CONDUCTING POLYMER-BASED ELECTRODES FOR ELECTROCHEMICAL SUPERCAPACITORS

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Applied

Science

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| MASTER OF APPLIED SCIENCE (2018) | McMaster University |
|---|---------------------|
| Department of Materials Science and Engineering | Hamilton, Ontario |

TITLE: conducting polymer-based electrodes for electrochemical supercapacitors

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NUMBER OF PAGES: XIII, 106

Abstract

The growing interest in the application of polypyrrole (PPy) for electrodes of electrochemical supercapacitors (ES) is attributed to the relatively high specific capacitance (SC), low cost, high electrical conductivity, advanced chemical and mechanical properties of PPy. However, it is found that swelling and shrinkage occurred during charge-discharge, resulting in higher impedance, gradual adhesion loss and poor cycling behavior of PPy electrode. Moreover, mass normalized capacitance decreased significantly with increasing electrode mass, especially at high charge-discharge rates. Therefore, it is challenging to achieve good electrochemical performance, cyclic stability and good capacitance retention at high charge-discharge rates for electrodes with mass loadings above 20 mg/cm², which is required for many practical applications.

To address this problem, PPy-MWCNT (multiwalled carbon nanotube) composites were prepared using polycharged aromatic anionic redox active molecules as dopants for PPy and dispersants for MWCNT. New dopants offer the advantages of their reduced movement during charge-discharge process and reduced PPy swelling because of large molecular size. In addition, polycharged dopants, containing several charged groups, can be linked to different polymer macromolecules, thus increasing interchain mobility of charge carriers and increasing PPy conductivity. Moreover, new dopants exhibit redox active properties and thus contribute to the total electrode capacitance. The reasons for adding MWCNTs are following: first, they can enhance charge storage properties of PPy by increasing the conductivity of composites, which is more obvious when the scan rate is high. Second, the network formed by MWCNTs can restrict the swelling of PPy and improve the cyclic stability.

In this research, new promising PPy-MWCNT electrodes were fabricated. 7 different molecules were used as new dopants for chemical synthesis of PPy. The molecular size and functional groups of the anionic dopants and dispersants have great influence on the morphology and capacitive properties of PPy and PPy/MWCNT composites. Moreover, PPy-MWCNT-FeOOH composite was also prepared in order to shift the working voltage window of PPy/CNT composite to more negative direction, which can facilitate the utilization of PPy as negative electrode.

The results showed that dopants with large size, multiple charges and high charge to mass ratio can decrease PPy particle size, reduce agglomeration and thus improve PPy capacitive properties. The highest SC of 118.26 F/g was achieved at 2 mV/s by using PMSS-SR31 doped PPy-MWCNT electrodes. The highest SC of 65.09 F/g at 100 mV/s was achieved by using Potassium Benzene-1,2-disofulnate doped PPy-MWCNT electrodes. Adding FeOOH to PPy-MWCNT composite with mass ration between PPy and FeOOH of 7/2 allowed for enhanced performance in a working voltage window of -0.8 - +0.1 V, which facilitated the utilization of PPy as a negative electrode in asymmetrical device.

Acknowledgement

I hereby express my deepest gratitude to my supervisor Professor Igor Zhitomirsky for his intellectual guidance and continuous encouragement and support. Also, I appreciated the environment of enthusiasm towards nature and science Professor has created and I wish greater success for Professor Igor Zhitomirsky in the future.

I am grateful to my committee members for their time, patience and criticism as well. I also want to thank Jieming Li, Mustafa Ata, Cameron Wallar for their kindness of helping me all along my two years of Master's research life. To all my group colleagues, Ryan Poon, Ri Chen, Aseeb Syed, Jordan Milne and Xinya Zhao, Amanda Clifford, many thanks to your help and support. It is my honor to work with you.

I want to express gratitude to Canadian Centre for Electron Microscopy and other faculty and staff in MSE department and in McMaster University. I would not have accomplished my thesis research without you.

Last, I want to thank my parents for their unconditional support in mental and financial part. I really appreciate that. I will try my best to be the son you can be proud of.

