CHAPTER II
LITERATURE REVIEW

The previous chapter introduced a brief supercapacitors overview and purpose of carrying out the research. This chapter will review the some of the advantages and challenges associated with different kinds of polymer electrolytes that are used as separator in supercapacitor fabrication. The chapter will also further presents a review of the previous literature regarding the advantages and challenges that are associated with the CNTs. Prior to all these, the chapter will give an elaborate historical background of capacitor and the emergence of supercapacitor in technological industry.

2.1 Historical Background: From Capacitor to Supercapacitor

Historically, the invention in October 1745 of the Leyden jar by the German Ewald Georg von Kleist can be regarded as the beginning of capacitor technology. Pieter van Musschenbroek, who was a Dutch physicist at the University of Leyden, Independently, discovered the Leyden jar in 1746 (Conway et al., 1997a). The Leyden jar was constructed in such a way that, it consisted of a narrow-neck jar partially filled with water with an electrical lead brought through a cork in the neck of the bottle into the water. In accordance with von Kleist's implementation, his hands holding the jar formed the outer electrode, and amazingly, used the electrostatic generator to charge the jar which was connected. At times, von Kleist could feel the painful shock when he dare touch the lead in the water while still holding the jar.

The Dutch Leyden jar employed a foil electrode over the outside surface of the jar to form a true capacitor. Benjamin Franklin showed that the water in the jar was not an essential element as had been thought by the inventors; as a result, he was able to make flat capacitors consisting of a sheet of glass between foil electrodes (Ho et al., 2010). But later Faraday made major contributions to capacitor technology, including the concept of dielectric constant as well as the invention of the first practical fixed and variable capacitors. Some of the earliest capacitors since after the invention of the Leyden jar by Georg von Kleist were;

Wax paper and foil capacitor: invented in 1876 by Fitzgerald (see the example in Figure 2.1). The capacitor was made from wax-impregnated paper dielectric with foil electrodes. At that time, higher voltage capacitors were only achievable based on oil-impregnated paper and metallic foil.

Figure 2.1 Example of early wax paper and foil capacitors (Ho et al., 2010).

Mica dielectric capacitors: were invented by William Dubilier in 1909, who used silver mica, then, because mica was very reliable and its excellent dielectric with very good discharge resistance. Examples of these types of capacitors have been displayed in Figure 2.2.

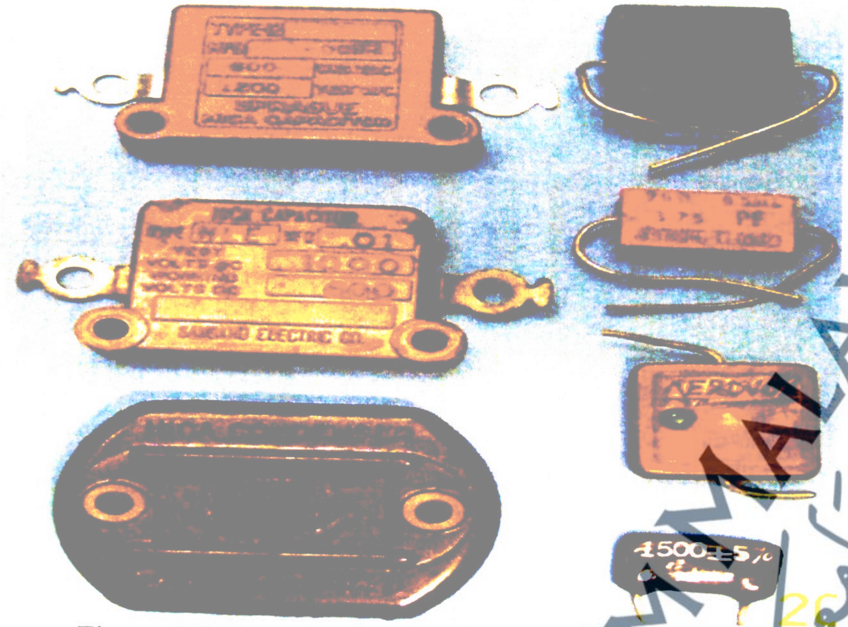

Figure 2.2 Example of early mica capacitors (Ho et al., 2010).

Ceramics Capacitors: Ceramics have been used as electrical insulation since the earliest studies of electricity. The Leyden jar, mentioned before was a ceramic capacitor. It was said that before and after the Second World War, mica was the most common ceramic dielectric for capacitors, although porcelain, steatite, cordierite, and rutile were also used.

Capacitors-based on titanium dioxide (rutile) were available commercially around 1926. Until the discovery of barium titanate in 1941 with a dielectric constant in the range of 1,000, about 10 times greater than any dielectrics known at that time, the attention has been focused on the barium titanate family of materials for a range of wartime applications, including capacitors (Ho et al., 2010) (see some sample examples of ceramic capacitors in Figure 2.3).

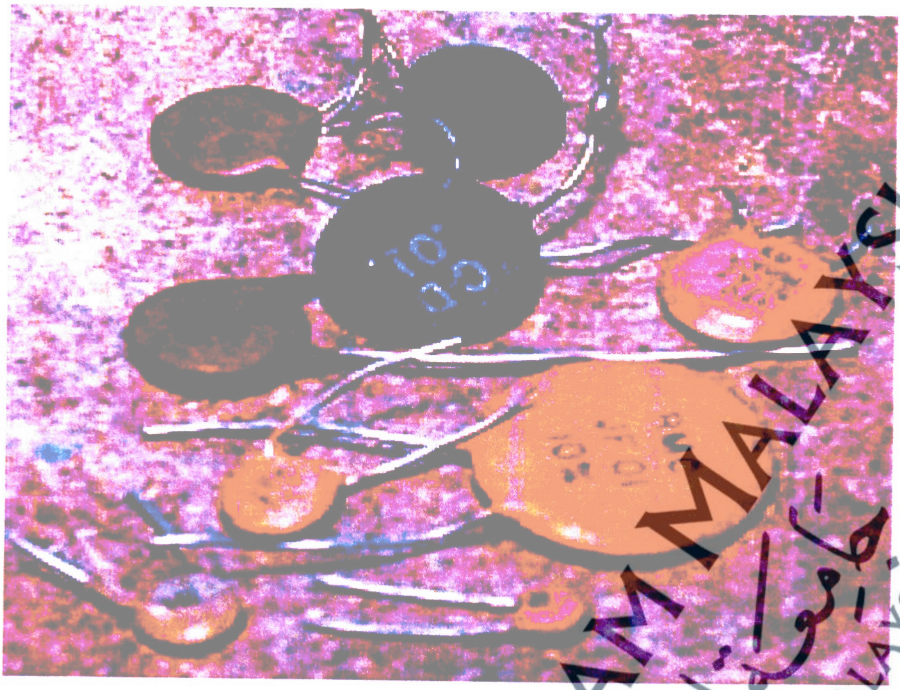

Figure 2.3 Example of early ceramic capacitors (Ho et al., 2010).

A metalized, self-clearing paper capacitor: Was patented by Mansbridge in 1900, and its assembly was based on metalizing with a metal particle-filled binder, which resulted in frequent shots through the paper. During the Second World War, Metalized paper capacitors becomes prominent, with Bosch manufacturing metalized paper capacitors using lacquer-coated paper and vacuum-deposited metal. The lacquer reduced electrolytic corrosion of the metal and increased insulation resistance. Starting from 1950 through 1954 further attention was given to metalized capacitor, to the extent; a 12 μm metalized capacitor film was produced in 1954 (Ho et al., 2010).

Double-layer capacitor: The concept of the double-layer capacitor was first explained by a German physicist, named Hermann von Helmholtz, in 1853. General Electric Company in 1957, first patented electrochemical capacitor (EC) based on the double-layer capacitance structure. The capacitor on those days consisted of porous carbon electrodes using the double-layer capacitance mechanism for charging. Thereafter, the Standard Oil Company, Cleveland, Ohio (SOHIO) patented a device that stored energy in the double layer interface (Sharma & Bhatti, 2010; Taleb, 2013). Nippon Electric Company (popularly known as NEC) of Japan licensed the technology from SOHIO and introduced the first EC products to the marketplace as memory back-up devices in computers in the year 1957 (Kurzweil, et al., 2012; Li & Wei 2013). At this time, SOHIO haven understands that, the "the 'double-layer' at the interface behaves like a capacitor of relatively high specific capacity." Advanced on to patent a disc-shaped capacitor in 1970 which make use of a carbon paste soaked in an electrolyte. In 1971, NEC takes the license of the technology from the SOHIO.

NEC was the first company to launch the first successful double-layer capacitors coined with the name "super capacitor" and to also send to the market. Then in 1980 and thereabouts, number of companies started producing the electro-chemical capacitor. The gold capacitor was developed by the Matsushita Electric Industrial Co., (otherwise known as Panasonic in the Western world) (Burke, 2009; Taleb, 2013). Pinnacle Research Institute, USA (PRI) developed the first high double-layer capacitor. The "PRI Ultra capacitor," developed from 1982, incorporated metal-oxide electrodes and was designed for military applications such as laser weaponry and missile guidance systems (Sharma & Bhatti, 2010).

2.2 Model of a Conventional Capacitor

A Conventional capacitor consists of two conducting electrodes separated by an insulating dielectric material. So, when a voltage is applied to a capacitor, opposite charges accumulate on the surfaces of each electrode. The charges are kept separate by the dielectric, thus producing an electric field that allows the capacitor to store energy. Figure 2.4 shows the illustration of this mechanism. (Halper & Ellenogen, 2006).

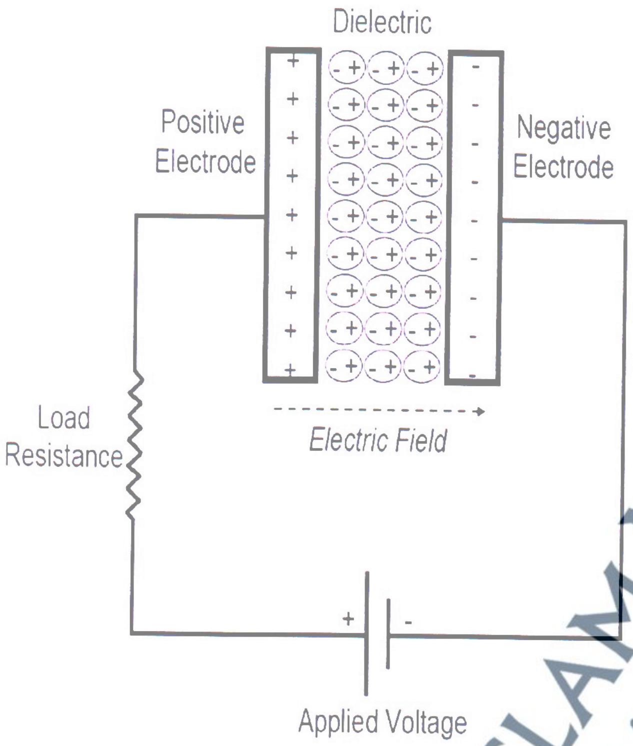

Figure 2.4 A simple electrostatic capacitor (Halper & Ellenogen, 2006).

The capacitance of a capacitor *C* is defined as the ratio of stored (positive) charge *Q* to the applied *V*, that is;

$$C = \frac{Q}{V} \qquad (2.1)$$

where *C* is capacitance in Farad, *Q* is the charge in Coulomb, and *V* is electric potential in the volt,

Again, capacitor, *C* in the conventional capacitor as shown the Figure 2.4 is directly proportional to the surface area *A* of each conducting plate and inversely proportional to the distance d between them;

Therefore,

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (2.2)$$

$\varepsilon_0\varepsilon_r$ are the product of dielectric constant (or permittivity) of free space and that of insulating material.

As for the energy density or energy stored *E* and power density, which are the main attribute of capacitor, we have;

$$E = \frac{1}{2}CV^2 \tag{2.3}$$

where *E* is the electrical energy stored in Joule and power *P* is the energy extended per unit time. Hence;

$$P = \frac{1}{4}\frac{V^2}{ESR} \tag{2.4}$$

where *P* is the maximum power measured in Watt and *ESR* is the equivalent series resistance,

Equation 2.4 shows clearly that *ESR*, limit the power of the capacitor. This entails all internal components of the capacitor such as current collector, electrode and dielectric materials.

2.3 Capacitor Classifications

There are four basic classifications of capacitors. These types could be subcategorized into sub-classes mostly depending on the choice of either electrolyte or the electrode.

