

Stable ternary nanocomposites of Multi walled Carbon nanotube/ Polyaniline/ Hydroquinone: electrodes for Supercapacitors

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Abstract

Multi-walled carbon nanotubes (MWCNTs) are widely used as supercapacitor electrode material. However, the specific capacitance of MWCNTs cannot achieve optimum value to facilitate required demand. Conducting polymers have been introduced to achieve optimum energy density and power density of supercapacitor electrode material. Conductive polymers are promising pseudo capacitive materials as they feature both good conductivity and high capacitance. Formation of composite using conductive polymers and carbon nanotubes is a proven technique in enhancing the material electroactivity. However, the cycling life and rate capability of PANI electrodes are unsatisfactory due to their large volume changes and slow redox reactions during charge-discharge processes.

This work describes the effect of HQ adding on MWCNT/PANI composite prepared by insitu polymerization technique in order to increase the cyclic stability of MWCNT/PANI.

PANI-HQ/MWCNT film offers intrinsic porous channels and promotes the transportation of charges and ions. Consequently, the PANI-HQ/MWCNT film electrode exhibits specific capacitance of 120 Fg^{-1} at a current density of 0.5 A/g whereas PANI/MWCNT film exhibits 130 F/g . Although PANI-HQ/MWCNT film electrode exhibits less specific capacity than PANI/MWCNT they presents a good cycling stability with 94% of capacitance retention after 1000 cycles, much higher than that of PANI/MWCNT film (74%) electrodes.

The excellent rate performance and cycling stability make it one of promising candidates for electrochemical energy storage.

Key words: Hydroquinone, Polyaniline, multi-walled carbon nanotube, cyclic stability

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List of abbreviations

- A = Surface area [cm^2]
A⁻ = Counter anions
AC = Activated carbon
APS = Ammonium Persulfate
CA = Carbon aerogels
CNTs = Carbon nanotubes
C = Capacitance (F)
C⁺ = Counter cations
C/dC = Charge /Discharge
CE = Counter Electrode (CE)
CV = Cyclic Voltammetry
D = Electrodes distance [nm]
DI = Deionised
dV/dt = scan rate [mV/s]
EIS = Electrochemical Impedance Spectrometry
EC = Electrochemical capacitors
ECPs = Electroactive Conductive polymers
EDLC = Electrochemical Double Layer Capacitors
EES = Electrochemical energy storage
ESR = Equivalent series resistance
F = Farad
SEM = Scanning ElectronMicroscopy
FTIR = Fourier Transform Infrared Spectroscopy
H₂ClO₄ = Perchloric acid
HQ = Hydroquinone
I = Current [A]
PANI = Polyaniline
Q = Charges [C]
RE = Reference Electrodes

V = Applied potential [Volts]

WE = Working electrode

t_c = Charge time [s]

t_d = Discharge time [s]

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1. Introduction

Concerns over the dramatic climate change, the availability of fossil fuels and energy security concerns, are driving efforts towards renewable and sustainable energy production. Although the use of these energy resources has grown significantly in recent years [1–3], further adoption of renewable energy will require the development of improved energy storage technologies to regulate and distribute power generated by intermittent sources such as solar and wind, the most abundant and readily available resources [4–6].

Given the intermittent nature of solar and wind energy, efficient energy storage systems are critically needed to make the best of the electricity generated from these sources since they can promote the reliability and effective use of the entire power system (generation, transmission and distribution) by storing energy when in excess while releasing it when in high demand. Among various energy storage systems, the most dominant is electrochemical energy storage (EES) system, including batteries, electrochemical capacitors (ECs) and fuel cells [7, 8]. These 3 device systems share the “electrochemical similarities” and customary options that the energy-producing processes occur at the section boundary at the electrode/electrolyte interface. To meet the increasingly higher requirements of future systems, from portable consumer electronics, hybrid and electric vehicles, to large-scale industrial power systems, the performance of EES devices has to be considerably improved by developing new materials and higher understanding of the basic chemistry processes at the interface.

The key parameters to evaluate the performance of EES systems and their potential for practical applications include energy density (Whk/g or Wh/L, energy stored per unit weight/volume), power density (Wk/g or W/L), specific capacitance (F/g), specific capacity (mAh/g), cycle life and calendar life, as well as cost and environmental safety [9-11].

To clearly compare the power and energy capabilities, **Figure 1.1** shows the Ragone plot of specific power versus specific energy for the most important EES systems. Fuel cells and batteries are often considered to be high-energy systems, while ECs (also known as super capacitors or ultra capacitors) and conventional electrostatic capacitors are considered to be high-power systems.

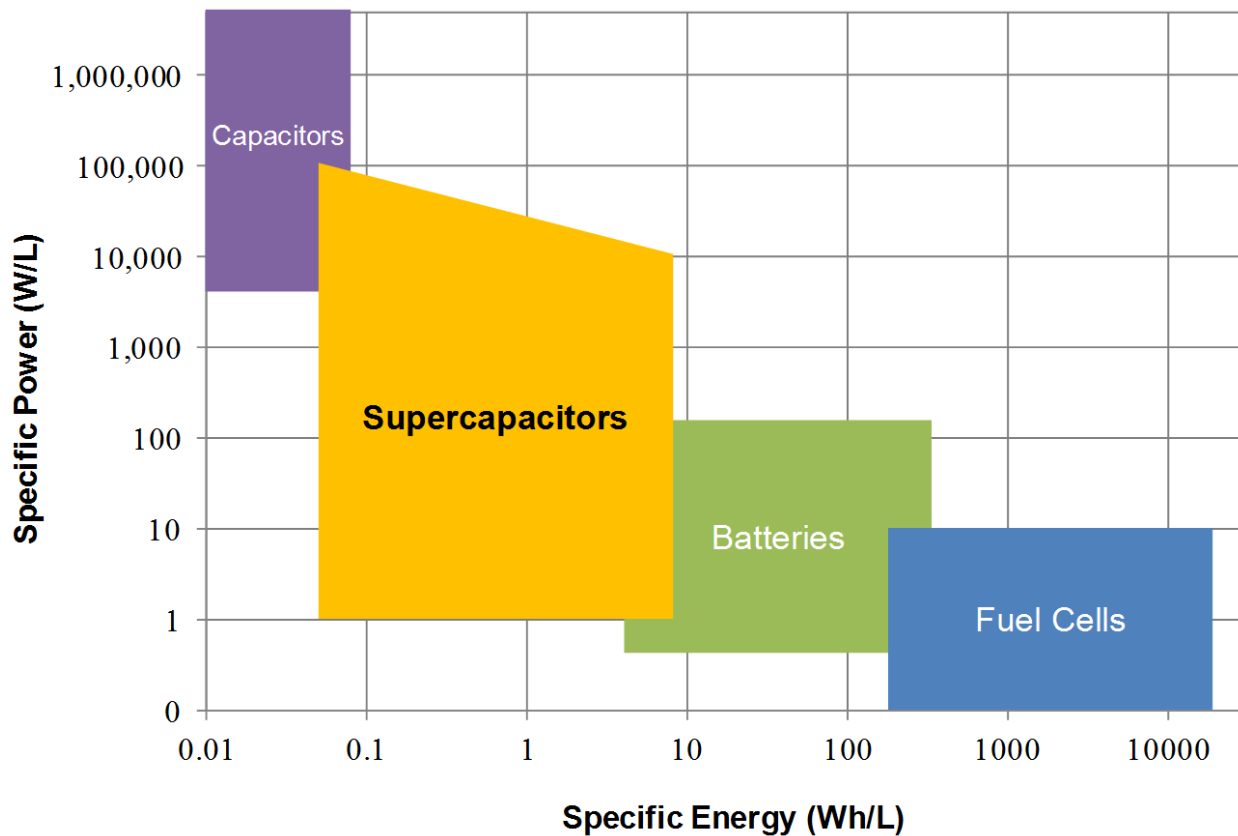


Figure 1. 1 Shows the Ragone plot of specific power versus specific energy for the most important EES systems [17].

Among these various energy storage systems, batteries and ECs are two key technological systems that have found a broad range of applications. The basic differences between batteries and ECs are their different charge storage mechanisms and their materials/structures.

Typically batteries are designed to provide high energy density by storing charge in bulk electrodes (bulk storage) through faradaic reactions, and they have been the technology of choice for many applications with nearly all transportable electronics relying on energy stored chemically in them. However, due to physical changes in materials/structures between the charged state and the discharges state, current battery technologies have performance limitations such as short cycle life and calendar life and slow charge/discharge rates (limited power capability).

In contrast, ECs are designed to take advantage of near-surface charge storage mechanisms (based on electrochemical double-layer capacitance or redox pseudocapacitance) to achieve much greater power density (1-2 orders of magnitude more than that of batteries) at some

expense of their energy density. Though limited in specific energy ($\sim 5\text{-}10 \text{ Whkg}^{-1}$ for ECs versus $\sim 100\text{-}250 \text{ Whkg}^{-1}$ for Li-ion batteries), ECs can provide the ability to store and release the energy within time frame of a few seconds, compared to tens of minutes or more needed to charge/discharge for batteries. Moreover, ECs exhibit superior cycle life that is typically measured in hundreds of thousands to millions of cycles, 2-3 orders of magnitude better than that of batteries [13, 17]. Last but not the least, ECs also offer high reliability and better safety versus batteries, leading to a much lower maintenance cost [13, 17].

Table 1. 1 Comparison of important characteristics between state of the art supercapacitors and electrochemical batteries [13, 17]

Characteristic	Supercapacitor	Electrochemical batteries (Lithium ion batteries)
Charge time (s)	~ 1 second	3-5 minutes
Discharge time(s)	~ 1 second	3-5 minutes
RC time constant	0.07-0.5s	$> 1000\text{s}$
Service life	> 1 Million	$< 5000\text{s}$
Energy density (Wh/kg)	5	70-100
Specific power (Kw/kg)	5-10	0.5-1
Cycle efficiency	$> 95\%$ to $< 75\%$	$> 90\%$ to $< 50\%$

While batteries are widely used in energy storage today, they are inherently limited in their power density: they store energy through chemical changes and reorganization of their bulk structure, a process which presents severe kinetic limitations [11–12]. These charge storage processes also limit the lifetime of batteries, making them unsuitable for applications requiring many charge/discharge cycles.

Capacitors are fundamental electrical circuit elements that store electrical energy within the order of microfarads and assist in filtering. Capacitors have two main applications; one amongst that could be a function to charge or discharge electricity. This function is applied to smoothing circuits of power provides, backup circuits of microcomputers, and timer circuits that make use of the periods to charge or discharge electricity. The other could be a function to dam the flow of DC. This function is applied to filters that extract or eliminate specific frequencies.