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1. Introduction

Developing new energy storage devices has attracted very much attention in recent years due to crisis of energy. Electrochemical Supercapacitor (ES), also called Supercapacitor or Ultracapacitor [1], has been investigated as an advanced energy storage device owing to its outstanding properties for decades. Based on the charge storage mechanism, the supercapacitors can be classified into 2 types, which are double layer capacitors and pesudocapacitors. When it compared to conventional capacitors, supercapacitors can store much more energy because of their high surface area and atomic size distance between the electrode surface and electrolyte surface. Besides, fast and reversible charging-discharging kinetics also make supercapacitors have much higher power density than batteries. Therefore, supercapacitor is a bridge filling the gap between batteries and conventional capacitors. The selection of electrode materials is a key factor to supercapacitors' electrochemical performance. Various kinds of materials can be used for the electrodes, including metal oxides, conducting polymers (CPs) and composites.

CPs based ES has been attracting significant interest due to high SC, high electrical conductivity, low cost, and easy fabrication [2]. PPy is one of the most promising CPs, which was investigated in this research. Electrochemical polymerization of PPy was widely used long time ago. However, this method is not suitable for the real industrial production because of its low efficiency in production and low loading of active

material (<1 mg/cm²). Recently, chemical polymerization of PPy has been commonly used since it has advantages in mass production, high loading of active materials (up to 40 mg/cm²) and high mass percentage of active materials in electrode [3]. Therefore, this method was also used in this research.

Anionic dopants play a vital role in charging & discharging of PPy, which corresponds to storing & releasing energy of ES. In this study, we used 7 different kinds of molecules as dopants, such as Ponceau-S, Potassium benzene-1,2-disulfonate and Aerosol S, to mechanistically investigate the effects of dopant structures on physical and electrochemical characteristics of PPy. Furthermore, my research aims at exploring and developing the general principles in selection of good dopants for PPy based ES.

A major factor that limits the application of PPy based ES is the degradation of bulky materials due to swelling and shrinkage during charging and discharging cycles. The loss in mass and decrease in mechanical properties of PPy are attributed to intercalation and deintercalation of ions during charging and discharging cycles. Another factor that prevents PPy based ES far from use is the relatively low electrical conductivity of chemically-synthesized PPy bulky powders, although PPy is a good conducting polymer. To increase electrode cyclic stability and electrical conductivity, multi-walled carbon nanotubes (MWCNTs) were introduced to fabricate the PPy/MWCNTs composite materials. MWCNTs with high aspect ratio and conductivity can form the network which can not only facilitate the charge transfer but also restrict the swelling of PPy during cycles. In conclusion, the factors that determine morphologies and capacitive behaviors of the composite material are the use of dopants, the selection of MWCNTs dispersing agents, and the PPy/MWCNTs mass ratio.

Because PPy's working voltage window is typically -0.5 - +0.4 V and PPy can only be p-doped, PPy is commonly used as positive electrode. Shifting the working voltage window to more negative direction is a good way to make PPy used as negative electrode. FeOOH has outstanding capacitive behavior at very negative working voltage range, which is usually used as negative electrode. In this sense, adding FeOOH to PPy to prepare PPy-FeOOH composite is a potentially promising way to shift PPy working voltage to more negative direction and facilitate utilization of PPy as negative electrode.

2. Literature review

2.1 History of supercapacitor

The concept that electrical energy storage in electric double layer formed at the interface of electrode and electrolyte was brought up in the late 1800s. In 1957, H.I. Becker from General Electric used porous carbon material to design the first ES based on double layer charge storage mechanism (U.S. Patent 2,800,616). Later in 1962, R.A. Rightmire from Standard Oil Company of Ohio (SOHIO) invented the device (U.S. Patent 3,288,641) in a format which is now commonly used. Rightmire's work was further developed in 1970 by D.L. Boos from SOHIO, whose patent (U.S. Patent 3,536,963) was the foundation for following study on supercapacitors. In 1975, a new mechanism of energy storage was developed by Conway, in which energy was generated and released from redox reactions taking place on electrode materials. After three years, supercapacitor was first commercialized and the license was held by SOHIO. During that time, electrochemical supercapacitors were only utilized as a back-up power source for volatile and complementary metal-oxide-semiconductor (CMOS) computer memories. The scope of supercapacitors' application has expanded drastically over the past 30 years. Supercapacitors have been already used as portable electronic devices and high-efficiency energy storage device for electric vehicles and hybrid electric vehicles. Many companies were involved in emerging development and applications of supercapacitors, such as SOHIO, NEC, ECOND, PANASONIC, ELIT, ELNA, MAXWELL, ESMA, CAP-XX, NIPPON CHEMI-CON and NESSCAP [4].

