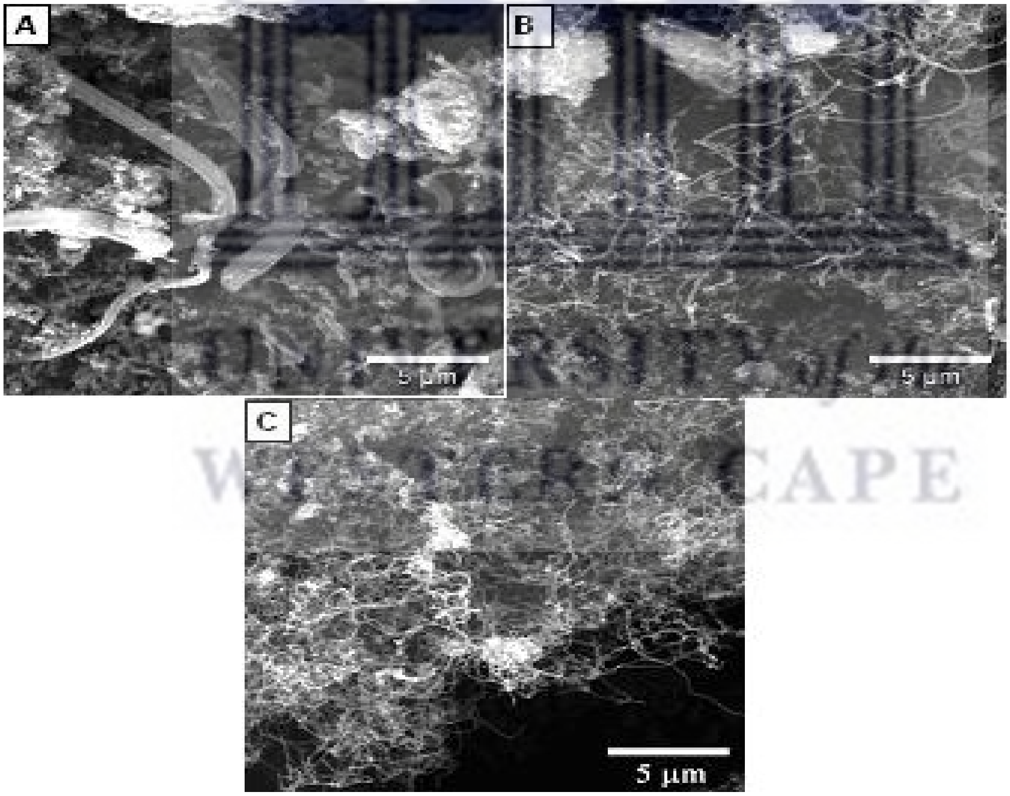


**Figure 2.4:** *SEM micrographs of CNT grown on Co foil (A), Ni foil (B), and Ni- porous membranes (C). Deposition temperature 800 $^0$C, LPG flow rate 0.35L/min, total deposition time 30 min.*

From the above results CVD and LPG pyrolysis was chosen for the synthesis of carbon nanotubes on the surface of the Ni micro-wires arrays.

**Temperature:** The growth, structure and yield of carbon nanotubes are strongly effected by the temperature in chemical vapour deposition. Carbon nanotubes are usually formed between 650 $^0$C and 1000 $^0$C with different structures and yields.

It has been reported [38] that carbon nanotubes produced at 650 $^0$C have similar morphology to those grown at 700 $^0$C and 750 $^0$C, but with smaller diameter and lower yield. Therefore as the temperature increases the yield and the diameter increase. At 800 $^0$C the carbon nanotubes are not uniform in diameter and start to show rough surfaces and curved shapes. At temperatures above 900 $^0$C the yield of carbon nanotubes is low. Carbon nanotubes produced at high temperatures (e.g. at 1000 $^0$C) are not pure nanotubes but a mixture of nanotubes and carbon particles. Therefore the appropriate temperature range to prepare carbon nanotubes by the chemical vapour deposition method is between 750 and 850 $^0$C, where one usually obtains pure carbon nanotubes with large yields. [38, 39 ]

**Table 2 1:** Summary of the production methods for carbon nanotubes

| Method | Arc -Discharge | Chemical Vapour Deposition | Laser Ablation |
|---|---|---|---|
| Pioneers | Ebbesen and Ajayan, NEC Japan 1992. | Endo Shinshu University Nagano Japan. | Smalley, Rice 1995. |
| How | Connect two graphite rods to a power supply, place them a few millimeters apart and turn switch. At 100 amps carbon vaporizes and forms a hot plasma. | Place substrate in oven, heat to $600^0$C and slowly add a carbon-bearing gas such as methane. As the gas decomposes it frees up carbon atoms, which recombine in the form of NT's. | Blast graphite with intense laser pulses, use the laser pulses rather than electricity to generate carbon gas from which the NT's form, try various conditions until hit on one that produces prodigious amounts of SWNTs. |
| Typical Yield | 30 to 90% | 20 to 100% | Up to 70% |
| SWNT | Short tubes with diameters of 0.6-1.4nm. | Long tubes with diameters range from 0.6-4nm. | Long bundles of tubes (5-20microns), with individual diameters from 1-2nm. |
| MWNT | Short tubes with inner diameter of 1-3nm and outer diameter of approximately 10nm. | Long tubes with diameter ranging from 10-240nm. | Not very much interest in this technique, as it is too expensive. But MWNT synthesis is possible. |
| Pros | Can easily produce SWNTs & MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible. | Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure. | Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure. |
| Cons | Tubes tend to be short with random sizes and direction often needs a lot of purification. | NT's are usually MWNTs and often riddled with defects. | Costly technique, because it requires expensive lasers 7 & high power requirements. |

## 2.3. The Role of catalysts in Carbon Nanotube growth

The synthesis of carbon nanotubes can be divided into two main categories: these are the non-catalytic and the catalytic methods.

- The non-catalytic category includes laser ablation and the electric arc discharge methods where graphite is used as the carbon source.
- The catalytic category includes the chemical vapour deposition method; transition metals such as nickel, cobalt and iron are used as pure metal catalysts for carbon nanotube growth. [40].

Transition metals such as nickel, iron and cobalt are the only three transition metals that can be used as pure metals.[41, 42, 43]. A number of reports have appeared in the literature regarding carbon nanotube synthesis where nickel, iron and cobalt were used either separately or in different methods or together as a composite catalyst. [44]. Transition metal catalysts such as nickel, iron and cobalt strongly influence nanotube diameter, growth rate, morphology and microstructure. [45]. The ability of these transition metals to form ordered carbon is thought to be related to a combination of factors. These include their catalytic activity for the decomposition of volatile carbon compounds, the fact that they form metastable carbides, and that carbon is able to diffuse through and over the metals extremely rapidly. [46, 47].

It was reported [45] that nanotubes grown from Ni have the largest diameter, the highest growth rate and the best alignment. They also exhibit reasonably good graphitized tubular microstructure. Nanotubes catalyzed by Co have the smallest diameter and lowest growth rate. Fe and Co both produce carbon nanotubes that have a thinner wall compared to Ni catalyzed nanotubes. Carbon nanotubes grown from Ni and Fe are relatively free of amorphous carbon, but those from Co are covered with amorphous carbon and carbon particles.

Since carbon nanotubes were observed, there has been extensive research on their synthesis using arc discharge, laser ablation, pyrolysis and plasma or thermal chemical vapour deposition methods. Among these methods chemical vapour deposition has many advantages of carbon nanotubes synthesis with high yield, high purity, selective growth and vertical alignment. However the growth temperature of thermal CVD is normally as high as 650-1000 $^0$C.

However a co-catalyst can be used to decrease the growth temperature of carbon nanotubes and also change the morphology of the carbon nanotubes. The two most promising co – catalysts are platinum (Pt) and palladium (Pd).

It has been reported [40] that Pd co-catalyst decreases the growth temperature of carbon nanotubes to 500 $^0$C, and Pt co-catalyst to 550 $^0$C. Pd co-catalyst causes the carbon nanotubes to have a bamboo-like structure, while Pt co-catalyst causes the carbon nanotubes to have a whiskers-like structure. [40].

## 2.4. Nanocomposite Materials

Composite nanomaterials can be considered as a kind of new material, which exhibits exotic physical and chemical properties different from the bulk material because of the size effect and the combination of various materials. An increasing interest has been focused on composite nanomaterials in science in technology in the field of chemical power sources. Nickel nanomaterials are widely used as electrode active materials in secondary batteries. [48]. Literature have reported that the addition of various nanomaterials such as carbon, polymers and various other metals to Bulk our nano-scale nickel to form a composite can alter the properties of the material. It was shown that the addition of nanosized carbon to the conventional Ni electrode greatly increase the specific capacity.[49,50 ].

### 2.4.1. Consolidated Composite Carbon Materials

The recent emphasis on solving material issues associated with fuel cells, supercapacitors and other emerging technologies for storage and conversion of energy is leading to a greater interest in high-surface area materials and nano composites such as consolidated composite materials. Nanoscale forms of carbon such as nanotubes and nanofibers are looking very promising because in addition to providing high surface area, excellent thermal stability and good electrical conductivity, they can also be combined with nanoparticles and other materials to form composite structures with customized electrical and chemical properties.

There is a growing demand for electronic devices that require high power density and long life cycle. It was illustrated by Robert. J. Hamers and co-workers [51] that composite based carbon nanotubes or nanofibers are particularly interesting for applications such as electrocatalysis, electrodes and fuel cells because of the carbon nanotubes or nanofibers arrangement that exposes edge-plane graphite along the side-walls, leading to increased electrical and chemical activity. Their work also demonstrates a method for producing nanostructured metal electrodes by functionalizing carbon nanotubes or nanofibers with metal particles.

Although carbon nanotubes or nanofibers provide a high-surface area substrate, Robert. J. Hamers and co-workers [48] have demonstrated a method for fabricating complex nanoscale structures that exhibit 10 times higher electrically accessible surface area than that of a nanofiber template, and 100 times higher than a planar surface. The high electrically accessible surface area is due to the metal particles attached to the nanotubes or nanofibers. By using a similar process for other metal electrodes it is suggested that this procedure may be useful for preparing a wide range of nanostructured metallic nanocomposites with novel electrical, catalytic and electrocatalytic properties.

Their work supports our novel concept to synthesize consolidated composite carbon materials. As explained in chapter 1 the consolidated composite carbon material will be synthesized by using a template technique to develop the nickel micro-wire catalyst and chemical vapour deposition to deposit the carbon nanotubes directly onto the catalyst.

## 2.5. Modern technologies in the preparation of consolidated nano-structured transition metals

Nano-structured transition metals have been shown to exhibit novel and significant improved physical, mechanical and chemical properties due to their nano scale dimensions when compared to their bulk structures. There are various ways to synthesize nano-structured transition metals: synthesis in powder form to form nanopowders or by template synthesis to form nano or microwires.

### 2.5.1. Synthesis and consolidation of metal nanopowders

There are basically four main directions of research and development in the field of nanoparticles. The first is that of obtaining nanoparticles by means of plasma chemistry, mechano-synthesis, electrical explosion of wires, low temperature reduction and sol-gel technology. The second direction is that of research on the properties and structure of nanoparticles and development of methods for characterizing and stabilizing them. The third direction is the development of new methods of obtaining nanoparticles (e.g. radiation-chemical synthesis, self-propagation high temperature synthesis). A large amount of research is performed on the formation of nanoparticles in polymer and inorganic matrices. The fourth direction is when the nanopowders are used as the basis for consolidated nanomaterials for various purposes as well as in an isolated form.
There has been a noticeable expansion in research in consolidated nanomaterials in areas such as catalytic, optical and biological properties of nanoparticles. [52].

Nanocrystalline and nanophase materials generally referred to as nanostructured materials, have many potential magnetic, electronic and structural applications. One of the main problems facing nano-science research is the economic reduction of nanopowders which is being pursued by a variety of techniques in order to meet the increasing demand for nanopowders

**Table 2.2:** Various techniques for synthesizing nanopowders

| No. | Nanopowder Synthesis Method | Metal/Ceramic nanopowder synthesis | Process Disadvantage |
|---|---|---|---|
| 1 | ***Ball milling/ Mechanical Attrition***: Powder particles subjected to severe mechanical deformation, with strain rates as high as $10^4$/sec. | Fe, Co, Ni, NiAl, TiAl and FeSn | Powder contamination due to WC or steel balls. Low production rates, 1-5g/hr, depending on material and size of milling. |
| 2 | ***Laser Ablation***: High energy focused laser beam, forms a plasma zone resulting in ultrafine particles. | AIN, MnO2, TiO2, Ti | Low production rate, 0.0lg/hr and high-energy consumption, is highly uneconomical. |
| 3 | ***Vapour Condensation:*** similar to physical vapor deposition (PVD), the difference being the use of a liquid nitrogen column to let the vaporized materials condense, instead of a substrate for deposition. | Fe, MgO, Cu, TiO2 | Low production rates, (l-5 g/hr) difficult to control particle size and particle size distribution. |
| 4 | ***Sputtering:*** a DC or RF sputter source is used for vaporizing the material, instead of laser as in laser ablation. | Al, Cu, Mn | A broad particle size distribution is obtained,<br>only 6-8%, of sputtered material, is reported to be < 100nm. (<4-S g/h) |
| 5 | ***Chemical Precipitation:*** involves mixing of two or more chemical 'precursors', and/or a catalyst, to form a 'gel'. The gel is dried under pre-determined temperatures, and further reduced under H2, to form nanopowders. | SiC, BaTiO3, W-Cu, MO-Cu | Production rates are close to l0-50 gm/day, agglomeration of powders and oxidation, from use of liquid chemical precursors are major disadvantages. |
| 6 | ***Induction Plasma:*** RF generator, coupled to copper coils, ionizes plasma gas. Temperatures, as high as l0.000$^0$C, are achieved. Material fed into plasma zone, vaporizes and recondenses as nanoparticles on the chamber walls. | Fe, AIN, Cu and metallic borides, nitrides and carbides. | High-energy consumption, uneconomical, electric field has to be converted to magnetic, which ionizes the gases. Efficiency is generally 50% or less. |

### 2.5.2. Transition metal nano or microwires and tubes synthesized using template techniques

Nearly any solid matter can in principle be synthesized within nanoporous templates provided a suitable chemical pathway can be developed. [53, 54]. However there are same asspects that need to be considered.

- Does the deposited material wet the pores?
- Will the deposition reaction proceed too fast resulting in pore blockage at the membrane surface before tubule/fiber growth can occur within the pores?
- Will the host membrane be stable (i.e. thermally and chemically) with respect to the reaction conditions.

By depositing metals into the nanopores, nanowires with a diameter predetermined by the diameter of the nanopores are fabricated. There are essentially several representative chemical strategies to carry template synthesis within the alumina and polymeric template membranes [51]. See **Figure 5** below.

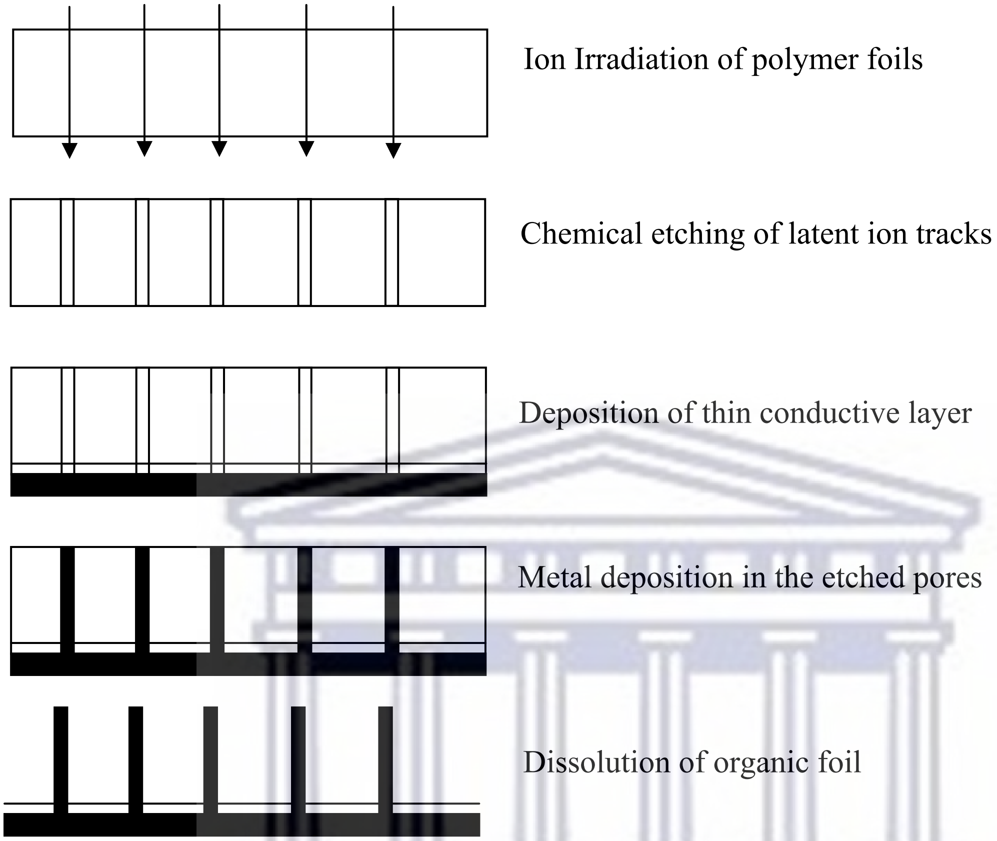


**Figure 2.5:** *Principal diagram of metal deposition into etched ion-track polymer membrane.*

A schematic representation of the process flow for synthesizing regular arrays of oriented nanotubes on a substrate by catalyst patterning and CVD is shown in **Figure 2.6**. The pattern was created on a hydrophilic substrate, such as glass, by the standard photolithography method, using a printed polymer foil as the photomask. To provide a better electric conduct, the hydrophilic substrates were metallized by thermal evaporation and photoresist lift-off. Aligned nanotubes were obtained previously by using CVD over catalysts embedded in mesoporous silica and over laser-patterned catalysts [55, 56].