(i) Electrostatic Capacitors: They contained mainly dielectric instead of electrolyte (Kurzweil, et al., 2009c) and their electrode is basically made of copper or aluminum as the dielectric between electrode air, mica, polymer firm or ceramics. These are used as components in electronics and high frequency filtering application which also requires operations at certain range of frequencies (Signorelli, 2009). However, their dielectric must be kept moisture–free in order to achieve a very high operating voltage. Although, the resistance-capacitance (RC) time constant -the time required to charge the capacitor, through the resistor, by ≈ 63.2 percent of the difference between the initial value and final value or discharge the capacitor to ≈36. 8 % - of this type of capacitor might be of the order of nanoseconds, with unlimited CD cycles and gravimetric and volumetric energy densities of approximately 1.5 Whkg^{-1}and 2 m Whl^{-1}.

(ii) Electrolytic capacitor: In this formation, anode is made from of rough aluminum firm coated with thin aluminum oxide film and the cathode is made of rough aluminum oxide layers (Jayalakshmi & Balasubramanian, 2008). These kinds of devices can achieve a high specific capacitance than electrostatic due to the thin nature of the aluminum oxide in conjunction with liquid electrolytes. However, their maximum voltages are lower than that of electrostatic capacitors, but higher in energy densities when compared to electrostatic capacitors. Again, electrolytic capacitors have RC time constants on the order of milliseconds, and are used in filtering applications that require bandwidth on the order of few KHz. They also possess volumetric and gravimetric capacitances that are higher than those of electrostatic and so their energy densities are also higher up to 30 kWhkg^{-1}and 120 mWhl^{-1}.

(iii) Electrochemical Symmetric Capacitor or Supercapacitor: In these types of devices, carbon electrodes and electrolytes of either aqueous of organic are made and no Faradaic reactions taking place either on the surface of the electrode. This is therefore similar to electrostatic and electrolytic capacitors. An ideal symmetric supercapacitor deliver RC time constant on the order of seconds, energy and power densities on the order of 5 Whkg^{-1}, 6 Whl^{-1} and 5 kWhkg^{-1}, respectively (Iwama et al., 2012; Qian et al., 2013).

(iv) Electrochemical Asymmetric Capacitors: They consist of two electrodes that differ in capacitance, meaning, they could be a hybrid between batteries and supercapacitors with the anode part representing carbon electrode and the cathode representing metal oxide electrode. Amazingly, the anode part operates as a supercapacitor and therefore does not involve Faradaic reaction (Kalinathan et al., 2008; Kurzweil, et al., 2009d), while, the cathode part which has oxide electrode operates in Faradaic reaction. The RC time constant deliveries on this kind of supercapacitors are slower - on the order of tens of seconds – and have the lower cycle ability compared to the normal supercapacitor, however, electrochemical asymmetric capacitor exhibit energy densities that double the symmetric supercapacitors for up to 10 Wh/kg and 12 Wh/l (Bockenfeld et al., 2013; Shirshova et al., 2013; Wang et al., 2013d).

2.4 Electrochemical Symmetric Capacitor

2.4.1 The Description

Supercapacitors (trade name of the first commercial device made by Nippon Electric Company (NEC) (Sharma & Bhatti, 2010), known as Electrochemical double layer capacitor (EDLC) (Lewandowski et al., 2010; Konno et al., 2010) or ultracapacitors’ (as it was recited by Pinnacle Research Institute (PRI) (Inagaki et al., 2010; Kaus et al., 2010; Inagaki et al., 2014f) or even ‘power capacitor’, ‘gold capacitor’, ‘power cache’ is based on the electrical double layer that forms at the interface between the charge solid and an electrolyte (Lee et al., 2011; Pint et al., 2011; McDonough et al., 2012; Ramya et al., 2013).

Supercapacitors are of utmost importance currently owing to as devices of utmost importance owing to their superior characteristics unmatched by other charge storage devices. Such characteristics include; high power densities (Orita et al., 2010; Khomenko, et al., 2010; Jampani et al., 2010; Yu et al., 2011; Lai et al., 2012; Dubal &

Holze, 2013; Dubal et al., 2013d;Venhryn et al., 2013;), at relatively high energy densities (less than that of lithium ion batteries (Eskusson et al., 2010) and long cycle life (Stepniak & Ciszewski, 2010; Zhao et al., 2011) and also broader range of working temperature (Li et al., 2010a), high coulombic efficiency (high reversibility) (Brouji et al., 2009), rapid CD capabilities (Zhang & Yang 2011), environmental friendliness – no heavy metals used – (Aravinda et al., 2013b; Aravinda et al., 2013c).

High cell specific capacitance may be achieved in EDLC compared to electrolytic or parallel plate capacitors in two ways;

(a) The active layer of the electrode is made of porous materials such as AC, carbon black (CB), and CNTs and so on, whose effective electrode surface area is several orders of magnitude higher than Euclidean surface area.

(b) Instead of dielectric, electrolyte is brought in to replace it, thereby filling the volume between the electrode and its voids. When the capacitor is charged, two double layers of charge between the electrode and electrolyte form at the cathode and at the anode. In simplest terms, the two electrical double layers can be explained as two capacitors in series (Signorelli, 2009).

Also, the two double layers of charge are characterized by a separation between the charges in the phase c_1 and c_2.

Even though both the phase c_1 and c_2 may differ due to the differences in radii - of the anion and cation in the electrolyte, they both have sizes on the order of few angstroms and this separation is in the order of magnitude less than the thinnest of the solid insulator (See Figure 2.5).

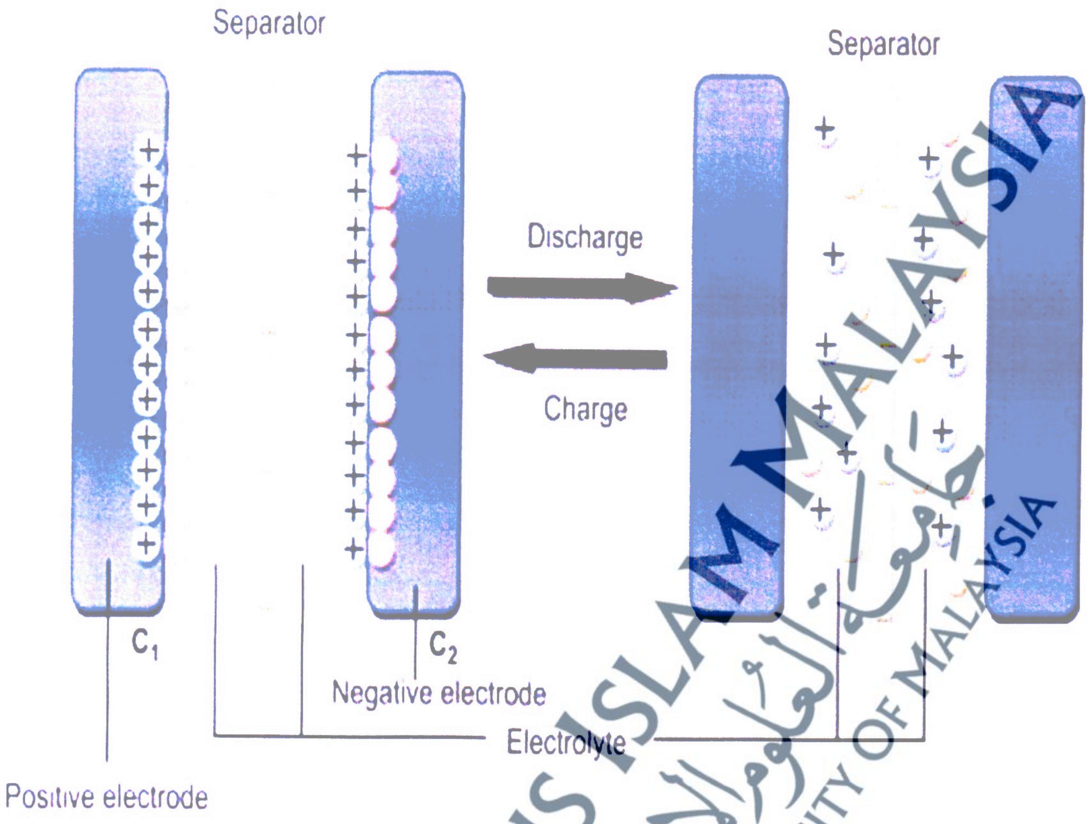

Figure 2.5 Charge and discharge stage of EDLC (Li & Wei 2013).

In terms of dielectric field strength at the double layer of charge, EDLC achieves one to two orders of magnitude higher at each electrode compared to electrolytic and electrostatic capacitors. Due to the high specific capacitance couple with the dielectric field strength that EDLC has, it's also volumetric and gravimetric energy density over other types of capacitors is also higher. In addition to the above, their power densities can reach up to ten times higher than those of batteries. Despite all these, they only achieve 5 % of the energy density of lithium batteries.

2.4.2 Supercapacitors Applications

The supercapacitors, which are characterized by good discharge rate and easy for maintenance have been on the demand, predictably, to be more extensive in frequency regulation applications. The other areas for significant growth is in regenerative braking for grid–connected light rail systems (Jampani et al., 2010), memory back-up devices in many electrical appliances, example, VCRs, cameras, etc. (Probstle et al., 2002); telecommunication devices, such as cell phones and pagers, stand-by power systems, which require high power in short pulse (Bittner et al., 2012; Dubal et al, 2013a; Dubal et al., 2013b; Dubal et al., 2013c; Dubal et al., 2013e; Zhao et al., 2013; Perera et al., 2013; Dubal et al., 2014) and electric/hybrid vehicles (Barsali et al., 2010; Tennakone & Buchanan, 2011; Inagaki et al., 2014f), lasers and uninterruptable power supply (UPSs).

In 1980s, the supercapacitors were also used for the energy source to drive wristwatches with solar cells. Since early 1990s, supercapacitors were used as actuator back-up sources for toys, electric appliances, home equipment, etc. Recently, supercapacitors with higher capacitances and lower resistances are under development for higher electric power sources in EV systems, electric power storage systems (Marie-Francoise et al., 2005).

2.4.3 Component of Supercapacitor Cell

Basically, there are three main components of a conventional supercapacitor cell (Kossyrev, 2012), these are:

- surface area electrode,
- separator, and
- electrolyte.

The surface area electrode; is composed of carbon or carbon related particles held together by a binder. The size of this electrode might differ as mentioned earlier depending on the type of the particles of the electrode leading to a moderate surface area.

The current collector; typically aluminum foil, supports the active layer to the EDLC terminal.

Electrolyte; composed of at least a solvent and a salt. Typical requirements of the electrolyte are electrochemical stability within the active layer of the electrode, high ionic mobility over a large range of ionic molarity and low cost. The ion mobility directly controls the equivalent series resistor (ESR) and consequently the EDLC cell. Organic electrolyte results in slower mobility than aqueous once, thereby given rise to higher cell ESR; although their high decomposition voltage makes them more preferable than aqueous electrolyte.

The function of the separator is to prevent short circuit between the electrodes and the permits ionic transfer from negative to positive electrode. This is very necessary, in that, as the capacitor charges, the concentration of the negative ions (with respect to the bulk concentration) increases at the cathode and decreases at the anode. Conversely, again, the concentration of positive ions increases at the anode and decreases at the anode. Separators are classified according to their conduciveness to permit ionic mobility, its dielectric strength, its weight, its ability to absorb electrolyte and its cost. Therefore, some of the qualities of good separators are; not electrically conductive, very thin (Carlson & Asp, 2013), capable of high temperature operation, highly porous, inexpensive and capable of being impregnated with electrolyte.

2.5 The Paradigm Shift from AC to CNTs

In recent years, most of the researches on supercapacitors focus on AC electrodes. Whereas today, due to the breakthrough in this area, CNTs and other re-engineered carbon electrodes have appeared to be the most promising electrodes for the fabrication of supercapacitors. This is due to the urgent need to improve the energy density that AC electrodes could not be able to achieve (Wang et al., 2013c).

Although there is an argument that AC electrode results in a high surface area, but then, that shows the irregularities regarding its pore sizes; as some pore is too wide for efficient utilization, while some are too small for the electrolyte ions to penetrate through (Wang et al., 2013d).

Energy density achieved in AC electrode is generally lesser due to the thickness of the electrode which results in leaving many portions of it un-accessed by the ions. Even the power delivered by the AC electrode is quite smaller compared to the CNTs due to the poor mobility of the electrolyte ions through the irregular path from the electrode surface to the current collector.

The characteristic performance of an EDLC can be adjusted by changing the nature of its electrolyte (Halper & Ellenbogen, 2006) and this made the researchers to find which among them will enhance the both the power and energy density of the EDLC especially between using either an aqueous (such as H_2SO_4, H_3PO_4 and KOH) or organic electrolytes. While the nature of the electrolyte is of great importance in supercapacitor design, the subclasses of EDLCs are distinguished primarily by the form of carbon that are used as electrode material.

Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides. Different forms of carbon materials that can be used to store charge in EDLC electrodes are ACs, carbon aerogels, and CNTs. However, currently the CNTs has an upper hand over other carbon materials due to the balanced power and energy delivery. A comparison of the power sources among different energy system is shown in the Ragone plot of Figure 2.6. The plot shows that EDLC that has CNTs as its active material delivers a balance power and energy densities over others.

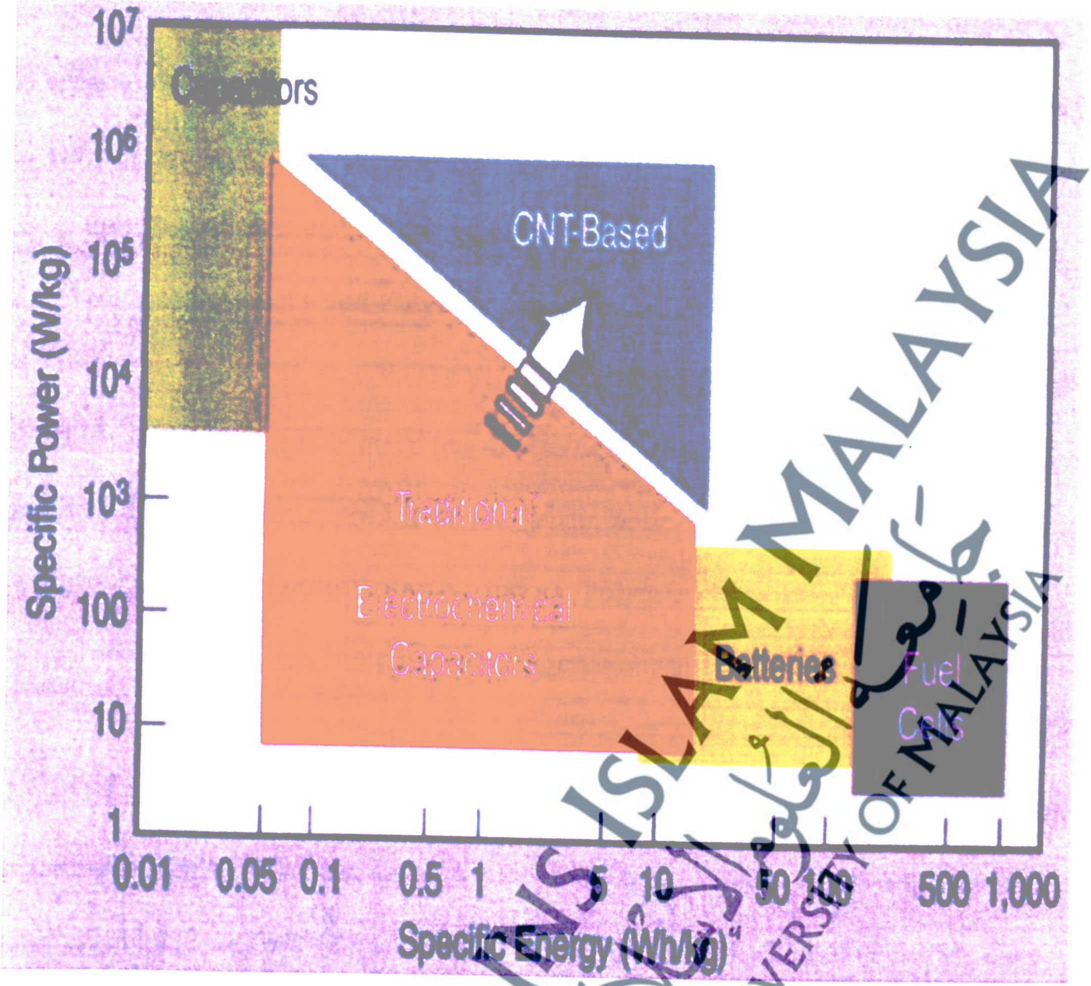

Figure 2.6 Ragone energy plot (comparison of power sources) (Hashmi, 2013b).

Though, AC is considered as the most popular electrode used in EDLCs due to its lower cost and high surface area, its major setback is the larger-distribution pore size (Wang et al., 2013c), which affects the attainability of the aforementioned power and energy densities. Carbon aerogel on the other hand, is a good electrode because of their formation of a continuous network of conductive carbon nanoparticles with interspersed mesopores (Halper & Ellenbogen, 2006), however, their "sticky-formed", made them not friendly in the fabrication of the supercapacitor.

Nevertheless, both symmetric and asymmetric types of supercapacitors have received tremendous breakthrough nowadays. While carbon aerogels, CNTs and graphitic carbon and alike are being selected for research in symmetric supercapacitors in order to enhance the energy and power density in supercapacitors, metal oxide, such as ruthenium and manganese oxides have been the choice of the asymmetric supercapacitor researchers (Kurzweil, et al., 2009f; Kurzweil., et al. 2009g).

2.6 What are Polymers and Polymer Electrolytes?

According to Helmenstine, (2013) a polymer can be regarded as a large molecule that is made up of repeating subunits connected to each other by chemical bonds. A polymer could be anything plastic, proteins, such as hair, nails, tortoise shell, cellulose in paper and trees, DNA, silly putty or even a rubber. Polymer electrolytes may be defined as membranes that possess, transport properties comparable to that of ionic solutions (Ganesh et al. 2008).

However, polymer electrolyte according to Noto, et al., (2011) refers to any macromolecular or supermolecular nano-aggregate system characterized by a significant ionic conductivity usually considered higher than approximately 10^{-7} Scm^{-1}. Therefore polymer electrolytes, generally, are all those materials where a supermolecular system is doped with ions and presents a significant conductivity.

Polymer electrolytes from poly(ethylene oxide) (PEO) with ionic conductivity were first discovered in 1973 by Fenton et al., (Noor et al., 2010; Kumar & Sundari, 2010; Tripath et al., 2012; Ulaganathan et al., 2012; Kuo et al., 2013; Yang et al., 2013) and Armand (Zhang et al., 2006; Ragavendran et al., 2004) who first described their exciting and electrochemical properties and presented them to the solid state ionics community at the 2nd International Meeting in this series, at St. Andrews, Scotland in 1978 (Kumar & Sundari, 2010).

Polymer electrolytes are promising materials for electrochemical device applications, namely, high energy density rechargeable batteries (Kuo et al., 2013), fuel cells, supercapacitors, Electrochromic displays (Livshits et al., 2005; Agrawal and Pandey, 2008; Noor et al., 2010).

They could also be used in sensors, actuators, and dye-sensitized solar cells which play the role of the either of the following; (i) to separate two electrodes; (ii) provide good electronic insulation; and (ii) allow a fast and selective transport of the desired ions.

To be suitable for application in a device, a polymer electrolyte must simultaneously satisfy three fundamental requirements, namely; give a good performance, should be very durable and most importantly, cost effective (Noto, et al., 2011). Figure 2.7 (a) and (b) below, describes the recent classifications of polymer electrolytes.

Figure 2.7(a) Classes of "Classic" polymer electrolytes (Noto, et al., 2011).

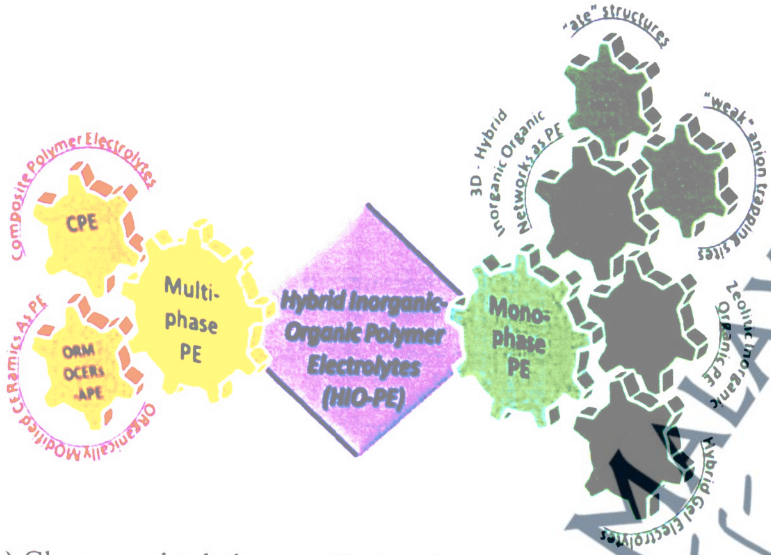

Figure 2.7(b) Classes and subclasses of hybrid inorganic–organic polymer electrolytes (HIO-PE): class A – multiphase polymer electrolytes, class B – mono-phase polymer electrolytes (Noto, et al., 2011).

In recent years polymer electrolytes (both solid and aqueous) attracted a lot of attention incorporated in many electronic devices (Dillip et al. 2008; Kurzweil, et al., 2009e) especially for the applications in laptops, phones, credit cards and so on (Yang, 2003).

2.6.1 Review on the Use of Polymer Electrolytes for Supercapacitor Fabrication

Clemente, et al., (1996) and Panero et al., (1996) in two of their separate but identical works, proposed a solid-state redox supercapacitor based on a polymer electrolyte and gel membrane respectively. In the first case, polymer electrolyte was prepared by immobilizing an ethylene carbonate-propylene carbonate (EC-PC) solution of LiClO, in a poly- (methylmethacrylate), (PMMA) matrix. Composition of the membrane (LiClO -EC-PCPMMA) in molar ratio was 4.5:19:46.5:30. While in the second case, the electrolyte membranes were prepared by immobilizing EC-PC solution of lithium perchlorate (LiClO,) in a PMMA matrix, and composition of the LiClO, -EC-PC-PMMA membrane was in the mole ratio of 4.5-49. 5-21-25. The authors also used two polymeric compounds, namely PMMA at high molecular weight (m.w. = 996 000) and PMMA at medium molecular weight (m.w. = 120 000) so the gel membranes with different wetting characteristics can be obtained. Although the performance of the fabricated supercapacitor was quite promising in both cases, their configurations have been the problem. For example, in the first case, the performance of the supercapacitor was good if and only if, the thick polymer film electrodes are employed and efficiently used. And in the second case, it was observed that, at higher current, the capacitance performance was low which was associated with the IR drop losses within the capacitors.

Again, in 1996, Morimoto and co-workers used organic electrolytes to fabricate the EDLC. Electrolyte solutions that was prepared by dissolving quaternary phosphonium (R_4P^+), quaternary ammonium (R_4N^+) and different lithium salts of different grades and qualities available in propylene carbonate (PC) distilled under low pressure and removing water by bubbling dry N_2. However the EDLC prepared from almost all the electrolytes was marred by degradation and low performance, especially as the temperature rises (above +25 ^{0}C) or lowered (below -25 ^{0}C). Like Morimoto et al., in 1996, Yata, et al., (1996) also fabricated two types of policing capacitor that they considered with extremely stable polyclinic semiconductor (PAS) as the positive and negative electrodes. The PAS was prepared by pyrolysis of phenol-formaldehyde resin molded with $ZnCl_2$ in advance. The PAS sample with the [H]/[C] molar ratio of 0.22 was used, which was heat-treated at a pyrolytic temperature of 510 ^{0}C in a N_2 atmosphere. Though this exploration leads to a significantly improve on the performance of the capacitance of the supercapacitor, better than that of Moriomoto et al., (1996), the performance was also constrained by the temperature rise and fall (within -30 to 70 ^{0}C).

Bonnefoi et al. (1999a), and Bonnefoi et al., (1999b), proposed their supercapacitor using a mixture of Norit SX Ultra AC as the active material and an electronic conductor which was added to the Carbon in order to ensure better electronic conductivity and thereafter, come up with the current collector from nickel foam. They further used cells that were then filled with electrolyte, which was a solution of acetonitrile (CAN) containing 1.7 M of NEt_4 $MeSO_3$. However, the electrolyte conductivity was only 20 Scm^{-2} at 25 ^{0}C and at 25 ^{0}C to -30 ^{0}C respectively.

Staiti et al., (2002), also made their contribution in this aspect of EDLC fabrication and used three different polymer electrolytes to test the efficiency of their supercapacitor. In their work, their three electrolytes that were tested in EDLC configuration are:

(a) Nafion 115, commercial membrane produced by DuPont (N115) and of 160 µm thickness of its swelled membrane.

(b) Nafion membrane obtained by casting procedure starting from 5 wt % Nafion ionomer solution by Aldrich (NRG50), with 50 µm thickness.

(c) microporous fiberglass matrix filled with sulfuric acid 1 M H_2SO_4 (FVH_2SO_4) of 200 µm thicknesses of its swelled membrane. But then, the overall conductivity of the electrolytes of the first two electrolytes was obtained as and 5.7 x 10^{-2} and 3.1 x 10^{-2} Scm^{-1} specific capacity of 13.2 Fg^{-1}. This may not be unconnected with the preparation procedure of the active components as admitted by the authors themselves.

