CHAPTER II
THEORY AND LITERATURE SURVEY

Carbon nanotubes (CNTs) and electrochemical capacitors (ECs) used in this work are respectively described in the initial section of this chapter. Consideration is then given the fundamental of electrochemistry. Finally, the detail of electrostatic spray deposition is described.

2.1 Carbon Nanotubes

2.1.1 History of Carbon Nanotubes

Fullerenes are large, closed cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis and detection of the small fullerenes C_{60} and C_{70}, it was generally accepted that these large spherical molecules were unstable. However, some scientists had already calculated that C_{60} in the gas phase was stable and had a relatively large band gap. As in the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley found strange results in mass spectra of evaporated carbon samples. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started. Since the discovery in 1991 by Iijima [1] and coworker with adding transition-metal catalysts to the carbon in an arc discharge, carbon nanotubes (CNTs) have been investigated by many researchers over the world. They can be seen as the nearly one dimensional form of fullerenes. Therefore, these materials are expected to possess additional interesting electronics, mechanic and molecular properties. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one dimensional structure on molecular and electronic properties.

2.1.2 Types of Carbon Nanotubes and Related Structures

Carbon nanotubes (CNTs) are hexagonal array of rolled carbon sheets with several microns in length and a few nanometers in diameter [2], which can have a length-to-diameter ratio greater than 1,000. The bonding in CNTs is sp², with each carbon atom joined to three neighbours, as in graphite. The tubes can be considered as rolled up graphene sheets. More interestingly, there are three distinct ways that a graphene sheet can be rolled into a tube. The structure of CNTs can be specified by chiral vector (C_h) which defines how the graphene sheet is rolled up. In Figure 2.1, the integer n and m are the number of unit vectors along two directions in the honeycomb crystal lattice of graphene, a_1 and a_2 are the lattice vectors. Chiral vector can be defined by the vector $C_h = na_1 + ma_2$. If $m = 0$, the nanotubes are called zigzag. If $n = m$, the nanotubes are called armchair. Otherwise, they are called chiral. The different chiralities of CNTs are illustrated in Figure 2.2.
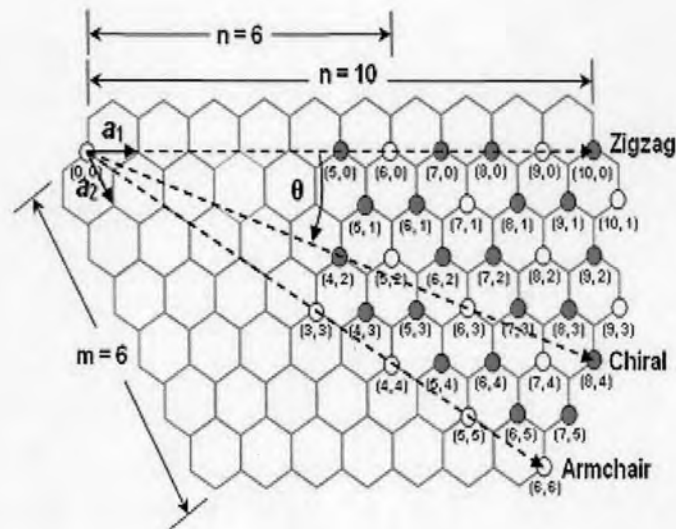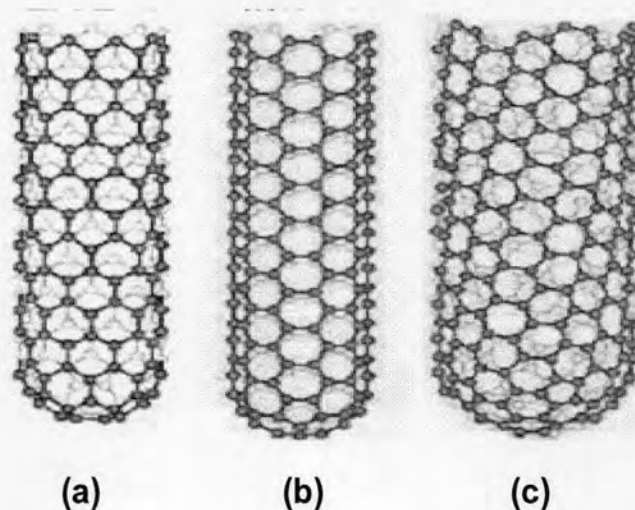

Figure 2.1 Chiral vector, C_h

**(a)**   **(b)**   **(c)**

Figure 2.2   The difference in structure of the tubes (a) Zigzag structure,

(b) Armchair structure and (c) Chiral structure.

More importantly, CNTs can be categorized into two different types:

2.1.2.1 Single-Walled Nanotubes

Single-walled nanotubes (SWNTs) is a rolled up tubular shell of graphene sheet as showed in Figure 2.3. In addition, SWNTs has a diameter of close to 1 nanometer with a tube length. The body of the tubular shell is mainly made of hexagonal rings of carbon atoms where as the ends are capped by a dome-shaped half-fullerene molecules. The natural curvature in the sidewalls is due to the rolling of the sheet into the tubular structure whereas the curvature in the end caps is due to the presence of topological (pentagonal ring) defects in the otherwise hexagonal structure of the underlying lattice. The role of the pentagonal ring defect is to give a positive curvature to the surface which helps in closing of the tube at the two ends.
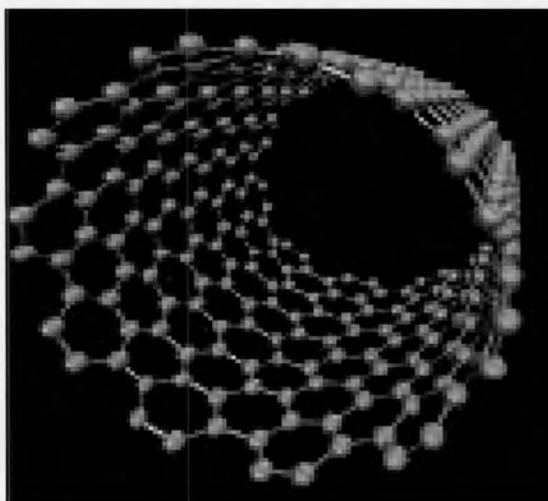
Figure 2.3 Single-Walled Nanotubes (SWNTs).