Electrolytic capacitors are next generation capacitors which are commercialized in full scale. ECs are similar to batteries in the deployment of renewable energies as primary energy sources is highly dependent on the development of efficient energy storage devices with both high energy density and high power density, thus electrochemical technologies are one of the most promising to achieve this goal [14].

ECs are similar to batteries in cell construction, the anode and cathode materials remain the same. Most common electrode materials are aluminum, tantalum and ceramic capacitors where they use solid/liquid electrolytes with a separator between two symmetrical electrodes [14, 17].

The third generation evolution is the electric double layer capacitor, where the electrical charge stored at a metal/electrolyte interface is exploited to construct a storage device. The interface can store electrical charge in the order of $\sim 10^6$ F [15]. The main element in the electrode construction is activated carbon. Though this idea was initialized and industrialized some 40 years ago, there was a stagnancy in research until recent times; the need for this revival of interest arises due to the increasing demands for electrical energy storage in some current applications like digital electronic devices, implantable medical devices and stop/start operation in vehicle traction which need very short high power pulses that could be fulfilled by electric double layer capacitors (EDLCs) [16]. They are complementary to batteries as they deliver high power density and low energy density. They also have longer cycle life than batteries and possess higher energy density as compared to conventional capacitors. This has led to new concepts of the so-called hybrid charge storage devices in which electrochemical capacitor is interfaced with a fuel cell or a battery. These capacitors using carbon as the main electrode material for both anode and cathode with organic and aqueous electrolytes are commercialized and employed in day to-day applications. Fig.1.2 presents the three sorts of capacitors depicting the essential variation in their design and construction [17].

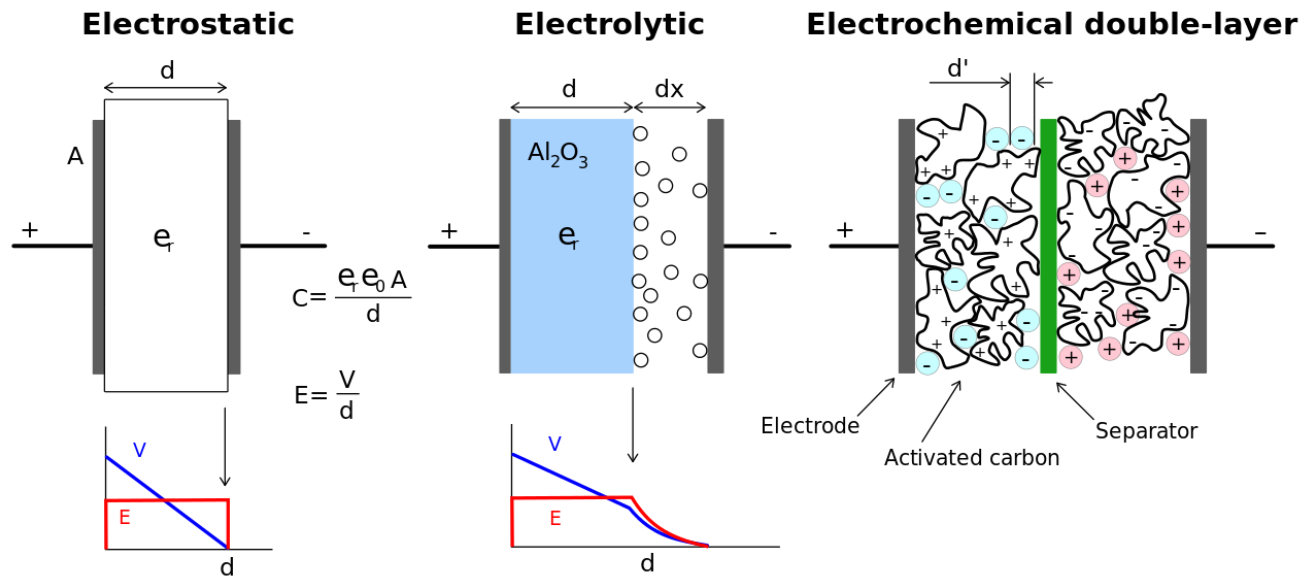


Figure 1. 2 The three sorts of capacitors depicting the essential variation in their design and construction [17].

However EDLCs suffer from low energy density. To rectify these issues, recently researchers try to incorporate transition metal oxides beside with carbon in the electrode materials. When the electrode materials contain transition metal oxides, the electrosorption or redox processes enhance the value of specific capacitance ca. 10 -100 times counting on the nature of oxides. In such scenario, the EDLC is called as supercapacitor by becoming pseudocapacitor. This is the fourth generation capacitor. Performance of a pseudocapacitor combines at the same time two kinds of energy storage, i.e. non-faradic charge as in EDLC capacitors and faradaic charge similar to processes proceeding in batteries [19].

Supercapacitors as clean energy-storage devices have attracted great attention owing to their high power density, long cycling life, and high charge-discharge rate. Electrode materials are the key components, which determine the whole performance of full devices [20–22].

When being used as an electrode material for supercapacitors, multi walled carbon nanotube (MWCNT) is stable but the capacitance is relatively low (around $100\text{--}270 \text{ F g}^{-1}$) because it mainly stores energy through the electric double-layer capacitor mechanism [23–25]. Pseudo capacitances materials are alternative electrode materials based on a Faradic mechanism and have much higher specific capacitance but poor stability [26–28]. To combine the virtues of the two types of materials, composites of CNT and nano-structured pseudo capacitance materials were prepared and studied [29–31].

Polyaniline (PANI), as one of the typical conducting polymers, has been extensively studied for pseudo capacitors mainly due to its high specific pseudo capacitance, ease of synthesis, good environmental stability, and low cost [32]. However, the cycling life and rate capability of PANI electrodes are unsatisfactory due to their large volume changes and slow redox reactions during charge-discharge processes [33]. Furthermore, the low conductivity of PANI also weakens its performance in supercapacitors [34]. To solve these problems, PANI was frequently blended with carbon nanomaterials to improve its conductivity, mechanical and electrochemical stabilities, and the kinetics of redox reactions [35].

Recently, researches on developing CNT based PANI composite films have been attracted a great deal of interest owing to their enhanced performance [36-37]. However, the cycling stability of most PANI/MWCNT composite films usually unsatisfactory. Herein, a special PANI-HQ/MWCNT film reported.

Hydroquinone (HQ) is very attractive as redox molecule due to the unique two electron redox behavior and stable reversibility [38-39], which is added in PANI/MWCNT composite material in order to achieve higher cycling stability.

PANI-HQ/MWCNT film offers intrinsic porous channels and promotes the transportation of charges and ions. Consequently, The PANI-HQ/MWCNT film electrode exhibits 120 F/g at a current density of 0.5 A/g. Furthermore, the PANI-HQ/MWCNT film electrode presents a good cycling stability with 97% of capacitance retention after 1000 cycles, much higher than those of PANI/MWCNT film (74%) electrodes.

The excellent rate performance and cycling stability make it one of promising candidates for electrochemical energy storage.

1.2. Objective of the study

The improvement of the electrochemical performance of electrochemical capacitors and batteries is currently the objective of researchers worldwide. Carbon based material for electrode super capacitors have been explored by researchers tremendously. However, the performance of this type of material still has its gap in achieving excellent energy storage requirement. In order to fill the gap, researchers introduced conducting polymer to produce carbon-conducting polymer material in order to enhance the performance of the electrochemical super capacitor. Conducting polymer are pseudo capacitive material which means the bulk of the material undergo as a fast redox reaction to provide capacitive response and they exhibit superior specific energy to the carbon based super capacitor.

Polyaniline (PANI) is one of the known conducting polymers used in Supercapacitor researches. PANI possesses several excellent properties such as light weight, good conductivity, mechanical flexibility and low cost. PANI is also easily to polymerize by oxidation polymerization at relatively low temperatures and can be doped from a conducting to an insulating state using simple protonic acids. Despite of all the advantages, this conducting polymer has been known to easily swell and contract substantially during charging and discharging, alternately. Consequently, its life-cycle is poor compared with carbon-based supercapacitors which generally only charge via adsorption and desorption of ions. For this thesis, the objective is to modify multi-walled carbon nanotubes (MWCNTs) with polyaniline (PANI) and Hydroquinone to form stable electrode for supercapacitors

In this thesis, the following properties were aimed to be achieved:

- Ideal capacitive behavior with fast charging/ discharging characteristic
- Improved cyclic stability

2. Background and literature review

2.1. Energy Storage Mechanisms and Materials for Electrochemical Capacitors

Distinct from conventional electrostatic capacitors which store charges in an electric field imposed across a thin layer of dielectric material, electrochemical capacitors store charges at the electrochemical interfaces between the high surface area, porous electrode material and the electrolyte. The effective capacitances of Electrochemical Capacitors are typically several orders of magnitude greater than those obtained by conventional capacitors as a result of much larger specific surface area (500-2000 m² g⁻¹ for ECs) and shorter distance between the electrode and electrolyte ions (in the order of nanometer, 10⁻⁹ m). The specific capacitance, C (F g⁻¹) of an EC can be described according to Eq. 1

$$C = \epsilon_r \epsilon_0 A / d \dots \dots \dots (1)$$

Where ϵ_r is the relative electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, d is the distance between electrolyte ions and the electrode (nanoscale charge separation distance) and A is the specific surface area of the electrodes.

Depending on the energy storage mechanisms, Electrochemical Capacitors can be classified into 2 general categories: Electrochemical double-layer capacitors (EDLCs) and pseudocapacitors (**Figure 2.1**).