In the same year, Pröbstle et al.,(2002) then proposed bottom cell supercapacitors using monolithic carbon aerogels and impregnated potassium hydroxide (KOH) as an electrolyte in it. The results seem to be promising, but the compatibility between the cell casing and the electrode was always the stumbling block towards getting efficient results in this kind of setup.

Another interesting literature is the work of Wu et al., (2003), where three different ECs of magnetite in aqueous electrolytes used in the fabrication of pseudocapacitor were charecterized. In their contributions to this knowledge, capacitive behavior of magnetite in aqueous electrolytes included sodium sulphite, chloride and phosphate, and potassium hydroxide were characterized, and are categorized into three syndicate groups. Sodium sulfate (Na_2SO_4) and chloride electrolytes gave capacitances of ~5 Fg^{-1} for Fe_3O_4 which they said was close to the space-charge capacitance of the oxide. They further added that, Potassium hydroxide and sodium phosphate yielded a higher capacitance of ~7 Fg^{-1} which they attributed to a surface redox reaction which involves hydroxide ions. And lastly Sodium sulphite resulted in the highest capacitance which, depending on the dispersion of the magnetite crystallites on the conductive matrix, reaches as high as 510 Fg^{-1} for the Fe_3O_4 with an operating voltage range of 1.2 V. This correlation study is a promising one, however, it is a known fact that, one of the set back of pseudocapacitor is because it involves faradaic reaction, use of heavy metals and consequent effect to the environment could sometimes be alarming.

In trying to solve the problem of corrosiveness, bulky design and low energy density associated to redox supercapacitors, Hashmi, et al., (2004), introduced a 1,5-diaminoanthraquinone-based all solid-state redox supercapacitors with the solid polymer electrolyte, PVA–H_3PO_4 blend and polymeric gel electrolyte poly methyl methacrylate–ethylene carbonate (EC) –propylene carbonate (PC) –tetra ethyl ammonium perchlorate ($TEAClO_4$) system. The results were commending and their work mark one of the major breakthrough in the optimized redox supercapacitor at that time. Having done that, Yang, et al., (2005), prepared "all solid supercapacitors" using

AC as an electrode with a mixture of PVA and KOH and electrolyte compared with EDLC using PP/polyethyle (PE) as separator. Their results greatly emphasized the noble of PVA over PP/PE separator, the reason why we choose PVA as one of our precursor in this research.

Arbizzani et al., (2007), Mastragostino & Soavi (2007) and Lazzari et al., (2007) used ionic liquids (IL) as their main electrolytes for the enhancement of supercapacitor performance. In their paper, the made their optimization of electrode materials for IL-based supercapacitors featuring a hybrid configuration with carbon negative electrode and poly (3-methylthiophene) (pMeT) as positive operating at 60 °C with the ILs *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR$_{14}$TFSI) and 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI). In another breakthrough, still the same group of researchers consisting Arbizzani et al., (2008), and Lazzari et al., (2008) come up with the solvent-free ionic liquid electrolytes and hydrophobic IL electrolytes in two in two of their separate but identical works. Although ILs used has proved to improve the capacitance of the capacitor, their cost is the major setback of using them.

Acrylamide-based polymer gel electrolyte was prepared and used by Ganesh et al., (2008) for the AC-based supercapacitor. However, the result was found not to be impressive as, only 3 Fg^{-1} of specific capacity was recorded after 10,000 cycles.

In another development, EDLC performance of the porous carbons was investigated in an organic electrolyte of 1M LiClO4 in propylene carbonate and dimethoxy ethane. The hierarchical porous carbons exhibited large specific double layer capacitance of capacitor 120 Fg^{-1} due to their large surface areas (Yamada et al., 2007).

(The analysis of the hierarchy only contributed to the 8.4 for the mouse/macropores and 8.1 μFcm^{-2}).

Wei et al., (2009) proposed gel ionic liquid as their electrolyte used in their fabricated supercapacitor. Their "room temperature ionic gel" otherwise RTIL electrolyte was prepared in composing of 1-butyl-3-methylimidazolium chloride ([BMIM]) and cellulose of 6 wt.% cellulose, which forms a totally transparent electrolyte when dried and therefore used it as a separator. The performance of the supercapacitor however, was not impressive as it only recorded 22 Fg^{-1} of capacitance with the 1 V window capacity.

In their work entitled "Allyl-functionalized IL as electrolytes for electric double-layer capacitors" Orita et al., (2010) used electrolytes that were prepared by dissolving the salts in propylene carbonate (PC), dimethylcarbonate (DMC), or γ-butyrolactone (GBL). They also added that; all the electrolytes were prepared with a glove box of Ar atmosphere. We used 1.4M 1-ethyl-3-methylimidazolium (EMIm) BF4/PC, EMIm–TFSA/PC, and TEMA–BF4/PC as typical electrolytes. The authors, however, they could not clearly state neither the conductivity of the electrolyte nor the performance of the capacitor achieved.

One of the recent work of supercapacitor enhancements, especially electrolyte and separator is work done by Zhou and his co-workers, where all-solid-state supercapacitors were fabricated using a polyvinylidene fluoride (PVDF) /lithium trifluoromethanesulfonate (LiTFS) membrane as the separator and poly (ethylene oxide) (PEO) /lithium perchlorate ($LiClO_4$) as the polymer electrolyte in the porous carbon electrodes. Two types of mediators, NaI/I_2 and $K_3Fe(CN)_6$/$K_4Fe(CN)_6$, were added into the PEO/$LiClO_4$ polymer electrolyte that was used to fabricate the electrodes (Zhou, 2011). They reported also to have achieved the voltage window in which the

SCs operated was 2.5–3 V. Though, they also reported high reversibility on one of the cells due to the high resistance.

Karabelli et al., (2011) also reported Macroporous separators based on vinylidene fluoride (VdF) homopolymers and copolymers that were prepared by a phase inversion technique using a solvent/non-solvent mixture. They then made the comparison and demonstrated that, among the fluorinated polymers, the homopolymer PVdF was rated to be the most suitable grade to be implemented in supercapacitors. The authors further asserted that, separator provided higher conductivities than the commercial separator cellulose and above all CelgardTM. They, however, admitted that, they could not give account for the grade of the supercapacitor in terms of energy or power density as optimization is currently on going.

Yamagata et al., (2012) also contributed in this area, in their paper titled "Chitosan-based gel electrolyte containing an ionic liquid for high-performance nonaqueous supercapacitors" used this Nonaqueous gel electrolytes based on Chitosan and 1-ethyl-3-methylimidazolim tetrafluoroborate (Chi/EMImBF4) are prepared for EDLCs. The transparent, colorless gel sheet has higher levels of mechanical strength and ionic liquid retention required in EDLC cells. But our investigation revealed that the thickness of the gel might have been the major cause of degradation after 5000 cycles.

Effect of aqueous electrolytes on the electrochemical behaviors of supercapacitors based on hierarchically porous carbons was the work of Zhang et al., (2012) where the Hierarchically porous carbons (HPCs) were prepared by solegel self-assembly technology with nickel oxide and surfactant as the dual template. The group also added that, the porous carbons are further activated by nitric acid. The electrochemical behaviors of supercapacitors using HPCs as electrode material in different aqueous electrolytes, such as $(NH_4)_2SO_4$, Na_2SO_4, H_2SO_4 and KOH were studied by cyclic voltammetry (CV), galvanostatic CD, cyclic life, leakage current, self-discharge and electrochemical impedance spectroscopy. Their results showed that the supercapacitors in various electrolytes perform different capacitive behaviors; especially in 6 M KOH electrolyte; they also argue that the supercapacitor represents the best electrochemical performance, the shortest relaxation time, and nearly ideal polarisability. This report though was promising, however, the capacitance values, energy and power densities where not clearly stated.

With the introduction of graphene into the scene of supercapacitor, Tsai et al., (2012), in their effort to improve the performance of supercapacitors, induced yet again the IL incorporated with graphene. The authors used KOH-activated microwave exfoliated graphite oxide ('a-MEGO') electrodes of specific surface area (SSA about 2000 m^2g^{-1}) porous in a eutectic mixture of IL (1:1 by weight or molar ratio N-methyl-N-propylpiperidinium bis(fluorosulfonyl)imid (PIP_{13}-FSI) and N-butyl-N-ethylpyrrolidinium bis(fluorosulfonyl)imide (PYR_{14}-FSI)) as the electrolyte for supercapacitor applications. They also claimed the supercapacitors working temperature was within the range of -50 to 80 °C with a capacitance of more than 100 Fg^{-1} at below room temperature. Indeed, this is an outstanding performance, even though the sour cost of the materials and reagent are for sure one of the alarming area of concern.

The same improvement on the capacitance of the EDLC that is based on the two identical ideally polarizable microporous titanium carbide-derived carbon electrodes and using IL was cited by Tonurist, et al. (2012), and Tonurist et al., (2013) using the popular (1-ethyl-3-methylimidazolium tetrafluoroborate) and the same conclusion can be derived as was done to other related works.

Yu and co-workers used egg shell membrane as separator in supercapacitor (Yu et al., 2012). Although it seems to be a new breakthrough, the reported voltage window was quite minimal, (1 V) even, when they used AC electrode which is known to have a high surface area. This shows the separator, (eggshell membrane) pore sizes might not be so promising in transporting the electrolyte ions through the electrodes and to the current collector.

We conclude this review with a recent report in the graphene-supercapacitors enhancement, Tamilarasan & Ramaprabhu (2013) report the fabrication of all solid supercapacitors based on graphene with the IL polyacrylonitrile (PAN/[BMIM][TFSI]) electrolyte. (The low range of working temperature reported by the authors was a point of concern).

2.6.2. Our Approach to Polymer Electrolytes Preparation Used in the Supercapacitor Fabrication

As mentioned earlier, in this research, solid polymer of two forms were used namely; the pure solid and hybrid polymer electrolytes for the supercapacitor fabrications. The polymer electrolytes were prepared from PVA and H_3PO_4 percentage rate (0 wt.%-70 wt.%) in a multiple of 10 until a desired conductivity is reached and achieved. Normally the sample takes four to six weeks (under room temperature) for it to dry and become a solid film. This work has been successfully presented elsewhere (Hashim et al., 2012; Sa'adu et al. 2014a; Sa'adu et al., 2014b; Hashim et al., 2014).

2.7 Reviews on Supercapacitor Fabrication

Number of several researchers have been working tirelessly on coming-out with a better material (both electrodes and electrolytes) for a good performance supercapacitor. Starting with the electrode for example, AC has been widely used due to its less expensiveness and possession of high surface area.

Let's begin this review with the work of Tassin et al., (1997) on his work on the Effects of three-dimensional current collectors on supercapacitors' characteristics where they checked the beneficial effect of using metallic foams as electrode collectors with three different methods of electrode preparation as well as two electrode compositions. They found in all three cases, the capacitors were made of two identical carbon electrodes with a porous PP sheet as separator in between (CELGARD 55 11). The authors also used the electrolyte solution of TEAMS (tetraethylammonium methane sulfonate) in acetonitrile. An AC (NORIT SX ULTRA) of high surface area was also used in each of the cases, mixed with carbon fibers or graphite and a binder (methyl cellulose). Their electrode preparation was done by filtration, spraying and pasting, thus; by filtration, electrodes were prepared (1 dm^2) on expanded nickel grids or nickel foams (NITECH) with different numbers of pores per inch (ppi 125 and 45). The mass of active material was 1.5 g dm^{-2}. Twenty-five millilitres of a solution having the following components were prepared; 4002:1.5 g of Carbon fibers RVC, 1.5 g of Norit SX Ultra, 20 ml of methyl cellulose (30 g l^{-1}), and 20 ml of ethanol. For spraying method, the nickel-foil and nickel form (NITECH) with an average pore diameter of 0.30 mm (foam ppi 125 - international ppi appellation) were used as the electrode current collectors. A homogeneous suspension was then prepared with AC, graphite, methyl cellulose and ethanol they then sprayed this mixture was then on the collector and allow to dry at 80 °C overnight and pressed under 2.5 tones dm^{-2}. And lastly by posting, pasted electrode was prepared on nickel foam collectors (NITECH, ppi 125). The viscosity of the mixture prepared for spraying was adapted to the pasting process due to the limited quantity of ethanol. Electrodes were then dried at 80°C overnight and pressed under a 30 tones dm^{-2} pressure. During testing, however, no any genuine method of either CV of CD is used to ascertain the capacitance of the capacitor.