2.1.2.2 Multi-Walled Nanotubes

Multi-walled nanotubes (MWNTs), as presented in Figure 2.4, is a rolled up stack of multi graphene sheets into concentric SWNTs, with the ends again either capped by half-fullerenes or kept open. The interlayer distance in MWNTs is close to the distance between graphene layers in graphite, approximately 0.3 nanometers. Moreover, the length and the diameter of these structures differ a lot from SWNTs
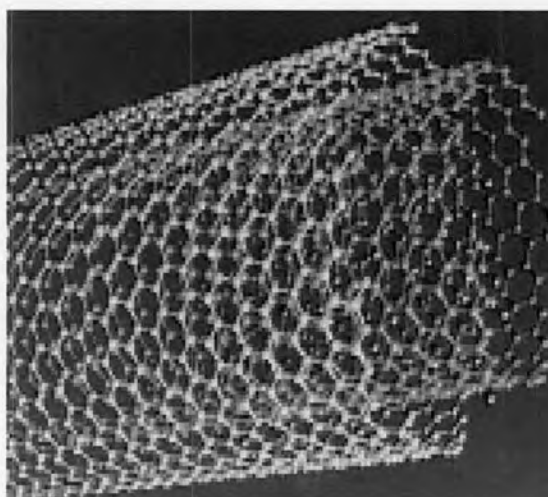
Figure 2.4 Multi-Walled Nanotubes (MWNTs).

2.1.3   Properties of Carbon Nanotubes [3]

The properties of CNTs are determined to a large extent by their dimensional structure. The most important properties of CNTs and their molecular background are stated below.

2.1.3.1   Chemical Reactivity

The chemical reactivity of CNTs, compared with a graphene sheet, is enhanced as a direct result of the curvature of CNTs surface. The reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has showed to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. However, the study of chemical modifications on nanotube behavior is difficult as the nanotube samples are still not pure enough.

2.1.3.2   Electrical Conductivity

Depending on their chiral vector, CNTs with a small diameter are either semiconducting or metallic. The differences in conducting properties are caused by the molecular structure that results in a different band structure and a band gap. The differences in conductivity can easily be derived from the graphene sheet properties. It was showed that a (n, m) nanotube is metallic as accounts that: $n = m$ or $(n - m) = 3i$, where i is an integer, n and m are defining the nanotube. Moreover, the conductivity of CNTs is determined by quantum mechanical aspects and proved to be independence from the nanotube length.

2.1.3.3 Thermal Conductivity and Resistance

All nanotubes are the excellent good thermal conductors along the tube, exhibiting a property known as ballistic conduction but good insulators laterally to the tube axis. CNTs are able to transmit up to 6,000 W/m/K at room temperature; compare this to copper, a metal well known for its good thermal conductivity, which only transmits 385 W/m/K. The temperature stability of carbon nanotubes is estimated to be up to 2,800 degrees Celsius in vacuum and about 750 degrees Celsius in air.

2.1.3.4 Mechanical Strength

CNTs are one of the strong materials known in terms of tensile strength as listed in Table 2.1. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. Besides, CNTs have a very large Young's modulus in their axial direction. The nanotube as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties. However, CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo when placed under compressive, torsional or bending stress.

Table 2.1 Young's modulus, tensile strength and density of carbon nanotubes compared with other materials.

Materials	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm^3)
Single-walled nanotubes	1,054	150	-
Multi-walled nanotubes	1,200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

2.1.4 Application of Carbon Nanotubes

CNTs provide electrical conductivity, heat conductivity, stiffness, light weight, high specific area, chemical stability and mechanical properties. These extraordinary characteristics give CNTs potential in numerous applications.

2.1.4.1 Field Emission Applications

CNTs are the best known field emitters of any material. This is understandable given their high electrical conductivity and the sharpness of their tip because of the smaller tip's radius of curvature. Moreover, the more concentrate will be an electric field leading to increased field emission that is the same reason lighting rods are sharp. The sharpness of the tip also means they emit at especially low voltage, an important fact for building low power electrical devices that utilize this feature. CNTs can carry an astonishingly high current density that possibly as high as 1,013 A/cm^2. Furthermore, the current is extremely stable. An application of this behavior receiving considerable interest is in field emission flat panel displays. Instead of a single electron gun, as in a traditional cathode ray tube display, in CNTs-

based displays the electron gun for each individual pixel in the display. Their high current density and operating voltages make CNTs very attractive field emitters in this application. Other applications utilizing the field-emission characteristics of CNTs include general types of electron microscope sources.

2.1 4.2 Conductive Plastics

The history of plastics over the last half century has involved their use as a replacement for metals. For structural applications, plastics have made headway. Sometimes, electrical conductivity is required for their application because plastics are the electrical insulators. This deficiency is overcome by loading plastics up with conductive fillers such as carbon black, and larger graphite fibers which the ones used to make golf clubs and tennis rackets. The loading required to provide the necessary conductivity using conventional fillers is typically high resulting in heavy parts. More importantly, plastic parts whose structural properties are highly degraded. It is well established that the higher the aspect ratio of filler particles, the lower of the loading required, needed to achieve a given level of conductivity. CNTs are ideal in this sense, since they have the highest aspect ratio of any carbon fiber. In addition, their natural tendency to form ropes provides inherently very long conductive pathways even at ultra low loadings.

2.1.4.3 Energy Storage

CNTs have the characteristics desired in materials to use as the electrodes in batteries and capacitors. CNTs have a high surface area about 1,000 m^2/g and good electrical conductivity. Importantly, their linear geometry makes their surface highly accessible to the electrolyte. Research has showed that CNTs have the highest capacity of any carbon material for use in lithium ion batteries. More interestingly, CNTs are outstanding materials for supercapacitor electrodes and are now being marketed for this application. CNTs also have applications in a variety of fuel cell components. They have a number of properties including high surface area and thermal conductivity which make them useful as electrode catalyst supports

in fuel cells. Moreover, they may also be used in gas diffusion layers as well as current collectors because of their high electrical conductivity. CNTs' high strength and toughness characteristics may also prove valuable as part of composite components in fuel cells that are deployed in transport applications.

2.1.4.4 Conductive Adhesives and Connectors

The same properties that make CNTs attractive as conductive fillers for use in electromagnetic shielding, ESD materials, etc. make them attractive for electronics packaging and interconnection applications, such as adhesives, potting compounds, coaxial cables and other types of connectors.

2.1.4.5 Molecular Electronics

The idea of building electronic circuits by CNTs has seen a revival the past five years and is a key component of nanotechnology. In any electronic circuit, particularly as dimensions shrink to the nanoscale. The interconnections between switches and other active devices become increasingly important. Their geometry, electrical conductivity and ability to be precisely derived, make CNTs to be the ideal candidates for the connections in molecular electronics. In addition, they have been demonstrated as switches themselves.

2.1.4.6 Thermal Materials

The thermal conductivity of CNTs is enabling many applications where heat needs to move from one place to another. Such an application is found in electronics, particularly advanced computing where the chips routinely reach over 100°C. The technology for creating aligned structures and ribbons of CNTs is the step toward realizing effective heat conduits. In addition, composites with CNTs have been shown to dramatically increase their bulk thermal conductivity, even at very small loadings.