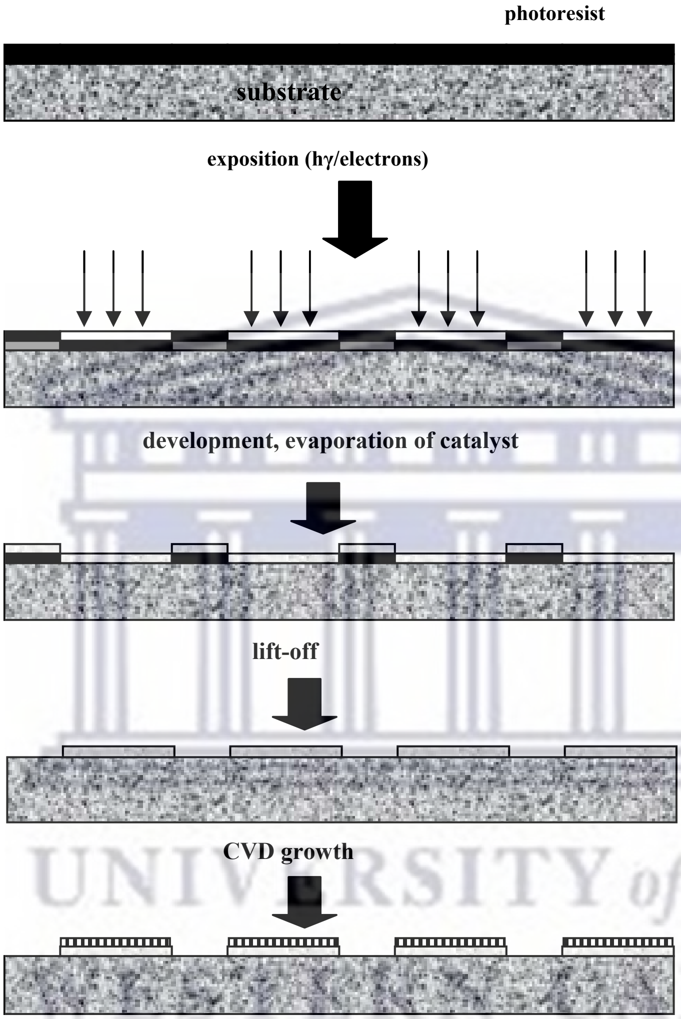


**Figure 2.6:** *Schematic process flow for the synthesis of regular arrays of oriented nanotubes on a substrate by catalyst patterning and chemical vapour deposition (CVD).*

**Electrochemical deposition**: This is one of the most widely used methods to fill conducting materials into nanopores to form continuous nanowires with large aspect ratios. One of the great advantages of the electrodeposition method is its ability to create highly conductive nanowires. This is because electrodeposition relies on electron transfer, which is fastest along the highest conductive path. Another important advantage of the electrodeposition method is the ability to control the aspect ratio of the metal nanowires by monitoring the total amount of passed charge. This is important for many applications where, for example, the optical properties of nanowires are critically dependant on the aspect ratio. [57].

Electrodeposition of a material within the pores of the matrix is preceded by coating one face of the template with a metal film and using this metal as a cathode for electroplating. This method has been used to prepare a variety of metal nanowires including copper, platinum, gold, silver and nickel in both track-etched and alumina templates. The length of these nanowires can be controlled by varying the amount of metal deposited. By depositing a small amount of metal, short wires can be obtained; alternatively by depositing large quantities of metal, long needle-like wires can be prepared. [58].

**Electroless deposition**: In electrochemical deposition the electrodes required for the reduction of metal ions are supplied by an external current. In electroless deposition the electrons required for reduction are supplied by the catalytic or electrocatalytic oxidation of a reducing agent. Electroless deposition involves the use of a chemical agent to plate a material from the surrounding phase onto a template surface. [50]. Electroless deposition differs from electrochemical deposition in that the surface to be coated need not be electrochemically conductive.

In electroless deposition the material deposition in the pores starts at the pore wall. Therefore after short deposition times, a hollow tubule is obtained within each pore, whereas long deposition times result in solid nanowires. Unlike the electrochemical deposition method where the length of the metal nanowires can be controlled at will, electroless deposition yields structures that run the complete thickness of the template. [59].

**Chemical polymerization**: Different conductive polymers can be synthesized by the polymerization of the corresponding monomer to yield tubular nanostructures. [60, 61]. Chemical polymerization is a process that can be accomplished by simply immersing the membrane into a solution containing the desired monomer and a polymerization reagent. The polymer preferentially nucleates and grows on the pore walls, resulting in tubules at short deposition times and fibers at long deposition times.

**Sol – gel**: Synthesis within the pores of templates can be conducted to create both tubules and fibers of a variety of materials. [62]. Sol-gel deposition is a process that typically involves preparation of a solution of a precursor molecule to obtain firstly a suspension of colloid particles (the sol) and then secondly a gel composed of aggregated sol particles which is thermally treated to yield the desired nanostructure within the pores of the template.

## 2.6. Porous Templates used to synthesize transition metal nano or microwires

In template synthesis of nanostructures, the chemical stability and mechanical properties of the template as well as the diameter, uniformity and the density of the pores are important characteristics to consider. There are a number of different templates that have been used for nanowire synthesis; these include anodic alumina, nano-channel glass, ion track-etched polymers and mica films. The frequently used templates for nanowire synthesis are anodic alumina and track-etched membranes.

### 2.6.1. Porous Alumina templates

Porous anodic alumina templates are produced by anodizing pure Al films in various acids. [63]. Under carefully selected anodization conditions the resulting film possesses a regular hexagonal array of parallel and nearly cylindrical channels. The organization of the pore structure in an anodic alumina template involves two coupled processes. Firstly a pore formation with uniform diameter and secondly pore ordering. The pores form with uniform diameters because a balance exits between the electric-field-enhanced diffusion which determines the growth rate of the alumina and the dissolution of the alumina into the acid electrolyte. The pores are believed to self – order because of mechanical stress at the aluminum-alumina interface due to expansion during anodization. The stress produces a repulsive force between the pores, causing them to arrange into a hexagonal lattice. [64].

## 2.6.2. Track-etched membrane templates

Track-etched membranes have been widely used recently as templates for the synthesis of micro and nanostructures. Track-etched membrane production follows a two step process. The first is the formation of latent tracks by heavy ion irradiation which is followed by the subsequent enlargement of tracks to pores by chemical etching. Variation of the irradiation and etching conditions enables the production of suitable membranes with pores of different geometries, sizes and aspect ratio.

There are two basic methods of producing latent tracks in the polymer films to be transformed into porous membranes. [65].

The first method is based on irradiation with fragments from fission of heavy nuclei such as californium (Cf) or uranium (U). Exposing uranium to a neutron flux, a nuclear reactor initiates the fission of $^{235}$U. Typical energy loss of the fission fragments is about 10keV/nm. The second method is based on the use of ion beams from accelerators. [66]. The intensity of the beam should be at least $10^{11}$ $s^{-1}$ to be competitive in the track membrane industry. Modern accelerators provide beams of higher intensities. The energies of the accelerated ions are a few MeV per nucleon. The beams can be pulsing or continuous. To irradiate large areas a scanning beam is normally used.

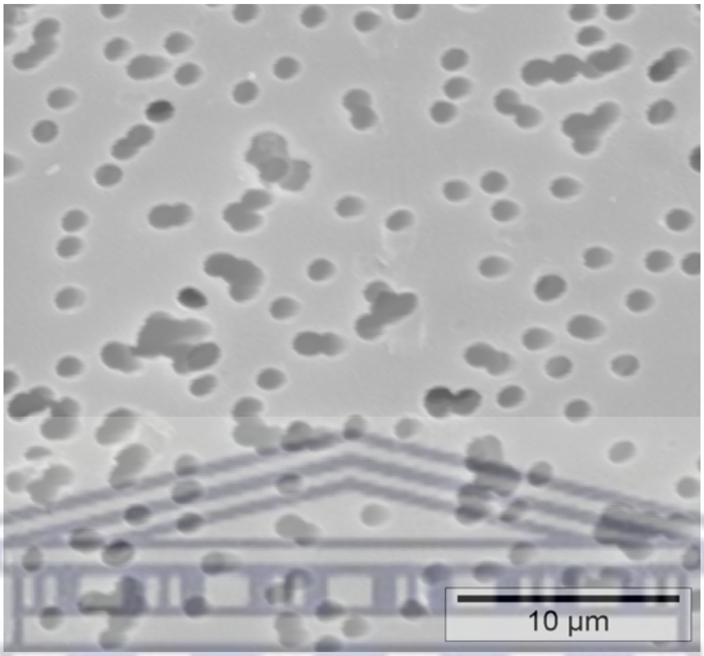


**Figure 2.7**: *SEM image of the surface of a track- etched membrane.*

Track-etched membranes have advantages over conventional membranes because of their precisely determined structure. However, many large scale applications are insensitive to such a brilliant property. Track membranes occupy a niche in biological, medical, analytical and scientific applications. These types of membranes are indispensable for manipulations with small particles of living and other matter. [67].

Track-etched membranes seem to be the best porous material for providing controllable transport of solutes. Further progress in track-etched membrane technology can be connected with the creation of membranes having particular properties for a particular use. For example membranes that do not adsorb proteins, membranes with various functional groups on the surface etc, might be developed and introduced into industry.

## 2.7. Nickel impregnation into polymer templates via electrochemical deposition

Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive aqueous solution of nickel salts. It is the electrolytic deposition of a layer of nickel on a substrate. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). [68]. Direct current is applied between the anode (positive) and the cathode (negative). Conductivity between the electrodes is provided by an aqueous solution of salts. When nickel salts are dissolved in water, the nickel is present in a solution as divalent, positively charged ions ($Ni^{2+}$). When current flows, divalent nickel ions absorb with two electrons ($2e^-$) and are converted to metallic nickel ($Ni^0$) at the cathode.

The reverse occurs at the anode where metallic nickel dissolves to form divalent ions. The electrochemical reaction which takes place is:

$$Ni^{2+} + 2e^{-} \leftrightarrow Ni^{0}.$$

Because the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode, the nickel plating process can be operated for long periods of time without interruption.

Nickel electroplating basically consists of an electrolyte that contains nickel sulphate, ammonium chloride and boric acid. Nickel sulphate is the principle source of nickel ions, ammonium chloride improves the anode dissolution and increases the solution conductivity, while boric acid helps to produce smoother, more ductile deposits. [57]. Anionic anti-pitting or wetting agents are required to reduce the pitting due to the clinging of hydrogen bubbles to the products being plated.

## 2.8. Novel applications of carbon nanotubes in power generation devices

Carbon nanotubes have generated an interest amongst scientists and engineers since its discovery by Iijima in 1991 [13] that surpasses almost any material known to man. Carbon nanotubes have been found to possess a wide variety of extremely remarkable properties, most notably high electrical and thermal conductivity, mechanical strength and catalytic surface area. These properties imbue carbon nanotubes with tremendous potential for a variety of power generation and storage devices.

### 2.8.1. Carbon application in electrode preparation for fuel cells

The major motivation for the use of carbon nanotubes in PEM fuel cells is due to the fact that it has the potential for significant enhancement of electrical conductivity and metal support. [69]. The incorporation of carbon nanotubes in PEM fuel cells allows for enhanced oxidation of $H_2$(g), electron transport from the anode to the cathode and reduction of $O_2$(g). [70]. The current technology uses platinum supported carbon powder-based electrodes to promote these processes; recent work has shown the potential for platinum supported MWNTs as a viable material. [71].

## 2.8.2. Carbon electrodes for acid batteries and Li-ion batteries

Carbon nanotubes used in $Li^+$ batteries are an appropriate choice since the anodes are conventionally constructed from graphite. The addition of carbon nanotubes has shown to improve the batteries capacity due to its higher electrical conductivity and specific surface area compared to graphite. [72]. The nanosized pore structures of CNTs may provide hosting sites for storing large amounts of $Li^+$, good chemical stability, high mechanical strength and elastic modulus that could make it possible for CNT electrodes to have a long life cycle and high electrical conductivity. [73].

## 2.8.3. Carbon Nanotubes as possible material in polymeric solar cells

Single wall carbon nanotubes have recently been incorporated into poly(3-octylthiophene) (P3OT) to promote exciton dissociation and improve electron transport in polymeric solar cells. [58]. In the photovoltaic community, conducting polymers like P3OT have attracted significant attention since they produce excitons (quantum mechanical particles consisting of bound electron-hole pairs) upon optical absorption. [74]. The use of SWNTs in these polymers is an appropriate dopant choice since the electron affinity is higher for SWNTs compared to P3OT and electron transport is typical of a ballistic conductor.

### 2.8.4. Carbon Nanomaterials for hydrogen storage

Reported for the first time by Dillon *et al* [75], was the excellent hydrogen properties of single walled carbon nanotubes. Its nanosized hollow core or interlayer/intertube space may provide holding sites for hydrogen molecules/atoms. Tremendous interest has been aroused in hydrogen storage in CNTs since they were first reported in 1997. Unfortunately because of significantly diverse results reported and lack of clarity concerning the mechanism, the future of hydrogen storage in CNTs remains obscure.

## 2.9. Conclusion of literature review and scope of investigation:

The literature review shows that one of the challenges faced in modern nanotechnology is the preparation of finely dispersed powders, metals, compounds and superfine grained materials, intended for various areas of science and engineering. Consolidated composite materials have attracted fundamental and applied interest. The chemical vapour deposition method, based on the pyrolysis of carbon source gas, is currently actively used for the synthesis of consolidated composite carbon materials. This method allows for the fabrication of carbon nanotubes directly onto various supports, such as powders, films and nano and micro-wires.

A catalyst is required for the synthesis of carbon nanotubes via chemical vapour deposition. At present it is known that transition metals are the best catalysts for carbon nanotube synthesis (as explained early in the literature review). In this investigation Ni micro-wire arrays were chosen as the catalyst, for carbon nanotubes which were synthesized via template synthesis. Template synthesis is based on the use of ultraporous polymeric and inorganic templates, and is currently actively used for synthesizing consolidated materials. This method allows for the fabrication ensembles of nano or microstructured tubes and wires. The structure of these materials is an exact replica of the template matrix. By combining the Ni micro-wire arrays and the carbon nanotubes one would expect a new form of composite material, with properties that would differ from the bulk materials and individual components.

The fundamental purpose of this research is to synthesize consolidated composite carbon materials using scientifically proven technology. Carbon nanotubes were selected as one of the ideal materials. The reason for this is because nanoscale forms of carbon such as nanotubes and nanofibres are intriguing as, in addition to providing high surface areas, excellent thermal stability and good electrical conductivity, they can be combined with metal particles and other materials to form composite structures with tailored electrical and chemical properties.

The objectives of this study were as follows:

- To determine the optimal conditions for homogeneous growth and, in addition, to identify the deposition parameters, namely overpotential, temperature and electrolyte solution, required for the growth of nickel micro-wire catalyst. Track-etched membranes with various pore diameters (i.e. 1µ, 0.4µ and 0.2µ) were used as templates.
- To determine the optimal conditions for synthesis of carbon nanotubes directly onto the surface of nickel micro-wire arrays using LPG pyrolysis and chemical

vapour deposition. To determine the deposition parameters, namely time of deposition, temperature and flow rate of LPG gas.

- To investigate the influence of carbon nanotubes on the surface of the Ni micro-wire arrays. To study the structural parameters and properties of the composite material by SEM and TEM analysis.
- To investigate the electrochemical and physico-chemical properties of the consolidated composite carbon materials. The electrochemical methods used for analysis will be cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS)
- To determine the thermal stability of the consolidated composite carbon material. The thermal stability will be analyzed by thermo-gravimetric analysis (TGA).
- To investigate the crystallinity of the synthesized consolidated composite carbon material by the XRD technique and to determine the influence of the carbon nanotubes on the crystallinity of the nickel micro-wire arrays.
- To investigate the capacitance of the consolidated composite carbon materials via electrochemical impedance spectroscopy (EIS) and its comparison with various carbon based materials.

## Chapter 3: Materials and Methods

In this chapter the methodology and materials that were used to synthesize the novel consolidated Ni micro-wire structured catalyst will be presented, as well as the consolidated composite carbon material which was prepared via chemical vapour deposition. The synthesis of the novel consolidated Ni micro-wire arrays was undertaken via template synthesis. Electrochemical deposition was used to synthesize the stable nickel structures inside the pores of track-etched membranes to form nickel wires.

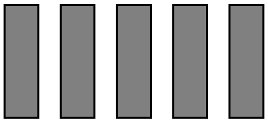
### 3.1. Template synthesis technique for Ni micro-wires using track-etched templates

The template that was used to synthesize the Ni micro structured catalyst was a porous track-etched membrane, properties of which are shown in **Table 3.1** below.

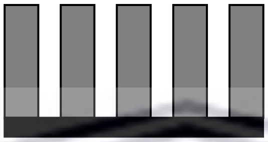
**Table 3.1**: Properties of track-etched membranes

| | |
|---|---|
| Supplier | Joint Institute of Nuclear Research Russia |
| Polymer | Polyethylene terephthalate (PET) membrane |
| Pore diameters | 1μ, 0.4μ, 0.2μ |
| Thickness of template | 23μ |
| Porosity | 1μ = 15%, 0.4μ = 12%, 0.2μ = 10% |

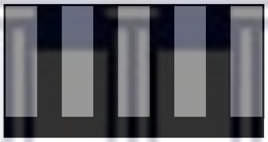
A brief illustration of how the novel consolidated Ni micro-wire arrays were synthesized is shown below.



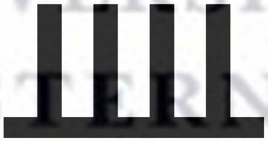
a) Porous track-etched membrane



b) Deposition of conductive layer by sputter coating



c) Electrochemical deposition of nickel into the membrane



d) Removal of template by dissolution

## 3.2. Magnetron sputtering of conductive layer on track-etched membranes

Good adhesion between the polymer foil and the metal layer was found to be essential to prevent the electrolyte from slipping between the conductive layer and the polymer surface during electrodeposition of the wires. A suitable thickness of the platinum (Pt) layer had to be chosen. If the layer is too thin it will not conduct and it will not be possible to clad it with nickel. If the layer is too thick, stress will be induced on the surface of the polymer and the platinum layer will separate.