EDLCs, which store charges electrostatically via reversible ion absorption at the electrode/electrolyte interface (Figure 2.1(a)), commonly use carbon-based active electrode materials with high surface area [6, 20]. In contrast, pseudocapacitors use fast and reversible redox reactions at the surface of electroactive materials for charge storage (Figure 2.1(b)). The large specific pseudocapacitance of faradaic electrodes (typically 300-1000 Fg⁻¹) exceeds that of carbon-based materials (typically 100-250 F g⁻¹) using double layer charge storage. Typical active pseudocapacitive materials include transition metal oxides such as RuO₂, Fe₃O₄, NiO, and MnO₂ [21, 22], and electronically conducting redox polymers such as polyanilines, polypyrroles, and polythiophenes

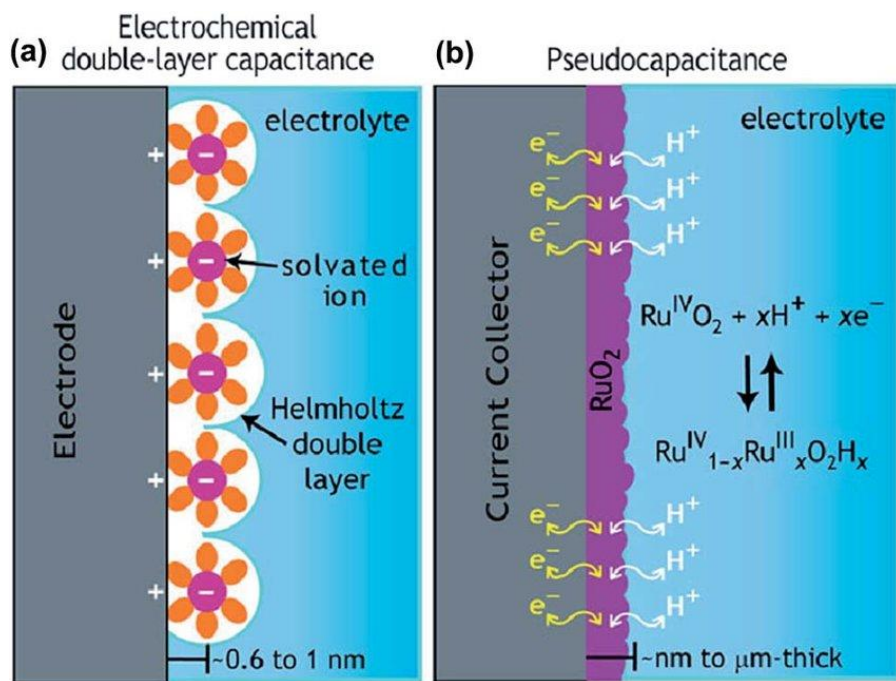


Figure 2. 1(a) Electrochemical double-layer capacitors (EDLCs) and (b) Pseudocapacitors [20].

A comparison between the properties of EDLC and pseudo capacitance is shown in Table 2. 1.

Table 2. 1 Comparison of EDLC and Pseudo capacitance [9, 25]

Electric double layer capacitance	Pseudo capacitance
Higher voltage operation	Lower voltage operational range. Limited by electrochemistry and decomposition of solvent
High power operation (90 ⁰ phase angle)	Phase angle function of frequency
Higher power capability	Kinetic limitation for high charge discharge rates, therefore limited the power capability
Non reversible	Highly reversible
Capacitance constant with voltage	Capacitance dependent on voltage
20-50μF/cm ²	Up to 2000 μF/cm ²

2.1.1 Electrochemical Double-Layer Capacitors

Currently the foremost common and commercially available ECs are EDLCs where electrical energy is stored by electrostatic accumulation of charges within the electric double-layer at all electrode/electrolyte interfaces (**Figure 2.1(a)**). Electrochemical Double Layer Capacitors (EDLC) is constructed by two electrodes being immersed in an electrolyte with a separator [36, 40]

EDLCs can give very high power and long cycle life due to their fast and near-surface electrochemical process. However, the energy stored in EDLCs is often limited by the finite electrical charge separation at the active electrode materials / electrolyte interface, and by the operating voltages that is primarily determined by the stable potential window of the electrolyte. This can be clearly seen from the following equation for the specific energy (E) of the EDLC [7-10],

$$E = 2CV \dots \dots \dots (2)$$

Where C is the cell-level specific capacitance and V is the operating voltage of the EDLC cell. Each component is crucial to the final performance of the EDLC. The specific capacitance depends strongly on the electrode material, and can be optimized by choosing high surface area, electronically conducting materials, such as carbon-based nanomaterials [10]. On the other hand, the electrolytes need be carefully chosen and evaluated to maximize the operating voltage. Non-aqueous electrolytes with good ionic conductivity are often used for high-energy and high-power EDLCs owing to their large operational voltage window (up to 3.5 to 4 V), as opposed to a more restricted potential window by aqueous-based electrolytes (generally <1.2 V). It should be noted that according to Eq. 2, a three-fold increase in voltage (V) results in nearly an order of magnitude increase in energy (E) stored at the same capacitance.

2.1.1.1 Electrode Materials for EDLC

Various forms of carbon nano materials have been investigated and used as active materials in EDLC electrodes since these carbon-based materials offer the advantageous features including high conductivity, electrochemical stability and open porosity. Besides activated carbons (ACs) which are the most widely used active materials for EDLC applications, many other forms of nano structured carbons, including aerogels [25], nanotubes [26, 27], carbide-derived carbons

(CDCs) [28], onion-like carbons (OLCs) [29], and graphene [11, 19, 30], are being explored as alternatives to activated carbon for improving energy density while maintaining high power density in the ultimate EDLCs.

Table 2. 2 properties and structure of different carbon materials used in EDLCs [36, 40]

Materials	Carbon nanotubes	Graphene	Activated Carbon	Carbon Aerogel
Dimension	1-D	2-D	3-D	3-D
Surface Area (SA) m ² /g	>2000 (market)	~2600	1000-3000 (market)	400-800
Conductivity (S/cm)	High 5000S/cm	High ~5000S/cm	low	Low (50-100 S/cm)
Specific capacitance (F/g)	~80-130 F/g	~100 F/g 25 μF/cm ³	50 μF/cm ³ 50-100 F/g	50-100 F/g
Cost	Moderate to High	Moderate	Low	Moderate

Considering many recent reviews that cover more extensively on carbon-based electrode materials for ECs [31-34], despite these advancements made on developing new electrode materials, the ultimate specific energies of EDLCs are still basically restricted by their reliance on double-layer capacitance as the primary energy storage mechanism. It is troublesome to further promote the performance of ECs based on pure carbon to fill the gap between batteries and ECs.

Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) have been discovered in 1991 [41]. After its discovery, many researchers have focused their investigations on the synthesis, structure, electrochemical properties, mechanical properties and the proper applications [42-46] of CNTs. In general, carbon can be found in three forms: diamond, graphite and fullerenes/nanotubes. Carbon nanotubes are tiny strong cylinders with a length reaching up to 1 mm and an average diameter of 0.3 to 2.6

nm. CNT exists in 2 types containing more than two concentric cylindrical shells of graphite sheets; single wall nanotubes (SWNT) which have a single graphite sheet and smaller structure; and multi-walled nanotubes (MWNT) that encompass several graphene cylinders [17-19].

The structure of CNT makes it distinctive and extraordinary material; particularly the helicity of the arrangement of the carbon atoms on the surface honeycomb lattice [18]. The diameter and folding angle in CNTs can modify it from a metal-like material to semiconducting material by increasing the width that will lead to decrease the band gap [20].

Both types of CNTs have been used in supercapacitor applications due to their unique properties. CNTs with conducting polymers are widely used in super capacitor applications.

2.1.2. Pseudocapacitors

In contrast to EDLCs, pseudocapacitance arises from fast and reversible electron exchange reactions at or near the electrode surface (**Figure 2.1(b)**). Given the nature of the Faradaic process (redox reactions) involved in energy storage, pseudocapacitors can increase specific capacitance and energy density but at some cost of power density and cycle life when compared to EDLCs.

2.1.2.1. Common Pseudocapacitive Materials

There are two general kinds of pseudocapacitive materials: transition metal oxides and electronically conducting polymers. The most commonly known pseudocapacitive metal oxides include ruthenium oxide (RuO_2) [36, 37], manganese oxide (MnO_x) [22], iron oxide (Fe_3O_4) [21], nickel oxide (NiO) [38], and others [23].

Typical electronically conducting polymers for redox pseudocapacitance are polyanilines, polythiophenes, polypyrroles, and other π -conjugated conducting polymers [23].

Transition metal oxides have been widely explored for supercapacitor applications due to their wide variety of oxidation states and their unique layered structure [9, 11]. The pseudocapacitance of metal oxides is due to a highly reversible surface chemical reactions or extremely fast and reversible intercalation of metal ions into the lattice (e.g. H^+ , Na^+ , K^+) [11, 30] One of the commonly investigated metal oxides is ruthenium oxide (RuO_2); the capacitance is achieved through the insertion and removal, or intercalation of protons into its amorphous structure [22, 33, 34]. Ruthenium oxide pseudocapacitors achieve high energy and power densities in its hydrous form [33, 34].

Fairly high specific capacitance, up to 700 F/g could be achieved [14]. However, its potential application in the industry is severely limited by its high cost [7, 44]. Another metal oxide being actively researched is manganese dioxide [11, 15, 16]. Manganese dioxide has two advantages over ruthenium oxide which makes this material a promising one in this field [16]. This material is low production cost and highly compatible with various environmentally friendly aqueous electrolytes.

Conductive polymers

Another common pseudo capacitive material is conductive polymers. Conducting polymers possess good intrinsic conductivity from semi-conducting to metallic range [30]. They exhibit fast charge/discharge kinetics owing to the fast doping and de-doping characteristic [7, 9]. Conductivity is achieved through the conjugated π bond system on the polymer backbone. Conductivity is ranged from a few S cm^{-1} to 500 S cm^{-1} in the doped state [30]. In order for the polymer to be conductive, a charge carrier counter ions (e.g. Cl^-) is required to cause delocalization of electrons and create conductivity. The process is known as doping. Conducting polymers can be either p-doped which the polymer chain become oxidized (positively charged) intercalated with counter anions (A^-), or n-doped with counter cations (C^+) when reduced (negatively charged) [18, 30, 31].

Conducting polymers are attractive as they have high charge density. Moreover, they are relatively cheap compared to metal oxides [7, 32, and 41]. From the literature, carbon based supercapacitor devices can achieve a specific power of $3\text{--}4 \text{ kWkg}^{-1}$ and a specific energy of $3\text{--}5 \text{ Whkg}^{-1}$ [31], while for conducting polymer based supercapacitor achieves a slightly lower power at 2 kWkg^{-1} but the specific energy is doubled (10 Whkg^{-1}) [32].

In terms of specific capacitance, ECP based materials can achieve up to 400 - 500 F/g in contrast to about 100F/g for double layer capacitor. However, the application of conductive polymer in supercapacitors is limited by their poor cycling stability. The ECP electrode would start to degrade within less than a thousand cycles due to the physical structure changes caused by the doping/de-doping of electrolyte ions [31-33]. This volume change or swelling eventually causes mechanical failure of the polymer backbone under prolonged charge/ discharge cycles. And therefore degrades the faradic transfer process [7, 8, 30, 42]. Although a higher specific energies can be achieved by increasing the doping level. However it leads to a consequence that the higher degree of counter ions insertion and de-insertion would worsen the volume change effect [8, 30].