2.1.4.7 Structural Composites

The superior properties of CNTs are not limited to electrical and thermal conductivities but also include mechanical properties, such as stiffness, toughness and strength. These properties lead to a wealth of the exploiting applications including advanced composites which requiring high values of one or more of these properties.

2.1.4.8 Fibers and Fabrics

Fibers of pure CNTs have recently been demonstrated and are undergoing rapid development along with CNTs composite fibers. Such super strong fibers will have many applications including body, vehicle armor, transmission line cables, woven fabrics and textiles. CNTs are also being used to make textiles stain resistant.

2.1.4.9 Biomedical Applications

CNTs in biomedical applications have significant potential. Since a large part of the human body consists of carbon, it is general of as a very biocompatible material. Cells have been showed to grow on CNTs, so they appear to have non toxic effect. The cells also do not adhere to the CNTs, potentially giving rise to applications such as coatings for prosthetics as well as anti-fouling coatings for ships. The ability to functionalize the sidewalls of CNTs also leads to biomedical applications, such as vessel, neuron growth and regeneration. It has also been showed that a single strand of DNA can be bonded to nanotubes which can then be successfully inserted into a cell.

2.1.4.10 Ceramic Applications

Ceramic material reinforced with CNTs has been made by material scientists at University of California, Davis. But the new material is far tougher than conventional ceramics conducting electricity. Furthermore, it can both conduct heat and act as a thermal barrier depending on the orientation of the nanotubes. Ceramic materials are very hard and resistant to heat and chemical attack which make them useful for applications, such as coating turbine blades. However, they are also very brittle. The researchers mixed alumina or aluminum oxide with 5 to 10 percent of CNTs and a further 5 percent of finely milled niobium. Then, they treated the mixture with an electrical pulse in a process called spark-plasma sintering. This process, which consolidates the ceramic powders, is more quickly and lower temperatures than conventional process. The new material has up to five times of the fracture toughness and this material shows electrical conductivity 7 times that of previous ceramics. It also has interesting thermal properties which conduct heat in one direction along the alignment of the nanotubes but reflecting heat at right angles to the nanotubes makes it an attractive material for thermal barrier coatings.

2.1.4.11 Other Applications

There is a wealth of other potential applications for CNTs, such as solar collection, nanoporous filters, catalyst supports and coatings of all sorts. There are many unanticipated applications for this remarkable material that will come to light in the years ahead which may prove to be the most important and valuable ones of all. Many researchers are looking into conductive and water proof paper made with CNTs. CNTs have also been showed to absorb infrared light and may be applications in the optic industries.

2.2 Capacitors

2.2.1 Traditional Capacitors [4]

The simplest traditional capacitor consists of two parallel conducting plates separated by a distance. As presented in Figure 2.5, the capacitance and energy storage of such as a device is directly proportional to the surface area of the plates and inversely proportional to distance between them.
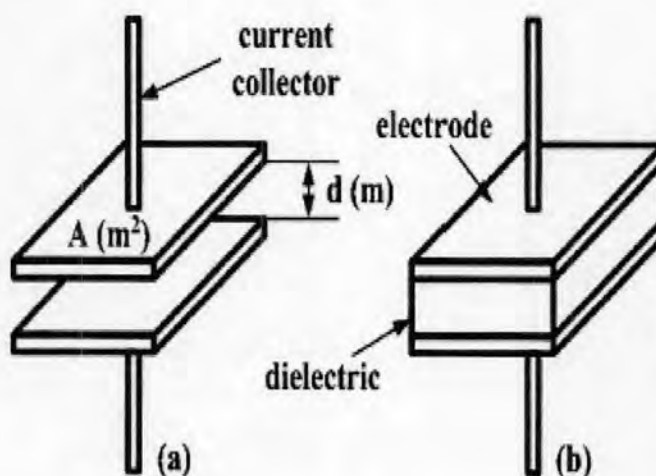
Figure 2.5 The basic components of capacitor: (a) without dielectric and (b) with one.

The addition of a polarizable insulator, called a dielectric, between the plates of a capacitor increases its characteristics in three ways. First, because dielectrics breakdown and allow charge to flow at higher potentials than air or vacuum, higher potentials, which may be applied to the capacitor, cause the greater energy storage within the capacitor. Second, since dielectrics are insulating, they allow the plates to be brought very close together without making contact, thereby increasing capacitance by reducing plate separation. Third, dielectrics reduce the electric field between the plates by a constant factor which reduces the work require to move a charge from one plate to the other. This result in the capacitance being increased by the same constant factor, as is the amount of energy that may be stored within the device.

The development of traditional capacitors has focused on improving one or more of the three factors to suit the needs of particular applications.

Initial efforts focused on controlling the geometric relationships of the capacitor increasing the surface area by rolling thin plates together while minimizing the distance between them. Parallel plate capacitors, typified in column (a) of figure 2.6, can withstand high voltages when utilizing ceramic dielectric, but are limited to energies of a few microWatt-seconds due to their overall small (picoFarad) capacitance values. Rolled capacitor, column (b), achieve higher (nanoFarad) by closely rolling together thin sheets of conductors separated by thin dielectric film and energies of milliWatt-seconds. The selection of the dielectric affects not only the capacitance but also the potential range, resulting in a two-fold impact on energy storage.

Diverging from such solid state capacitors, electrolytic capacitors, column (c) and (d), replace one electrode with a conducting electrolyte solution. The surface area is increased by the atomic level of the interaction between electrolyte and remanding metallic electrode. A thin oxide layer forms on the metallic electrode, serving as an insulator that separates the two electrodes by distances on the order of hundreds of nanometers. High capacitances may be achieved with such small separation but potential is limited to tens of Volts by the breakdown voltage of most applicable electrolytes. Typical energies of electrolytic capacitors are in the range of several milli-to Watt-seconds.

Figure 2.6 summarizes typical values of capacitance and energy storage associated with the various types of capacitor technologies. The final column, column (e), introduces electrochemical capacitors, which are typified by much greater capacitance values than any conventional capacitor technology.

	(a)	(b)	(c)	(d)	(e)
Typical Capacitance (F)	1×10^{-12}	1×10^{-9}	1×10^{-6}	1×10^{-3}	1000
Example	Plate capacitors with 50 pF. Left: an element from an old vacuum-tube radio in the form of two plates rolled to a cylinder, max. 450 V. Right: modern ceramic element, max. 100 V	Rolled capacitor with 51 nF, max. 63 V	Electrolytic capacitor with 10 mF, max. 35 V (bent wire is positive electrode)	Electrolytic capacitor with 1000 mF, max. 25 V (positive electrode left)	Electrochemical capacitor with 1500 F, max. 2.5 V (positive electrode left)
Energy Storage	10^{-6} Ws (μWs)	10^{-3} Ws (mWs)	10^{-3} Ws (mWs)	several Ws (Ws)	Watt hours (Wh)
Applications	High frequency technology: e.g. radio, TV, PC	Low frequency technology: general electronics, e.g. audio amplifiers	Low frequency technology: general electronics, e.g. audio amplifiers	Power supply units	Novel applications in power electronics: e.g. in electric cars, and replacing batteries

Figure 2.6 Characteristic examples of the various existing capacitor technologies, comparing typical capacitances, energy storage and application.