2.2 Energy Storage devices

2.2.1 Comparison between Devices

In the past 30 years, consistently burning fossil fuel has induced two biggest problems, which are environmental pollutions caused by greenhouse gas emission and shortage of fossil fuel [5]. Energy revolution is inevitable. Therefore, green and renewable energy supplies, like solar energy, wind power, hydro power have attracted great attentions over the past decades [6]. However, considerable disadvantages, like instable support (solar & wind energy), low efficiency (solar), limited life cycle of device (solar), geographic restrictions (wind & hydro power), and potential risks (nuclear energy), become obstacles for vast applications of these energy forms [7]. To solve reliability issue of the green energy supplies, energy storage systems play an important role. Such systems store and release energy whenever needed to satisfy industrial and social demands. There are mainly four types of energy storage systems and devices, including conventional capacitors, batteries, fuel cells and electrochemical supercapacitors [8]. Conventional capacitors store electric energy by inserting a dielectric material between two conducting metals plates. The dielectric materials are polarized when connected to an external power source and being charged. The amount of energy depends on charges accumulated on metal plates. The maximum potential applied to conventional capacitors is limited by the breakdown field strength of dielectric material [9]. An ideal electrostatic capacitor is characterized by a constant capacitance C, which is the

capability of charge storage and can be calculated by the amount of accumulated charge (Q) and the applied potential (V).

$$C = \frac{Q}{V}$$
 2-1

Capacitance is an important parameter of capacitor devices and it is determined by properties of dielectric materials inserted between the conducting plates. The capacitance can be expressed in the following way [10],

$$C = \varepsilon \frac{A}{d}$$
 2-2

where A is the total area of one conducting plate, d is the distance of two conducting plates and ε is the permittivity of dielectric material. The capacitance of the doublelayer supercapacitors can be estimated in a similar way. Energy stored in capacitors can be characterized by the following equation,

$$W = \int_0^Q V dq = \int_0^Q \frac{q}{c} dq = \frac{1}{2} \frac{Q^2}{c} = \frac{1}{2} C V^2$$
 2-3

where C is the capacitance and V is the potential applied to it. And maximum power of capacitors is determined by the equation shown here,

$$P = \frac{W}{t} = \frac{1}{2}VI = \frac{1}{4}\frac{V^2}{R}$$
 2-4

where R is the equivalent series resistance. The parameters are always mass or volume normalized.

In comparison, batteries provide energy by outputting Faradaic current generated by reduction or oxidation of some chemical substrates at electrodes with phase change [11]. Fuel cells convert chemical energy directly to electrical energy by reduction of oxidant and oxidation of fuel through internal electrolyte, usually with help of high efficient catalyst (Pt) [12]. ES, stores and releases energy by achieving non-Faradaic charge adsorption and desorption at the electrode/electrolyte interface (double-layer capacitors), or fast and highly reversible Faradaic reaction inside the bulky electrode (pseudo-capacitors) [9], or combination of the above two (hybrid capacitors) [13].

From Ragone plot [14], we can see the difference between these four common electric devices in terms of energy density and power density. Energy density is how much energy can be stored in the device, while power density is how fast energy can be delivered. Fig 2-1 presents mass normalized parameters, from which we can clearly conclude that conventional capacitors have highest power density but lowest energy density. In capacitors, the energy is stored by electrostatic adsorption of electrons onto the conducting plates. From the equation 2-3, the energy of conventional capacitors

depends on capacitance and breaking field strength. Breaking field strength is related to dielectric material, and capacitance has something to do with dielectric material, total conduct area of conducting plates and distance between conducting plates. Even though breaking field strength can be increased by using good dielectric material, it is very hard to increase the contact area for metal plates and their distance can not decrease to atomic level. Therefore, their energy is not high. However, it doesn't involve any chemical reaction, resulting in the energy can be released in a very fast way. Batteries and fuel cells obviously can store and generate much more energy but they have fairly low power density because of the redox reactions and ions diffusion they have to go through when delivering begins. Electrochemical supercapacitors, to some degree, bridge the gap between conventional capacitors and batteries. When they are compared to conventional capacitors, their large contact area, small distance between double layers and redox reactions occurring at electrode make them have higher energy density. In comparison with batteries, even though some redox reactions will also occur at supercapacitors' electrode surface, the reaction speed is much faster and the reaction occurs much shallower from electrode surface. Therefore, their power density is higher than batteries. For supercapacitors, they have high powder and energy densities at the level of 10^3 - 10^4 W/kg and 10^{0} - 10^{1} Wh/kg, respectively. Their advantages make them applicable for a wide scope of applications, including high power and energy densities, fast chargingdischarging kinetics (1-30 s), high efficiency (> 95%), long cycle life (> 106 cycles), easy processability, ecological friendliness and low cost[1,9,15].