Moreover another hindrance is the limited voltage window, it is reported that the voltage window for conductive polymer is within 1V [30], therefore application in a higher voltage range is restricted.

Table 2.3 summarizes the theoretical capacitance achieved by the ECPs polyaniline (PANI), Polypyrrole (Ppy) and Poly 3,4dioxiphiohene (PEDOT) [30].

Table 2. 3 Summary of the theoretical capacitance achieved by the ECPs polyaniline (PANI), Polypyrrole (Ppy) and Poly 3,4dioxiphiohene (PEDOT) [30, 39].

Conductive polymers	Mw (gmol ⁻¹)	Dopant level	Potential range (V)	Theoretical capacitance (F/g)	Conductivity (S/cm)
PANI	93	0.5	0.7	750	0.1-5
Ppy	67	0.33	0.8	620	10-50
PEDOT	142	0.33	1.2	210	300-500

Polyaniline

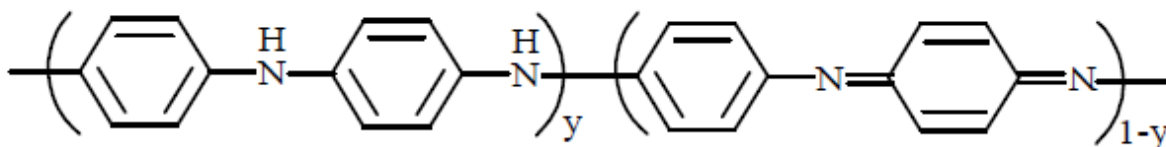
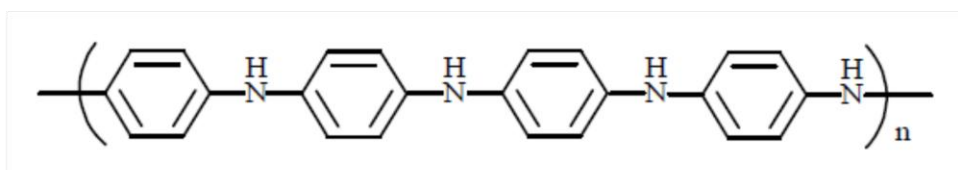


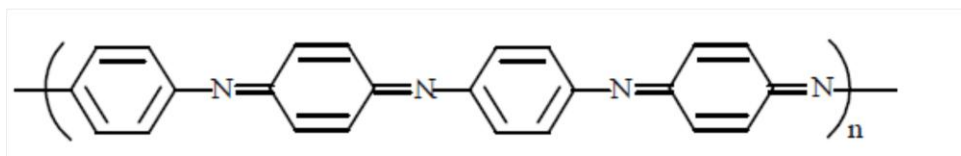
Figure 2. 2 General chemical formula of PANI [45]

One unique feature of PANI is that it exists in three different oxidation states. They are the Leucoemeraldine oxidation state (fully reduced), the Emeraldine oxidation state (half-oxidized), and the Pernigraniline oxidation state (fully oxidized) as shown in Figure 2.3 [39]. Moreover, these oxidation states are highly pH sensitive. Another interesting feature of PANI is that, besides doping induced by partial oxidation or partial reduction, oxidation states can be converted through proton exchange in contact with protonic acid [39, 52]. Non-conducting Emeraldine base (EB) form of PANI can be doped to a highly conductive Emeraldine salt (ES) without changing the total number of electrons associated with it [39,50]. Such doping process (Figure 2.4) is achieved by protonation of the –NH– group of EB by inorganic protonic acids and

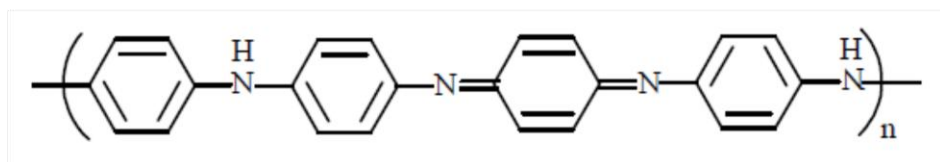
is known as ‘acid doping’ [15, 30, 45]. The acid doping process increases the conductivity of PANI by more than eight orders of magnitude [17, 38]. Positive charges accumulated on the polymer backbone during protonation of PANI are neutralized by the negatively charged counter ions of the dopant. The protonation is also accompanied by the drastic change in the electronic structure, crystallinity, solubility, etc. [58]. The degree of protonation and the resulting conductivity can be controlled by changing the pH of the dopant acid solution. Color changes from dark blue to emerald green can be observed upon the doped state is reached.



I. Leucoemeraldine base: the fully reduced form



II. Pernigraniline base: the fully oxidized



III. Emeraldine base: the half- oxidized

Figure 2. 3 Chemical structure of PANI at various oxidation states [39, 47]

It is composed of equal amounts of alternating reduced base and oxidized base unit

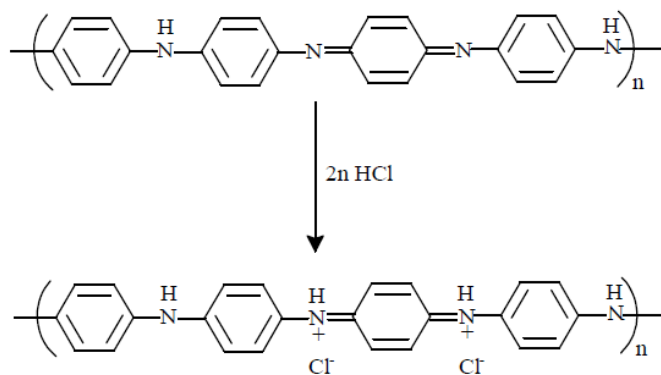


Figure 2. 4 Protonic acid doping of PANI Emeraldine base by HCl to conductive Emeraldine salt state with two polarons [39,47]

For polyaniline, similar to polypyrrole, APS and FeCl_3 can both be employed as oxidant. It is claimed that APS under acidic medium (1M HCl) in generally yield the highest conductivity. Other oxidants such as ceric ammonium sulfate, potassium dichromate, and hydrogen peroxide are also reported. The solvent for polyaniline polymerization is generally carried out in aqueous solvent.

Polyaniline exhibits many desirable properties in supercapacitor application; it has high electroactivity, a high doping level (0.5). High theoretical specific capacitance (up to 400–500 F g^{-1} in an acidic medium) can be achieved [31]. In addition, it has good environmental stability, controllable electrical conductivity (Ranged from 0.1 to 5Scm^{-1}) [48].

2.1.3. Hybrid Capacitors

In addition to EDLCs and pseudocapacitors, there is another special type of capacitor system, called ‘hybrid capacitors’, which usually combine one battery-type faradaic electrode (as energy source) with the other capacitive electrode (as power source) within the same Electrochemical Capacitor cell [10]. In such systems, the battery-like electrode provides high energy density while the EDLC electrode enables high power capability in the system. Although this type of ECs generally shows much enhanced capacitance and greatly improved energy density compared with EDLCs [43-45], there is still a significant drawback of these hybrid capacitor devices, namely, the limited cyclability of the faradaic electrodes (considering balanced capacities for positive and negative electrodes) [39].

The electrochemical performance of ECs can be achieved by introducing pseudocapacitance effects into hybrid composite electrode systems combining nanostructured carbons with

pseudocapacitive materials, such as transition metal oxide and electrically conducting polymers [46]. Forming hybrid structures with highly conductive carbons is one of the most adopted methods to improve the device performance of metal oxide electrodes with poor conductivities.

For carbon based composites, carbon materials such as carbon nano-fibers, activated carbon, graphene and carbon nanotubes have been actively studied [10, 12, 16, 34, 45, 46, 47]. The porous structure provided by the carbon base material network provides a high surface area which facilitates double layer charge storage and the deposition of the pseudo capacitive material. Moreover, this large surface area can also increase the contact with the electrolyte for effective pseudo capacitive charge storage.

Hybrid structures of CNTs and conducting polymers were extensively researched with the expectation that the high conductivity and high specific surface area of CNTs can greatly enhance the ECs performance of conducting polymers.

Generally, an improved electroactivity of the carbon/ECP composite materials can be obtained [42, 48, 49]. Studies discovered that the interaction between the two materials causes overlapping between the π -bonds surface of the MWCNTs and the π conjugates of the polymer chain. And therefore improves the electron mobility. Further, it is reported that the carbon material can also provide doping effect to the conductive polymers by forming a charge transfer complex. This can induced higher degree of protonation to the polymer chain and hence, the conductivity [42, 38, 49]. In addition, the carbon materials can also provide mechanical reinforcement to the conductive polymer in the composite. The swelling and physical shrinkage problem resulted from the doping and dedoping process can be compensated. The mechanical properties of the ECP can be reinforced by the MWCNTs. The interaction between the two materials causes micro-mechanical interlocking at the interface between the two materials. With carboxylic acid functionalization on the MWCNTs surface, chemical bonds can be formed between the two materials, and therefore facilitate stress transfer from the ECP to the MWCNTs [52].

From a study of **Mariana et.al**, it suggested that 10 wt% of CNT in Ppy/CNT composite can lead to 170% increase of stiffness of the polymer matrix [51]. As a result, it is believed that the cycling stability of conductive polymer can be improved by forming composite with MWCNTs. [20, 38, 34-36,45,50].

Nano-composite formed between polyaniline (PANI)/Graphene composites was found to have improved cycling stability by **Chun Li et.al.** Their study found that a laminated architecture of graphene can support the PANI fibers in place to suppress the swelling and shrinking mechanism. An increase of capacitance from 147F/g to 210F/g was observed [52].

Hammond et.al. deposited hybrid thin film electrodes of PANI nanofibers and functionalized MWCNTs by LbL assembly for electrochemical capacitors [46].

Highly stable cationic PANI nanofibers, synthesized from the rapid aqueous phase polymerization of aniline, were assembled with carboxylic acid (-COOH) functionalized CNTs into LbL films. These LbL-PANI/CNTs films within lithium cell can store high volumetric capacitance ($\sim 238 \text{ F cm}^{-3}$) and high volumetric capacity ($\sim 210 \text{ mA h cm}^{-3}$). In addition, rate dependent galvanostatic tests showed that LbL-PANI/CNTs hybrid structures can deliver both high power and high energy density ($\sim 220 \text{ W h L}^{-1}$ and $\sim 100 \text{ kW L}^{-1}$) and could be a good positive electrode material for thin film micro batteries or ECs.