Gu et al., (2000) in their composite-type of electrode in which its film was sized to 2 $cm^2 \times 2\ cm^2$, and 25 µm in thickness was prepared by mixing AC of specific surface area of 1200 $m^2\ g^{-1}$ with Lonza carbon (KS-6). The AC/KS-6 was mixed with Kynar 2801/*N*-methyl-2-pyrrolidone (NMP) solution. They then prepared the composite electrode films were prepared by coating this slurry on an aluminum foil current films with 5 wt.% KS-6. After solvent evaporation, the electrode films were vacuum dried at 110°C for six hourss. Their P(VDF-HFP) (Eif Atochem, kynal 2801) was dried under vacuum at 60 °C for 20 hours before using $LiClO_4$, they set it to dry under vacuum at 110 °C for 20 hours. Propylene carbonate (PC) and ethylene carbonate (EC) were all purchased and with LiClO4, was dissolved in PC–EC solution and allow to dry by storing it over molecular sieves. Therefore, their overall mole ratio of PC–EC–$LiClO_4$ was $PC_{10}EC_{10}LiClO_4$, and 25 wt.% P(VDF-HFP). The liquid electrolyte solution was homogeneously mixed by stirring. While for the polymer electrolyte film, it was prepared by heating at 115 °C for 15 min. The thickness of the electrolyte film was 100 µm.

Electrochemical measurements performed by them was promising one; good working voltage and efficiency up to only 1000 cycles. Though, no energy and power density results are mentioned.

In the Asymmetric area of supercapacitor fabrication, Wu et al., (2006) fabricated their electrochemical supercapacitor with following description; with a prepared graphite disc electrode of sizes 6 mm in diameter, the nickel foils of dimension 10 mm × 10 mm × 1 mm were degreased in a chemical detergent solution, rinsed in distilled water, and then electrochemically cleaned. $Ni(OH)_2$ thin films were electrochemically precipitated at room temperature onto the above two substrates, from a bath containing 1.5 Mol L^{-1} $Ni(NO_3)_2$ and 0.1 Mol L^{-1} $NaNO_3$ in a solvent of 50 %

(v/v) ethanol at a cathodic current density of 5.0 mA cm^{-2} respectively. They then run the deposition process for specified time in order to achieve different thickness of films. They also washed the deposited $Ni(OH)_2$ films in distilled water and delicately heated them in the air at some certain temperatures for two hours to obtain no films. After all this, they then allow the samples to cool automatically to room temperature. For an encapsulated graphite electrode, the epoxy coating was removed from the electrode before being heated in air, and after heating, the graphite electrode was re-insulated with epoxy coating but the electro-active NiO film. However, even when they claim to achieve the capacitance of 195 Fg^{-1}, the number of cycleablity the cell can withstand remained un-mentioned and consequently therefore the cell stability will be questionable.

Conducting polymers are also used for electrode materials due to their CD kinetics and low cost and fast doping and un-doping (Bhat & Kumar 2007). A composite electrode method using carbon and conducting polymer for the fabricating supercapacitor has been presented by Muthulakshmi et al., (2006) where they utilized an "Aldrich-rated" and it's in a form of "paste" by the help of *N*-methyl pyrrolidine along with a binder, PVDF, in the ratio of 70:30 using a pestle and mortar. The paste was then applied with a brush to a pre-weighed stainless steel current collector and allowed the mixture to dry at normal temperature.

For the incorporation of the conducting polymer, 98 % of payroll were distilled before it was put to use. An Indian branded 99 % Himedia of β-Naphthalene sulphonic acid (β-NSA) was used in as received condition as a dopant cum electrolyte. They then grow polypyrrole (PPy) at room temperature in a single compartment cell by galvanostatic polymerization using an electrochemical analyzer (BAS Electrochemical Analyzer 100 B). The working electrode was AC coated stainless steel (1 cm^2) and a

Pt plate (5 cm^2) was used as the counter electrode. All potentials were referred to a saturated calomel electrode (SCE). They also make use of a normal aqueous electrolyte solution of 0.5 M Payroll and 0.5 M β-NSA. PPy was electrochemically deposited onto the carbon material with a constant current density of 0.36 mA cm^{-2} for 300 s. At their final stage of the sample preparation, they conducted the electrochemical half-cell measurements a three-electrode cell equipped with a reference electrode (SCE), Pt as counter electrode while carbon/PPy composite electrode as the working electrode.

Furthermore, the cell assembly was in such a way that, an electrolyte-impregnated separator was sandwiched between two symmetrical AC/PPy composite electrodes (p/p). They also pre-wetted electrodes with an electrolyte before use. The capacitance was promising, but the cell performance in CV seems only fair enough, as it was degraded after running few tens of circles only.

Wei et al., (2009) had in the Asymmetric type of capacitor determined the cycleability mechanism of Manganese oxide electrode. Using 0.3 M $MnSO_4$ solutions, with and without 0.2 M ethylenediaminetetraacetic acid (EDTA) disodium, by anodic electro-deposition, Nanocrystalline MnO_2 coatings were deposited. They the adjusted electrolyte pH value to 7.0, deposition current density to 100 mA cm^{-2}, and electrolyte temperature to 70 °C. Moreover, at the electro-deposition, they introduced agitation with a magnetically driven Teflon® coated stirring bar at a speed of 300 rpm. The mass of the MnO_2 nanocrystals on the Pt electrodes was controlled to be 0.20–0.25 mg cm^{-2} of the electrode surface area. They then rinsed the working electrodes after electro-deposition, with deionized (DI) water, dried at 100 °C for 60 min in the air and then stored in a vacuum desiccator before they put them to test and analysis electrochemically.

Having done all those, they then characterized cells using Gamry instrument modeled PC4/750 potentiostat/galvanostat under CV and electrochemical impedance spectroscopy (EIS) modes with an electrolyte inside (0.5 M Na_2SO_4). Their CV recorded to be only within the range of −0.1 and 0.8 V at 100 mVs^{-1}. Apart from that, the energy and power density were also unknown.

We have noticed another important work by Xu and coworkers (Xu et al., 2009; Xu et al., 2010) in two of their separate but identical works on the preparation of high-capacitance carbon electrode using poly(vinylidene chloride) (PVDC). The elaborate lab work was that; the porous carbons were simply prepared by PVDC carbonization at high temperature without activation or any other additional processes. The PVDC-derived carbon is microporous with Brunauer–Emmett–Teller (BET) surface area about 1200 m^2 g^{-1}couple with high-volumetric capacitance in aqueous EDLCs. Under the protection of nitrogen and kept there for one hour to accomplish pyrolysis, They heated the homogeneous PVDC to the carbonization temperature (400–900 °C) at 10 °C min^{-1} after which, it was left for cooling to room temperature, then the PVDC-derived porous carbons were obtained finally obtained afterwards. As for the assembly of the cell, a pellet of electrode from a mixture of 87 wt.% of PVDC-derived carbon, 10 wt% of acetylene black and 3 wt% of (polytetrafluoroethylene) PTFE binder. And the button-type capacitor was assembled with two carbon electrodes separated by a PP membrane using 6 mil L^{-1} KOH aqueous solutions as electrolyte. Although the capacitance of the capacitor achieved was quite amazing, but the energy and power densities were not that encouraging.

In trying to enhance the energy properties of supercapacitor, Rakhi & Alshreef (2011) come up with a composite-type of supercapacitor consisting of Graphene nanosheets (GNs), SnO_2 nanoparticles and MWCNTs. They had first functionalized the

MWCNTs by refluxing in conc. Nitric acid (5 N) at 60 °C for 4 h to make them more dispersible in DI water. And in the electrode preparation, they spread 10 mg of functionalized MWCNTs 40 ml of DI water by ultrasonication with subsequent addition of 1 ml of HCl (38 %) and 1 g of hydrous $SnCl_2$. Then the resulting mixture was sonicated for 5 min and then stirred for 60 min at room temperature. Using distilled water they then filtrated and washed completely the precipitate and before it was put to dry in air at 90 °C for six hours. Both energy and power densities achieved were impressive indeed (224 Fg^{-1} and 17.6 $kWkg^{-1}$), however there was no clear conductivity study on the electrolyte used.

Kossyrev (2012), single handedly explore the novel of CB as an electrode in supercapacitors in two different approaches of fabrications. In the first approach, the electrodes were produced by the traditional coating procedure of casting of CB ink containing 2 wt.% of solids on top of a 25 µm thick conductive vinyl current collector of Intelicoat Tech. Brand. While, the solids in ink constituted of binder - 10 wt.% of PTFE - and 90 wt.% of SC3 CB of Cabot Corp. Brand, all of which were ultrasonically dispersed in isopropyl alcohol solvent. For coatings, we used a Mayer rod, which produced a 25 µm thick wet coating and around 1 µm thick electrodes after drying at 60 °C overnight. After which a prototype supercapacitor assemble in the HS test cell (Hohsen Corp.) was sandwiched after cellulose separator of 30 µm in thickness is fused between the two CB electrodes. Furthermore, a 25 % KOH, was used as electrolyte.

In their second fabrication approach, Kossyrev (2012), highlighted that, thin CB electrodes were produced directly on separator membranes by inkjet printing from the Fujifilm Dimatix printer. They then posited on one or both sides of the CB electrodes of around 1 µm in thickness. Their separator was either cellulose one from TF4030, Nippon Kodoshi Corp. Brand was of 30 µm thick or PP from Celgard 2500 brand which was about 25 μm thick. In the case of cellulose separator, they printed the electrodes on one side of the separator and then folded the membrane so that the electrodes face each other. Prior to folding, they implored the use of expanded graphite which was manually rubbed the top of carbon block electrodes so as to serve as current collector. As such, they found out that, the graphite flakes were good-entrapped within fibrous cellulose separator. Herein, again, they use 25 % KOH as their electrolyte which was spread on the cellulose separator. Well, in the case of PP separator, they spread supercapacitor electrodes on opposite sides of one membrane and they used no current collector in this case, so that the CB electrodes directly contacted the HS test cell positive and negative terminals. And they used the electrolyte made of 1.8 M of triethylmethylammonium tetrafluoroborate in acetonitrile ($TEMABF_4$/AN) from a spread on PP separators. However, in all the aforementioned cases, the researcher could not clearly indicate his achievement in terms power or energy density, neither did he disclose the cycleability of the two cells or range of working voltage.

Paul et al., (2012) in their work titled "Factors affecting the performance of supercapacitors assembled with PPy/MWCNT composite electrodes" proposed composition of PPy/MWCNT as symmetric supercapacitor using three different synthesis before the fabrication process. In the first case which was a synthesis of PPy/MWCNT composites in water (PPy/MWCNT-W), 100 mg of MWCNTs was first well stirred in 50 ml of an aqueous solution containing anhydrous ferric chloride (1.94 g $FeCl_3$). And they drop-wisely added 500 μL of the pyrrole monomer into this solution before they allow polymerization to continue for four hourss. The precipitated composite was filtered by suction, washed thoroughly with water, and then dried in a vacuum oven at 60 °C. They also calculated MWCNT content in the composite was from the weight of the added MWCNTs and the total weight of the PPy/MWCNT composite obtained after completion of the reaction. As for the second synthesis, i.e. Synthesis of PPy/MWCNT composite in DCM (PPy/MWCNT-D) 4 ml of aqueous $FeCl_3$ (18 mmol) was added to 40 ml of DCM, and the resulting solution was stirred well, then, 100 mg of MWCNTs was added into the aforementioned solution and agitated for one hour, they also drop-wisely added 500 μL of pyrrole and the reaction was continued for another four hours and other processes like before. In their last synthesis; Synthesis of PPy/MWCNT composite in *n*-hexane–AOT (PPy/MWCNT-H), they dissolved 4.5 g of AOT initially in 40 ml of hexane after which stirring continued with the addition of 4 ml of an aqueous $FeCl_3$ solution (10.5 mile). Moreso a 100 mg of MWCNTs was added into this solution and well agitated. Then, they added 500 μL of pyrrole monomer was added drop wise and the polymerization reaction was allowed to continue for four hours also. The resultant material was suction filtered, washed well with methanol, and finally dried in a vacuum oven at 60 °C.

In the fabrication process, they fabricated supercapacitor cells using the PPy-based composites containing 20 wt.% MWCNTs synthesized in the different solvents. They also added the Super-P as a conducting additive and PTFE and polyvinylpyrrolidone (PVP) were used as binder materials. All they had composite: Super-P:binder ratio was maintained at 75:15:10 but kept the ratio of the PTFE:PVP binder material was kept constant at 7:3 when used together to prepare the slurry. In addition, they prepared the slurry without the addition of PVP (10% PTFE binder only) and ultrasonicated. All of the ingredients for 16 hours and films (~60 μm) were cast onto a titanium current collector foil. The films were dried at 80 °C in a vacuum oven overnight and then, 1 cm^2 area of the electrode material was cut from the foil. They symmetric cells were fabricated in 1.0 M aqueous electrolyte solutions of KOH, H_2SO_4, Na_2SO_4, and potassium chloride (KCl) using a paper separator (thickness: 40 μm, Nippon Kodoshi Co. Ltd.) in between the two electrodes. After the whole processes the characterization was made by first cyclic voltammograms and the cycleabilty was stacked after 1000 cycles only with a negligible working voltage of 0.6 V only. This might not be un-connected to the type of electrolytes used as for aqueous solution the voltage window can go as far as 1.99 V.