A conductive layer of platinum, of a thickness estimated to be 100 nm was deposited on one side of the track-etched membrane using a magnetron sputter coater see table 3.3.

**Table 3.2**: Conditions for the deposition of Pt conductive layer on Track – etch membranes.

| | |
|---|---|
| Sputter Coater | Bal-Tec Mac 240 Sputter Coater |
| Target | Platinum (Pt) |
| Pressure | 8 x 10 $^{-5}$ mbar |
| Current | 60 mA |
| Time | 300 seconds |
| Gas | Argon (Ar) |

## 3.3 Method used for the deposition of Ni micro-wire arrays in porous materials

Electrochemical deposition is a technique that is commonly used for depositing coatings, but it can also be used to fabricate both metallic and semiconducting micro / nanowires. In this study nickel was electrochemically deposited into the pores of porous track-etched membranes to form nickel micro-wires.

Electrodeposition of a material within the pores of a matrix is preceded by coating one face of the template with a metal layer and using this metal layer as a cathode for electroplating. In electrodeposition the pores are continuously filled beginning from the pore bottoms. Therefore the length of the structures can be controlled by varying the amount of the material deposited. Both metal and conductive polymers can be synthesized using the electrodeposition method. [76].

In this study, electrodeposition of nickel within the pores of the track-etched membranes was accomplished by coating one side of the membrane with a platinum (Pt) layer which was used as a cathode for electroplating. The membrane was then placed in an electrochemical cell (see figure 3.1) so that the deposited surface faces the anode; the electrochemical cell employed in this study consisted of two electrodes, a working electrode or cathode and a counter electrode or anode.

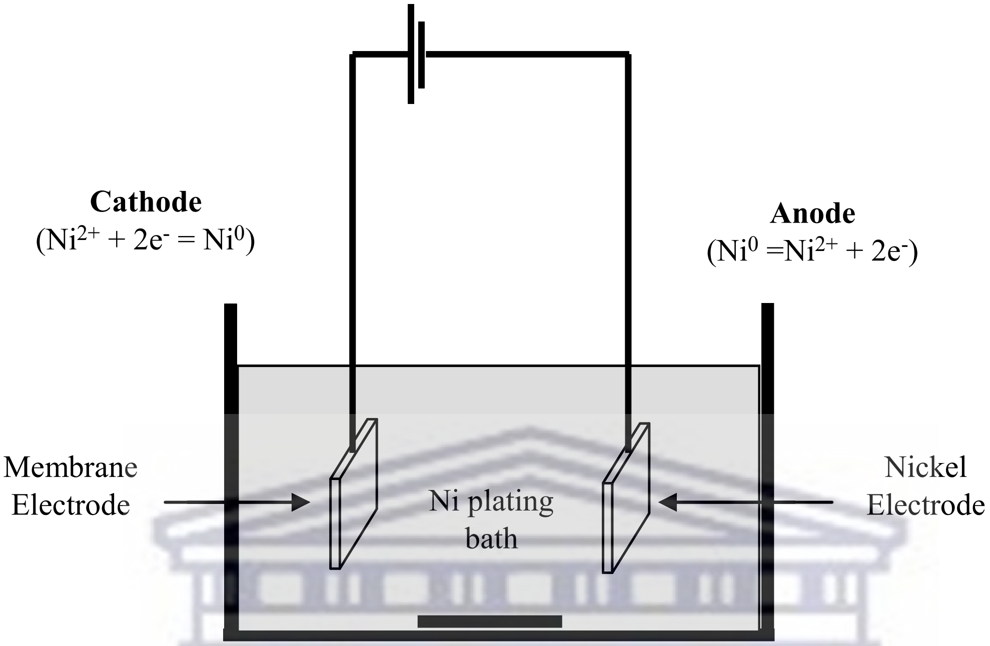


**Figure 3.1**: *Schematic view of the experimental setup used to perform electrochemical deposition of nickel in track-etched membranes.*

The nickel electrodeposition was carried out by the steady-state galvanostatic technique using a nickel plating bath. The electroplating solution used in this investigation was prepared using de-ionized water (Millipore, 18.2 MΩ-cm). The measurements were performed in a 500 $cm^3$ cell with the anode and cathode electrodes 5 cm apart. The electrolyte that was employed in the electrochemical cell was a nickel sulphate solution shown in **Table 3.2**.

**Table 3.3**: Composition of Ni plating bath

| Components | Nickel plating bath |
|---|---|
| $NiSO_4.7H_2O$ | 180g/dm$^3$ |
| $NH_4Cl$ | 25g/dm$^3$ |
| $H_3BO_3$ | 30g/dm$^3$ |
| pH | 5.6 – 5.9 |
| Bath temperature | 35 – 40 $^0$C |
| Current Density for deposition inside template | 0.70 A/dm$^2$ |
| Current Density for Support of template | 1.50 A/dm$^2$ |
| Anode | Nickel (geometrical area of 3 x 10cm$^2$) |

The electrochemical deposition was carried out galvanostatically at temperatures between 35 to 40 $^0$C in an open cell. The deposition of the nickel within the pores of the membrane was done by applying two different current densities 0.70 Acm$^{-2}$ for 10 minutes to deposit Ni within the pores of the template. The template was then covered with a layer of candle wax to prevent over-growing of the Ni wires. This was done by melting a candle and then pouring the candle wax directly on the surface of the track-etch membrane were the Ni micro-wire growth was initiated, the candle wax was then allowed to dry to form a solid wax layer on the surface of the membrane.  The current density was then increased to 1.40 Acm$^{-2}$ for 30 minutes, to increase the support and to prevent the structure from becoming brittle. The membrane was then etched to remove the organic layer. Etching was done in a 6M KOH + 10% ethanol ($C_2H_5OH$) solution for 24 hours.

Under these conditions the resulting nickel micro-wire arrays were polycrystalline and homogeneously covering the pore entrances.

## 3.4. Conditions affecting the structure and the properties of Ni micro-wire arrays

The selection of the electrolyte and the related deposition conditions are of primary importance. Numerous studies have shown that mechanical properties of the nickel coatings depend strongly on the deposition parameters and the bath conditions. [77]. The electrolyte used in electrodeposition should be free from impurities; this is due to the fact that electrode reactions can be extremely sensitive to impurities in the solution. Therefore the salts should be of the highest available purity or recrystallized and the solvents should be carefully purified. There are a number of conditions that influence the characteristics of electrodeposited metal wires; they are namely, current density, concentration of electrolyte, temperature and pH.

At low current densities the discharge of the ions happens at a slow rate, allowing for ample crystal nuclei growth time. The deposit obtained under these conditions exhibits a coarse crystalline structure. As the current density increases, the rate of discharge of the ions also increases. The resulting deposit consists of smaller crystals. Therefore, the increase in current, within certain limits, yields deposits that are finer grained. But there is a definite limit to this improvement, because at very high current densities the crystals tend to grow out from the cathode towards regions where the solution is more concentrated, therefore creating overgrowth within the membrane. Increasing the concentration of the electrolyte can largely offset this effect.

There are two factors that counter one another if one increases the temperature in electrodeposition. Firstly, it promotes the diffusion of ions to the cathode, thereby preventing impoverishment, which leads to roughness of the deposit. Secondly, it increases the rate of growth of the crystal nuclei, so that the deposit will have a tendency to be coarse. When operating at moderate temperatures, such as those generally applied to electroplate nickel, the first of the above mentioned effects predominates, thus the deposits are improved. But at high temperatures the quality of the deposit deteriorates.

The pH of the solution influences the discharge of hydrogen ions, thus causing the solution in the cathode layer to become alkaline and precipitate hydroxides or basic salts. Significant amounts of these compounds will make the resulting deposit exhibit a fine grain structure, but it will be dark in colour or spongy/powdery in character.

Conditions for the growth of the Ni micro-wire catalyst are described in **Table 3.2**.

## 3.5. Synthesis of carbon nanotubes via Chemical Vapour Deposition (CVD) using LPG pyrolysis

Chemical vapour deposition involves the dissociation and chemical reaction of gaseous reactants in an activated (heat, light or plasma) environment, followed by the formation of a stable solid product. The deposition involves homogeneous gas phase reactions, which occur in the gas phase, and heterogeneous chemical reactions which occur in the vicinity of a heated surface leading to the formation of powders or films. [78].

In this study chemical vapour deposition was used to synthesize carbon nanotubes directly onto the nickel micro-wires to form consolidated composite carbon material. To synthesis carbon nanotubes through CVD one needs a catalytic substrate. These are usually transition metals (Fe, Ni, Co) or an alloy of the three metals. Also required is a carbon source; previous studies have shown that the pyrolysis of hydrocarbons over metals can result in the formation of carbon nanotubes. [79]. **Figure 3.2** illustrates the setup that was employed to synthesize carbon nanotubes in this study.

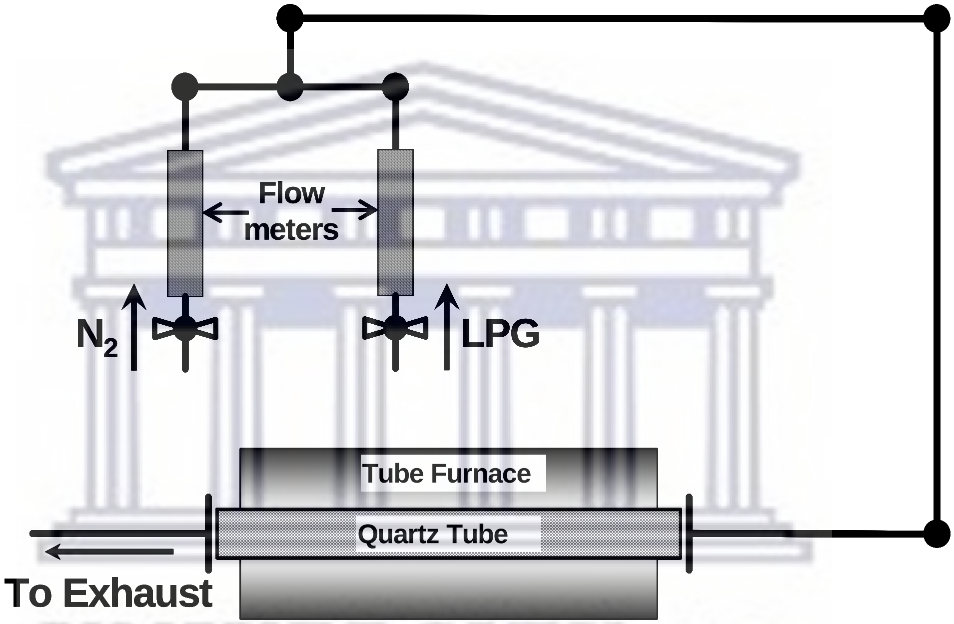


**Figure 3.2:** *Schematic view of the experimental setup used to perform chemical vapour deposition.*

Parameters employed for Carbon Nanotube synthesis via chemical vapour deposition (CVD).

| | |
|---|---|
| **Flushing gas:** | **Nitrogen gas (UHP) supplied by Afrox** |
| **Carbon source:** | **Liquid Petroleum Gas (LPG) supplied by Afrox** |
| **Temperatures:** | **650, 700, 750, 800, 850, 900$^0$C** |
| **Flushing gas flow rate:** | **20 L/min** |
| **Carbon source flow rate:** | **20 L/min** |

**Times of deposition: 2, 5, 10, 15, 20 minutes**

In this study nickel micro-wires were used as the catalytic substrate and liquid petroleum gas (LPG) was used as the hydrocarbon source. To grow CNTs on the nickel micro-wires, the sample was secured in a stainless steel frame to prevent the sample from deforming under the CVD conditions used; this was then loaded into a quartz tube located inside a horizontal tube furnace. Once appropriately sealed, the system was flushed with nitrogen and then heated to 800 $^{0}$C under nitrogen. After the temperature had stabilized the nitrogen flow was terminated and liquid petroleum gas was introduced into the system for 5 minutes. Samples were cooled to ambient temperature under nitrogen. The consolidated composite carbon material was then removed from the furnace. The optimal condition for carbon nanotube synthesis was found to be at 800 $^{0}$C and time of deposition 5 minutes.

## 3.6. Morphological and structural analysis of Ni micro-wires and consolidated composite carbon material

The morphological and structural analysis of novel consolidated composite carbon material was systematically investigated by scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD). The information obtained from these surface techniques are discussed in Chapter 4.

### 3.6.1. Scanning Electron microscopy (SEM)

Scanning electron microscopy (SEM) is a versatile imaging technique capable of producing three-dimensional images of material surfaces. SEM is one of the most frequently used instruments in material research today because of the combination of high magnification, large depth of focus, greater resolution and ease of sample observation.

The basic operation in SEM entails the interaction of an accelerated highly mono-energetic electron beam, originating from the cathode filament, with the atoms at the sample surface. The electron beam is focused into a fine probe which is rastered over the sample. The scattered electrons are collected by a detector, modulated and amplified to produce an exact reconstruction of the sample surface and particle profile. [80].

A prerequisite for effective viewing is that the surface of the samples should be electrically conductive. During operation electrons are deposited onto the sample. These electrons must be conducted away to earth thus conductive materials such as metals and carbon can be placed directly into the SEM whereas non-metallic samples have to be coated with a gold metal layer to be observed.

For SEM/EDS (energy dispersive spectroscopy) measurement, Hitachi x-650 microscope and a Noran Voyager 300EDAX (energy dispersive analysis of x-rays) in the Department of Physics was employed at the University of the Western Cape. The microscope beam energy can be varied over the range from 5 – 40KeV, with a maximum resolution of 10nm. The EDAX analyzer is equipped with window range, allowing light elements analysis from carbon upwards.

Parameters for SEM analysis are given as follows:

| | |
|---|---|
| **Working distance (mm):** | **15** |
| **Accelerating gun filament:** | **Tungsten** |
| **Filament Current (µA):** | **75 – 80** |

**Accelerating voltage (KeV): 25**

### 3.6.2. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) probes the internal structure of solids and provides access to micro-structural details. In consolidated composite carbon materials characterization studies, TEM is almost exclusively used in the investigation of the consolidated composite shape and distribution of the metal particles. TEM was utilized to determine if the carbon nanotubes were deposited on the Ni micro-wire arrays and to observe if any Ni particles were attached to the carbon nanotubes during the CVD process.

In TEM operation, a narrow electron beam originating from a tungsten filament is concentrated onto an ultra-thin sample surface using a series of magnetic lenses. The electrons interact with sample atoms while penetrating the thin sample structure leading to the transmittance of electrons and the production of secondary electrons. Secondary electrons pass through an aperture to produce an image on a fluorescent screen. For the consolidated composite carbon material, Ni particles appear as dark areas and low atomic weight elements such as carbon appear as light areas in the resultant micrographs due to differences in electron transmittance with increasing atom weight. [81, 82].

TEM samples were prepared by scraping the composite carbon material from the template using a scalpel. A spatula tip of the composite carbon material was dispersed in 5 ml methanol solution, followed by sonication of the suspension. One drop of the suspension was deposited on a carbon/formvar film-coated copper grid. The methanol was allowed to evaporate at room temperature. Samples were mounted in a sample holder which was introduced directly into the shaft of the microscope (LEO EM 912 and Hitachi H – 800 EM).

Experimental parameters are given below:

| | |
|---|---|
| **Accelerating voltage (kV):** | **175** |
| **Current (µA):** | **20** |
| **Condenser aperture:** | **1** |
| **Objective aperture:** | **3** |
| **Exposure time (seconds):** | **3** |

### 3.6.3. XRD analysis of crystallinity of the Ni micro-wires and the consolidated composite carbon material

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter, ranging from thin films and fluids to powder and crystals. XRD is an indispensable method for material characterization. XRD is a powerful tool in the study of crystallinity and atomic structure of materials and forms and integral part of a comprehensive characterization study of the consolidated composite carbon material. It is used extensively in the determination of the Brava's lattice types and unit cell dimensions. For the purpose of this study XRD was used in the investigation of the crystallinity of the structure.

In XRD, crystalline solids are bombarded with a collimated x-ray beam which causes crystal plane atoms, serving as diffraction gratings, to diffract x-rays in numerous angles. Each set of crystal planes (hkl) with inter-plane spacing ($d_{hkl}$) can give rise to diffraction at only one angle. The diffraction angle is defined from Bragg's law (nλ=2dsinθ), where the intensities of the diffracted x-ray are measured and plotted against corresponding Bragg angles (2θ) to produce a diffractogram.

The intensities of the diffraction peaks are proportional to the densities of the abundance of the corresponding crystal facets in the material lattice. Diffractograms are unique for different materials and can therefore qualitatively be used in material identification.

In the XRD analysis, the samples were mounted on a glass sample holder and the surface was flattened to allow maximum x-ray exposure. Experimental parameters for the XRD analysis are given as follows:

| | |
|---|---|
| **X-ray Diffractometer:** | **Bruker multipurpose powder diffractometer (D8 Advance)** |
| **Tube:** | **Copper** |
| **Detector:** | **Sodium Iodide** |
| **Monochromator:** | **Graphite** |
| **Generator operation:** | **40kV and 40mA** |
| **Electron intensity (KV):** | **40** |
| **X-ray source:** | **CuKα1 (λ = 1.5406Ǻ)** |
| **Scan range (2θ):** | **Scan rate ($^0$/min): 0.05** |

## 3.7. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a materials thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. In this investigation the thermal stability of the consolidated composite carbon material was studied using thermal analysis.

Thermal characterization of the consolidated composite carbon material was conducted using thermogravimetric analysis (TGA). TGA involves the continuous weighing of solids, using a thermo-balance, while they are heated at a constant rate. Samples are generally heated in inert environments and undergo increases in kinetic motion resulting in physical and chemical changes which result in the thermal decomposition of solids to form products that are detectable. The output signal is a thermogram which is a plot of weight loss, or change in weight, as a function of increasing temperature. Weight loss or change in weight may be credited to thermal events such as phase transition, melting, volatilization, thermal decomposition, sublimation, oxidation or dehydration.