Gao et. al. synthesized PANI/SWCNT hybrid films through an *in situ* electrochemical polymerization/degradation process [47]. Cyclic voltammetry (CV) tests revealed good electrochemical properties of the free-standing PANI/SWCNT hybrid films. PANI/SWCNT hybrid films with 90 electrochemical polymerization cycles showed the highest specific capacitance of 501.8 Fg^{-1} . And this value reached 706.7 F g^{-1} after the electro-degradation process, an improvement of $\sim 40\%$, which was attributed to more available charge transfer channels and increased polycrystalline PANI regions that were produced by the dissolution of off-lying disordered PANI.

Chen et. al. demonstrated transparent and flexible supercapacitors assembled from PANI/SWCNT hybrid thin film electrodes [48]. The ultrathin, optically homogeneous and transparent, electrically conducting films of the PANI/SWCNT hybrid showed a large specific capacitance due to combined electrochemical double layer capacitance and pseudocapacitance mechanisms. A supercapacitor cell assembled using these electrodes with a SWCNT density of 10.0 mg cm^{-2} and 59 wt% PANI yielded a specific capacitance of 55 F g^{-1} at a current density of 2.6 Ag^{-1} , showing its potential for transparent and flexible energy storage.

Ternary hybrid structure

In addition to binary hybrids that have been explored to improve the electrochemical performance of conducting polymers and metal-oxides, ternary hybrid structures have been

recently explored as a new design that could combine the advantages from all components: conducting carbon and pseudocapacitive metal oxides and conducting polymers [49]. By taking advantage of the synergistic effects from the ternary hybrid, it is possible to effectively utilize the full potential of all the desired functions of each component. Thus, this ternary hybrid structure provides a direction toward solving the potential problems and is promising for the next generation high-performance electrochemical electrodes.

These novel ternary hybrid systems take advantages of the synergistic effects from the hybrid structures, and make possible to effectively utilize the full potential of all the desired functions of each component. The new ternary hybrid system shows the advantages of high loading of active materials, excellent power and energy density, long cycling life, and provides a new perspective for designing electrode architectures for next generation high-performance ECs.

3. Electrochemical Techniques

3.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is a useful technique for studying macroscopic electrochemical surface reaction of electrode materials. The charges response with regard to a changing voltage, and therefore the capacitance can be measured. In cyclic voltammetry experiment for single electrode, a half-cell three electrodes setup is incorporated.

In this three electrodes cell, the working electrode (WE), which is the tested electrode makes contacts to the electrolyte and a desired DC potential is applied to the system in order to facilitate transfer of charge between the electrodes and electrolyte. The reference electrode (RE) acts as the other half of the cell with a known potential. It is placed close to the polarization layer of the WE in order to measure the voltage difference between the WE and the RE [50]. The counter electrode (CE) takes on the roles of supplying electrons to allow flow of current between working and counter electrode, it provides current required to balance the current observed at the working electrode [52,55].

The measured charge current from CV is plotted against the applied voltage to generate a cyclic voltammogram plot. The following information can be obtained from a CV plot:

- 1) The reversibility of the charge/discharge process,
- 2) Indication of any noticeable stages in charge / discharge of the electrodes.

- 3) Total charge accumulated over a potential range and
- 4) The dynamic electrode charge discharge behavior with increasing scan rates [56]

3.2 Galvanostatic Charge /Discharge

Galvanostatic method consists of applying a constant current pulse to the cell and measuring voltage response over time. Cyclic Charge Discharge is a standard technique for testing the performance of EDLCs and batteries. A repetitive loop of charging and discharging is named a cycle. The measurement is conducted under constant current until a set voltage is reached. The charge of each cycle is measured and the capacitance C, in farad (F) can be calculated. Since

$$dV/dt=I/C \dots\dots\dots 3$$

$$C=Q/V \dots\dots\dots 4$$

Therefore the capacitance equals to

$$C=Idt/dV \dots\dots\dots 5$$

Where V is the cell potential in volts (V), I is the cell current in amperes (A), and (Q) is the charge in coulombs (C) or ampere-seconds (As). [59].

3.3. Experimental

3.3.1 Materials

MWCNTs, Perchloric acid, Sulfuric acid, Nitric acid, Acetylene black, and the aniline used were received from sigma Aldrich. Ammonium Persulphate (APS) was used as oxidizing agents acquired also from sigma Aldrich. All these reagents used were analytical grade.

3.3.2 Functionalization of MWCNT

MWCNTs acid treated using H₂SO₄/HNO₃ mixture under reflux condition to improve their dispersion and surface reactivity and also to remove other carbonaceous materials produced during synthesis.

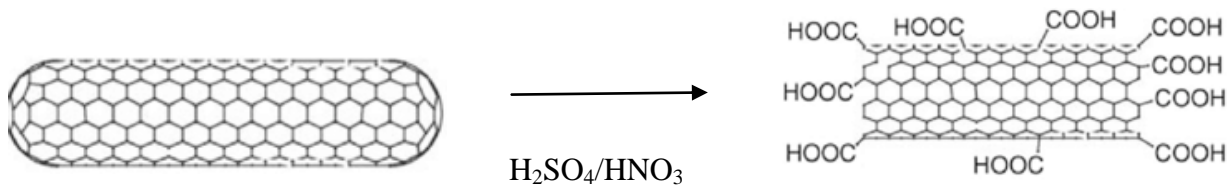


Figure 3.1 Functionalization of MWCNT

Surface modification and functionalization of MWCNTs were made by using acid boiling reflux treatment. For this, MWCNTs (0.5 g) were suspended in 6M H₂SO₄ and 6M HNO₃ in a ratio of 3:1v/v to introduce the carboxylic group into the surface of MWCNTs. The suspension was refluxed with vigorous stirring at 80°C for 12 h. After cooling to the room temperature, the mixture was filtered with filter paper. The filtrated solid was then washed thoroughly with DI water until neutral pH, and then washed with ethanol. The collected product was dried in vacuum oven at 60°C for 12 h. This product is referred to as functionalized MWCNTs (f-MWCNT) [23].

3.3.3 Preparation of MWCNT/PANI

F-MWCNTs/PANI composites were synthesized by an *in situ* oxidative polymerization. Primarily, the MWCNTs were purified and functionalized by the process mentioned above. Then, 0.3g of the purified MWCNTs was dispersed in 50 ml of 1M HClO₄ with ultrasonic treatment for 0.5 h. In the meantime, 50 ml of 1M HClO₄ solution with 1.5 ml of aniline monomer was treated by stirring for 1 h at room temperature. Then, the above two solutions were mixed together and sonicated for another 0.5 h and stored in a refrigerator for 2 hour (~5°C). Next, 0.9 g of APS was added in to 1M HClO₄ and stored in refrigerator for 2 hour (~5°C) after that it was then poured to the above mixture and the mixture was left at refrigerator for another 2 hour. Next the mixture was stirred for 5 h at 9°C and immersed in H₂O for 10 hours. Finally, the mixture was filtered and washed with deionized water three times and then dried at 80°C overnight.

3.3.4 Preparation of ternary MWCNT/PANI/HQ composite

0.3 g of the purified MWCNTs was dispersed in 50 ml of 1M HClO₄ with ultrasonic treatment for 0.5 h. In the meantime, 50 ml of 1M HClO₄ solution containing 1.5 ml of aniline monomer and 1g HQ was treated by stirring for 1 h at room temperature. Then, the above two solutions were mixed together and sonicated for another 0.5 h and stored in a refrigerator for 2 hour (~5°C). Next, 0.9 g of APS was added in to 1M HClO₄ and stored in refrigerator for 2 hour (~5°C) after that it was then poured to the above mixture and the mixture was left at refrigerator for another 2 hour. Next the mixture was stirred for 5 h at 9°C and immersed in H₂O for 10 hours. Finally, the mixture was filtered and washed with de ionized water three times and then dried at 80oc overnight.

3.3.5 Composite electrode preparation

In electrode preparation, additive carbon black along with a polymeric binder was used to create a good adhesion and conductivity between the composite materials and the current collector. Metal foil (stainless steel) was used as current collector.

Working electrodes were fabricated by mixing of 75 wt % active materials, 15 wt % acetylene black, and 10 wt % polytetrafluoroethylene (PTFE) to form homogeneous slurry. Then, the slurry was coated onto the platinum current collector and dried at 60 °C for 12 h. Finally, each working electrode containing about 0.25 mg of electroactive materials was tested in 1 M H₂SO₄ solution using a saturated calomel electrode (SCE) and a platinum electrode as reference and counter electrodes. Cyclic voltammetry (CV), galvanostatic charge–discharge (GC), and cycle-life stability tests were employed.

3.4. Characterization

3.4.1. Physical Characterizations

3.4.1.1. Scanning Electron Microscopy (SEM)

Morphology of the synthesized composites strongly influences the electrochemical properties. *Hitachi S2-5200 HR-SEM* machine was used to provide images with detailed information of the composite material morphology. Different magnifications (> x10000) is able to study the micro, nanostructure. The surface morphology of the composite can be studied to correlate the study of material electrochemical performance.

3.4.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) method allows one to characterize vibrations in molecules by measuring the degree of Infrared energy absorption of that correspond to the excitation of the molecules. From the excitation at different wavelength of a FTIR spectrum, the presence of certain characteristic bonds confirms the successful polymerization of ECP in the composite.

3.4.2. Electrochemical measurement

The electrochemical tests of cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were performed using 1 M H₂SO₄ as electrolyte

solution in a three-electrode cell, in which platinum foil and Ag/AgCl electrode were used as counter and reference electrodes, respectively.