Tourist, et al., 2012 used what they called "two identical ideally polarizable microporous titanium carbide-derived carbon electrodes" with a room temperature ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) for the fabrication of their EDLC cell. In their work, Tonurist and co-workers employed the used of commercial PVDF, of 530000 g Mol^{-1} in molecular weight, 99.8 % of N,N-dimethylformamide (DMF) and 99.8 % of N,N-dimethylacetamide (DMA,) and acetone without even further purification. They then dissolved various amounts of PVDF DMA (TUX5) or in DMF-acetone mixture in the ratio of 8:2, w: w for the TUX7, TUX8 and TUX10-TUX12. Furthermore, they used an electrospinning method to prepare the PVDF membranes at different conditions. They also added that in order to come-up up with self-made separately, they investigated the material's structure, which was by the use of scanning electron microscopy (SEM). And to compare the electrochemical performance of the electrospun membranes, they were studied the already established commercially available separator TF4425 at the same electrochemical conditions as the PVDF separators. The authors also used by the chlorination method to synthesize titanium carbide-derived carbon (TiC–CDC). The electrode paste was prepared from TiC–CDC and PTFE binder (2.4 % dispersion in H_2O). The paste was roll-pressed to form a flexible layer of the active electrode material with a thickness of 105 ± 5 μm. After drying under vacuum, the electrode material was covered from one side by a pure Al layer (~ 3 μm) by magnetron sputtering method. Although the capacitance achieved in this experiment was high (about 170 Fg^{-1}), the cycleability of all the prepared samples was just fair, and CD also remained unknown.

He at al., (2013) worked on efficient preparation of biomass-based mesoporous carbons for the fabrication of the supercapacitor. From self-prepared peanut shell, that was turned to a CB, the researchers came up with the electrode using the following steps. They molded the electrodes of 89 wt.% mesoporous carbons (MCs), CB (5 wt.%) with a BET surface area of 550 $m^2\ g^{-1}$, and PTFE (6 wt.%) at 15.0 MPa for 10 s, which they dried at 383 K for one hour under vacuum. Thereafter, they assembled the button-type capacitor from two carbon electrodes and a separator. The two different separators and electrolytes were; for the 6 M KOH electrolyte, the separator used was PP membrane, while for the 1 M Et_4NBF_4/PC electrolyte, the separator was TF4050. Although the researchers achieved a fascinating current density (20 A g^{-1}) in one of the results, the number of cycles that the instrument can attain is not known or disclosed, which raised some questions about the cycleability of the whole system.

Another work worthy of mentioning in this review is the work done by Mateyshina et al., (2013) where they synthesized from some organic precursors, some nanoporous carbon materials and later converted it to electrode materials for supercapacitors. In their work, in the presence of alkali, three samples, namely Kem-1, Kem-3, and Kem-4 of nanoporous carbon materials were prepared by carbonization of organic precursors at 700 °C. They then used precursors made up of individual organic compounds, these include; the mixture of 1, 2, 3-benzotriazole and urea, hydroquinone, and PVA. After washing off the alkali excess and dried at the temperature of 105 – 110 °C until reaching a constant weight, the prepared product yielded of nanoporous carbon material (Kem-1) was 17.3 % mass. Kem-1 was obtained by repeated carbonization in a muffle at the temperature of 900 °C for 27 min to prepare sample

Kem-2. Kem-3 was obtained from Kem-1 by carbonization at the temperature of 900 °C in a flow reactor during 5 min in the inert atmosphere. Similarly, from other precursors, the samples Kem-4 and Kem-5 were obtained by the researchers. For the fabrication study, the researchers used a symmetric two-electrode cell, while an aqueous solution of sulfuric acid (1 M H_2SO_4) and 6 M KOH were also used as the electrolytes. They then prepared the electrodes by mixing the carbon powder with CB with the weight ratio of 80:20, and the mixture was molded onto the surface of a graphite rod. Again, they deposited 10–30 mg of NCMs on the electrode with the area of 1 cm^2. And lastly, they pressed the two identical electrodes through a separator they coded as film PORP-A1 that was soaked with 1 M solution of H_2SO_4 (or 6 M solution of KOH). The capacitance of the capacitor in all the cells was promising indeed, but the voltage through which it operates was small couple with the fact that, the liquid electrolytes used will adversely affect the life cycle of the fabricated supercapacitor.

Lei et al., (2013) reported an outstanding work of the porous carbon contact for the fabrication of the supercapacitor. In their report, they prepared the composite carbon electrode from a blend of AC of Sigma–Aldrich brand and of specific surface area of 1000 m^2g^{-1}, acetylene, CB from Alfa Aesar Company and PVDF. They then mixed all the chemicals at a weight ratio of AC: CB: PVDF = 90:5:5 in l-methyl-2-pyrrolidinone (NMP) to form a slurry, they then coated the slurry was onto an aluminum foil, and dried in an oven at 150 °C for two hours. Their EDLC cells were fabricated using a symmetrical electrode configuration and they placed a soaked-piece of filter paper of electrolyte and placed it between the carbon electrodes to act as a separator. Their electrode working area was fixed to 2 cm^2 in all the devices. The device assembly was sealed in a plastic bag with vacuum and their electrolyte was 1 M $TEABF_4$ (Sigma–Aldrich, purity 99 %) in the PC (Sigma–Aldrich, anhydrous, purity 99.7 %). How this work did not give any account of what was achieved as regards to the energy or power densities, cycleability of the cells as it only concentrated on the internal resistance that have been identified as a result of the cell assembly.

2.8 Literature Review Related to CNTs

CNTs - which were discovered by Iijima and coworkers in 1991 for MWCNTs and in 1993 for single-walled CNTs (SWCNTs) at NEC Laboratories, Japan (Nakashima, 2005; Tunckol et al., 2012)- are carbonaceous materials, with novel hollow-tube structure, excellent electrical conductivity of about 3000-4000 Sm^{-1} (Kuilla et al., 2010), optical activity, chemical reactivity, mechanical strength and high surface areas (Xiao & Zhou, 2003; Akbar & Taimoor, 2009; Tunckol et al., 2012). They can be seen as the nearly one-dimensional form of fullerenes (large, close-cage, carbon clusters and which have some properties peculiar to them alone and not found in other compound before their invention). These unique properties that carbon nanotube has, offer them great potential for the high-power applications of supercapacitors (Trigueiro et al., 2009), even though their specific capacitance is relatively low. The other areas of applications may include; molecular electronics, chemical sensors, scanning probes (Dong et al., 2007), special capillaries and electrochemical actuators (Balasubramanian et al., 2004). Hence, the use of CNTs to boost the performance of carbon-based supercapacitors should be a good choice (Yi et al., 2011; Inagaki et al., 2014c).

CNTs have some defect and structures that exist in different shapes of fullerenes ranging from cone-types, spheres, tubes to a more complicated and strange one. But some of the important and best structures are;

(a). SWNTs: this can be considered as long wrapped a graphene sheet having a length of about 1–10 μm and diameter of roughly 1–2 nm (Nakashima, 2005; Tunckol et al., 2012), therefore their length to diameter ratio is about 1000 (so can be considered as nearly one-dimensional structures). SWNTs also consist of two separate regions with different physical and chemical properties. The first one is the sidewall and the second is the end cap of the tube. The structure of the end of the cap is similar to or derived from smaller fullerenes, such as C_{60}. The cylinder is one other structure which SWNTs are composed of. This can be generated when we wrapped a graphene of a certain size in a certain direction (Daenen et al., 2003; Dai, 2002).

(b). MWNTs: are collections of concentric SWNTs with different diameters. They are having a length of about 1–10 μm and diameter of roughly 2–50 nm (Nakashima, 2005; Tunckol et al., 2012), therefore their length to diameter ratio also is about 1000 (so can be considered as nearly one-dimensional structures). Both the length and properties of MWNTs are different from that of SWNTs (Daenen et al., 2003). Figure 2.8 describes the structure of SWNTs and how MWNTs are formed.

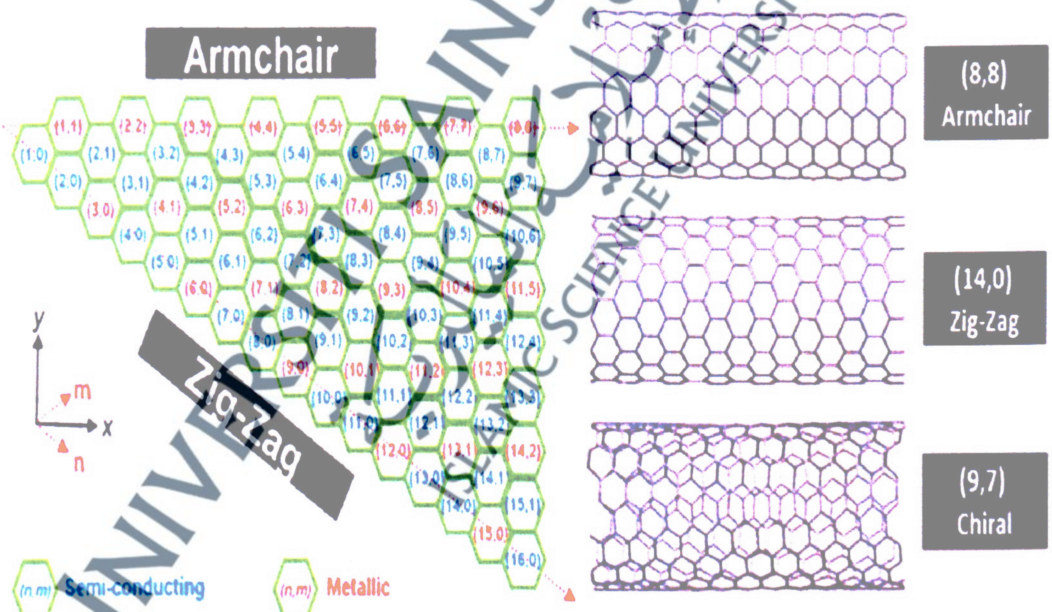

Figure 2.8 (a) The left hand side is the chiral plane where all possible structures of SWNT can be formed from the chiral vector lying in the range given by the Figure. Where n and m are integer and $m \leq n$ or $\theta < 30^{\circ}$. The right hand side is charities in SWNTs: this can be observed from the open end of the tube: armchair structure, zigzag structure and the chiral structure (Daenen et al., 2003).

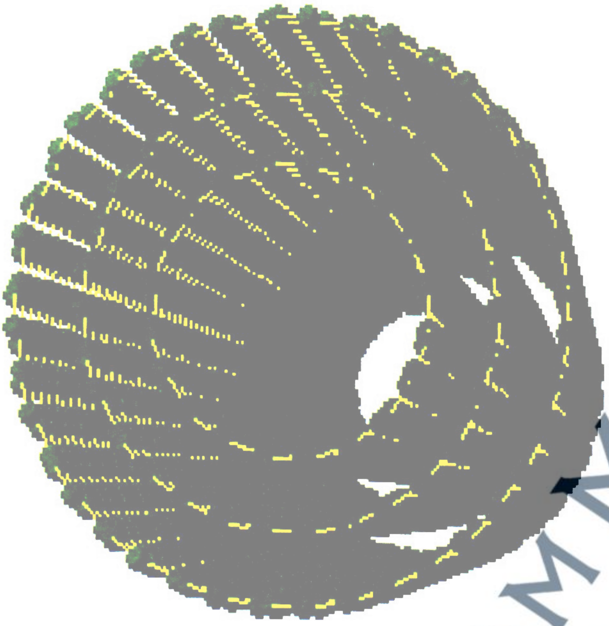

Figure 2.8 (b) Collections of concentric SWNTs with different diameters.

There are so many inspirations nowadays about the use of CNTs as an active material in supercapacitor fabrication (Wu et al., 2012).

Recently, much interest has been focused on nanocarbon materials as electrodes for EDLCs because of their accessibility, ease of processing, and relatively high specific surface area (Hsieh et al., 2012).