In terms of the consolidated composite carbon material, structural defects and porosity have pronounced influences on thermal behaviour. In addition, the morphology of nanomaterials leads to thermal behaviour that deviates from the bulk materials. Typical thermograms for carbonaceous solids have three distinct regions. Firstly, the evaporation of surface moisture; secondly, the evaporation of volatile adsorbed molecules from micro or nanopores, and lastly the thermal decomposition of the carbon matrix. [83, 84].

TGA was conducted using a simultaneous thermal analyzer (Rheometric Scientific STA 1500) in an air atmosphere. Samples were ramped from ambient to 850 $^0$C at a 5 $^0$C / min heating rate.

## 3.8. Electrochemical Characterization techniques of Ni micro-wires and the consolidated composite material

Electrochemical methods cover a wide range of analytical techniques. The fundamental signal measured is electric in nature, either current (Faradaic) or voltage (potentiometric), resulting from redox reaction. In this study three electrochemical techniques were used. These were cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).

### 3.8.1. Cyclic Voltammetry (CV):

Cyclic voltammetry (CV) can be used in the study of electrode surface reaction, the behaviour of electrochemically-active species, and to investigate the quality of the electrocatalyst. CV is a widely used technique for acquiring information about an electrochemical reaction due to the fact that it provides information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions.

CV entails cycling a potential applied to an electrode immersed in an electrolyte solution, containing an analytic species, through a defined potential range and measuring the resultant current. [85]. The measured current is a result of electron flow through the electrochemical circuit and is due to diffusional mass transfer of electroactive species as migration and convection are minimized. The applied potential is swept back and forth between two designated potentials at a constant current, by a potentiostat.

Typically a three-electrode system consisting of a working electrode, a reference electrode and a counter electrode is used. The working electrode is the electrode of interest at which a potential is applied. An essential feature of a working electrode is that the electrode should not react chemically with the solvent or solution components.

The counter electrode completes the circuit and is usually Pt wire, graphite or glass carbon. [86]. The purpose of the counter electrode is to supply the current required by the working electrode without limiting the measured response of the cell. [87].

The reference electrode experiences zero current and has a known standard potential against which all other potentials are measured. The role of the reference electrode is to provide a fixed potential which does not vary during the experiments.

In this investigation, CV was used to study the electrochemical activity of the Ni-micro arrays and the Ni-micro arrays modified by carbon nanotubes. CV experiments on the Ni-micro arrays and the Ni-micro arrays modified by carbon nanotubes were conducted at room temperature.

Cyclic Voltammetry experimental parameters are given as follows:

| | |
|---|---|
| **Voltammetric assembly:** | **Metrohm** |
| **Potentiostat:** | **Eco-Chemie Autolab PGSTAT** |
| **Working Electrode:** | **Ni micro – wires / Ni micro wires modified by CNTs** |
| **Reference Electrode:** | **Ag/AgCl** |
| **Counter electrode:** | **Platinum wire** |
| **Electrolyte:** | **0.1M KOH.** |
| **Sweep rate:** | **50mV/s** |
| **Potential range:** | **0.6V to -1.4V.** |

## 3.8.2. Chronoamperometry (CA):

It is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current occurring at the electrode (caused by the potential step) is monitored as a function of time. Because the experiment is diffusion controlled, after a certain time almost all molecules that are able to reach the electrode are reduced (oxidized). The analysis of CA data is based on the Cottrel equation. The equation defines the current-time dependence for linear diffusion control.

$$i = \frac{nFAD^{1/2}C^{*}}{\pi^{1/2}t^{1/2}}$$

Where $i$ is the current, $n$ number of electrons, $F$ is the Faradays constant, $A$ area of the electrode, $D$ diffusion coefficient, $C^*$ concentration and $t$ time. This equation can be used to calculate the surface area of an electrode or the concentration of analyte in solution.

In this study Chronoamperometry (CA) was used to look at the hydrogen evolution reaction that takes place at the electrode surface. CA experiments were carried out at room temperature using a two electrode system. CA experimental parameters are as follows:

| | |
|---|---|
| **Potentiostat:** | **Eco-Chemie Autolab PGSTAT** |
| **Working electrode:** | **Ni micro – wires / Ni micro wires modified by CNTs** |
| **Counter electrode:** | **Platinum Cage** |
| **Potentials:** | **1.4V to 2.0V** |
| **Time:** | **300 seconds at each potential** |
| **Electrolyte:** | **1M KOH** |

### 3.8.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the characterization of electrochemical systems. The electronic properties of a system can be defined in terms of its ability to store and transfer charge (i.e. its capacitance and conductance). EIS is used to determine double-layer capacitance, and characterization of electrode processes and complex interfaces.The use of EIS records the response of the system to a small applied perturbation (i.e. AC signal), over a pre-determined frequency range. The technique is non-destructive and is particularly sensitive to small changes in the system.

In this study EIS was used to determine the double-layer capacitance and subsequently calculate the surface roughness factor of the composite carbon material. The double-layer capacitance $C_{dL}$ obtained from impedance measurements was calculated using the equation below.

$$C = \frac{-1}{2\pi f Z''}$$

Capacitance is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is as follows:

$$C = \varepsilon_o \varepsilon_r \left( \frac{A}{d} \right)$$

*Where;* $C$ = *capacitance [F]*
$A$ = *electrode surface area* [$m^2$]
$d$ = *electrode distance [m]*
$\varepsilon_o = 8.854 \times 10^{-12}$ *[F/m]*
$\varepsilon_r$ = *relative dielectric constant*

The electrochemical impedance measurements were performed using methods adapted from Shervedani et al. [88]. Electrochemical Impedance spectra were recorded using an A.C. signal of 1 mV, over a 10 mHz-100 kHz frequency range. These measurements were carried out using an AUTOLAB PGSTAT30 (FRA) instrument, and a 6 M KOH solution.

# Chapter 4: Results and Discussion

The synthesis of the consolidated composite carbon material is a complex process which involves two steps. Firstly, the synthesis of Nickel micro-wire arrays via electrochemical deposition and secondly, the deposition of carbon nanotubes via chemical vapour deposition. In this chapter an in-depth study of the consolidated composite carbon material will be discussed which includes the synthesis method and characterization of the material.

## 4.1. Development of consolidated Ni micro-wire catalyst using template synthesis technique

The synthesis of the Ni micro-wire arrays was performed by template synthesis. The template that was used was nuclear track-etched polyethylene terephthalate (PET) membrane. Nickel was deposited in the pores of the membrane. Due to the nature of the PET membrane (organic in nature) the membrane had to be made conductive by deposition of a metal layer on one side of the membrane in this case was platinum (Pt). The conductive layer was estimated 100 nm thick.

The 100 nm layer of Pt provides an electroactive surface for the growth of the Ni micro-wires in the pores of the PET template. The method used to deposit the Pt ‘backing layer’ on the surface of the PET membrane is critical. If the backing layer does not sufficiently adhere to the PET template, then during the actual micro-wire growth step the PET template may simply separate from the backing layer and thus no micro-wire formation will be observed. The backing layer protocol used produced a platinum layer that adhered to the membrane well enough to effect the growth of the Ni micro-wires without the PET template separating.

Nickel micro-wire arrays were fabricated inside the pores of microporous polyethylene terephthalate (PET) membranes. The experimental method for the deposition of Ni wires is described in Chapter 3. Three different types of PET membranes were obtained from the Joint Institute of Nuclear Research Russia with pore diameters of 1µ, 0.4µ and 0.2µ.

During electrodeposition of nickel wires the initiation and growth rate (current density) of the wires is important; it could determine whether the wires become solid or tubular. [89]. It can also influence the electrical contact resistance.

During the nickel electrodeposition process, the potential as a function of time was recorded. A typical current-time dependence at a constant potential maintained on the cell is shown in **Figure 4.1** below.

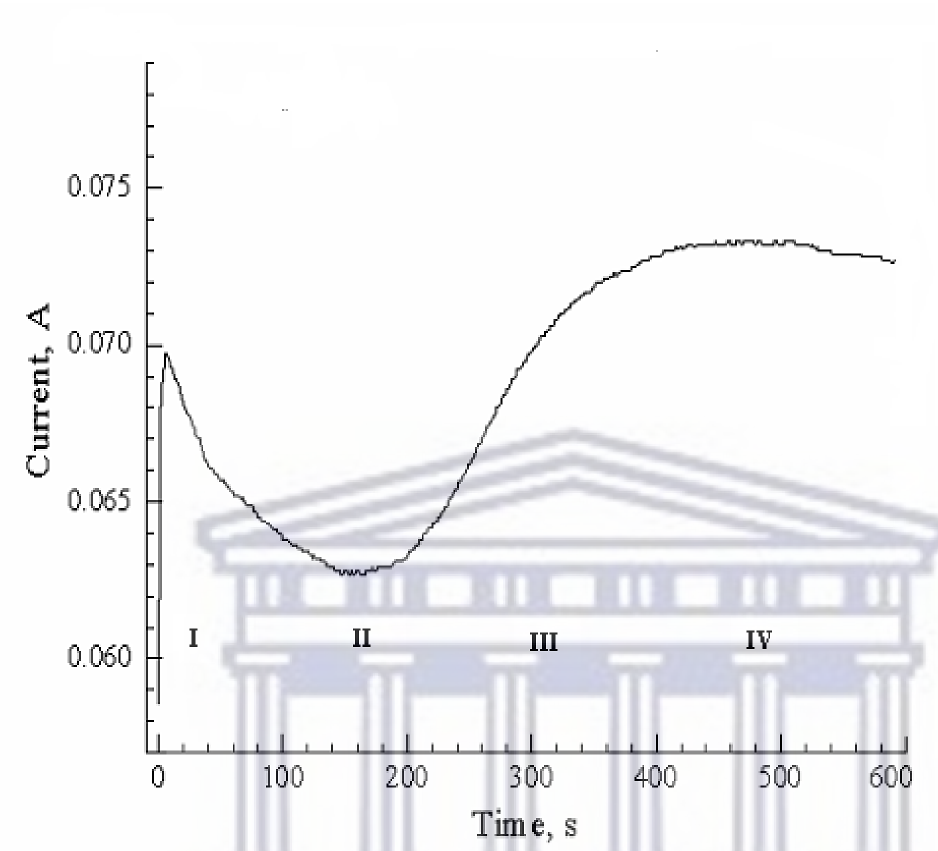


**Figure 4.1:** *A typical current-vs.-time curve for electrodeposition of nickel wires in polyethylene terephthalate (PET) templates. The applied potential was 0.7V using Ni hard bath.*

Four different zones can be distinguished. At stage **I** there is an initial current increase of the process; this is due to the electrical charge of the double layer and the diffusion layer. [90, 91]. The current decreases later as a result of metal ion depletion in the pores or the formation of the diffusion layer. At stage **II** the current remains nearly constant during the growth of the nickel wires in the pores. At stage **III** the current increases as soon as the wires reach the surface, causing covering of the template with nickel. At stage **IV** the process continues with the growth of macroscopic nickel over the whole template. The electrodeposition of nickel can be stopped during stages **II** and **III**, to obtain only wires or wires with caps respectively.

## 4.2. Morphological study of Nickel micro wire arrays

Scanning electron microscopy (SEM) was used to study the morphology of the Ni micro-wire arrays. The nickel was deposited into the pores of the PET membrane by using a 'Nickel hard bath' (as described in **Chapter 3**). The geometry of the wires depends on the irradiation and etching conditions of the PET template as well as the electrolyte. Therefore the surface smoothness of the Ni micro-wire arrays depends on several factors such as the quality of the polymer and the etching process. Previous studies have shown [92] that the use of different nickel baths have an effect on the Ni wire morphology, there are various baths that can be used such as Ni watts bath, Ni mirror bath and the Ni hard bath. In this study the Ni hard bath was used as the electrolyte for the deposition of Ni to form Ni micro-wires, due to the fact that the mirror bath and watts bath take considerably longer to fill the pores of the PET membrane when compared to the hard bath. The quality of the Ni micro-wires indicates that the geometry of the wires directly reflects that of the pores of the PET template during electrodepsoition (shown in **Figure 4.2**). This clearly emphasizes the quality of the polymer and etching conditions. Typical SEM images of the PET template and Ni micro-wires arrays are shown below in **Figure 4.2**.

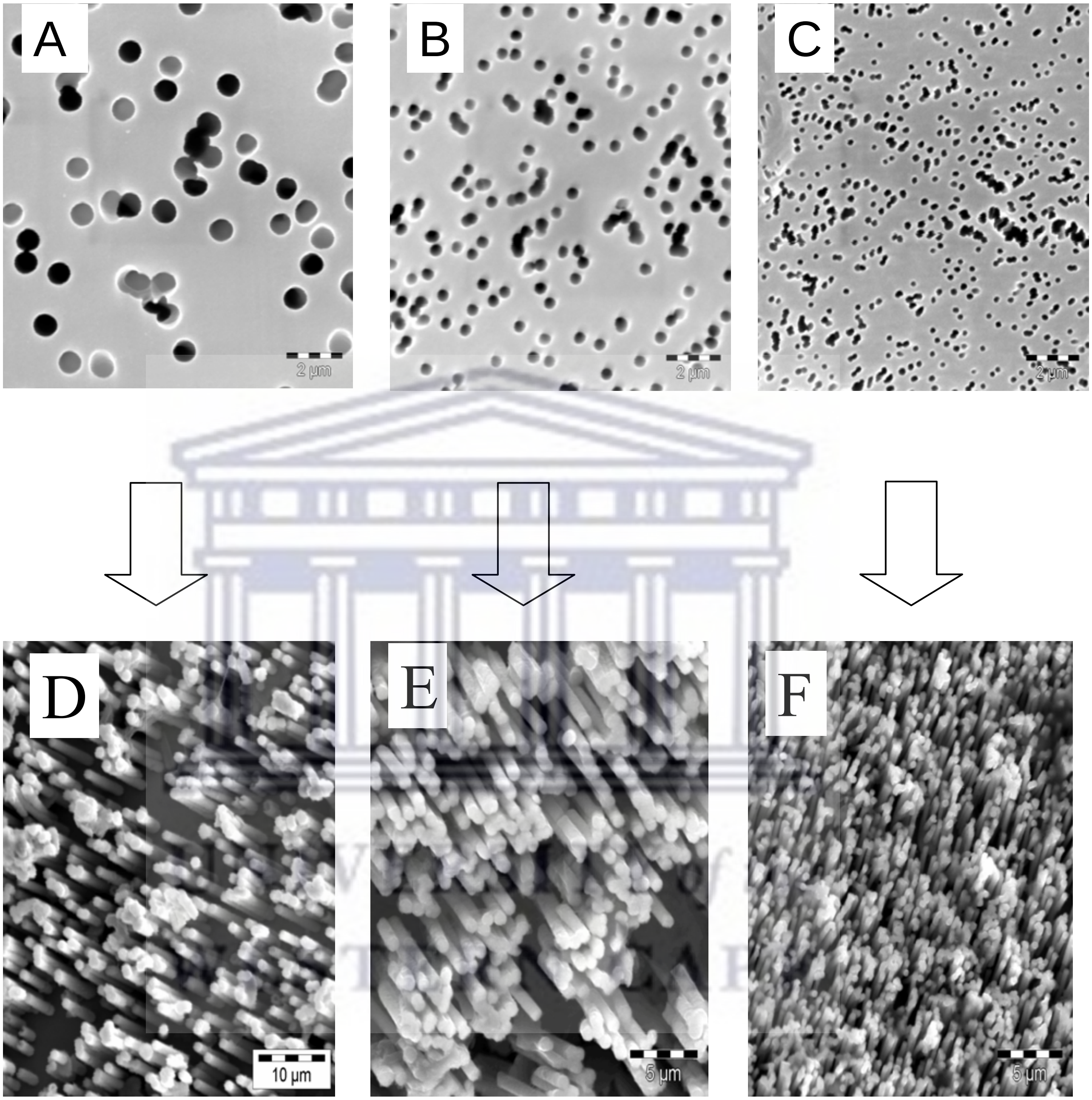


**Figure 4.2:** *SEM template images (A) 1µ PET, (B) 0.4µ PET and (C) 0.2µ PET. SEM image in (D) Ni micro-wires grown in a 1µ PET template, image (E) Ni micro-wires grown in 0.4µ PET template and image (F) Ni micro-wires grown in 0.2µ PET templates.*

The SEM examination of the samples revealed straight cylindrical structures with diameters larger than the pore size of the template, a distribution of the structures similar to that of the original template, and the length shorter than the membrane thickness. (See Table 4.1 below)

**Table 4.1**: Thickness and length of the Ni micro-wire arrays.

| PET template pore diameters | Diameter of Ni micro - wires | Length of Ni micro - wires |
|---|---|---|
| $1\mu$ | $1.14\mu$ | $12.2\mu$ |
| $0.4\mu$ | $0.53\mu$ | $12.1\mu$ |
| $0.2\mu$ | $0.31\mu$ | $11.8\mu$ |

The Ni wires exhibit a larger diameter than that of the diameter of the pores of the PET template. The PET template is a polymer and unlike metal oxide templates, such as alumina the polymer can be stretched by the growth of the metal wires in the pores and thus the increase in the nickel wire diameter is expected.

The SEM images revealed that the wires are in general free standing structures, however, in a very few of the regions examined there were some wires that had slightly bent over and were lying against other free standing wires (shown in **Figure 4.3**). If the wires in the arrays bend and come into contact with adjacent wires or a wire, this can potentially reduce the electro-active surface area of the system. From the SEM examination on the structures there were no significant bends or breaks observed within the Ni micro-wire arrays.