The specific capacitance was calculated from the galvanostatic discharge process according to the following equation:

$$C_s = I\Delta t / (m\Delta v)$$

Where,

I = the discharge current (A)

m = mass of working electrode (g)

ΔV = potential window (V)

Δt = discharged time (hours)

4. Results and Discussion

4.1. Physical Characterization Results

4.1.1. SEM Results

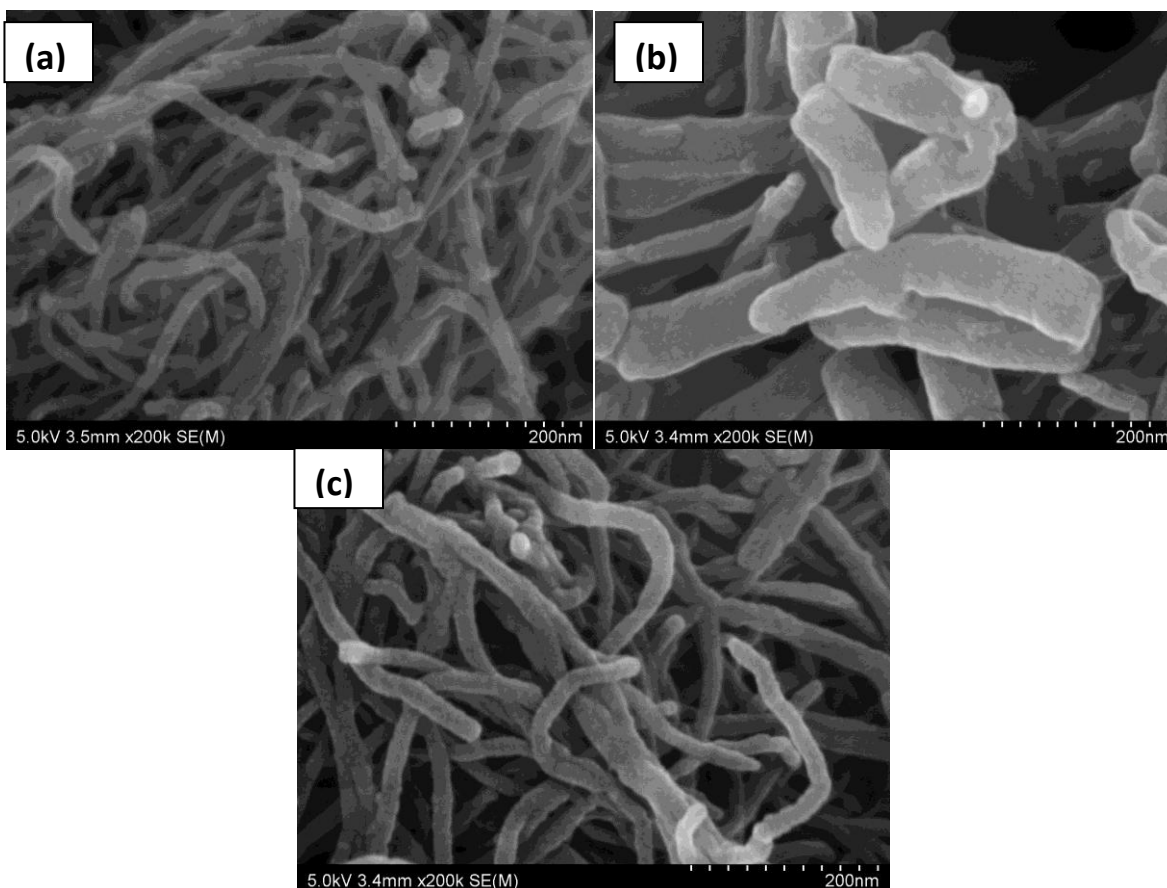


Figure 4.1. 1 Cross-section SEM images of (a) MWCNT, (b) PANI/MWCNT, (c) PANI-HQ/MWCNT

Figure 4.1.1 shows the cross-section SEM images of MWCNT, PANI/ MWCNT, PANI-HQ/MWCNT. As we can see from the image PANI is coated on the surface of MWCNT uniformly (Fig. 4.1.1b). It is hard to identify the presence of Hydroquinone since Hydroquinone is a small molecule, but we can simply identify them by further electrochemical characterizations.

4.1.2. FTIR RESULTS

Functionalized multiwalled carbon nanotube

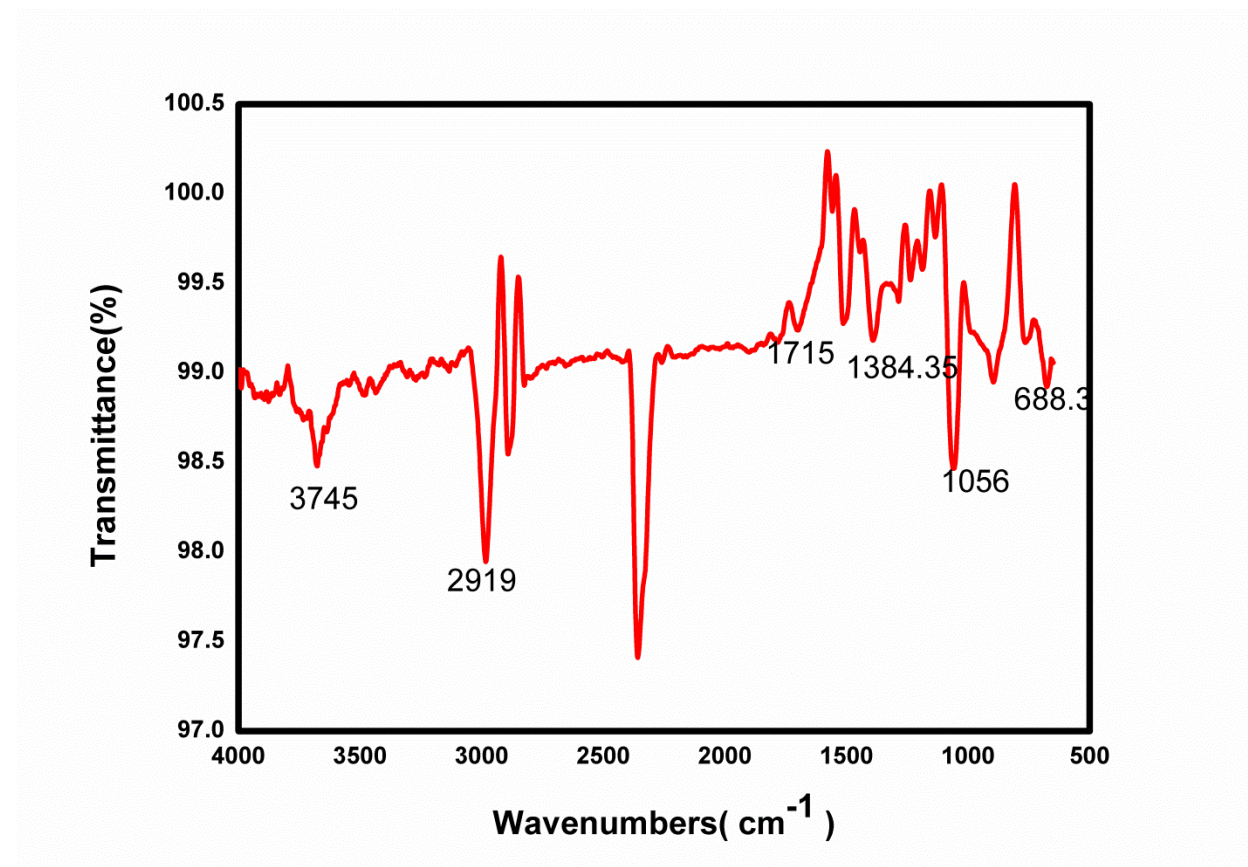


Figure 4.1. 2 FTIR result of functionalized multiwalled carbon nanotube.

Noticeable peaks at 1715 cm^{-1} and 1056 cm^{-1} appeared in MWCNT oxidized by the mixture of H_2SO_4 and HNO_3 . The occurrence of these bands are contributed to the existence of C=O and C-O stretching vibrations of the carboxylic groups (-COOH), respectively. This formation was caused by the oxidation of some carbon nanotube by strong acids. The peak at 3745 cm^{-1} is ascribed to the free hydroxyl groups.

The infrared spectra of the MWCNT/PANI, and PANI-HQ/MWCNT film were measured to verify the composite film. As shown in Fig. 4.1.3 for MWCNT/PANI, the characteristics peaks at 1572 and 1476 cm^{-1} are assigned to the C=C stretching of quinoid rings and benzenoid rings, respectively. The characteristics peaks at 1290 and 1105 cm^{-1} are assigned to the C-N stretching vibration of the secondary aromatic amine group and aromatic C-H in plane bending vibration

respectively [23]. The peak at 1232 cm^{-1} is owing to conducting form of polyaniline indicating that the polyaniline exist in conducting emeraldine form [24].

As shown in Fig. 4.1.3 for PANI-HQ/MWCNT, the band at 1623 cm^{-1} is assigned to C=O stretching vibration, indicating the presence of quinone. The bands at 1540 , 1477 and 1431 cm^{-1} can be assigned to the vibrations of aromatic rings and C=C bonds in the backbone of HQ. Accordingly, the typical bands of PANI and HQ appear in the spectrum of PANI-HQ/MWCNT, indicates the existence of PANI and HQ in composite film.

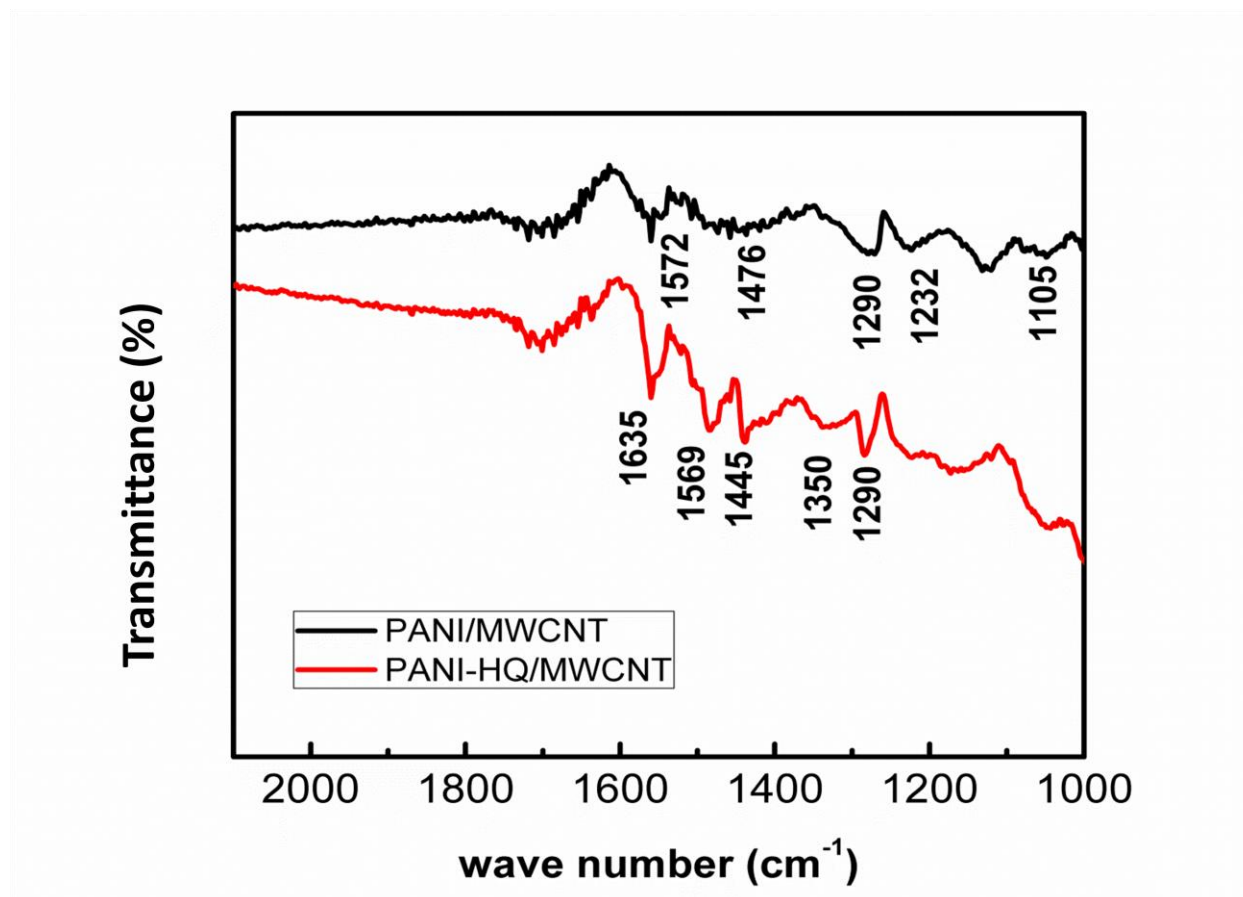


Figure 4.1. 3 FTIR result of PANI/MWCNT and PANI-HQ/MWCNT.