Fig 2-1 Ragone Plot (Power density of several kinds of energy storage devices versus Energy density) [16]

2.2.2 Applications of Electrochemical supercapacitors

Due to their high power density and energy density, electrochemical supercapacitors potentially can have many important applications [17]. First, supercapacitor is a promising and ideal device for small applications involving high power output and uninterruptible power supply, such as flash light of smart phone, turning on of smart phone and power source for desktop or laptops [18]. Besides, supercapacitors can also be used in hybrid vehicles and automobiles. Supercapacitors can collect wasted energy generated from braking or deceleration and release huge power in a limited period of time to provide energy for acceleration of vehicles or climbing uphill, which can increase the efficiency of engine and prolong the effective life [19]. Furthermore, supercapacitors also have applications in huge industrial machines like mining shovel. Supercapacitors capture and collect energy from swing deceleration and deliver burst energy to assist lifting operations, which is reportedly said to be able to save 25% of fuels demanded [20]. Last but not least, since supercapacitors can act as extra power source, they can provide back-up energy if there is a power shutdown of main power source in houses, aircraft doors and data centers and thus enhance safety of daily human life and information security.



Fig 2-2 Applications of supercapacitors in portable electronics, hybrid vehicles, huge industrial machines, houses, aircraft doors and data centers

2.3 Energy Storage Mechanism of Electrochemical Supercapacitors

It has been 30 years since ES was first investigated. At the initial stage, supercapacitors were only based on double layer mechanism, which induce low energy density and fairly high cost [9]. After Conway brought up another mechanism of energy storage

system in 1975, the research about supercapacitors underwent historical change, which is energy generated from Faradaic charge exchange. ES can be divided into three categories based on energy storage mechanism: (1) Electrochemical Double Layer Capacitors (EDLCs), (2) Pseudocapacitors and (3) hybrid capacitors.

2.3.1 Double layer Capacitors

The double layer refers to two parallel layers of opposite charges adjacent to electrode surfaces. The basic theory for EDLCs is storing and releasing energy by non-Faradaic charge adsorption and desorption at electrode/electrolyte interface without any redox reaction. Many other theories were proposed to explain the structure of EDL and to quantitatively derive related parameters, such as those by H. Helmholtz, L.G. Gouy and D.L. Chapman, O. Stern, D.C. Grahame, J.O. Bockris and M.A.V. Devanthan and K.A. Müller, etc [12].

In 1853, EDL was first theorized by Helmholtz's model. This theory thought two layers of positive charge and negative charge, functioning as metal plates, attract each other on the two sides of electrode to store charges. However, after 50 years, L.G. Gouy and D.L. Chapman begun to doubt that theory and brought up a new model, since they observed that the capacitance of EDLC is related to ionic concentration of electrolyte. They believed EDL should be considered in a more dynamic way. Therefore, a diffuse model was introduced to replace the rigid and static molecular dielectric. The charge distribution of ions was expressed as a function of distance from the electrode/electrolyte interface following the Maxwell-Boltzmann statistics. However, their theory still can not illustrate the phenomenon they observed. In 1924, O. Stern combined Gouy-Chapman's model and Helmholtz's work and proposed a composite theory. As asserted, some ions attached to the electrode and form the so-called "Stern layer", meanwhile, other ions form a diffuse layer next to the Stern layer. The diffusion layer decays in a non-linear potential fashion with distance [21]. In 1947, D.C. Grahame suggested that Stern layer was supposed to be further divided into two sections. One is the inner Helmholtz plane (IHP), where the ions are directly adsorbed to the electrode without a solvated coat. The other is the outer Helmholtz plane (OHP), in which the solvated ions are at their closest distance from the electrode. Grahame's model was further developed by J.O. Bockris, M.A.V. Devanthan and K.A. Müller in 1963 [22]. They took the distribution and action of interfacial solvent molecules into consideration and brought up BDM model, which is commonly accepted today. The BDM model, suggests that solvent molecules form a major portion of the first layer (OHP) adjacent to the electrode surface and this first layer of solvent can orientate to electric field depending on the charge. The IHP and OHP contribute to most of the potential drop. By contrast, the diffuse layer is further outside the OHP and gives the non-linear potential drop. Therefore, the Stern layer forms the major part of the whole capacitance. the capacitance of EDLC can be expressed as [23]:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$
 2-5