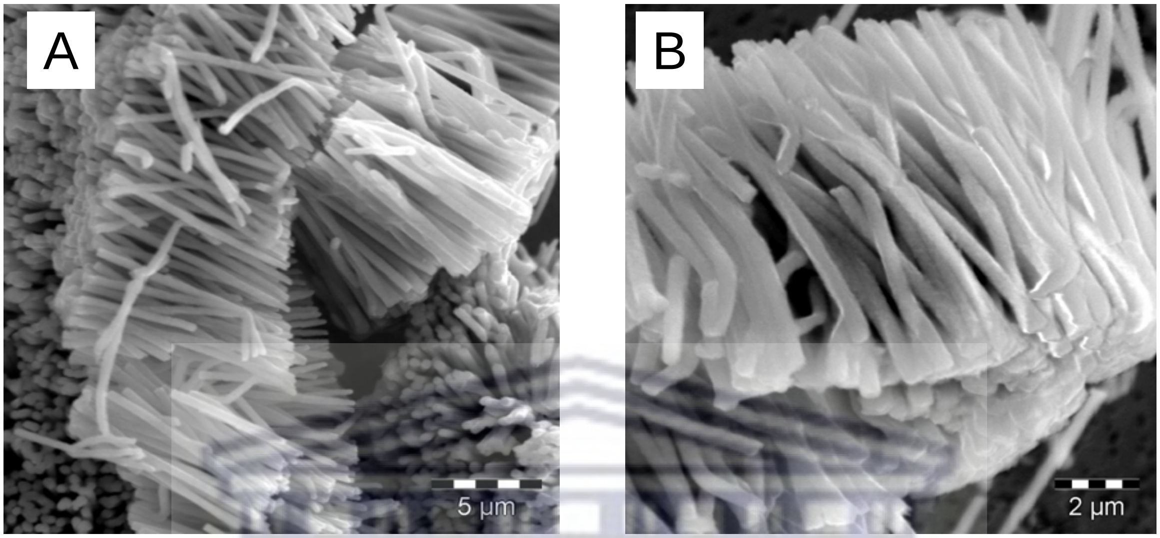


**Figure 4.3**: *SEM image (A) is of Ni micro – wires grown in 0.2µ PET template, image (B) is of Ni micro – wires grown also in 0.2µ PET template but at a higher magnification. The surface of the array was purposefully scratched with a pair of tweezers to obtain a side view.*

## 4.3. Carbon Nanotube deposition on the surface of Ni micro-wire catalysts by LPG pyrolysis

Carbon nanotubes were deposited on the surface of the Ni micro-wire arrays by chemical vapour deposition (CVD). The CVD set up consists of a furnace using a heating coil to transfer energy to the gaseous carbon molecules, liquid petroleum gas (LPG) as the carbon source and Nitrogen gas ($N_2$) to flush the system, the method employed is described in **Chapter 3.** The synthesis of carbon nanotubes in this current approach using the CVD method is based on the fact that the hydrocarbon source decomposes to carbon.

This is then followed by the carbon dissolving into the metal catalyst, saturating the metal catalyst and finally precipitating to form carbon nanotube structures. [93, 94]. How fast this process occurs is a function of the crystalline structure of the metal catalyst.

To synthesize carbon nanotubes via chemical vapour deposition a catalyst is required which is usually one of the transition metals such as Ni, Fe and Co. Therefore, due to the fact that the micro-wire arrays are Ni in nature it's quite natural to use the micro-wire array as a catalyst for carbon nanotubes synthesis. By using the Ni micro-wires as a catalyst, the carbon nanotubes will grow directly on the surface of the wires. Carbon nanotubes were deposited on the Ni micro-wires using deposition times of 2, 5, 10, 15 and 20 minutes, and it was shown that the deposition time of 5 minutes was the best time for deposition of carbon nanotubes on the Ni micro-wires. Above 5 minutes the Ni micro-wire catalyst is consumed in the CVD process. It was observed that after 20 minutes the entire template was destroyed.

SEM images of the samples after chemical vapour deposition see **Figure 4.4**, clearly illustrate the presence of an extensive mat of carbon nanotubes on the nickel micro-wire arrays and random distribution of isolated carbon nanotube islets on the surface of flat nickel. From these results it can be seen that Ni micro-wire is a superior catalyst to flat nickel for carbon nanotube synthesis. From the SEM images, the carbon nanotubes grow preferably from the nickel micro-wires and not the nickel support. SEM examination of the backing layer (reverse side with no nickel micro-wires) showed mainly amorphous carbon structures and no carbon nanotube growth. This result highlights the importance of the nickel micro-wires in the distribution and growth of carbon nanotubes.

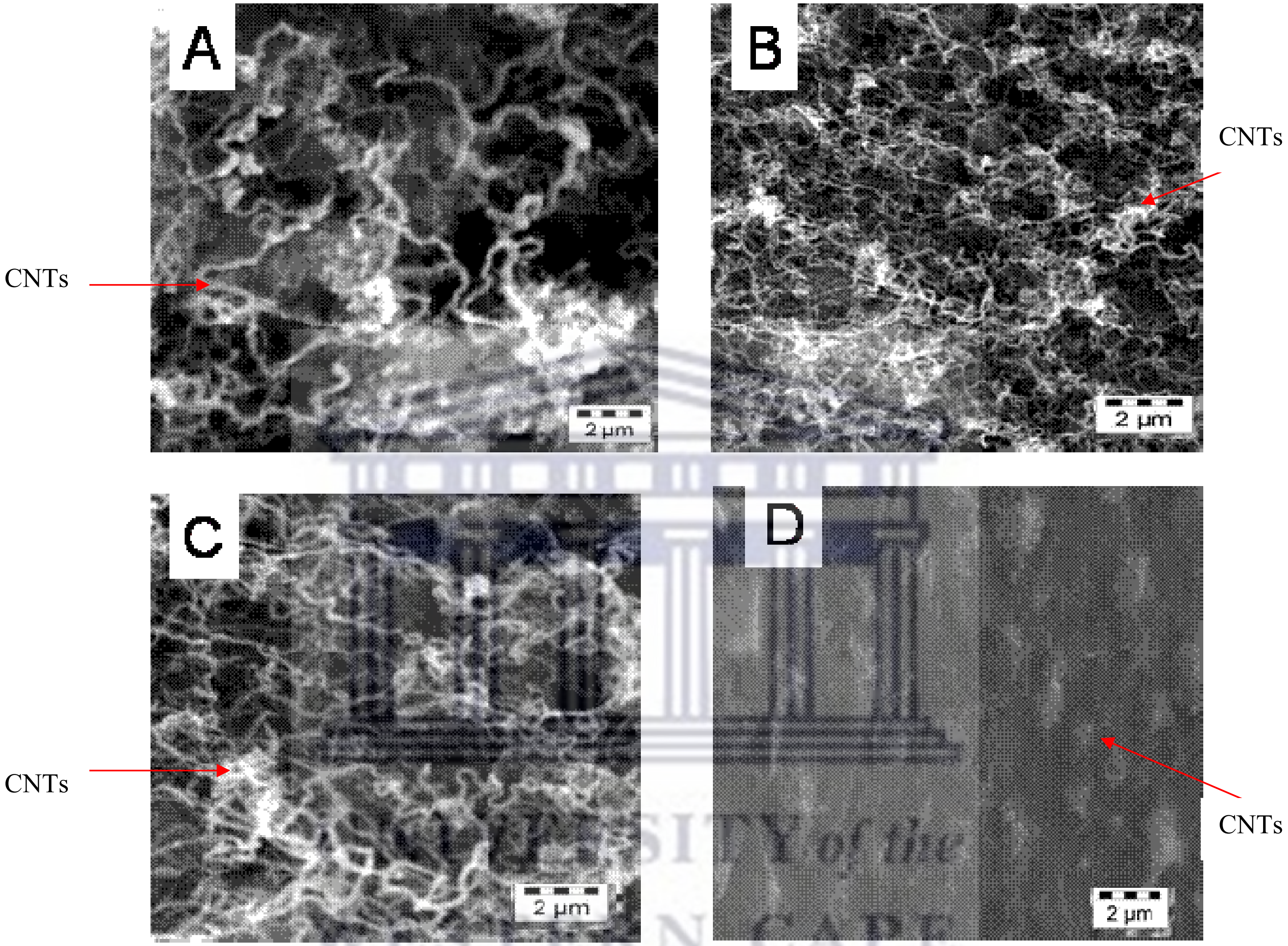


**Figure 4.4:** *SEM images of CNT mat produced after CVD synthesis, on top of Ni micro – wire arrays, (A) on 1µ template, (B) on 0.4µ template, (C) on 0.2µ template. (D) SEM image of Flat nickel with carbon nanotubes grown on it. After pyrolysis of LPG for 5 minutes at temperature of 800* $^{0}$*C.*

From an in-depth look into the growth of the carbon nanotubes on the nickel micro-wires, it can be clearly observed from the SEM images in **Figure 4.5** that the nanotube growth starts from between the nickel micro-wires and then starts to move up to the surface of the wires to form a mat over the nickel micro-wires. Based on current mechanisms for the growth of CNT in a CVD set-up [95], the length of the carbon nanotubes can be indicative of where the growth of CNT initiated. From the SEM images below one can observe that the longer nanotubes are attached at the bottom of the Ni micro-wires and the shorter nanotubes are found on top of the Ni micro-wires. Therefore it can be concluded that the nanotube growth initiated at the bottom end of the micro-wire array, and other CNT initiated later at the top ends.

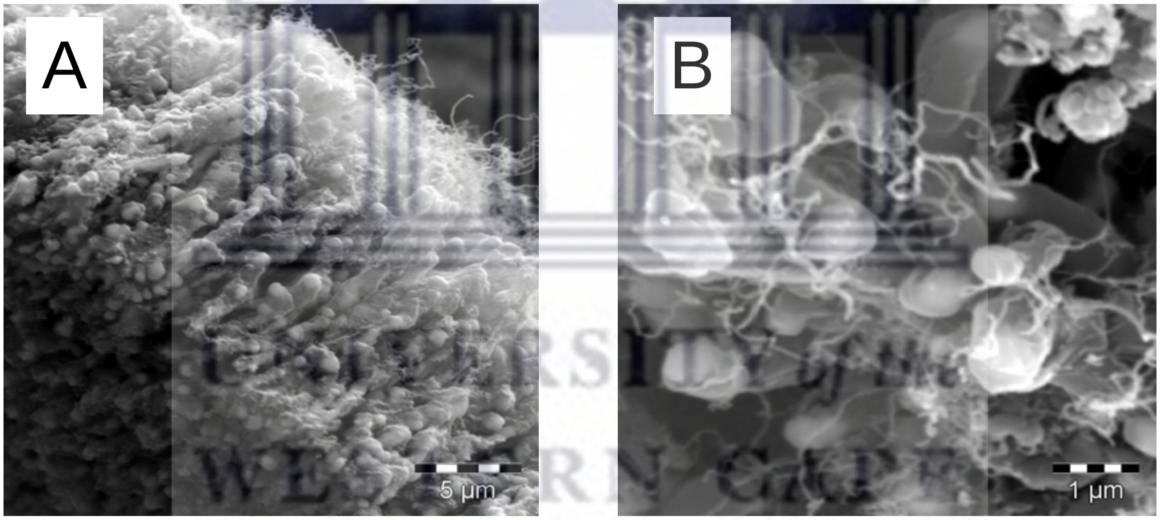


**Figure 4.5:** *SEM image in (A) is of the Ni micro – wires + carbon nanotubes on a 0.2µ PET template. The surface of the array was purposefully scratch with a pair of tweeze to obtain a side view. Image (B) is a high magnification of the lower part of the Ni micro – wires + carbon nanotube arrays on a 0.2µ PET template.*

The images in **Figure 4.5** clearly illustrate that the nanotubes directly attach to the nickel micro-wires and grow between the arrays of micro-wires as well as on top. The SEM images show that the Ni wires and the carbon nanotubes are bonded together. Therefore the consolidated composite carbon material was expected to have very interesting properties.

TEM was performed on the consolidated composite carbon material to observe the more detailed morphology of the carbon nanotubes. From **Figure 4.6** below it can be clearly observed that multi-walled carbon nanotubes were synthesized. This is evident from the fact that the walls of the nanotubes are relatively thick. From the images one can clearly observe that some of the end caps of the tubes are open. If one looks at **Figure 4.6: (B)** below, it clearly shows that nickel particle attached to the carbon nanotubes during the synthesis method.

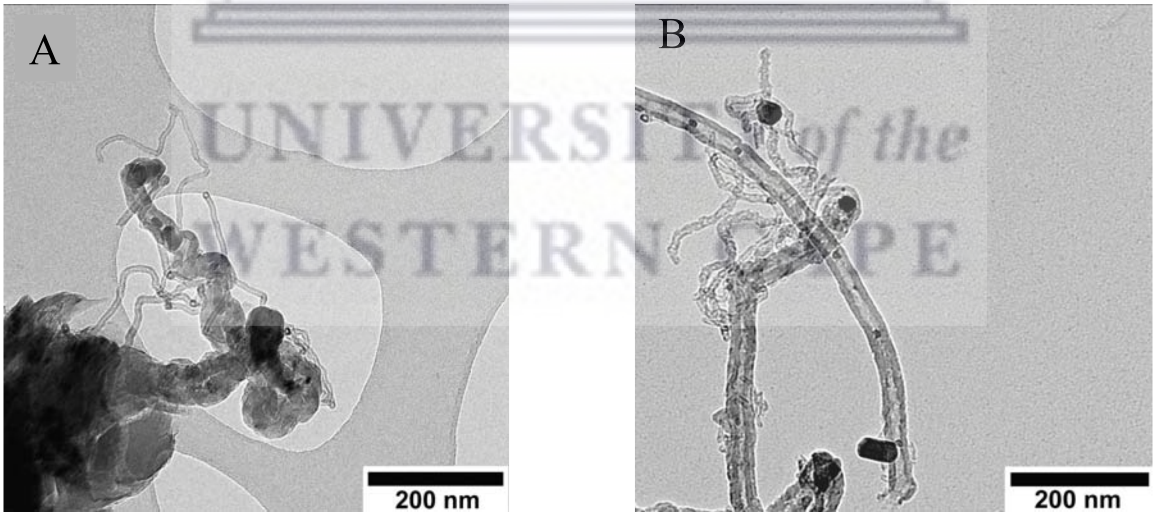


**Figure 4.6**: *Image (A) TEM image of carbon nanotubes with open end caps, Image (B) TEM image of carbon nanotubes with Ni particles attached.*

The addition of carbon nanotubes to the nickel micro-wires to form the consolidated composite carbon material has a two fold function. The functions include the increase of the surface area of the arrays and to provide a dynamic surface that can be easily modified with any chemical group of interest. Such functionalities can include metal nanoparticles, polymers or any bio-active group. Thus the carbon nanotube expands the practical use of the nickel arrays in electrochemical device application.

## 4.4. Study of the crystalline nature of the consolidated composite carbon material

The crystallinity of the consolidated composite carbon material was determined using XRD. The XRD analysis of the structures is shown in **Figure 4.7.** The XRD analysis on the structures corroborated the initial assessment of EDS analysis by conclusively showing that the cylindrical structures were crystalline nickel with no nickel oxide peaks.

The X-ray diffraction patterns of the nickel micro-wires clearly show the characteristic reflections expected for nickel with face centered cubic (FCC) structure. [96, 97].

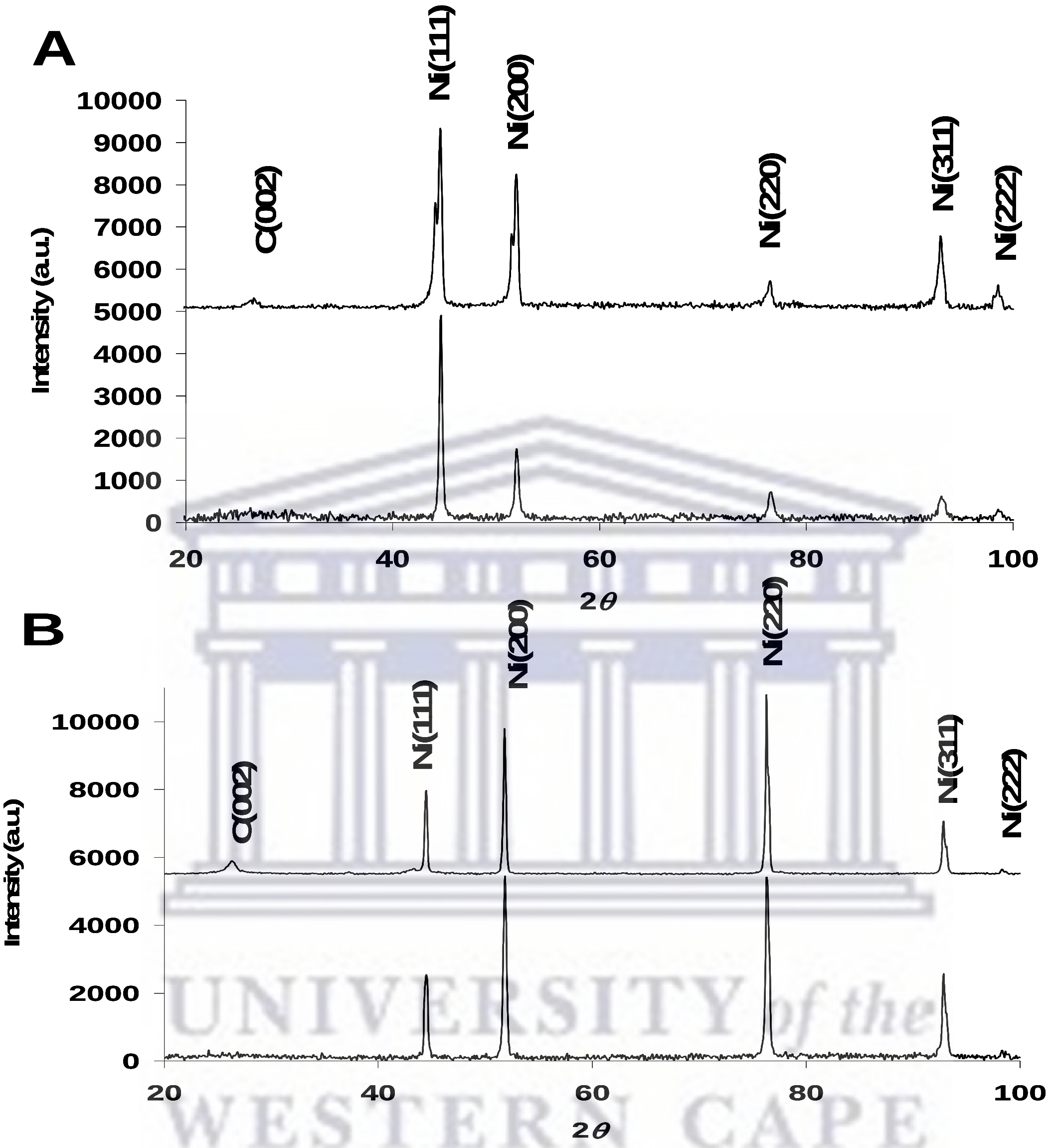


**Figure 4.7:** *The XRD spectrums presented in image (A) were obtained from the 0.2µm Ni micro - wires before CVD growth of CNT (lower spectrum) and the Ni micro – wires with CNT after CVD are shown in the upper spectrum. The XRD on the other Ni micro – wire sample (0.4 and 1.0 µm) and Ni micro –wire + CNT samples displayed similar spectrums. Image (B) is the Ni foil with micro – wires before (lower spectrum) and after (upper spectrum) CVD growth of CNT.*

Common to all Nickel micro-wire structures were 5 peaks, the Ni (111) at $2\theta = 44.50^0$, Ni (200) at $2\theta = 51.88^0$, Ni (220) at $2\theta = 76.50^0$, Ni (311) at $2\theta = 92.96^0$ and Ni (222) at $2\theta = 98.64$. On the flat nickel substrate the same peaks were identified, however, when the nickel micro-wires were compared to the flat nickel substrate there was a notable difference in the peak intensities of the Ni (111). With the nickel micro-wires the dominant peak is the Ni (111), whereas on the flat Ni the dominant peak is Ni (200). This difference is attributed to the change from bulk nickel structure to a micro-crystalline structure.