Starting with the review on the fabrication of supercapacitor using carbon nanotube, is the work done by Portet et al., (2005). In their work, they presented the performances of 4 cm^2 supercapacitors cells assembled with 200 μm thick active material films which consist of AC and CNTs mixture in organic electrolyte. The 4 cm^2 electrodes were made by laminating active material onto treated aluminum current collector foil (which also have conducting paint in its treatment) of the thickness 200 μm. Carboxymethylcellulose (CMC, from Prolabo) and PTFE (obtained from Dupont de Nemours) were used as binders while the active layer composition is x wt.% AC, y, wt.% CNT, 3% CMC and 2% PTFE, with $x + y = 95$. Before they finalize the composition to be used, they studied different active material varying from 0 to 50% of the CNTs content in the active material. The electrode thickness was kept constant at 200 µm. After that, they then assembled the supercapacitor cells with 4 cm^2 electrodes between two PTFE plates in a glove box where water and oxygen are controlled (less than 1 ppm). Their two electrodes were then separated by a 50 µm thick porous polymeric film separator. Stainless steel clamps were used in order to maintain the stack under pressure. The organic electrolyte (1.5 M NEttBF4 in acetonitrile), with water content lower than 10 ppm were also employed. Although the researchers achieved a modest capacitance (90 Fg^{-1}), the voltage window was not known and the maximum current achieved was just 0.002 mA cm^{-2}.

Xu et al., (2006) assembled EDLCs using CNTs as the electrodes and a novel binary room temperature molten salt (RTMS) composed of lithium bis(trifluoromethane sulfone)imide ($LiN(SO_2CF_3)_2$, LiTFSI) and acetamide as the electrolyte. In their simple but interesting work, the electrode was made from a mixture of 87 wt.% CNT, 10 wt.% acetylene black and 3 wt.% PTFE binder pressed into a pellets of diameter 11 mm. After that, the electrodes were allowed to dry in the vacuum for 12 hours at 120 °C. Furthermore, they assembled the button-type capacitor with two CNT electrodes separated by PP membrane, then they soaked all in the as-prepared molten salt electrolyte, in an Ar-filled glove box of MBraun LabMaster 130 brand. Although the working voltage of the capacitance was good (2 V), the capacitance obtained was quite low (22 – 30 Fg^{-1}).

Zhang et al., (2007) contributed in this aspect as well, in their title work "Electrochemical properties of ultra-long aligned, carbon nanotube array (ACNTA) electrode in organic electrolyte (Et4NPF6/propylene carbonate electrolyte)" where they tried to justify that the fabricated EDLC works good in the organic electrolyte than in aqueous electrolyte with the argument that, the specific capacitance of the ACNTA electrode in an organic electrolyte is 24.5 Fg^{-1}, was larger than that obtained in an aqueous electrolyte. There CNT was developed by themselves and the EDLC was fabricated using a 500μm of ACNTA, with the 6mm × 4mm apparent area, which was removed from the silica substrate with a razor blade. A layer of graphite milk branded from DAG-2, Qingdao Xiyou Fine Graphite Chemicals Industry Co. Ltd., and of 50 μm in thickness was then cast on to a 4.0 cm × 0.8 cm nickel foil and then the ACNTA were pasted immediately on the nickel foil to prepare an electrode. After pasting, the film was dried in an oven at 120 ºC for an hour. In order to prove their work right and also to provide a material for comparative studies, they fabricated another EDLC from an AC branded by ground apricot stone. The AC powder was mixed and kneaded with 3 wt.% PTFE and 5 wt.% acetylene black and then pasted on a nickel foil current-collector with the assistance of graphite milk. However the comparison yielded negative results as the AC electrode tends to achieve more capacitance than that of their prepared ACNTA and the capacitance as earlier mentioned was very small (24.5 Fg^{-1}).

In 2008, Ma and co-workers produced a three-sandwiched type of a cell from Birnessite-type manganese dioxide (MnO_2) that was coated with CNTs by employing a spontaneous direct redox reaction between the CNTs and permanganate ions (MnO_4^-). The three-electrode electrochemical cell was were measured in such a way that two lithium foils were used as the counter and reference electrodes, respectively. The working electrode consisted of a mixture of the MnO_2/CNT nanocomposite, a conducting agent and a binder, while either of CNT of 28 wt.% or acetylene black was used as the conducting agent, and 5 wt.% PVDF dissolved in *N*-methylpyrrolidone was also selected as the binder. They then coated the slurry of the mixture on titanium foils, which was followed by drying at 100 ^{0}C for 12 hours and each working electrode with a 1 cm ×1 cm area contained 1mg of the dried slurry. The electrolyte was 1M $LiClO_4$ in PC. The authors claimed to achieve a capacitance of 250 Fg^{-1}, however, the number of cycles recorded and seems suitable for the cell was only 10. Another setback of the work is the exorbitant cost of the manganese dioxide, which may not favor the market value of the cell.

Just as in Ma et al. (2008) case, Yan et al. (2009) also used the same composite compositions of CNTs and MnO_2 on one hand and CB on the other hand. In the fabrication process, the working electrodes composites consisted of CB and PTFE were mixed in a mass ratio of 75:20:5 and dispersed in ethanol. They then coated the resulting mixture onto the nickel foam substrate (1 cm × 1 cm) with a spatula, which was followed by drying at the 100 ^{0}C for 12 hours in a vacuum oven. All electrochemical measurements were done in a three electrode setup: A Ni foam coated with CNT/MnO_2 composites as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The result was promising (even better than that of Ma et al., (2008), because of the effectiveness that MnO_2 has in terms of capacitance but its costly nature is what discourages its usage.

A composition of CNTs grown on a polyacrylonitrile (PAN) based AC electrodes were presented by Huang et al., (2009). The PAN-based AC fiber used thickness of 0.4–0.6mm, BET surface area of 1200 m^2g^{-1}, and pore volume of 0.59 $cm^3g^{-1}$was in the form of woven cloth, having. The authors used nickel as the catalyst for the growth of CNTs on the carbon cloth. They then deposited the catalyst on carbon cloth sized 6 cm × 6 cm using sputtering deposition (performed for 5 min at a working pressure of 5×10^{-2} Torr, an argon flow rate of 15 cm^3min^{-1}, a radio-frequency power of 50 W, and an electrode distance of 5 cm), in which the nickel target was made up by 99.99 % in purity. After the catalyst seeding, CNTs were grown on the cloth using a thermal chemical vapor deposition (CVD) method. Prior to that, they treated the catalyst on the cloth with 1 atom of H_2 at the 400 °C for one hour. The growth of CNTs was performed at 800 ^{0}C for one hour under atmospheric pressure, using methane as the carbon source and hydrogen as the balance gas at a CH_4/H_2 ratio of 3/17. As for the supercapacitor assembly and characterization, the two electrode cells, which consisted of 1 cm^2 carbon cloth, 2M H_2SO_4 as electrolyte at the ambient temperature and stainless-steel foil as the current collector were used to examine the electrochemical performance of the carbon fiber specimens. The cells were constructed using a usual process of sandwiching a pair of the electrodes with cellulose fiber filter paper as separator. The result was, however fair enough in an aqueous solution with 1 V working voltage and capacitance of 117 Fg^{-1}, although the cycleability was not clearly stated.

Ko & Kwang (2009) presented composites of MnO_2 and AC nanotube as their electrode in the supercapacitor fabrication. The active materials included Multi-walled CNTs which was prepared using chemical vapor deposition with an aspect ratio (L/D) of 5 μm/20 nm = 250 and other chemicals. They then used a high purity Ti foil as current collector, after which it was cleaned for two minutes by using a chemical etching solution of the ratio; H_2O:HNO_3:HF = 92:6:2, v/v/v. After the etching, they then rinsed and sonicated the electrode in water for at least 10 minutes, and finally dried to obtain a strong adhesion of the active material to the Ti foil. As for the activation of the carbon nanotube the researchers mixed the CNT with KOH at a weight ratio of KOH/CNT = 5. The mixture was heated under the nitrogen gas (N_2) flow at a heating rate of 5 °C min^{-1} until 800 °C, maintained for one hour at that temperature, and cooled down at a slow rate under N_2 gas flow. After cooling, the sample was washed with an abundant amount of water and dried in vacuum at 80 °C. As for other active materials used, the researcher's selected 40 wt.% of the CNT anticipating of achieving higher capacitance of the capacitor. Having done that, they prepared composite of MnO_2/(A-CNT or CNT) by dispersing them separately in $KMnO_4$ solution by sonicating for one hour and stirring for 15 min so as to ensure good dispersion state of the CNT. Manganese acetate solution was added drop by drop for one hour to the CNT-dispersed solution being stirred, and the stirring was continued overnight. The precipitate was filtered, washed with an excess amount of water, and finally dried under vacuum at 70 °C for 12 hours. While the fabrication of the aforementioned composite electrode was made in such a way that the powdered 90 wt% of the MnO2/(A-CNT or CNT) was first ball-milled for 12 hours at 100 rpm, mixed with the binder solution of the 10 wt% of P(VDF-HFP), which was dissolved in *N*-methyl-2-pyrrolidone solvent, and finally, ball-milled again for another 48 hours at 400 rpm to ensure a well-dispersed state. After that, they then spread and cast it on the pre-cleaned Ti foil and finally air-dried overnight and then dried under vacuum at 70 °C for 24 hours and roll-pressed to enhance the contact and adhesion to the collector foil. However after careful analysis of the promising result achieved in Ko and Kim work, we observed that high capacitance were recorded (184 - 250 Fg^{-1}), but as mentioned in our previous arguments regarding the use of manganese oxide as precursor, it's very clear here also that exorbitant nature of the aforementioned metal oxide may not be welcome by many researchers as one of the aims and objective of introducing any new discovery that could be marketed out is to be achieved (affordable) and efficient.

Still on the composite electrode, Yan et al., (2009) considered using RuO_2/carbon nanotube as their choice of electrode for supercapacitor fabrication. In their work, they claim to develop a simple and efficient way to decorate MWCNTs with RuO_2 nanoparticles for use of electrochemical supercapacitor. In their procedure they synthesized RuO_2 nanoparticles and later attached it to MWCNTs in the mixture with a

$RuCl_3$ solution by microwave-assisted irradiation. The mixed solution of nanocomposites was then dripped onto the polished surface of home-made carbon paste electrode (CPE) and dried under room temperature. Their result indicated a very low achievable current (0.0008 A), although the calculated capacitance was quite promising.

Liu et al., 2009 also reported the promising performance of supercapacitor using Nickel hydroxide powder electrode with different carbon conductor and nickel hydroxide/MWCNT composite electrode. The $Ni(OH)_2$ was loaded onto the purified MWCNT consisting of; an Aldrich brand of $Ni(NO_3)_2{\cdot}6H_2O$ (0.05 M, 0.02 M), urea (DC Chemical Co., Korea) (0.3 M) and 1 g purified MWCNT were dissolved in 200 ml of de-ionized water. The solution was heated to 353 K and kept for two hourss with a stirring (400 rpm speed). When the solution reached room temperature, they then filtered the solution with precipitate and washed with distilled water to neutral pH. Then the solid was dried in oven at 393 K for 12 hours. The 85 wt% $Ni(OH)_2$/MWCNT composite was mixed with 10 wt.% of Superp, 5 wt% of binders (2.5 wt% CMC and 2.5 wt% SBR) and 3 times on the total electrode weight water together. They further stirred the mixture was at room temperature until to form slurry with proper viscosity. The electrode was fabricated by coating the slurry on 2 cm × 2 cm of pressed Ni foam (110 PPI, Jin Cheng Bo Co., China) as a current collector. The prepared electrode was dried in vacuum at 333 K for 10 hours and pressed again. Their average thickness of the sample electrodes was about 280 μm (with current collector inclusive). They achieved a modest capacitance (118 – 221 Fg^{-1}), however the cyleability was not worthy of mentioning.

Liu et al., (2010) also reported what they called "A simple, two-step method for constructing flexible sheets of supercapacitors fabrication". Their construction was based on painting a sheet of flexible plastic electrolyte with a composite material made of a conducting polymer and CNTs. The total capacitance of the supercapacitor consisted of pseudocapacitance produced by the polymer and electrical double-layer capacitance produced by CNTs. In detail; the two step construction of the capacitor sheet was made in such a way that, the powdered and Sigma–Aldrich-branded (PVA) was mixed with water in a ratio of 1:9 by weight. They then mixed the PVA wih 85 % of H_3PO_4, with a ratio of 1:1 by volume. Later they come up with the films (of about 0.3 mm) of PVA first casting the final mixture on a glass surface and then peeling the cast off from the surface after the water had evaporated. They again dispersed the purchased 0.1 ml of polyaniline (PANI) in xylene and then mixed 0.003 g of SWCNTs (Carbon Solutions) in N-dimethylformamide. Using a paint brush, the researchers transferred the PANI–CNT aqueous mixture on both sides of a PVA film to form and define the shape of a capacitor, then transferred into an oven at 40 °C for water to be evaporated. The two-dimensional size of the capacitor was about 5 mm × 5 mm. Electrical contacts were made by either using metallic clips or copper sheets. As for the measurements, they used a commercial potentiostat to carry out the CV of PANI and galvanostatic charging–discharging measurements of capacitor sheets. They also used conventional three-electrode cells with a commercial Ag/AgCl (3 M KCl) electrode as the reference electrode and a platinum wire as the counter electrode as their electrochemical cell assembly. But the voltammetry measurements were made with electrodes immersed in 0.5 M H_2SO_4 aqueous electrolyte. However, the capacitance recorded was just 16 Fg^{-1} and the cycles of the capacitance quickly diminished (8 Fg^{-1}) as it reaches only 600 cycles.