4.1.3. XRD RESULT

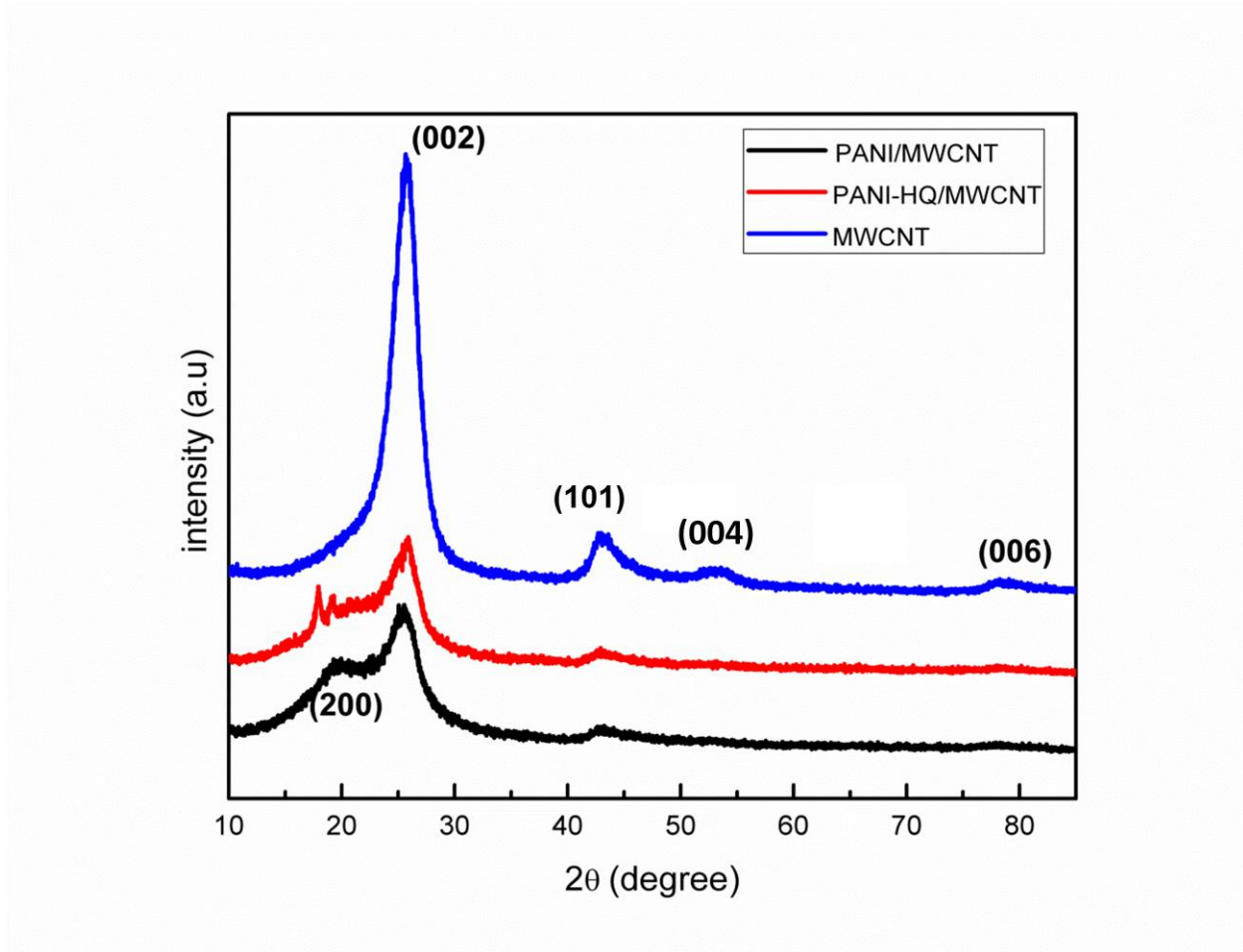


Figure 4.1. 4 The XRD pattern of PANI-MWCNT, PANI/F-MWCNT/HQ and pure MWCNT

The XRD pattern of PANI-MWCNT, PANI/F-MWCNT/HQ and pure MWCNT are shown in figure 4.1.4. the four diffraction peaks of MWCNTs at 25.6°, 43.2°, 52.8°, and 78.5° could be indexed as (002), (101), (004), and (006) reflection respectively[20]. The same diffraction peaks also emerged in the PANI/F-MWCNTs, suggesting that the crystalline structure of MWCNTs was not destroyed after the compositing process. The x-ray pattern of the PANI/F-MWCNT displays the presence of a broad peak at ~25.28° assigned to (200); this peak assures the presence of PANI in the composite. This peak in PANI may arise due to regular repetition of monomer unit of aniline. The data indicates that no additional crystalline order has been introduced into the composite. Compared with functionalized MWCNT, the obvious characteristic peaks in PANI/MWCNT can be ascribed to the formation of crystal appearing on the outer layers of

nanotubes. This result shows that the homogeneous coating of PANI onto the CNTs indicating that CNTs were well dispersed in polymer matrix. In PANI/HQ-MWCNT sample additional peak at ~17.80 shows the presence of hydroquinone in the composite.

4.2. Electrochemical Analysis

Figure 4.2 shows the cyclic voltammogram and charge-discharge curves of all samples.

Specific capacitance for all samples was calculated using the charge discharge analysis from Fig. 4 (a). The CV profiles of PANI and PANI/MWCNT film electrodes have distinct two pairs of redox peaks, which are attributed to the leucoemeraldine/emeraldine and emeraldine/parnigraniline transitions of PANI. While the CV profiles of HQ electrode at different scan rates have a pair of redox peak as seen from other reported literature, Additionally, The CV profile at a high scan rate of 200 mV s^{-1} keeps well indicates the good rate performance and excellent reversibility of HQ electrode [34]. More interestingly, the CV profile of PANI-HQ/MWCNT film electrode shows three pairs of redox peaks, which is caused by the synergistic effect among PANI, HQ, and MWCNT in the composite film. Moreover, three of the redox peaks are well separated and symmetric in shape, indicating that the electrochemical reactions involved are reversible. The peak current density and the CV loop area of the hybrid increase clearly with the increase in scanning rates, demonstrating the excellent rate property of the hybrid

Fig. 4.2c shows galvanostatic charge-discharge curves of MWCNT film, PANI, PANI/MWCNT and PANI-HQ/MWCNT composite at a current density of 0.5 A/g , and the specific capacitance are 120 F/g for PANI/MWCNT and 130 F/g for PANI, HQ/MWCNT.

Calculated by equation

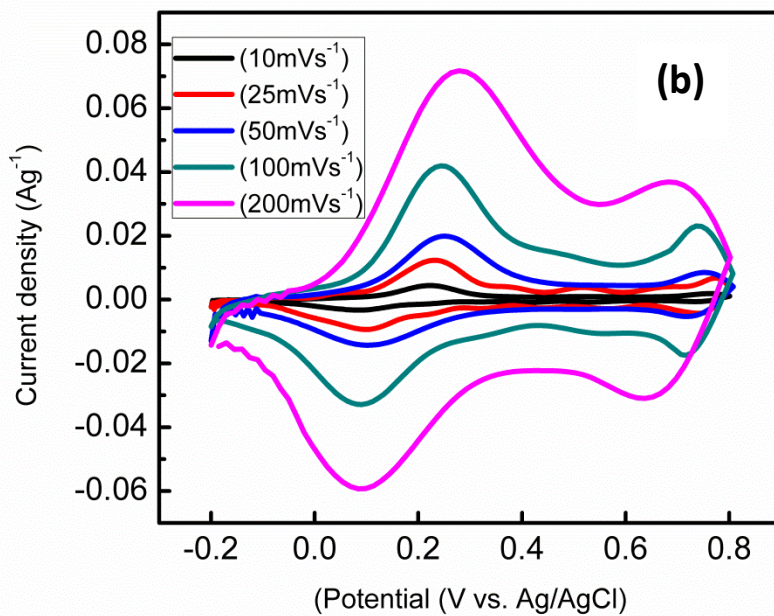
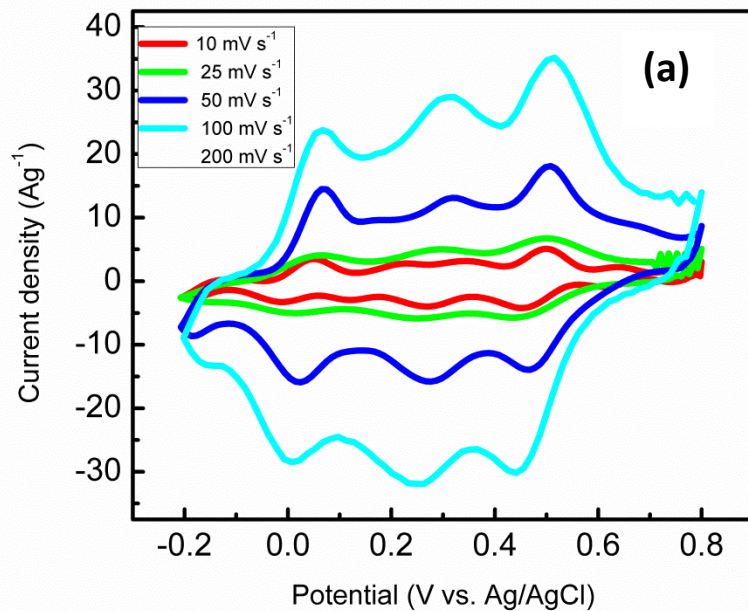
$$C_s = \frac{I\Delta t}{m\Delta v} \quad \text{Where, } I = \text{the discharge current (A), } m = \text{mass of working electrode (g)}$$

$\Delta V = \text{potential window (V), } \Delta t = \text{discharged time (hours)}$

The PANI/MWCNT electrode possesses larger specific capacitances than other electrode materials. This can be due to the fact that the transmission of protons and electrons between the PANI surface and H_2SO_4 electrolyte, which can maintain the faradaic pseudocapacitance property of PANI. The specific capacitance of PANI, HQ/MWCNT electrode is also not far from the PANI/MWCNT electrode this can be due to the fact that the HQ formed on the surface of

MWCNTs/PANI produces large double-layer capacitance and this kind of nanostructure does not obstruct the transmission of protons and electrons between the PANI surface and H₂SO₄ electrolyte, which can maintain the faradaic pseudocapacitance property of PANI.