XRD analysis on the samples after CVD revealed a peak at $2\theta = 24.6^0$, identified as C (002) which is characteristic for ordered or crystalline graphite in a curved configuration such as nanotubes or nanofibers. It is interesting to note that the nickel peak intensity of the Ni (111) face is still the most dominant peak after CVD on the nickel micro-wires and that the Ni (200) is still dominant on the flat Ni and thus the nickel micro-wires are preserved through the CVD process. This is shown in the SEM image of **Figure 4.5 B** where it can be observed that the Ni micro-wires are still present after carbon nanotube growth via the CVD process.

## 4.5. Thermal stability of the consolidated composite carbon material

TGA and DSC are thermal analysis techniques utilized to measure the weight loss and heat flow as a function of temperature and time. The combination of both techniques can give valuable information on phase transitions and decomposition temperatures as well as heat capacity for physical and chemical changes to the sample. From the thermograms of the consolidated composite carbon material the TGA curve shows three main zones and the DSC curve shows one main peak, shown in **Figure 4.8**.

Thermogravimetric analysis was conducted, under air flow, from ambient to 850 $^0$C, to study the thermal stability of the consolidated composite carbon material.

Zone (**I**) in the TGA curve is the stable state, in this zone the composite carbon material is relatively stable, and there is not a huge weight change, until it reaches the next zone. Zone (**II**) occurs due to the oxidation of carbon nanotubes, and a weight change is observed. This zone ranges at 520 $^0$C to 660 $^0$C. After zone **(II)** all the carbon nanotubes are removed from the surface due to oxidation and only nickel is left. In zone (**III**) the nickel starts to react with the air to form nickel oxide, which causes an increase in the weight.

The DSG revealed one peak for all the samples; this is an exothermic peak that is caused due to the oxidation of the carbon nanotubes.

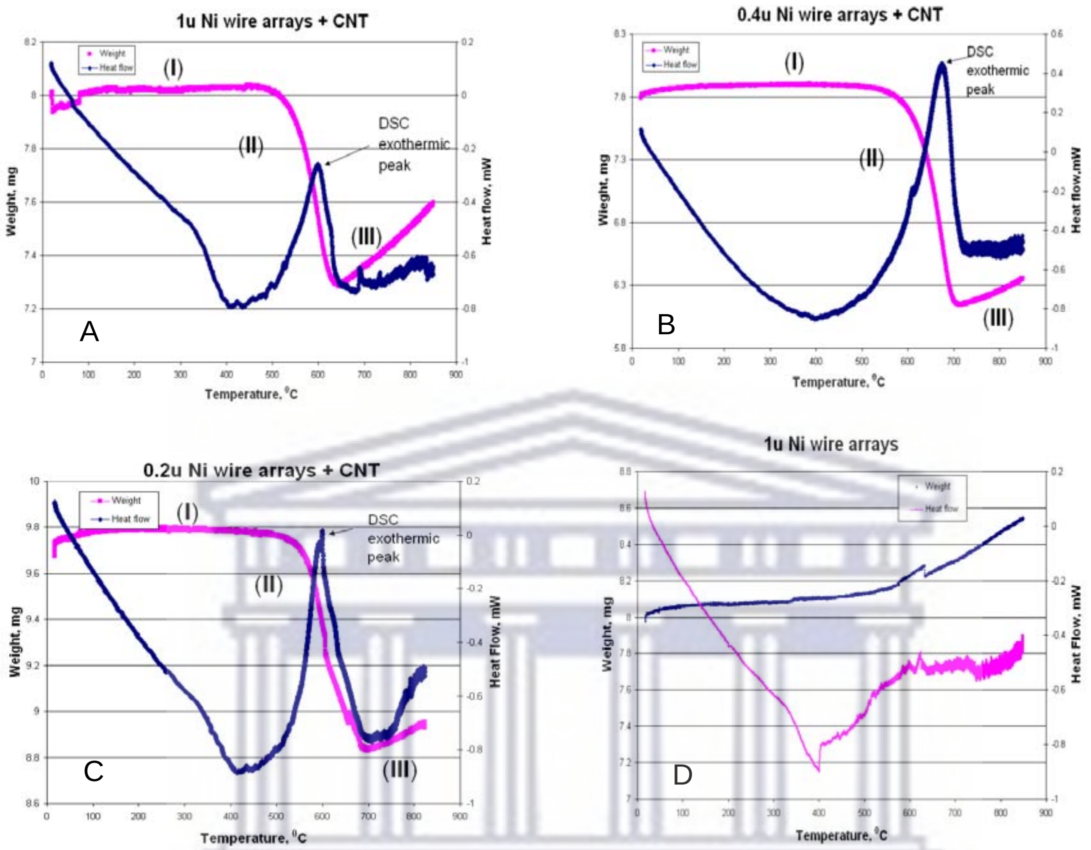


**Figure 4.8:** *TGA and DSC curves of the consolidated composite carbon material, (A) is of a 1µ Ni micro – wires + CNTs , (B) is of a 0.4µ Ni micro – wires + CNTs, (C) is of a 0.2µ Ni micro – wires + CNTs and (D) is of 1µ Ni micro – wire arrays*

The thermograms of the consolidated composite carbon material revealed that the composite material is relatively stable until about 520 $^0$C. This is due to the fact that above 520 $^0$C carbon nanotubes start to oxidize. This was evident in all the samples; the template pore diameters did not have a great effect on the thermal stability of the composite material.

The TGA thermogram of the Ni micro-wire arrays showed and increase in weight due to nickel oxide formation, which was expected because the experiment was run in air. The TGA of the flat Ni showed no phase changes on the sample, only nickel oxide formation occurred.

From the thermograms of the consolidated composite material one can determine the amount of nanotubes that were deposited on the surface of the nickel wires. This is shown in **Figure 4.9**.

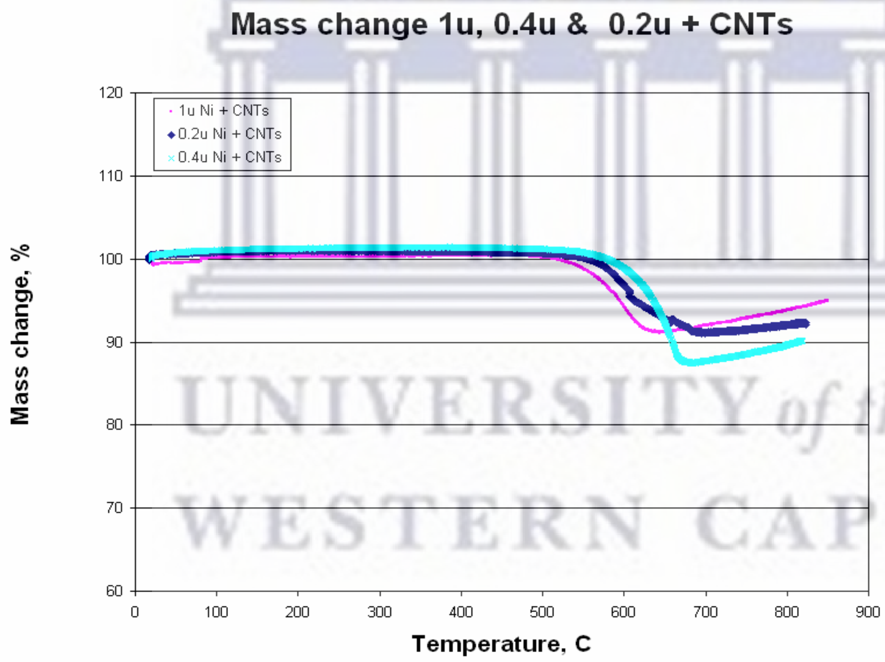


**Figure 4 9:** *Mass change of different consolidated composite carbon material*

The above figure illustrates that approximately only 10% of the sample is carbon nanotubes and 90% of the sample is nickel. This is due to the fact that during the CVD process the time of deposition of nanotubes was only 5 minutes.

## 4.6. Electrochemical characterization of the consolidated composite carbon material

In this study the PET membrane is easily removed after growth of the micro-wires by simply dissolving the template in KOH solution. Besides easy removal, the PET template can be obtained commercially (or prepared) with different porosities. Different porosities can result in different surface coverage or micro-wire density in the resulting micro-wire array and as a result varying surface area.

For example, a 1.0 cm x 1.0 cm nickel plate will have a surface area of 1.0 $cm^2$; whereas an array made using a 20µm thick PET template with pores having a diameter of 200 nm and a porosity of $1 \times 10^6/cm^2$ has a surface area of approximately 1.13 $cm^2$ (the surface area of the flat plate plus the surface area of the micro – wires). Increasing the porosity by an order of magnitude increases the surface area accordingly, and thus a porosity of $1 \times 10^7/cm^2$ has a theoretical surface area of 2.3 $cm^2$ and theoretical values of 13.6 $cm^2$ and 126 $cm^2$ for porosities of $1 \times 10^8/cm^2$ and $1 \times 10^9/cm^2$ respectively. Thus from this simple treatment of the surface area effect of an array of micro-wires has on flat surface, it does suggest that arrays may be suited for electrochemical application. The platinum backing layer provides a very good electrical contact to the nickel wires and the nickel wires plus carbon nanotubes. Thus the nickel wires or the composite can be easily addressed in any electrochemical system of choice.

A principle focus of modern research in eletrocatalysis is to discover electrode materials that exhibit excellent electrochemical stability and show interesting activity towards typical electrochemical reactions. [98]. It is also desirable that these materials be inexpensive, abundantly available, etc. Electrocatalytic hydrogen and oxygen evolution on various electrode materials and from various electrolyte solutions, are two of the most frequently studied electrode reactions. The reason for this is both theoretical and practical, since the two gases represent major products or by-products of several industrial electrocatalytic processes.

The hydrogen electrode reaction $2H^{+} + 2e^{-} \leftrightarrow H_2$ is a heterogeneous catalysis where an electrode material acts as a catalyst. [99]. A three-electrode, cylindrical electrochemical cell was used with Ni micro – wires / Ni micro-wires plus CNTs as a working electrode, platinum as a counter electrode and Ag/AgCl as a reference electrode. The geometric surface area of the working electrode and the counter electrode were 0.126 and 3.35 cm$^2$ respectively. The electrochemical behaviour was studied by applying a potential sweep rate of 10mV/s at room temperature.

**The Cyclic Voltammetry** (CV) experiments can be divided into seven separate electrodes that can be classified into one of three different categories; these are, a flat Ni substrate electrode, the Ni micro-wire (1.0, 0.4, or 0.2µm micro-wires) based electrodes and the CNT plus Ni micro-wire composite (CNT grown on the 1.0, 0.4, or 0.2µm micro – wires) electrodes.

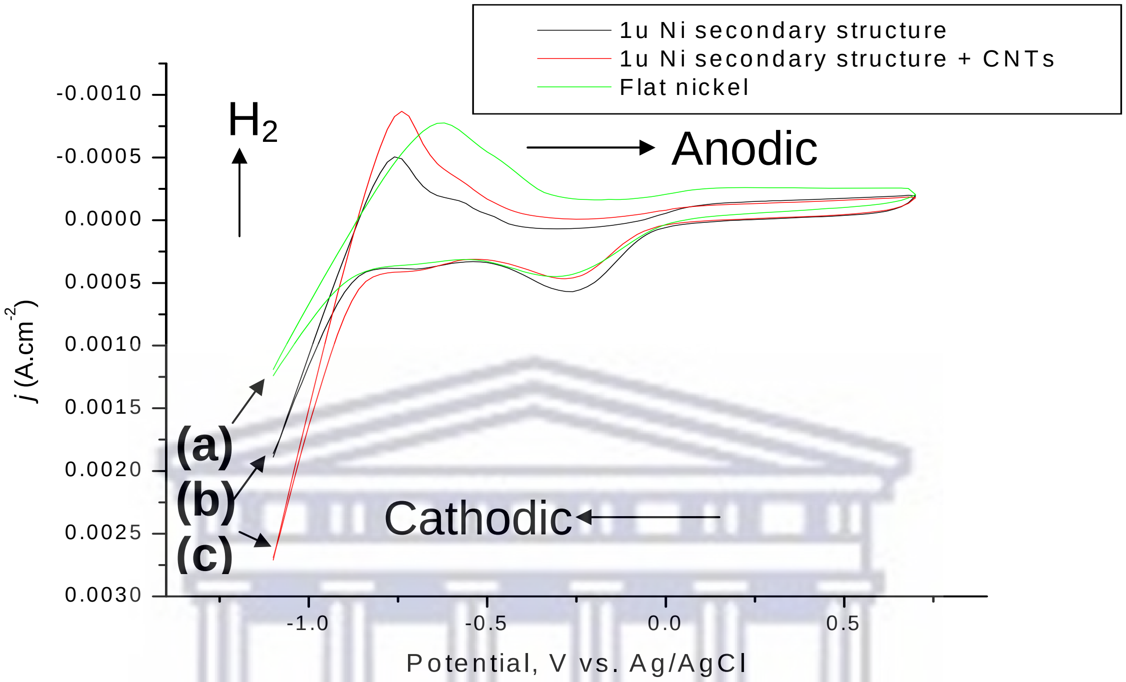


**Figure 4 10:** *CV on the flat Ni substrate (a), the Ni micro – wires (b) and the Ni micro – wires + CNT composite (C).*

All cyclic voltammograms show only one anodic peak and similary only one reduction peak in the range of potential from -1.4V to 0.6V vs. Ag/AgCl. The anodic peak appears for the electrochemical formation of $Ni(OH)_2$, which takes place in the region between -0.75V and -0.60V. The oxidation of $Ni(OH)_2$ to NiOOH takes place at a different potential, in the oxygen evolution reaction (OER) part of the voltamogram therefore its not observed. In the cathodic sweep, the reduction of NiOOH to $Ni(OH)_2$ occurs at a potential between -0.25V and -0.15V, while reduction from $Ni(OH)_2$ to Ni is not observed because of the hydrogen evolution reaction (HER). [100,101]

A general trend was seen between the flat Ni substrate, the Ni micro-wires and the CNT plus Ni micro-wire composite electrodes, shown in **Figure 4.10**. The anodic peak current density ($j_{PA}$) increased in the following order: Flat Ni substrate electrode ≤ Ni micro-wire electrode ≤ CNTs plus Ni micro-wire electrode. This increase in the $j_{PA}$ may be indicative of the higher electrocatalytic activity of the Ni micro-wire electrodes towards the anodic surface reaction compared to the flat Ni electrode.

In addition the anodic peak potential ($E_{PA}$) shifts to a more cathodic potential (-0.75 V vs. Ag/AgCl) when using the Ni micro-wire electrodes, compared to the more anodic $E_{PA}$ of the flat Ni electrode (-0.63 V vs. Ag/AgCl). The higher activity in the cathodic peak ($E_{PC}$ = -0.26 V vs. Ag/AgCl) and the more elaborate current tailing (higher peak current density at the maximum cathodic potential of 1.10 V vs. Ag/AgCl) of the Ni micro-wire based electrodes and the CNT plus Ni micro-wire composite electrodes is also indicative of higher electrocatalytic activity of these electrodes towards the hydrogen evolution reaction, when compared to that of the flat Ni electrode. [102, 103, 104].

## 4.7. Chronoamperometry (CA) of the consolidated composite carbon material

In this investigation water electrolysis was carried out in a 1M KOH aqueous solution at room temperature. The experiment was conducted in a standard two-electrode system. The working electrode was the sample and the counter-electrode was a platinum cage. The experiment was conducted by applying a constant potential to the working electrode and monitoring the current density over a specific time until it remained constant; this was done for a period of 5 minutes at each potential.

The efficiency of hydrogen production by water electrolysis was qualitatively evaluated and compared with the current density value at a certain voltage. Since the amount of hydrogen gas is proportional to the electric current, the current density value becomes a good index to represent the electric power necessary to produce a certain mass flux of hydrogen when compared amongst data of the same voltage.

It can be seen from **Figure 4.11** below that there is an increase in current density due to the hydrogen evolution reaction on the Ni secondary structures plus CNTs composite when compared to the Ni micro-wires and that of flat Ni. This may be due to the fact that the surface areas of the electrodes are different and therefore they give rise to different current densities.