2.2.2 Electrochemical Capacitors

Electrochemical capacitors (ECs), which are known supercapcitors or ultracapacitors, become the excellent energy storage devices. The energy storage is achieved either by faradaic or non faradaic process at the electrode-electrolyte interface. ECs have long durability (over 10^6 cycles), greate energy density, high specific power. Importantly, they are non toxic materials [1-6]. Moreover, loading of ECs can be performed at high current density which decreases the loading time needed. Recent trends in miniaturization have led to many applications which require micropower in the range of milliWatts to Watts. Microelectromechanical systems (MAMS), microsensors and transmitters, as well as consumer electronics, such as mobile phones, PDAs and laptop computers are all examples of applications of ECs

[4,7]. The behavior of ECs is intermediate that of existing battery technologies and traditional capacitor. The large specific capacitances of ECs allow them to store significantly greater energy than traditional capacitors, nearly as much some type of batteries. The current delivery of ECs is not as limited by the oxidation-reduction reaction rates that limit batteries, giving them greater power of traditional capacitors. Ragone plots, such as the one showed in Figure 2.7, graphically demonstrate the typical specific energy and specific power of energy storage devices and display the intermediately characteristics of ECs.
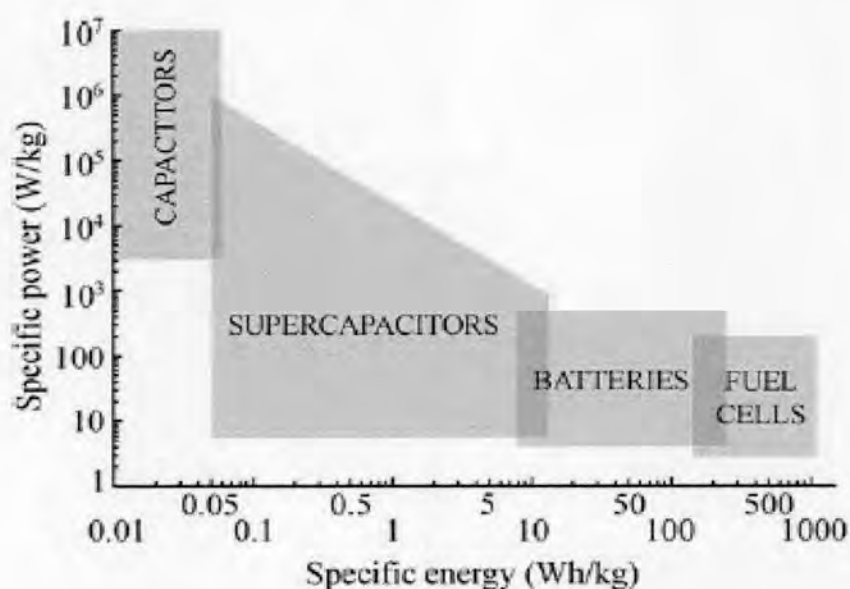
Figure 2.7 Sketch of Ragone plots for various energy storage and conversion devices.

In addition, ECs can be made from a variety of materials which the selection depends on the type of capacitance to be utilized as presented in Figure 2.8. Carbon in general and especially, carbon nanotubes (CNTs) form an attractive material for ECs applications as they have a large active area determining the capacitive performance. In this case, the large surface area is the important factor in achieving the high capacitance. More interestingly, they are relatively cheap, low density, friendly environmental and highly polarisable materials which make application, ever more attractive. Due to the microtexture, defect and catalyst contamination of CNTs, their specific capacitance is restricted to low value. Recently,

there have been considerable efforts to improve the capability of CNTs-based ECs by various techniques such as activated CNTs with heat or acid treatment to improve the micropore volume of CNTs and modification of CNTs with conducting polymers or with contain transition metal oxides.
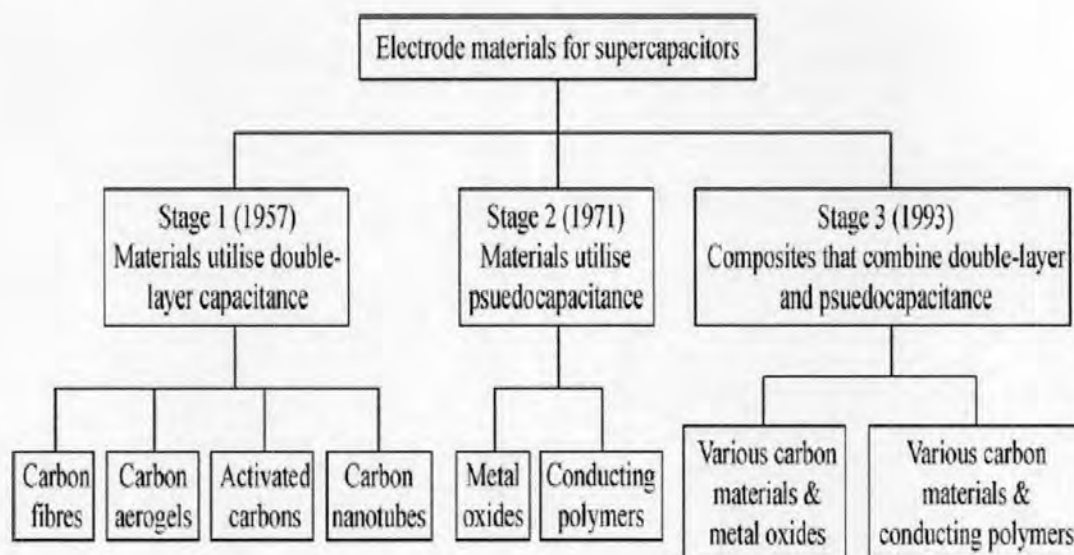

Figure 2.8 Taxonomy of the capacitor materials.