Where ε_r and ε_0 are the relative dielectric constant of double layer and the permittivity of vacuum; A and d correspond to the surface area and thickness of the double layer, respectively. In a system where solvent molecules firmly adhere to electrode surface with few isolated charges crossing the OHP layer, the ions at OHP determine the quantity and contribute to a majority of the capacitance. Such characteristics lead to a highly reversibility of charging and discharging cycle and a good effective cycle life of EDLC devices.



Fig 2-3 Models of double layer: (a) Helmholtz model, (b) Gouy-Chapman model

and (c)Stern model with IHP indicating inner Helmholtz plane and OHP indicating outer Helmholtz plane. ψ_0 and ψ are potentials at the electrode surface

and the electrode/electrolyte interface, respectively [9]

The double layer thickness d is in the order of ion diameter (3-8 Å). It is way smaller than the distance between the plates in conventional capacitors. Improvement in capacitance can also be achieved by increasing surface area A with porous materials having high specific surface area (SSA) and excellent electric conductivity. Porous carbon material is usually used to prepare the electrodes for EDLCs. In a nutshell, reduced thickness and increased surface area of the double layer dramatically improved the capacitance from the 10^{-9} - 10^{-6} F (conventional capacitors) to 10^{0} - 10^{1} F. EDLC consists of two electrodes, and each electrode in EDLC is an individual capacitor and one EDLC can be considered as two capacitors connected in series. The total capacitance of an EDLC is:

$$C_{cell} = \left(\frac{1}{C_1} + \frac{1}{C_2}\right)^{-1}$$
 2-6

Where C_1 and C_2 are the capacitances of the two capacitors.

2.3.2 Pseudocapacitors

Another type of electrochemical supercapacitors is pseudocapacitor and when a potential is applied to a pseudocapacitor, fast and reversible redox reactions take place on the electrode material. Therefore, it is faradaic process. Pseudocapacitors can be classified into three types based on different mechanism, which are underpotential deposition, redox pseudocapacitance and intercalation pseudocapacitance [24].

The first model is based on surface adsorption of ions from electrolyte. Different from OHP, ions are directly adsorbed to the electrode surface without solvated molecules [25]. The second model is based on Faradaic current generated from compound formation via redox reaction in the bulk electrode material, but only limited to certain depth which is very closed to its surface [2]. Therefore, we can say adsorption and redox reaction occur at the electrode/electrolyte interface, which are highly affected by SSA of electrode. Metal oxides are usually prepared as electrodes for pseudocapacitors based on first two models.

The third model is to specifically describe the mechanism of conducting polymer (CP) based PS [24]. With applied potential or current density, CP-based PS device can store and release energy from the doping/de-doping process occurred in the whole bulk of electrode. Since this doping and de-doping processes are not limited to the surface, SSA of the bulk materials is not the key factor affecting CP-based PS capacitance performance. Its performance is more related to the permeability of electrolyte infiltration into bulky electrode and the electric conductivity of CPs. It should be pointed out that it is difficult to classify an ES system into either pure non-Faradaic or pure Faradaic process because both storage mechanisms often coexist.



Fig 2-4 Different pseudocapacitive mechanisms: (a) underpotential deposition, (b) redoxpseudocapacitance and (c) intercalation pseudocapacitance [9]

2.3.3 Hybrid Supercapacitors

According to the equation 2-3 & 2-4, the energy density and power density are proportional to the voltage square. Increase in the voltage window can improve stored energy and power output of whole device. However, the open circuit voltage of traditional symmetrical ES device equals to the voltage window of single electrode, which restricts the stored energy and power output of device [25, 26]. By contrast, hybrid supercapacitor based on the application of EDLC capacitor and the use of different PS materials for electrodes asymmetrically in a single cell can expand the working voltage window a lot [28]. When the electrode materials are carefully selected with a certain voltage window, the optimized HS devices have an enhanced open circuit voltage higher than the sum of the two, which means much larger stored energy and

power output [25, 28].