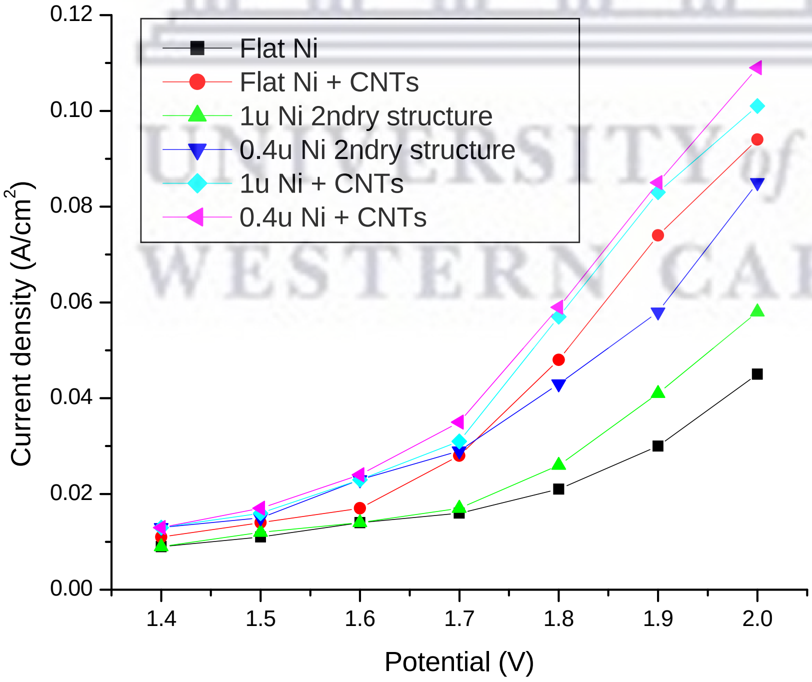


**Figure 4.11**: *Activity of the different electrodes for hydrogen production.*

Maximum electrocatalytic activity was observed on the Ni micro-wire plus CNT composite. This is most likely due to the larger electrochemical surface area caused by the growth of the CNT on the surface of the Ni micro-wires. During CVD growth of CNT, the catalyst used, such as Ni in this case, can be found on the tips of the CNT [105], and the metal particle can be encapsulated or partially exposed and thus available for any electrochemical process.

## 4.8. Electrochemical impedance spectroscopy of the consolidated composite carbon material

A key factor controlling the practical utilization of high surface-area electrodes is the extent to which the surface area is electrochemically accessible. The double-layer capacitance ($C_{dL}$) of the consolidated composite carbon material was determined using electrochemical impedance spectroscopy (EIS). EIS measured the real (Z') and imaginary (Z'') parts of the complex impedance of the open circuit potential in a 6 M KOH solution. The double-layer capacitance was then extracted as a function of frequency (*f*) using the equation below.

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

The double-layer capacitance $C_{dL}$, obtained from the impedance measurements, was calculated using equation 1, and typical Nyquist plots along with the capacitance is presented in **Figures 4.12 and 4.13**.

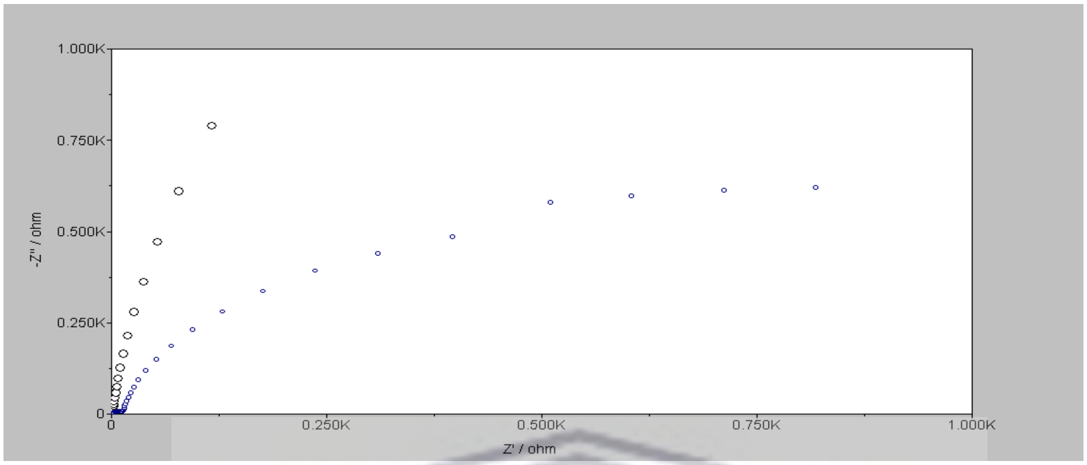


**Figure 4.12:** *Typical Nyquist plots on the Ni micro – wires (large circle in image), and the Ni micro – wires + CNT composite (smaller circle in image)*

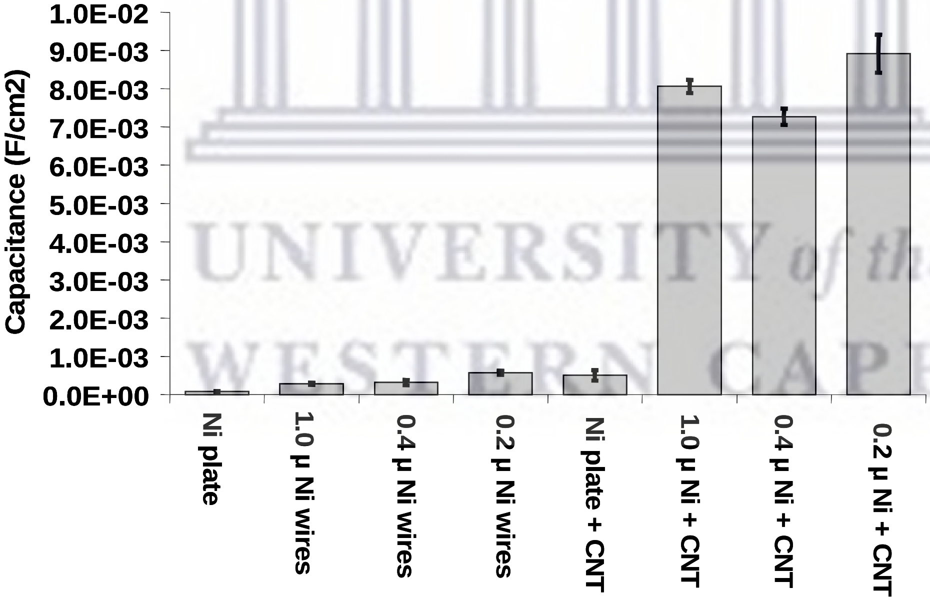


**Figure 4.13:** *The difference in capacitance between the flat Ni substrate, the 1µ, 0.4µ and 0.2µ Ni micro – wires, the flat Ni substrate with CVD deposited CNT, the 1µ, 0.4µ and 0.2µ Ni micro – wires with CVD deposited CNT.*

The $C_{dL}$ increases from 0.078 on the Ni plate to 0.282, 0.318 and 0.576 mF on the 1.0 µm, 0.4 µm and 0.2 µm Ni micro – wire arrays. This slight increase in the $C_{dL}$ can be attributed to the increase in surface area of the micro-wire arrays. The greatest increase in $C_{dL}$ is observed after the CVD growth of CNTs on the Ni micro-wires, where the $C_{dL}$ is 8.062, 7.267 and 8.916 mF on the 1.0 µm, 0.4 µm and 0.2 µm Ni micro-wires plus CNT composite electrodes. It is interesting to note that the growth of CNT on the Ni plate (with no micro-wires) resulted in an increase in $C_{dL}$ comparable to that seen on the Ni micro-wires (0.505 mF). This result highlights the importance of the synergistic effect of the Ni micro-wires and the CNT in the composite.

The surface area of the consolidated composite carbon material was then determined by using the equation 2 below. Capacitance is formed when two conducting plates are separated by a non- conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is as follows.

$$C = \varepsilon_o \varepsilon_r \left( \frac{A}{d} \right) \qquad (2)$$

*Where;* C = capacitance [F]

A = electrode surface area [$m^2$]

d = electrode distance [m]

$\varepsilon_o$ = 8.854 x $10^{-12}$ [F/m]

$\varepsilon_r$ = relative dielectric constant

The conducting plates were two Ni plates with surface area of 1.2 $cm^2$, the dielectric was 6 M KOH solution and the distance between the plates was 2 cm.

If measuring different samples with surface area $A_1$ and $A_2$ in the same electrolyte and experimental set-up, $\varepsilon_o$, $\varepsilon_r$ and d will be constant.

Hence,
$$\frac{A_1}{A_2} = \frac{C_1}{C_2} \qquad (3)$$

By measuring the capacitance of the different samples and comparing it to the area and capacitance of a Ni plate, we can thus calculate the surface area of the sample by using equation 3. The surface area of the flat Ni was calculated to be 12.33 $cm^2$ and the capacitance $6.24 \times 10^{-5}$ F. The surface area of the Ni micro-wires and the Ni micro-wires plus CNT composite, is shown in **Figure 4.14.**

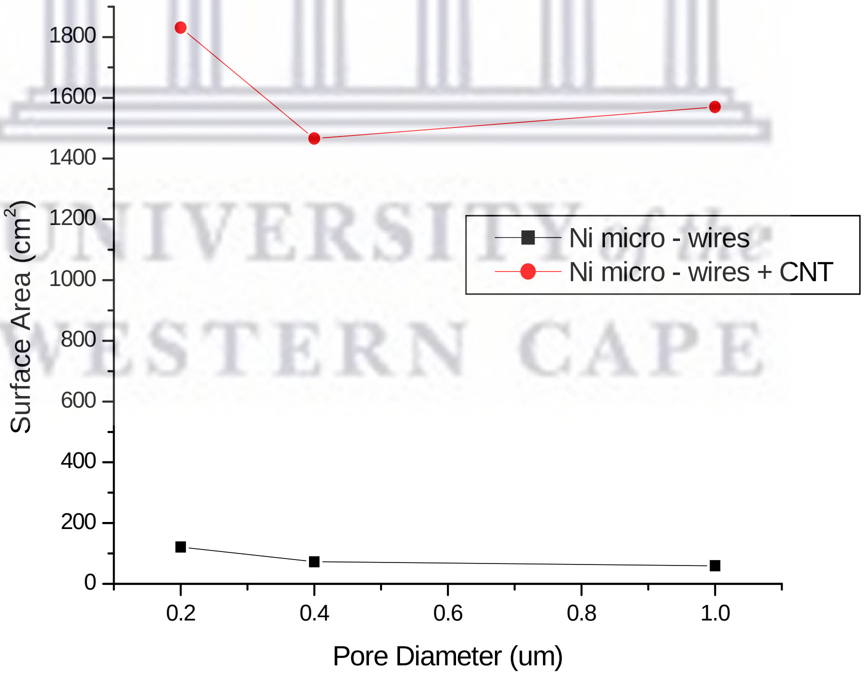


**Figure 4.14**: *Comparison of the surface area of the Ni micro – wires and the Ni micro – wires + CNT composite.*

The above figure illustrates that the addition of carbon nanotubes to the Ni micro-wires not only increases the capacitance but also increases the surface area of the material. From **Figure 4.14** it can be observed that the Ni micro-wires plus CNT composite, has a surface area 10 times higher than that of the Ni micro-wire arrays.

From the CV results, the higher activity in the hydrogen evolution reaction is only seen in the composite arrays of Ni micro-wires plus CNT and not in the Ni plate plus CNT electrode, thus higher activity in the hydrogen evolution reaction can be attributed to the increase in the $C_{dL}$ and surface area.

## 4.9. Comparison of the capacitance of consolidated composite carbon material against various carbon based materials

In recent years there has been a great increase in research for alternative material that can be used as anode material in lithium ion batteries. Presently carbon material such as graphite is used as anode material in lithium ion batteries. Most carbonaceous materials can react reversibly with lithium to some extent. Therefore they can be used as negative electrodes in lithium batteries. Research on anode material for lithium ion batteries is focused on searching for carbon alternatives with large capacities and better cycling performance.

The capacitance of various materials was measured in this study that may, possibly be used as anode material in lithium ion batteries. These included graphite plates, carbon cloth, Ni micro-wires, Ni micro-wires plus CNT composite and a commercial anode obtained from China (which consists of carbon anode materials on a copper foil support).

From **Figure 4.15** it can be seen that the capacitance of the Ni micro-wires plus CNT composite is the largest when compared to the commercial anode, graphite plates, carbon cloth, Ni plates, Ni plates plus CNT and Ni micro-wires. From **Figure 4.15** it is clearly seen that the consolidated composite carbon material has a higher capacitance than that of the commercial anode. This could be attributed due to the composite carbon materials high specific surface area, excellent electronic semi-conductivity and conductivity of the carbon nanotubes.

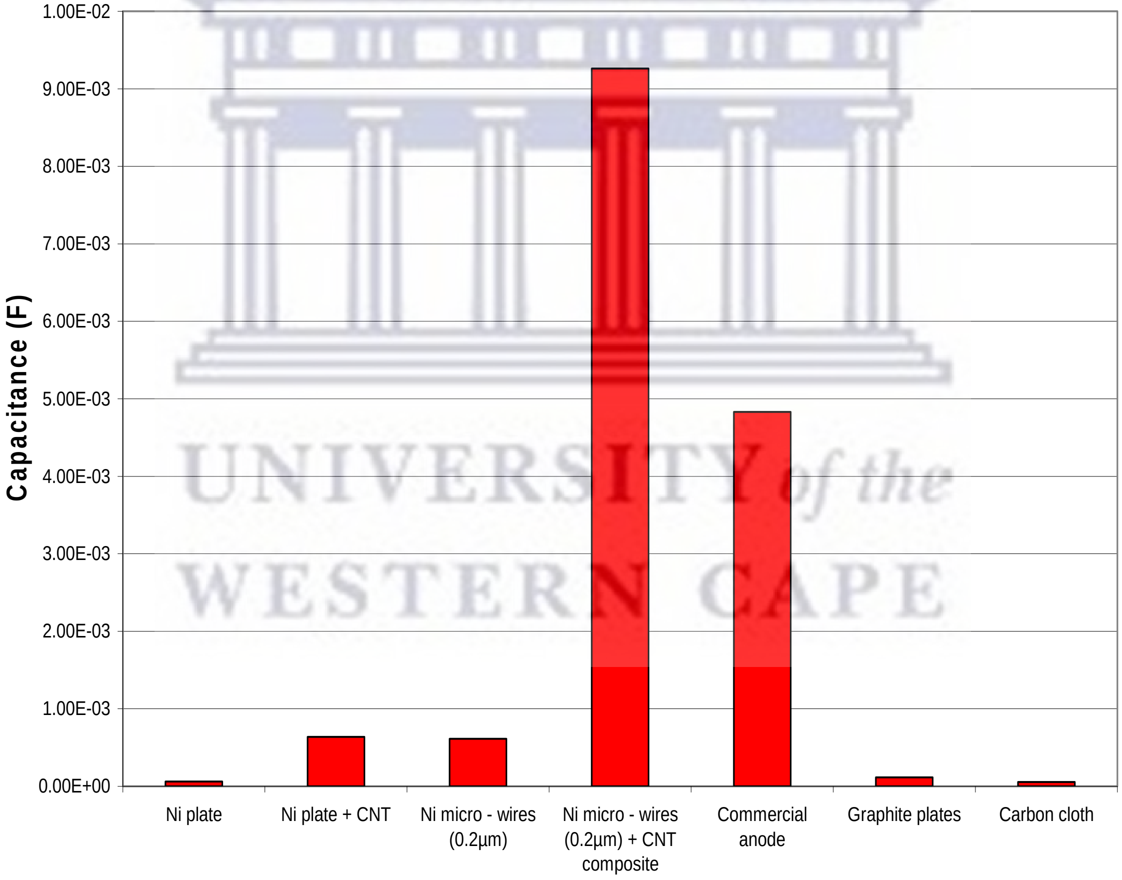


**Figure 4.15**: *Comparison of the capacitance of various materials that can possibly be used as anode materials for lithium ion batteries.*

## 4.10. Modification of the consolidated composite carbon material

Water electrolysis has gained importance in recent years because of its promise of economic production without adverse environmental impact. For water electrolysis to become more competitive and an efficient process, energy loss has to be minimized and equipment cost lowered. From a technological standpoint, the cost of electrolytic hydrogen is directly dependant on the voltage used to operate an electrolyzer at significant current densities. The operational voltage depends on the overpotentials for cathodic and anodic reactions and on the internal resistance of the cell. Due to the high cost and stability consideration, very few materials can even be considered for use as anodes and cathodes in practical electrolytic cells.

Two properties play an important role in selecting catalytically active materials for hydrogen evolution. These are the actual electrocatalytic effect of the material and its long-term stability. Materials for alkaline water electrolysis were reviewed by various authors [106, 107] who reported on the properties of platinum materials as viable cathode material for hydrogen evolution. Although platinum is an expensive metal, but due to its electrocatalytic effect on the formation of hydrogen at the cathode, it is the most widely used metal for electrolysis in industry.

In this study, an attempt was made to enhance the electrochemical activity of the consolidated composite carbon material for hydrogen production. This was done by modifying it with Pt group metals.

## 4.11. The influence of Pt deposits on the consolidated composite carbon material and on the hydrogen evolution reaction

Platinum is a versatile but expensive catalyst or material. [108]. Pt is one of the best electrocatalysts for hydrogen production. Pt was deposited on the consolidated composite carbon material by electroless deposition. The electrolyte that was used for Pt deposition consisted of a solution containing 1 mM of chloroplatinic acid ($H_2PtCl_6$) and 0.1 M HCl made up to 1 liter. The deposition of Pt on the consolidated composite carbon material was done by using a sacrificial electrode. This was performed by using 1.2 $cm^2$ of the consolidated composite electrode and clipping it to a 2 $cm^2$ stainless steel mesh using a steel paper clip. The deposition of Pt was performed at room temperature by placing the consolidated composite electrode in a beaker containing 50 ml of the electrolyte. The time of deposition was 30 minutes.

Platinum distribution on the consolidated composite material was determined by SEM. From the SEM analysis (see figure 4.16) it can observe that platinum was deposited on the composite material. It can be seen that the platinum was deposited on the carbon nanotubes as particles. This deposition of Pt on the nanotubes is expected due to their unique structure that allows particles to attach to their surface.