According to the mechanism of energy storage, ECs can be basically classified into two classes:

2.2.2.1 Electrochemical Double Layer Capacitors [7-9]

Electrochemical double layer capacitors (EDLCs), based on carbon electrode, store their electrical energy from double layer capacitance obtained by charge separation at the interface between charged surface of electrode and electrolyte ions as illustrated in Figure 2.9. This contact determines the amount of charge store. Thus, high surface of carbon materials, such as activated carbon, activated carbon fibers and carbon aerogels are commonly used as electrode materials for EDLCs. In addition, the capacitance of EDLCs is proportional to the permittivity of electrolyte and the distance of charge separation.
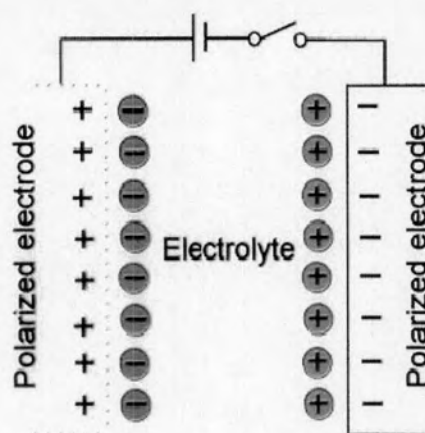
Figure 2.9 Electrochemical double layer capacitors (EDLCs).

2.2.2.2 Pseudo Capacitors [8-12]

Pseudo capacitors arise from the fast and electrochemical faradic redox reactions which occur at or near a solid electrode as showed in Figure 2.10. This is responsible for the charge storage of pseudo capacitors. The most widely used electrode materials for these capacitors are conducting polymers and transition metal oxides.
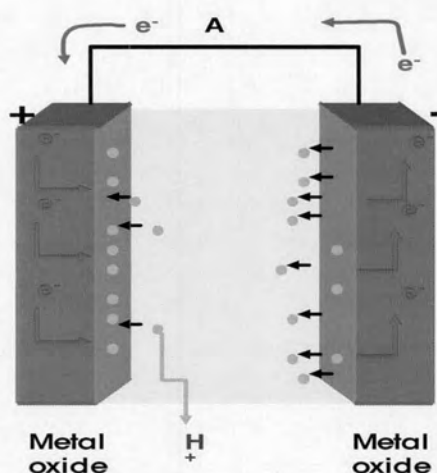
Figure 2.10 Pseudo capacitors.

As the polymer electrode materials do not have long-term stability and cycle life owning to their degradation. Thus, transition metal oxides have been studied recently due to their enhanced stability and high conductivity.

2.3 Faradaic and Non Faradaic Process

Two types of process occur at electrodes. One kind comprises reactions like those just discussed in which changes are transferred across the material-solution interface. Electron transfer caused oxidation or reduction to occur. Since reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes. Sometimes the electrodes, which faradaic processes occur, are called charge transfer electrodes. Under some conditions, a given electrode-solution interface will show a range of potentials where no charge transfer reactions occur because the reactions are thermodynamically or kinetically unfavorable. However, processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface can change with charging potential or solution composition. These processes are called non faradaic processes. Although charges do not cross the interface, external currents can flow when the potential, electrode area or solution composition charges. Both faradaic and non faradaic processes occur when the reaction of electrode takes place. Although the faradaic processes are usually of primary interest in the investigation of an electron reaction, the effects of non faradaic processes must be taken into account in using electrochemical data to obtain information about the charge transfer and associated reactions.

2.4 Fundamental of Electrochemistry [13-15]

Electrochemistry compasses chemical and physical processes that involve the transfer charge. There are two categories of electrochemical processes, potentiometry and electrolytic method, that are applied to quantitative measurements. Potentiometry is the field of electroanalytical chemistry in which potential is measured under the conditions of no current flow. The measured potential may be used to determine the analytical quantity of interest, generally the concentration of some components of the

analytical solution. Unlike potentiometry, where the free energy contained within the system generates the analytical signal, electrolytic methods are an area of electrochemical chemistry in which an external source of energy is applied to drive an electrochemical reaction which would not normally occur. The externally applied driving force is either an applied potential or current. When the energy is applied, the resultant potential is the analytical signal. Techniques which utilize applied potential are typically referred to as voltammetric methods while those applied the external source are referred to as impedance spectroscopic and galvanostatic. Electrochemical measurements utilize a conventional three-electrode cell including working electrode, counter electrode and reference electrode in electrolyte solution along with the potentiostat instrument. In this section cyclic voltammetry, impedance spectroscopy and galvanostatic charge-discharge used in this work are considered respectively.

2.4.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemistry reactions. The power of CV results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogenous electron-transfer reactions, and on coupled chemical reactions or absorption processes. CV is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process.
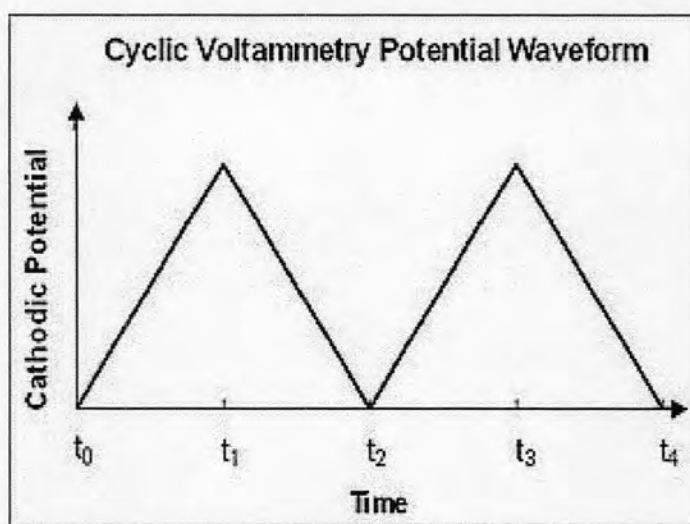
Figure 2.11 Potential-time excitation signal in cyclic voltammetric experiment.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode, using a triangular potential wave-form as showed in Figure 2.11.

During the potential sweep, the potentiostat measures the current resulting from the applied potential. The relationship between the potential applied and the current obtained is called cyclic voltammogram as presented in Figure 2.12.
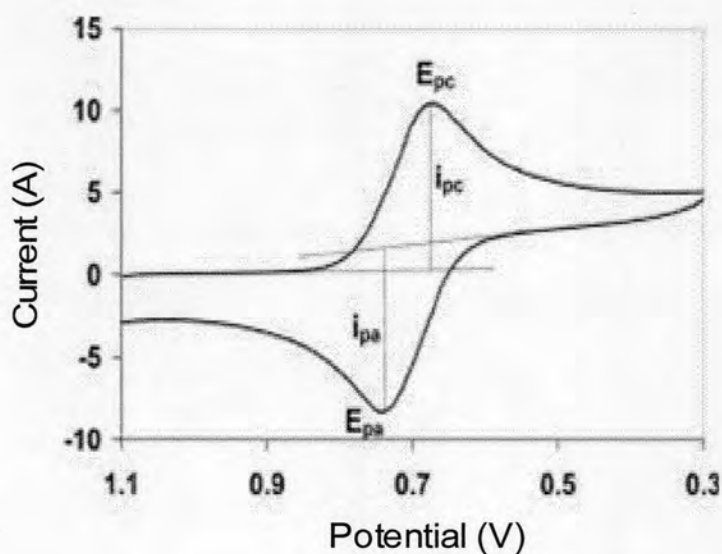
Figure 2.12 The relationship between the potential and the current.