2.4 Electrode materials for electrochemical Supercapacitors

As discussed before, electrochemical supercapacitors can be classified into two major types based on their different charge storage and release mechanism. EDLCs require the electrodes to be porous and highly conductive. By contrast, for PS, the attention should be put on whether the electrode material is redox active. Therefore, different types of electrode material are selected depends on what type of electrochemical supercapacitors are prepared [22, 29].

2.4.1 Porous Carbon Material

•

For EDLCs, the surface area and electric conductivity are the two key parameters determining performance of ES devices. Since 1957, carbon in various forms have been considered as good candidates for EDLCs' capacitors. Activated carbon (AC), carbon nanotubes (CNTs) and graphene have been all investigated and found to meet the requirements [31].

Since electrolytic ions travel through pores, pore size and size distribution of the carbon materials play important roles. In 2008, P. Simon and A. Burke [32] theorized the pore size network in activated carbon grain. The theory is applicable to various carbon forms.

According to the theory, pores can be classified into two types, which are closed pores and open pores. The closed pores are those stable void spaces totally surrounded by active materials. Those pores are unavailable for electrolyte and do not contribute to energy storage. By contrast, the open pores are accessible for electrolyte. These pores form the electrode/electrolyte interface for energy storage. The pore sizes can be further divided into three groups: (1) micropores (<2 nm), (2) mesopores (2-50 nm) and (3) macropores (>50 nm).

It was long believed that among the three types of pores, micropores make little contribution to charge storage, because they are smaller than solvated electrolytic ions and those ions can not penetrate the pores.



Fig 2-5 Schematic network for pore size distribution in active material grain [32]

However, recent researches revealed that ultrahigh capacitance for EDLCs can be achieved by micropores. The theory is that with pore sizes in 1.5~4 nm, the free space for electrolyte infiltration is reduced, restricting motions of electrolytic ions and thus reducing capacitance. However, as shown in Fig 2-6, when the pore size decreases to lower than 1.5 nm, solvated ions will distort or even lose part of their solvation shells for entering the narrow spaces. The reduced space actually makes ions closer to the electrode surface and enhances the capacitance via Faradaic process in electrode materials [33].





comparable data in the same electrolytes [32]

Besides SSA and pore size, the other key parameter that determines ES performance is the electric conductivity of bulk carbon [34]. It is well known that sp³- and sp²hybridization are most common carbon atoms connection in carbon materials. In sp³ hybridization, four stable σ -orbits are formed in one carbon atom. In sp² hybridization, three σ -orbits are formed and one electron is left in the remaining p-orbit, forming π bond when its electron cloud approaches and overlaps with nearby p-orbits. The p-orbit electron is delocalized in the whole π cloud region, providing the essential charge transfer route for electric conductivity. A high ratio of sp2 hybridization carbon is vitally important for high electric conductivity. Right now, graphene is the most important carbon materials used as electrode of EDLCs [34, 35]. Graphene can be regarded as one atomic thick of graphite. It is a 2D crystalline of carbon (~100% sp²-hybridization). Therefore, it has superb electric conductivity (>1700 S m⁻¹), surpassing AC (~10-100 S m^{-1}). Besides, graphene has an ultrahigh SSA (2630 $m^2 g^{-1}$) and a theoretical capacitance of 550 F g⁻¹, making it promising for ES Application [37]. As most carbon materials are fragile and amorphous, certain current collectors are usually occupied in fabricating ES devices. In 2012, M.F El-Kady [38] reported the fabrication of pure graphene electrode without other current collectors and obtained a high capacitance of 276 F g⁻¹.

2.4.2 Transition metal oxide and Conducting polymers

Capacitance generated from Faradaic charge transfer also exists in carbon-based materials, but the contribution is so little that we can even overlook. Metal oxides and conducting polymers, however, are predominantly manipulated by redox reactions.