The cycling performance of PANI, HQ/MWCNT and PANI/MWCNT for 1000 cycles was also tested. PANI, HQ/MWCNT specific capacitance retention is 94 %, revealing good cycle performance and stability of the hybrid. The improved stability is mainly attributed to the architecture with synergistic effect of HQ, MWCNTs and PANI. Firstly, MWCNTs acts as a framework to make PANI effectively accommodate the mechanical deformation caused by the swelling and shrinking of the nanostructures during the long-term Galvanostatic charge discharge process. Secondly, the HQ covering on the surface of MWCNTs/PANI can suppress the volume change of PANI from the outside, which avoids the destruction of the electrode material and leads to outstanding stability. Although the specific capacitance of PANI-HQ/MWCNT film electrode is lower than those of PANI and PANI/MWCNT film electrodes at 0.5 A/g, PANI-HQ/MWCNT shows excellent cyclic stability after 1000 cycle than PANI/MWCNT as shown in Figure 4.2d



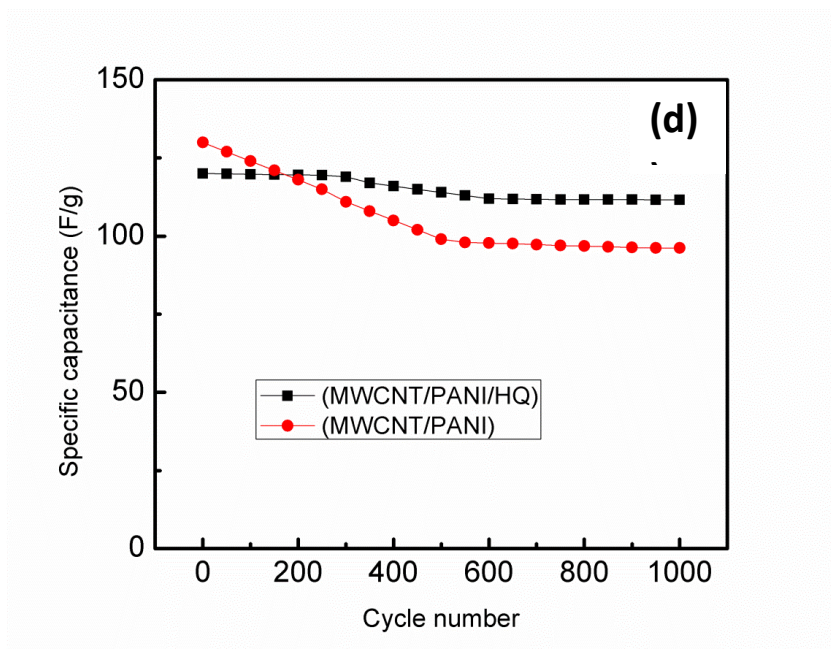
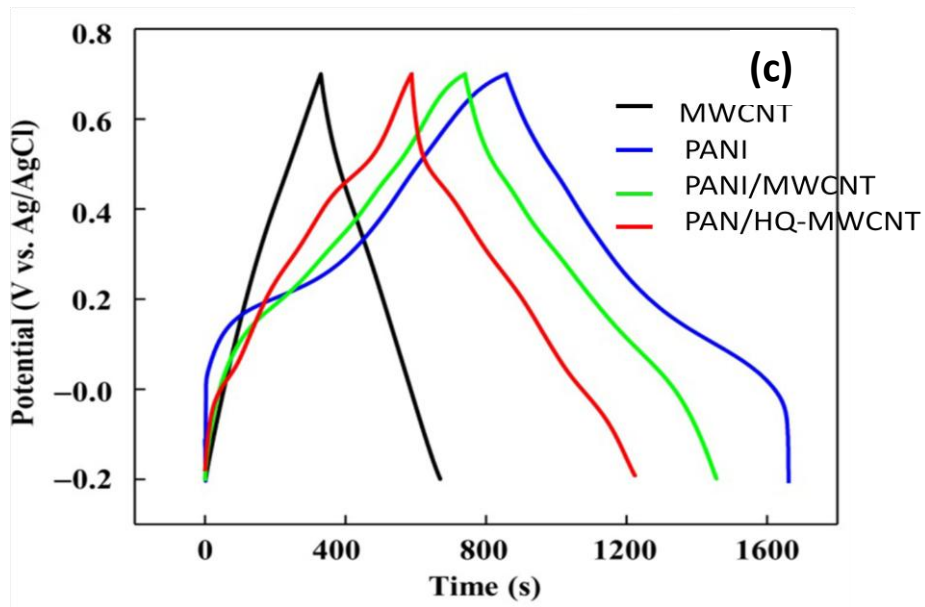


Figure 4.2 Electrochemical properties of, PANI/MWCNT film, and PANI-HQ/MWCNT film electrode materials: (a) CV profiles of PANI-HQ/MWCNT film at different scan rate, (b) CV profiles of PANI/MWCNT film at different scan rate, (c) Galvanostatic charge-discharge curves

5. Conclusion

Multi-walled carbon nanotubes (MWCNTs) are widely used as supercapacitor electrode material. However, the specific capacitance of MWCNTs cannot achieve optimum value to facilitate required demand. Conducting polymers have been introduced to achieve optimum energy density and power density of SuperCapacitor electrode material. Conductive polymers are promising pseudo capacitive materials as they feature both good conductivity and high capacitance. Formation of composite between conductive polymers and carbon nanotubes is a proven technique in enhancing the material electro activity. However, the cycling life and rate capability of PANI electrodes are unsatisfactory due to their large volume changes and slow redox reactions during charge-discharge processes.

The addition of Hydroquinone on MWCNT/PANI composite prepared by in-situ polymerization increase the cyclic stability of MWCNT/PANI due to addition of pseudo capacitive effect of Hydroquinone.

PANI-HQ/MWCNT film offers intrinsic porous channels and promotes the transportation of charges and ions. Consequently, The PANI-HQ/MWCNT film electrode exhibits specific capacitance of 120 Fg^{-1} at a current density of 0.5 A g^{-1} whereas PANI/MWCNT film exhibits 130 Fg^{-1} . Although PANI-HQ/MWCNT film electrode exhibits less specific capacity than PANI/MWCNT they presents a good cycling stability with 94% of capacitance retention after 1000 cycles, much higher than those of PANI/MWCNT film (74%) electrodes.

The excellent rate performance and cycling stability make it one of promising candidates for electrochemical energy storage.

6. Future works

In this study, from the material engineering perspective, an enhanced cyclic stability was achieved through combining conductive polymer (PANI), carbon nanotubes and hydroquinone in form of composite. The performance was aimed to be optimized through synthesizing PANI/MWCNT/HQ using insitu polymerization process. However, there are areas to be further improved from both composite materials engineering perspective and device design perspective. In order to further improve the power performance, and at the same time further increase the capacitance and cyclic stability closer to the theoretical limit. The following areas can be investigated.

6.1.1 CNTs surface manipulation

Parameters such as pore size and pore volumes of the carbon materials greatly influence the materials ionic conductivity, which is related to the mobility of ions inside the pores, and therefore the capacitance.

6.1.2 Increasing voltage window limitation

Since the energy is proportional to the capacitance (C) and the Voltage (V). In order to increase the capacitance the voltage window is still a limiting factor for both carbon and conductive polymers. The power performance can also be improved because the power is also proportional to the cell voltage. Commercialized organic electrolytes were used in supercapacitors device in order to achieve a higher voltage window up to 2.7V. But this electrolyte requires complicated assembly process and they are expensive [57]. On the other hand, ionic liquid electrolyte can improve the cell voltage window up to 3.5V. However, the conductivity of the electrolyte is low and has a very high viscosity, as a result they limits the specific power and high rate capability [58].

Therefore, instead of focusing solely on the electrolyte, the focus was shifted to the electrode materials itself. A study from **Susana et.al** suggested that constructing an asymmetric cell by varying the mass ratio between the cathode and anode can strategically increase the voltage window of the cell. Her work was conducted of activated carbon supercapacitor cell. The mass of positive electrode is greater than the negative electrode by a ratio of 2.46. The operating voltage window was increased from 1.2V to 2V in 0.5M K₂SO₄ neutral electrolyte [58]. High

cycling stability with retaining more than 75% of capacitance over 10000 cycles was obtained. Her work demonstrated that the loss of performance of the cell is mainly owing to the aging of the positive electrode. The asymmetric mass-balancing approach can be applied to study the cell performance with carbon nanotubes and conductive polymers composite electrodes. These attempts have not been reported from the literature. Moreover, the investigation of acidic or basic electrolyte should also be conducted.

6.2.3. Composition of active materials (ratio of PANI/MWCNT/HQ) study

In this study better stable nano composite of PANI/MWCNT/HQ was synthesized through in-situ polymerization process. However the composition of PANI/MWCNT/HQ was believed to affect the performance of these electrode materials.

Further addition of ECP and HQ content leads to formation of an aggregated polymer with a heterogeneous surface morphology. As a result diminishes the polymer conductivity. The poor interaction between ECP and MWCNT would also weaken the synergy in the electroactivity from the composite.

In order to get optimum ratio or favorite combination of PANI/MWCNT/HQ further study needed to be implemented.

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