where i_{pa} = anodic peak current

i_{pc} = cathodic peak current

E_{pa} = anodic peak potential

E_{pc} = cathodic peak potential

In addition, CV can inform the kinds of redox reactions occurred. The redox reaction can be classified into three types: reversible, quasi-reversible and irreversible illustrated in Figure 2.13 which gives the information in a system.
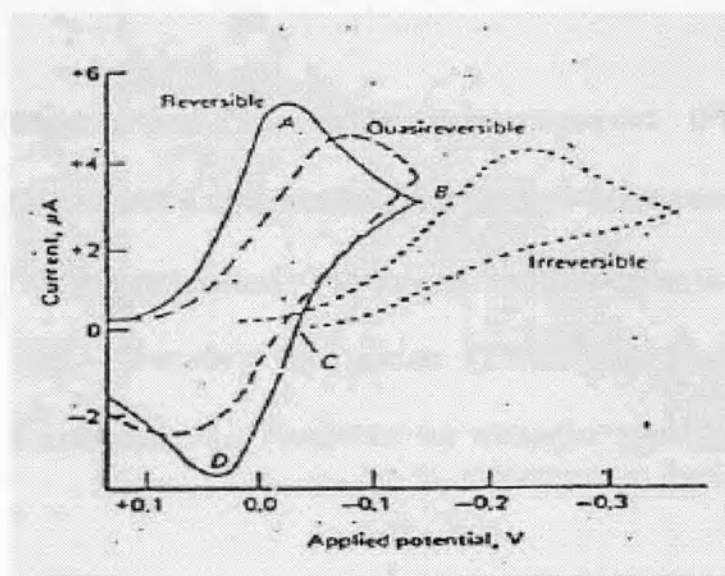
Figure 2.13   The cyclic voltammogram of three types of redox reactions.

For a reversible process, the separation between the peak potentials, is given by

$$\Delta E_p = E_{pc} - E_{pa} = 0.059/n$$

where E_{pc} = cathodic peak potential

E_{pa} = anodic peak potential

n   = number of electrons transferred

Moreover, the ratio of the reverse-to-forward peak current, i_{pa}/i_{pc}, is unity. For quasi-reversible system, the voltammograms are more drawn out and exhibited a

larger separation in peak potentials compared with a reversible system. For irreversible process, the individual peak was reduced in size and widely separated.

### 2.4.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is one of the most powerful techniques for measurement the resistance, capacitance and understanding the electrochemical behavior of electrode materials which is influenced by the frequencies. EIS is measured by applying the AC sinusoidal potential excitation to an electrochemical cell and measuring the current through the cell. The response to this potential is the AC current signal which contains the harmonic and the frequency, shifted in the phase as presented in Figure 2.14. Generally, the frequency range in EIS is from 0.1 Hz to 100 kHz.
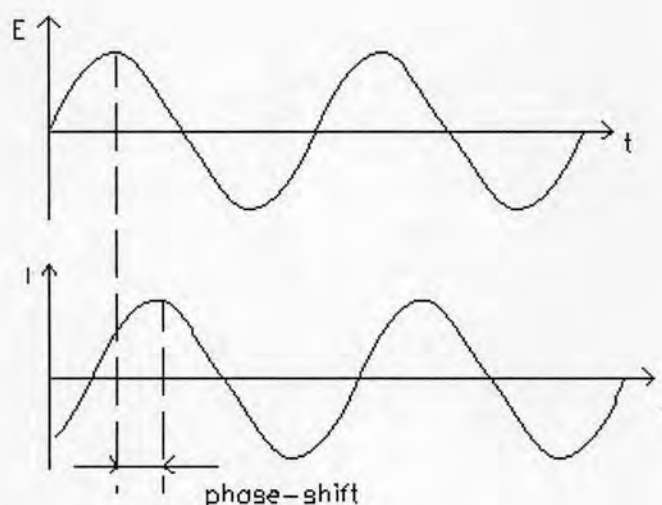
Figure 2.14 AC sinusoidal current response in electrochemical impedance spectroscopy.

In addition, the results of EIS are presented as the Nyquist plots (Z' vs Z'') where Z' and Z'' are the real variable and negative value of the imaginary variable of impedance, respectively as showed in Figure 2.15. The charge transfer process at electrode-electrolyte interface is determined by the region and represented by semicircular loop at high to medium frequencies. This process has a certain speed depending on the kind of reaction, temperature, concentration of the reaction products and potential. Whereas diffusion is represented by the straight line inclined at an

angle of 45^0 to the real axis at low frequencies. In the Nyquist plots the values are obtained from fixed curve calculated by electrochemical software.
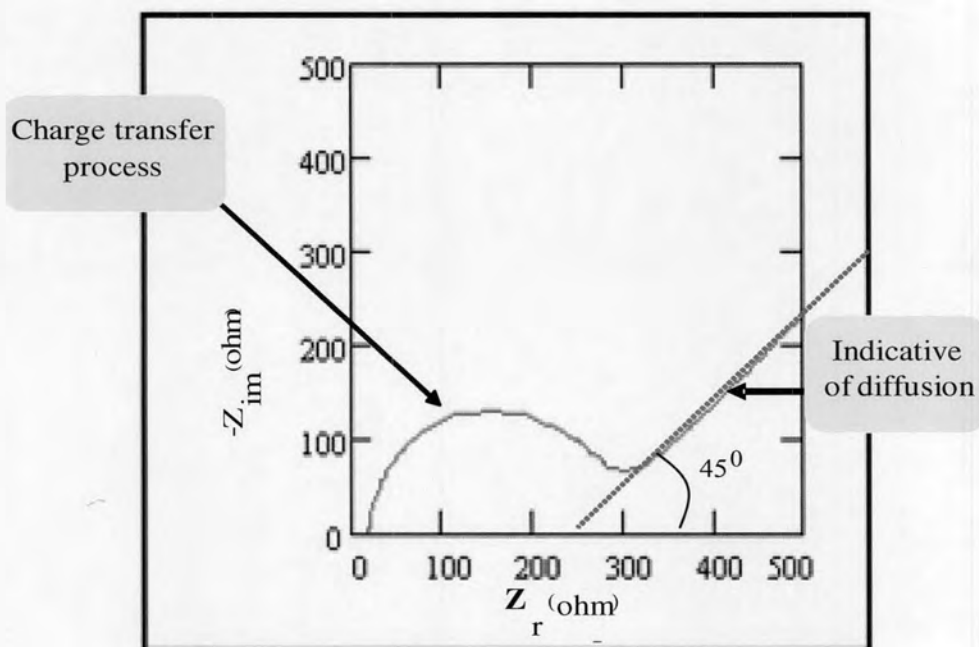
Figure 2.15 The Nyquist plot.