2.4.2.1 Transition metal oxide

Ruthenium oxides, manganese oxides, cobalt oxides, nickel oxides and vanadium oxides have been under investigation for applications in supercapacitors. Certain criteria are used to judge whether a metal oxide is suitable. First, the metal oxide should be electrically conductive. Second, the metal must have multiple valence states so that redox reactions can take place and protons can easily intercalate into and detercalate from the lattice during charging and discharging processes. For the transition metal oxide, double layer charge storage only contributes 10% of the total specific capacitance. The rest of specific capacitance is supplied by pseudocapacitance. Among the metal oxides, RuOx has attracted a lot of attention due to its 1.2 V potential range which is beneficial for energy and power densities of the device. In addition, redox reaction of RuOx is highly reversible which can elongate cycle life.

Pseudocapacitive behavior is highly affected by different environments, such as pH. For RuOx, the capacitive performance varies when pH changes. In an acidic environment,
the reversible redox reaction is shown by the following equation, with protons adsorbed on the surface of RuO₂ and Ru changes from Ru (IV) to Ru (II).

$$RuO_2 + xH^+ + xe \rightarrow RuO_{2-x}(OH)_x$$
 2-7

On the contrary, when RuO_2 is in alkaline environment, the changes in valence state are complicated. RuO_2 can end up in multiple forms such as RuO_4^{2-} , RuO_4^{-} and RuO_4 [39].

However, RuO₂ is not the ideal candidate for commercialized supercapacitor owing to its high cost[39, 40]. Recently researchers are making efforts to select substitutional metal oxides that are cheaper but perform as well as Ru oxides. However, it is hard to achieve a balance. Good capacitive performances of metal oxides require high concentration of proton, but metal oxides will be easily dissolved by strong acid [41, 42]. Neutral electrolytes are taken into consideration like Na₂SO₄ and KCl for manganese, cobalt, iron and nickel oxides. Among these metal oxides, MnO₂ has attracted very much attention with a theoretical capacitance reaching 1380 F g⁻¹[42, 43]. The charge-discharge reaction is shown in following Equation 2-8, which contributes to the capacitive behavior of manganese dioxide with the exchange of protons or cations and transitions in valence states of manganese.

$$MnO_2 + xC^+ + yH^+ + (x+y)e^- \rightarrow MnOOC_xH_y$$
 2-8

2.4.2.2 Conducting Polymers

Since the synthesis of polyacetylene [45] in 1970's, conducting polymers (CPs) have experienced a fast development for various applications over the past 40 years because of their unique physical and chemical properties [46]. Many CPs have been extensively studied as potential materials for ES utilization, such as polypyrrole (PPy) [47], polyaniline (PAn) [48], polythiophene (PTh) [49], poly(3,4-ethylenedioxythiophene) (PEDOT) [50].

| Polymer | Doping | Potential | Theoretical | Conductivity | Doping type |
|---------|--------|-----------|-------------|--------------|-------------|
| | level | range(v) | SC (F g-1) | (S cm-1) | |
| РРу | 0.33 | 0.8 | 620 | 10-50 | P-doping |
| PAni | 0.5 | 0.7 | 750 | 0.1-5 | P-doping |
| PTh | 0.33 | 0.8 | 485 | 300-400 | N,P-doping |
| PEDOT | 0.33 | 1.2 | 210 | 300-500 | N,P-doping |

 Table 2-1 Electrochemical properties of common CPs for ES application [24]

A common specification of CPs is the delocalized π -conjugated backbone of polymer chains, which can be ultra-conductive after certain redox or doping processes. Depending on the redox type reactions and polarity of dopant molecules, CPs are classified into two types: n-doped and p-doped [9]. N-doped CPs are reduced during charging and doped with cationic dopants while oxidation takes place on p-doped CPs when being charged. Doping level varies for different kinds of CPs because doping is related to how closely the positive or negative charges are spaced along the polymer backbone. For p-doped type of CPs, the doping level is approximately 0.3-0.5 dopant molecule per monomer. It has been reported that p-doped CPs are more stable than Ndoped CPs and also have wider scope of applications in electrochemical supercapacitors [50].



Fig 2-7 Schematic diagram of charging-discharging state for (a) p-type and (b) n-

type CP electrodes [9]

Compared to other carbon materials, CPs have better specific capacitance and relatively

lower SSA requirement used for capacitance due to fast and reversible reaction of doping-dedoping in bulk instead of at interface area. CPs are more electrically conductive, more environmental friendly, and less costly than metal oxides. Many factors, including selection of monomer, electrolyte and substrate, nano-morphology and dopant utilization, have important effects on the electrochemical applications of CPs. Among all the factors, dopant molecules greatly affect morphology, conductivity and capacitance of CPs.