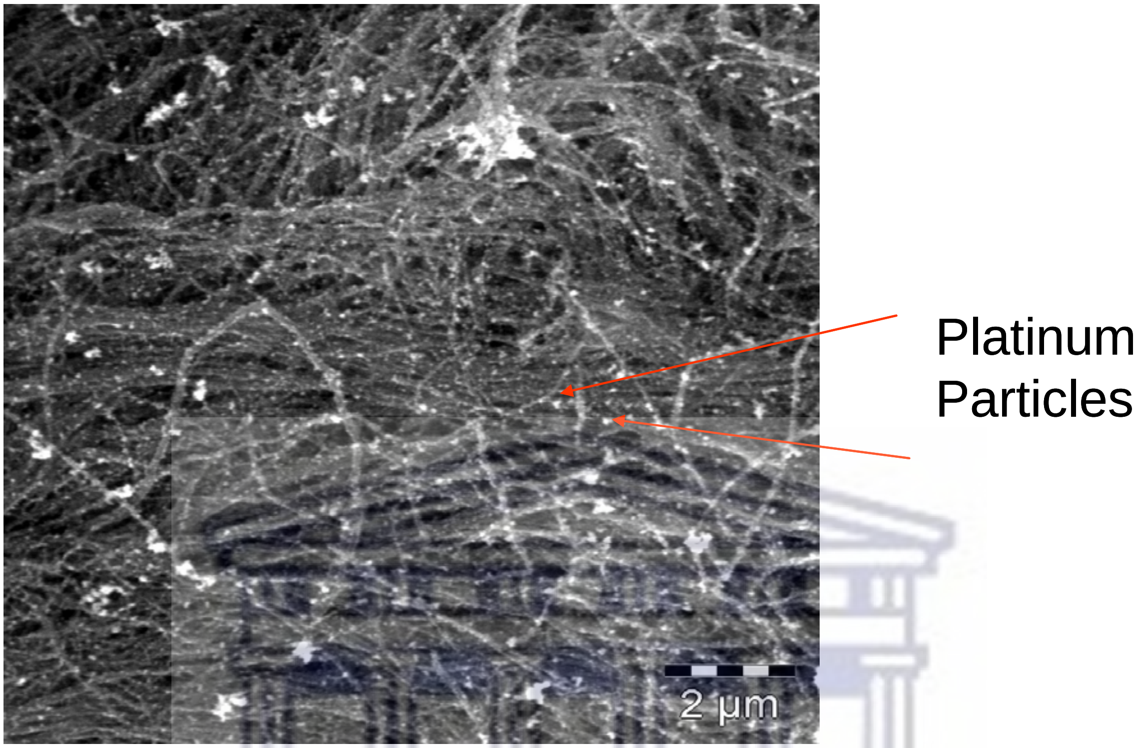


**Figure 4.16:** *SEM image of consolidated composite after modification with platinum in a chloroplatinic acid solution to enhance catalytic activity.*

Energy dispersive spectrometry (EDS) was further used in order to determine the chemical composition of the modified composite structure and to investigate the distribution of the elements on the electrode surface. The atomic percentage Pt on the consolidated composite is shown in **Figure 4.17**. The EDS data correspond to bulk particles and may differ from the surface values due to segregation. The EDS analysis of the sample resulted in a composition of 46.65 % Ni, 31.33 % C and 22.02 % Pt. This was recorded over an average of 10 samples. Literature shows that EDAX is a good qualitative and quantitative method for determining the composition of materials. [109].

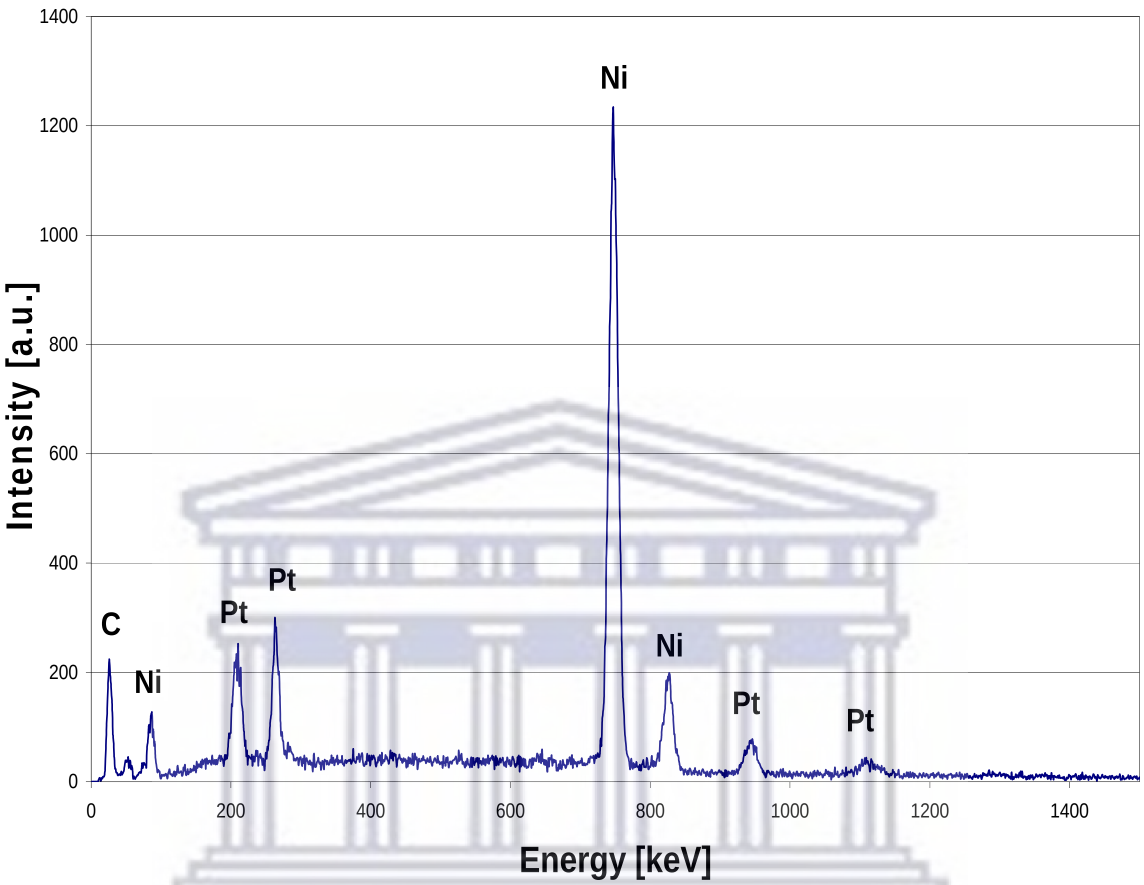


**Figure 4.17**: *EDS plot of the consolidated composite carbon material modified in chloroplatinic acid solution.*

The cathodic behaviour of the platinized consolidated composite carbon material was investigated using chronoamperometry to determine the current density of the modified composite electrode (see figure 4.18). A two-electrode system was employed as explained in Chapter 3.

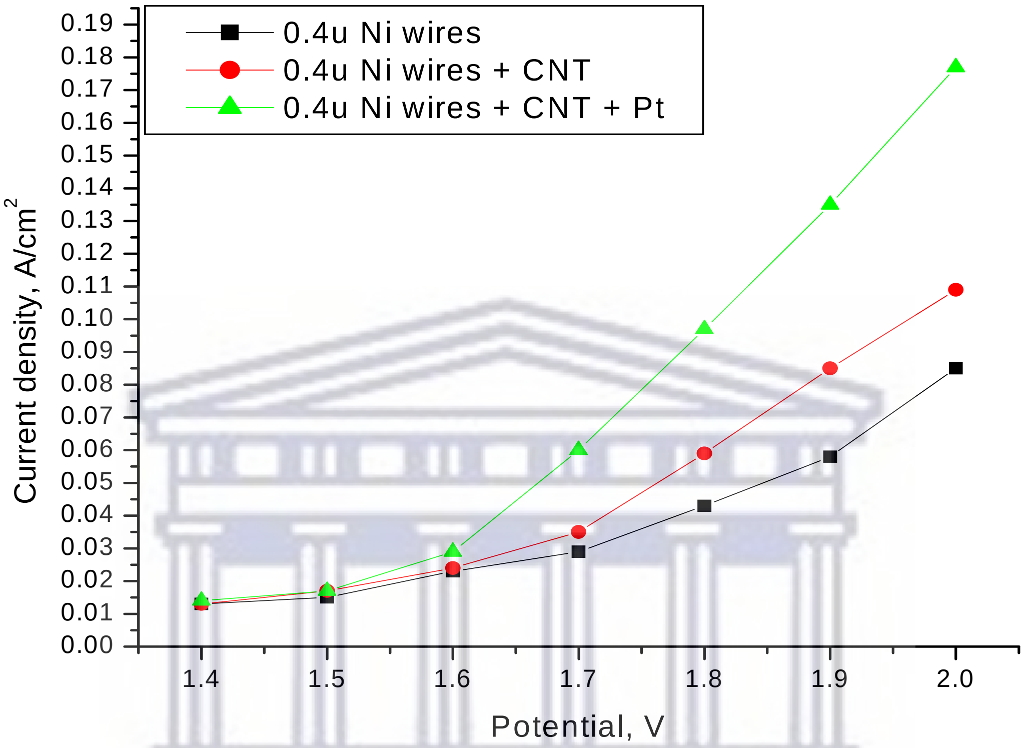


**Figure 4.18:** *Current-potential curves of the hydrogen evolution reaction of the nickel micro – wires, consolidated composite carbon material and the consolidated composite carbon material modified with platinum.*

Nickel micro – wires modified with carbon nanotubes and Platinum (Pt) showed a higher activity for hydrogen production when compared to the Ni micro – wires and the Ni micro – wires plus CNTs.

The current densities obtained from the structures modified with Pt particles are higher than that of the unmodified structures (as shown in **Figure 4.11**). From **Figure 4.18** it can be seen that enhancement of the cathodic activity of nickel for electrolytic hydrogen evolution has been demonstrated by the formation of Pt particles on the surface of the Ni micro-wires plus carbon nanotubes. Thus, the result clearly indicates that the catalytic activity for hydrogen evolution can be enhanced by modifying with platinum particles.

**Table 4.2**: Summary of current densities of nickel micro-wires '*before*' and '*after*' modifcation with carbon nanotubes or platinum at 25 $^0$C.

| Materials | Temperature $^0$C | Activated with | Current density [A/cm$^2$] (at 2.0 V) | (at 1.7V) |
|---|---|---|---|---|
| Flat Nickel | 25 $^0$C | - | 0.021 | 0.006 |
| Ni micro – wires 1µm | 25 $^0$C | - | 0.058 | 0.017 |
| Ni micro – wires 0.4µm | 25 $^0$C | - | 0.085 | 0.029 |
| Ni micro – wires 1µm | 25 $^0$C | CNTs | 0.101 | 0.031 |
| Ni micro – wires 0.4µm | 25 $^0$C | CNTs | 0.109 | 0.035 |
| Ni micro – wires 1µm | 25 $^0$C | CNTs + Pt | 0.146 | 0.051 |
| Ni micro – wires 0.4µm | 25 $^0$C | CNTs + Pt | 0.177 | 0.061 |

## 4.12. Conclusions of results and discussion

The purpose of this research was to synthesize consolidated composite carbon nanomaterials, by using Ni micro-wires as a catalyst and substrate, and to observe what affect the Ni micro-wires had on the synthesis of carbon nanotubes. From the fabricated consolidated composite carbon material the structure and the study of its properties, the following general conclusions can be made:

- Crystalline nickel micro-wires were produced by electrochemical deposition using a nickel hard bath by applying an applied potential of 0.7 V and a deposition time of 15 minutes, in PET etched ion - track membranes.
- The nickel micro-wires were successfully applied as a catalyst and substrate for the synthesis of carbon nanotubes, and to produce consolidated composite carbon nanomaterial.
- From the results obtained during SEM analysis, it was shown that carbon nanotubes grow preferably on the Ni micro-wire arrays as opposed to the Flat Ni surface. In addition, examination of the samples by SEM revealed that the Ni micro-wires physical morphology was moderatly altered by the CVD process. It was shown that the nanotubes are attached to the Ni micro-wires and an extensive mat of CNT is present on the surface of the Ni micro-wires. This phenomenon is extremely interesting because it shows that the two materials are attached to each other and one would, therefore expect very interesting properties which would be different to that of the individual components.

- From the TEM results it was observed that Ni nano-particles are present on the nanotube surface, and some of the CNT end caps are open which would result in greater electrochemical activity.
- Cyclic voltammetry experiments on the consolidated composite carbon nanomaterial and the Ni micro-wires determined that these electrodes had a higher electrocatalytic activity towards the hydrogen evolution reaction when compared to flat nickel; this increase is attributed to the increase in surface area resulting from the addition of CNTs to the Ni micro-wires and due to the presence of Ni nano-particles attached to the nanotubes after CVD.
- From electrochemical impedance spectroscopy measurements it was determined that the increase in the electrochemically active surface area of the composite array by a factor of 10 was due to the synergistic effect of carbon nanotubes and Ni micro – wires.
- The consolidated composite carbon material was successfully modified with platinum, and the presence of platinum on the surface of the nano-composite material improved the electrocatalytic properties in the HER.
- The results obtained during this research can be used not only in electrochemistry but in a wide range of research fields. From an evaluation of the results, further research is needed to better understand the structure and electrochemical behaviour.

# Chapter 5: Overall Conclusions and Future Research Directions

In the previous chapter the research results were discussed. In this the final chapter of this thesis, the discussion focuses on the main conclusions, recommendations and proposals for future research.

Consolidated composite carbon materials are a unique approach to synthesis of new materials with exceptional properties that can be used in a wide range of possible commercial and technological applications, including nano-devices, uses in analytical sciences (chemistry and biology), electronics and optics.

The consolidated composite material was synthesized using a novel approach specifically the combination of template synthesis and chemical vapour deposition. The template method is a simple and powerful process for the synthesis of the Ni micro-wire, which served as a catalyst and substrate, for the synthesis of carbon nanotubes. The electrodeposition method is capable of producing high quality micro and nanowires with desirable features. It was demonstrated that well defined arrays of nickel microstructures can be prepared using electrochemical deposition.

Chemical vapour deposition is a simple and highly favoured technique that is employed to synthesize carbon nanotubes, due to the fact that it produces relatively large yields with good purity, very adaptable, and is a method that can be scaled up relatively easily. Chemical vapour deposition via LPG pyrolysis was used to synthesis carbon nanotubes directly onto the surface of the nickel micro-wire arrays. The chemical vapour deposition methodology used to deposit carbon nanotubes onto the Ni micro-wires did not alter the crystallinity of the Ni micro-wires which was revealed by the XRD analysis.

The SEM images showed that the morphology of the Ni micro-wires where moderately altered after the CVD process.

In this study the feasibility of using the consolidated composite material as a cathode for the hydrogen evolution reaction in alkaline solution was studied. Electrocatalytic processes on consolidated composite electrodes, as surveyed using electrochemical techniques, almost invariably commence and terminate at reasonably well-defined potentials within the region 0.6V to -1.4V. The consolidated composite material showed higher current density values for the HER in alkaline solution when compared to Ni micro-wire arrays and flat Ni respectively (0.109 A/cm$^2$, 0.085 A/cm$^2$, 0.021 A/cm$^2$). This increase in current density was attributed to the increase in surface area from the flat Ni substrate to the Ni micro-wires to the Ni micro-wires plus CNTs shown by the EIS results. In addition, the TEM results showed that the end caps of the nanotubes are open, which would further increase the electrochemically active surface area of the CNT. TEM also revealed the presence of Ni nanoparticles attached to the nanotubes, another factor that can produce the increased activity observed.

Electrochemical impedance spectroscopy (EIS) revealed very interesting results; it showed that the consolidated composite material has a relatively high capacitance, and this increase in capacitance was only notable for the consolidated composite material. The capacitance of the consolidated composite carbon material was compared to a commercial anode for a Li ion battery; it was found that the composite material had a higher capacitance almost double than that of the commercial anode. The increase in capacitance is attributed to the synergistic affect between the Ni micro-wires and the carbon nanotubes, due to the carbon nanotubes excellent electrochemical properties.

Deposition of Pt particles from a suitable combination of $H_2Cl_6Pt$ solution on the consolidated composite carbon material produced electrodes with catalytic properties for hydrogen production. The hydrogen evolution reaction from Pt modified consolidated composite carbon materials showed that the electrocatalytic activity of these electrodes was significantly improved. The enhanced HER electrocatalytic activity observed on these electrodes was attributed to their chemical composition. Energy dispersive spectrometry was used to determine the chemical composition of the modified structure and to investigate the distribution of the elements on the electrode surface. The spectra showed characteristic peaks for Ni, C and Pt.

The synthesis of this novel consolidated composite carbon material has shown that it can be used in various areas in science and technology. From the preliminary investigations in alkaline solutions, the high current density for HER, suggests they can be used as possible cathode electrodes for hydrogen production. Also due to their high capacitance the material can be possibly used as anodes for Li-ion batteries.

## 5.1. Future work and recommendation

Based on the analysis and conclusions of this study, a number of suggestions regarding priorities for future research directions and areas of investigation are listed:

1. The template method is a useful approach for preparing nanomaterials. From this fundamental point of view it would be interesting to produce nanostuctures with smaller diameters (less than 100 nm) in order to explore more thoroughly the effects of size on the synthesis of the consolidated composite carbon material.

2. Investigate the synthesis of carbon nanotubes on the Ni wire arrays using different source gases such as methane and ethylene and observe what effect they have on the structure and properties of the composite material.
3. Investigate different catalysts, to observe what effect a) nanowires made up of alloys, b) nanowires made up of separate metal columns and c) doping Ni wires with different metal catalysts have on CNT diameter, and/or morphology control.
4. For cathode materials for HER, improving catalytic performance may be achieved by modifying the CNT surface with various combinations of transition metals such Pt-Pd, Zr-Pt and Ti-Pt. For anode materials for Li-ion batteries similar studies can be undertaken by modifying the surface with $MoO_2$ and $MnO_2$.
5. Different applications of the consolidated nanomaterials could be identified by modifying the CNT with various other materials such as metals, alloys and polymers.

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