Another presentation method is the Bode plot. The impedance is plotted with log frequency on the x-axis and the absolute value of the impedance, |Z| on the y-axis. The Bode plot is showed in Figure 2.16. Unlike the Nyquist plot, the Bode plot explicitly shows frequency information (ω).
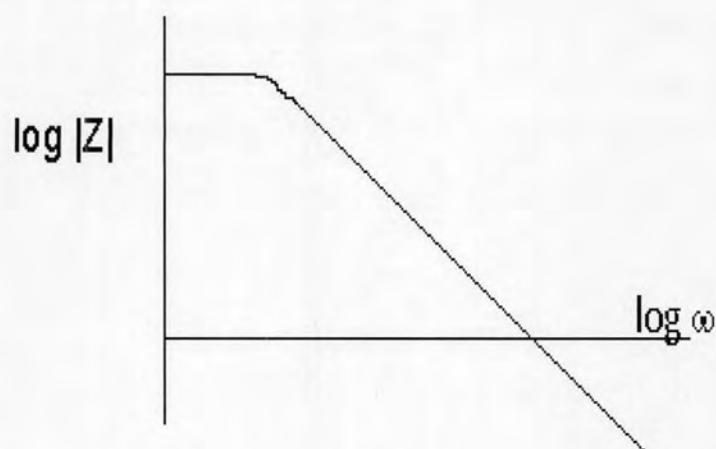
Figure 2.16 The Bode plot.

Moreover, the many values can be calculated by the impedance (Z) equations from the Bode plot as illustrated in Table 2.2.

Table 2.2 The impedance of common electrical elements

Component	Impedance
Resistor	$Z = R$
Inductor	$Z = j\omega L$
Capacitor	$Z = 1 / (j\omega C)$

where　$R =$ resistance

$L =$ inductance

$C =$ capacitance

$\omega =$ the radial frequency

$j =$ imaginary part $= \sqrt{-1}$

2.4.3 Galvanostatic

During galvanostatic testing, a constant current (I) is applied to the electrode material. Charge accumulates on the electrode in response to this current at the rate:

$$I = \frac{dQ}{dt} \qquad\qquad 2.1$$

The charge on the electrode is then given by:

$$Q = \int I \, dt \qquad\qquad 2.2$$

Capacitance is defined in the equation 2.3 as the charge in charge on the capacitor electrode divided by the change in voltage:

$$C = \frac{dQ}{dV} \qquad\qquad 2.3$$

Plotting the charge on the capacitor against its measured voltage, a linear region is observed during most of charging. In Figure 2.17, the slope of this region ($\frac{dQ}{dV}$) is the device's capacitance.
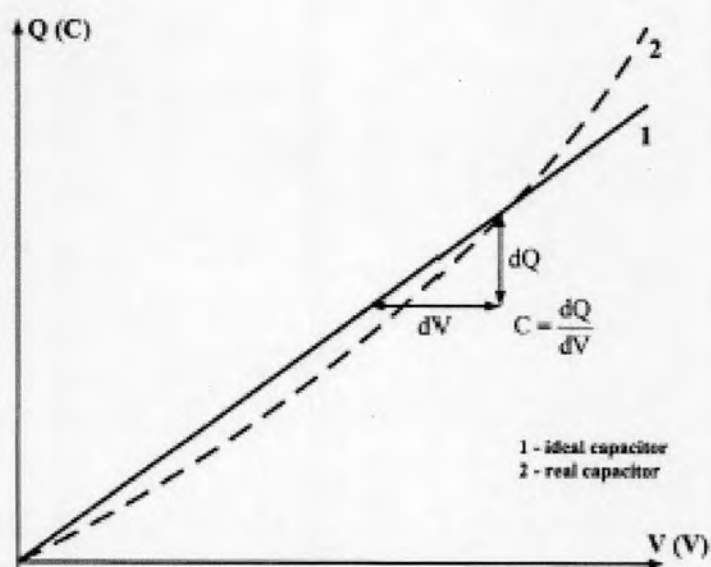
Figure 2.17 The method for determining capacitance value by plotting charge, Q (C) against potential, V (V) during galvanostatic charging.

When there is no straight forward method of plotting the charge on the capacitor electrode, the alternative method is available. The charge on capacitor is:

$$Q = CV \qquad\qquad 2.4$$

Combining of the equation 2.1 and 2.4 gives:

$$I = \frac{dQ}{dt} = C\frac{dV}{dt} \qquad\qquad 2.5$$

Rearranging the equation 2.5 expresses the capacitance value of the device as:

$$C = \frac{I}{(dV \, / \, dt)} \qquad\qquad 2.6$$

Hence, the capacitance of the device can be determined by using even the simplest oscilloscope to record the potential difference over time, and calculating the capacitance value as the current divided by the slope of the linear region as showed in Figure 2.18.
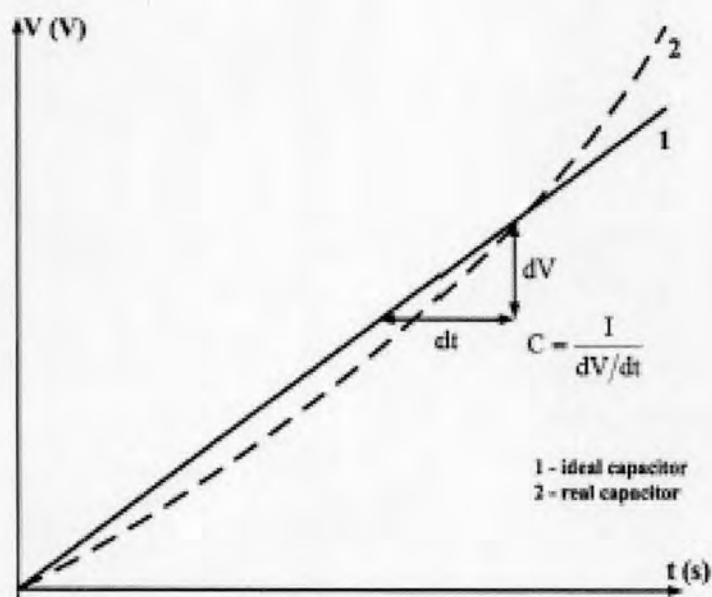

Figure 2.18 The method for determining capacitance value from charge in voltage over time during galvanostatic charging.