Li et al., (2010a) produced a large number of CNTs (of 50 nm in diameter and characteristic length of more than 10 μm) mixture in activated mesocarbon microbeads (AMCMBs) which was activated by potassium hydroxide in a stainless steel container at a temperature of 900 °C. Using buried-protection method with petroleum coke powders the product was fully protected during activation, they added. The electrolyte used was 6 M KOH aqueous solution.

In detail experimentation, they mixed the MCMB with KOH of 5:1, w/w in DI water to obtain a homogeneous slurry, and then they placed the slurry in a stainless steel container (with a movable cap) before heating at 2 °C min^{-1} up to 900 °C and held for two hours in a muffle furnace, in which the sample was protected buried in petroleum coke powders (with particle size of ~100 μ). After cooling down, they washed the produced AMCMB with 10 wt% HNO_3 so as to remove the metallic impurities and DI water and then dried in a vacuum. In the activation of the carbon, it was conducted in a horizontal cylindrical furnace under the protection of inert gas flow (N_2, Ar or He), in which the AC produce could be protected against air oxidation at high temperature. However, both the high cost of inert gases and the complexity of activation equipment are unfavorable for the practical production. Inert gases, petroleum coke was used acting as an air-insulating surrounding in the preparation of AMCMB. In order to study the electrochemical performances, the researchers prepared the as-prepared AMCMBs/CNTs compound into electrodes and assembled into supercapacitor cells by firstly, mixing the active substance with acetylene black and PTFE in the percentage ratio of 90:5:5, w/w/w in ethanol to form a sticky slurry, then the slurry was rolled into a film of 80 μm in thickness before they cut it into disk electrodes with a diameter of 10 mm. Thereafter, the cell assembly of the aforementioned fastener-type symmetric supercapacitor with a pair of disk electrodes divided by a piece of microporous separator. Finally, they used a Battery Tester to evaluate the capacitance of their supercapacitor miniature using CV and electrochemical CD. Although the resulting capacitance was impressive, the achievable current (0.0004 A) is not encouraging.

In 2010, Zhou and co-workers (Zhou et al., 2010) prepared a supercapacitor electrode from a composite form of Polyaniline/multi-walled carbon nanotube. The composites were synthesized by chemical oxidation polymerization of aniline monomers in the presence of MWCNTs treated with concentrated hydrochloric acid under ultrasonic irradiation. The thickness polyaniline layers were controlled effectively due to the varying the ratio of aniline monomers and CNTs. They then filtered the resulting composites and washed with DI water, then dried under vacuum at 80 °C for 24 hours.

The fabrications of the electrodes for supercapacitors were done by pressing the resulting composites into the nickel mash current collector under 5 MPa at 60 °C. They also recorded cyclic voltammograms on a CHI 1000A electrochemical working station, a CH Instrument, Inc. brand in 0.1 M H_2SO_4 aqueous solution by using a Pt wire as the counter electrode and Ag/AgCl as the reference electrode, while the Electrochemical impedance spectroscopy measurements for the resulting composite electrode were performed in a solution of 0.5 M H_2SO_4 under an open circuit potential of 0.5 V in an AC frequency range of 10^{2} - 10^{5} Hz. Though the capacitance recorded was quite magical (560 Fg^{-1}), there is lost in the cycles with more than 29 % of the capacitance diminishing after just 700 cycles.

Hsieh et al., 2012 have come up with a composite–type of supercapacitor where they investigated a composition of $RuO_2 \cdot nH_2O$/MWCNT/Ti electrodes for supercapacitors fabrication. Therein, they grow vertically aligned MWCNTs directly on a Ti current collector by chemical vapor deposition (CVD). They also claimed that the presence of hydrous ruthenium oxide in the mixture had resulted in the increase of surface area and electrical conductivity. However, from the characterization made, (both CV and CD) we observed that the highest achieving current had been 0.004 A/cm.

This is because of the composition used. It has been mention earlier that RuO_2 could though be a good material in supercapacitor, but the cost implication is higher compare to other materials.

Still on composite-typed supercapacitor, is the recent work of Chen et al., (2013) prepared an AC with coated CNT buckypaper, with the CNT buckypaper was firstly immersed into the PAN/$Zn(Ac)_2$–DMF precursor solution with different concentrations. The mass ratio of $Zn(Ac)_2$ to PAN was kept at 5:2, while the concentration of the solution was controlled by changing the total mass of PAN and $Zn(Ac)_2$. Pristine PAN/$Zn(Ac)_2$–DMF solution was also cast on a glass substrate to prepare pristine AC as a comparison. They further carbonized (850 °C for 100 min in argon pre-oxidation by air at 300 °C for 120 min) the all of the buckypapers immersed by. The nanotubes in the buckypaper were uniformly coated with a layer of AC, forming a core-shell structure. The Bucky paper-AC coated were obtained after, they added $Zn(Ac)_2$ was here as a pore-creator and activating reagent, which can be decomposed into zinc oxide by the process of carbonization. The carbonized samples were then immersed in 1 M HNO_3 for 48 hours to remove zinc oxide in the AC layer, and then they were washed by DI water for several times to remove the remnant HNO_3. After being dried, freestanding buckypapers coated by AC were obtained. (Energy and power densities were not known).

Jiang and co-workers (Jiang et al., 2013) made a fascinating work on nanocomposite firm used as a simple and portable supercapacitor device which they referred to as double-layer and triple-layer electrodes. The fabrication included an active layer made of a nano-composite of PVA and MWCNTs which were both synthesized by a multi-step methodology which first involved the preparation of an aqueous solution of PVA. The solution was prepared by dissolving the PVA powder in

DI water in 1:10 ratio by weight at 80 °C with magnetic stirring. There PVA of molecular weight 10,000–13,000 was obtained from Sigma Aldrich and was used for the purpose. They then mixed simultaneously the MWCNTs with acetone. Their resulting mixture was then sonicated in an ultrasonic bath for an hour to disperse the MWCNTs further and then heated at 60 °C till the acetone evaporated to yield a powder of dispersed MWCNTs. The powdered, dispersed MWCNTs were mixed with the PVA aqueous solution in the ratio 1:10 by weight at 60 °C with stirring which then resulted in the formation of a homogenous blend. The PVA/MWCNT solution was sonicated for 60 min, followed by de-aeration to remove any air bubbles introduced by the aforementioned step processes. They then came up with a nanocomposite of PVA/MWCNT that they used in the electrode fabrication.

Moreover, in the triple-layer configuration, the researchers made use of the three active layers, namely; silver nano-particle ink, PVA/MWCNT nano-composite, and a layer of solely MWCNTs. They then used either of the stainless steel or aluminum base substrate and coated it on one side using silver nano-particle ink - the silver nano-ink was solution cast on the substrate and cured at room temperature to yield a solid layer – and they coated over the solid silver nano-particle ink layer, the PVA/MWCNT nano-composite by a method they called "solution casting method" and allowed to cure overnight at room temperature to yield solid layers. Furthermore, they formed a "an only" MWCNTs layer at the preceding step, over the PVA/MWCNT layer by dispersing a sonicated mixture (in acetone for one hour in ultrasonic bath) and then the mixture was dispensed over the electrode substrate using a pipette and allowed to dry for five hours to evaporate the acetone. So, all in all, the configured three cells;

(i) The silver nano-particle ink and PVA/MWCNT nano-composite layers, made by the processes discussed previously;

(ii) The silver nano-particle ink and MWCNT only; and

(iii) The PVA/MWCNT nano-composite layer and MWCNT only. However, the capacitance achieved was smaller just as the authors also reported only 250 cycles as the achievable cycleability of the prototyped-supercapacitor.

Aravida et al. (2013c) had in one of their promising work of the year 2013, made a contribution in the ZnO/carbon nanotube composite in the supercapacitor domain. The authors come up with what they called "a facility, green and highly efficient method for the decoration of CNTs with ZnO" which was developed the fabrication of binder-free composite electrode for supercapacitor applications. Their nanocomposite was prepared by using reactive magnetron sputtering in Ar/O_2 environment. This was to take care of usual-uniform coating with tunable thickness, which most of the times affect the performance of the electrochemical performance of the nano composite electrodes. As for the electrode, it was prepared by sand witching two electrodes symmetrically, and were then separated by a thin PP separator in 0.1 M TBAPC/DMF (tetra butyl ammonium perchlorate in dimethylforamide) electrolyte. After that, they studied the electrochemical properties of the supercapacitor electrodes were obtained using CV, galvanostatic charge–discharge measurements, and electrochemical impedance spectroscopy (EIS) and few other need measurements. The optimum current density achieved for the CV of one of the cell was quite good (0.002 and 0.003 Acm^{-2}) and could be worthy of emulation.

Recently the use of Carbon nano Onion (CNO) - another family of the fullerense in the supercapacitors fabrications started attracting the attention of researchers with Gao et al., (2013) presenting the miniature of the supercapacitor from a chemically activated CNO. In their work, electrodes were fabricated by electrophoretic deposition (EPD) into Ni foams with 95 % porosity, 500 gm^{-1} surface area density, according to the supplier (MarkeTech International). CNOs were dispersed in ethanol containing 0.03–0.05 wt.% of $Al(NO)_3$ for stabilizing the CNOs. They then applied a DC voltage of 80 Vcm^{-1} was then between a Ni foam and a gold electrode to deposit the CNOs. After the EPD process, CNO electrodes were dried at 80 °C in a furnace for two hours. Using three electrode configuration, electrochemical measurements, including CV and galvanostatic charge/discharge (GCD), were carried out in a 2 Mol/l KNO_3 electrolyte on a CHI 760D (Shanghai Chenhua, China) electrochemical workstation. They also set the assembled 1 × 1.5 cm^2 CNO/Ni foam electrodes, a platinum gauze electrode, and an Ag/AgCl electrode used as the work, counter, and reference electrodes, respectively. However, after the measurement characterization, the capacitance achieved was only fair enough (about 100 Fg^{-1}) and the voltage window was quite low (less than 0.4 V) in all the cells.

Markoulidis et al. (2014) investigated the performance of supercapacitor cells if a small amount of MWCNTs is added to AC electrodes. The electrode structure investigated comprised AC, four different types of MWCNTs and two polymer binders, PVDF or PVA. In the sample preparation, they dispersed the MWCNTs in 1-methyl-2-pyrrolidinone (NMP) (or in water for the PVA binder) and sonicate it for half hour and then they vigorously mixed it for one hour at 15,000 RPM using a Wiggenhauser Homogenizer. After that, they added the MWCNT solution into either of the AC/PVDF binder-NMP solution or the AC/PVA binder-water solution. The slurry from which the above ingredients were mixed was then coated onto aluminum foil using a Film Applicator. The coating was dried in an oven at 120 °C for four hours; they however varied the spacing of the applicator to 30, 60 and 120 μm in order to obtain different coating thicknesses. Furthermore, the employed two different types of binders namely: PVDF soluble in organic solvents and PVA, a water soluble binder. Therefore, all porous electrode coatings contained AC, 0.15 or 1 wt.% MWCNTs, and 5 wt.% binder. For the fabrication of the cells, they prepared them using either of the 1 M of TEABF4/PC electrolyte or 1.5 M $TEABF_4$/AN electrolyte, and a separator from a Lens tissue. After the cell fabrication and sealing, they tested them as just sealed under a weight of 2.26 kg or in other cases they was immersed cell in the electrolyte contained in the "bag", with a feed-tube to replenish the electrolyte supply if the need arise, and they clamped it between two Perspex plates. Although they have outstanding results of the power and energy densities, and also the capacitance in all the cells, the authors did not give an account of the cycle life that cells might be able to attain.

2.9 Chapter Conclusion

The just concluded chapter reviewed the literatures on the polymer, CNT and different fabrication approaches towards attaining a promising supercapacitor device. Most importantly, the chapter discussed the classifications of supercapacitors; symmetric and asymmetric and approaches towards their making were highlighted. The next chapter will focus on the experimental procedures taken to produce both the electrode and electrolytes used for the fabrication of supercapacitor cells.