2.5 Electrostatic Spray Deposition [16-18]

Electrostatic spray deposition (ESD) technique, has been used for preparing thin film electrodes, is atomization of precursor solution into an aerosol when a strong electric field is applied between needle of a syringe and the substrate. More interestingly, this technique is simple and cost-effective deposition method. The result is electrostatical spray droplet being directed towards the heated substrate along

the electric field. In Figure 2.17, the ESD system is comprised of a precursor solution feeding unit, a power supply unit and a temperature control unit. The obtained film electrodes have resulted from the ESD process parameters, such as deposition temperature, distance of needle-to-substrate, precursor solution flow rate, electric field strength and deposition time.
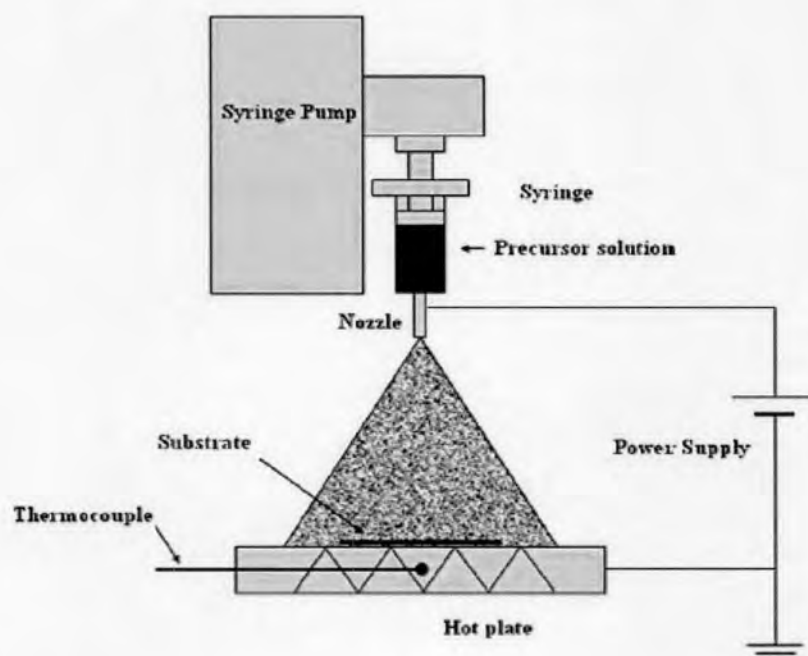
Figure 2.19 Schematic of electrostatic spray deposition system.

Several physical and chemical processes are involved in the ESD of materials layers and these occur either sequentially or simultaneously. The possible sequential steps are: (1) spray formation; (2) droplet transport, evaporation, disruption; (3) the preferential landing of droplets; (4) discharge, droplet spreading, penetration of the droplet solution, drying; (5) surface diffusion, reaction.

2.6 Literature Review

Q. Jiang and M.Z. Qu [1] studied the activated CNTs as electrochemical supercapacitor electrodes. The electrochemical capacitance of the activated CNTs, were produced by KOH, was 2 times that of normal CNTs. Moreover, the activated CNTs had 3 times BET surface area and 1.5 times pore volume than those of normal

CNTs. The reason that the activated CNTs had better than normal CNTs owed to the changes of CNTs structure during the activated process.

E. Frackowiak and K. Jurewicz [8] synthesized polypyrrole (PPy)/ MWNTs composite to increase specific capacitance of this material for supercapacitor application. The modified MWNTs by chemical activation with KOH is a significant enhancement of microporosity which increased in the specific capacitance of nanotubular material from 15 to 90 F/g. More importantly, the result of coated MWNTs by conducting polymer had been successfully realized and specific capacitance increased to 180 F/g because conducting nanotubular composite allowed an easy access of ions to the electrode/electrolyte interface and more effective contribution of the pseudofaradaic properties of PPy.

N.W. Kyung and K.B. Kwang [20] synthesized nickel oxide films by electrochemical precipitation of the $Ni(OH)_2$ films followed by heat treatment in the air at various temperatures. XRD results showed that nickel oxides obtained at 250^0C or above had a crystalline structure. However, it found that $Ni(OH)_2$ was not completely converted into NiO when heated at 250^0C and cyclic voltammogram presented a maximum capacitance of NiO at 300^0C which was 146.3 F/g.

S. Mukta and A. Girish [7] synthesized the composites of coconut-shell-based activated carbon and hydrous ruthenium oxide for supercapacitors. Cyclic voltammetric studies revealed an increase in the capacitance of the activated carbon from 100 to 250 F/g for the composite with 9 wt% ruthenium. Furthermore, electrochemical impedance analysis suggested that the energy storage process of these composite materials was limited by the mass transport of electrolyte ions in the pores of the activated carbon.

G.H. Deng and X. Xiao [19] demonstrated the preparation of $RuO_2.xH_2O/CNTs$ composites which grown on graphite substrate by chemical vapor deposition (CVD). Electrochemical properties of the synthesized electrodes were investigated by cyclic voltammetry and galvanostatic in 0.5 M H_2SO_4 electrolyte solution and found that

6 % w/w of RuO_2/CNTs electrode showed the excellent capacitive property and long-term cycle stability. More interestingly, the specific capacitance of this electrode was six times larger than that of CNTs electrode.

J.H. Kim and K.B. Kim [16] fabricated the binder-free CNTs film electrode by a novel process involving the electrostatic spray deposition (ESD) of an activated CNTs solution. This CNTs film electrode showed the mesopore structures with good adherence to the substrates, and the specific capacitance of 108 F/g was achieved for the electrode in 1 M H_2SO_4 electrolyte solution. Therefore, this CNTs film electrode shown the high rate capability while the binder-enriched CNTs film electrode may contained the impurities which could degrade its electrochemical performance.

Yan Shan and Lian Gao [6] prepared a novel MWNTs/Co_3O_4 composite electrode for supercapacitor which combined the acid treatment of MWNTs and in situ decomposition of $Co(NO_3)_2$ in n-hexanol solution at 140^0C for 10 hours. The result showed this composite electrode had the high capacitor property and displayed the different capacitive behavior depending on content of MWNTs. The best specific capacitance was up to 200.98 F/g which more than that of pure MWNTs (90.1 F/g).

A. Leela and S. Ramaprabhu [12] synthesized RuO_2/MWNTs, TiO_2/MWNTs and SnO_2/MWNTs nanocrystalline composites for supercapacitor electrodes. Electrochemical measurements of functionalized MWNTs gave the specific capacitance of 67 F/g whereas the nanocrystalline RuO_2/MWNTs, TiO_2/MWNTs and SnO_2/MWNTs composites gave the specific capacitance of 138, 160 and 93 F/g, respectively. The enhancement of the specific capacitance of composites from pure MWNTs was due to the progressive redox reactions occurred at the surface of transition metal oxides through faradaic charge transfer which from the morphological modification of MWNTs by the nanocrystalline RuO_2, TiO_2 and SnO_2. Especially, TiO_2 was suitable for developing ECs.