2.4.3 Composite material

Even though metal oxides and conducting polymers store much more charges than EDLCs made of carbon materials, carbon materials are more stable and have excellent electric conductivity and longer cycle life due to the reversibility of electrostatic adsorption/desorption of ions. By preparing metal oxides or CPs/ carbon materials composite, metal oxides and CPs will show better retention due to enhanced mechanical stability and good capacitive behavior because of improved conductivity. With the usage of carbon materials as a scaffold, electrode material can be more porous, which contributes to large capacitance due to higher specific surface area. Composite electrodes are made of one type of material incorporated into another material, typically a layer of pseudocapacitive materials have higher energy density, but low mechanical stability, cycle life, electric conductivity and power density. Therefore, optimal ratio between several components is important. Significant attention has been generated on pseudocapacitive material/MWCNT composites as electrode materials. The addition of MWCNTs is beneficial due to their high surface area and excellent electric conductivity. The conducting polymer-WMCNTs can enhance polymer cyclic stability and elongate cycle life, which can be backed up with the fact that after adding CNTs, Polypyrrole-CNT composite electrode material showed 85% of initial capacitance after five thousand cycles in comparison to pure polypyrrole's retention of 66% of the initial capacitance [52]

2.5 Electrolyte for electrochemical supercapacitors

In conventional capacitors, dielectric materials are important. Higher dielectric constant means capacitors are capable of storing more charges. In electrochemical supercapacitors, electrolytes are paramount because for EDLCs they can provide ions to form electrochemical double layers and for pseudocapacitors, they participate in redox reactions that contribute to capacitance.

Since electrolytes play the role of charge mediators, their conductivity is of vital importance, which is relevant to solubility of the electrolyte ions, mobility of free ions, dielectric constant of bulky solvent and viscosity of solvent. Conway demonstrated an equivalent circuit model of single pore, which is shown Fig 2-8. The liquid electrolytes

can be classified into three categories: (a) aqueous electrolytes, (b) organic electrolytes and (c) ionic liquids. Solid electrolyte and gel electrolyte are under massive investigation as well [53].



Fig 2-8 Transmission line model for a single pore

2.5.1 Aqueous Electrolytes

Aqueous electrolytes can be acid solutions including H₂SO₄ and HCl [54], alkaline solutions such as KOH and NaOH [54], and neutral salt solutions like LiClO₄, Na₂SO₄ and KCl [56]. Aqueous electrolytes present higher ionic concentration and lower resistance, which is beneficial for ES devices to obtain higher capacitance and power

density. In addition, aqueous electrolytes can be prepared in an easier way at lower costs and can be used under common conditions. However, the biggest problem for aqueous electrolytes is their small potential window of only about 1.2 V, which strongly restricts the energy and power densities of the devices since voltage window plays an important role in achieving high energy and power.

2.5.2 Organic Electrolytes

Unlike aqueous electrolytes, organic electrolytes have a much larger voltage window reaching 3.5 V, which is the major advantage of organic electrolytes. In this sense, higher energy density can be achieved than using aqueous electrolytes. Acetonitrile and propylene carbonate (PC) are most commonly used among organic electrolytes. More salts can be dissolved in acetonitrile than in other organic solvents, but it is at the cost of sacrificing environment. By contrast, concentration of salts in PC is lower, but PC is environmentally friendly and can provide larger voltage window and better electric conductivity. However, most of organic solvents have high resistance, which is 20 times higher than that of aqueous electrolytes [3]. What's more, lower solubility of ions in organic solvents than in aqueous electrolytes leads to low power, low retention, complicated production and high cost of fabrication.

2.5.3 Ionic Liquids

Ionic liquids (ILs) are molten organic salts that have low melting temperature and low vaporization pressure with large potential window. ILs consist of pure cations and ions and ionic liquids often have better electric conductivity at higher temperatures. Their potential window is determined by electrochemical stability of ions [57].

2.6 Fabrication Methods of Electrode based on Conducting Polymer

CPs are under intensive research now and the most commonly used CPs are Polypyrrole (PPy), Polyaniline (PAni), Polythiophene (PTh) and their corresponding derivatives. CPs have a lot of advantages, including high theoretical specific capacitance, high electric conductivity, high charge density, lower equivalent resistance, high flexibility and low fabrication cost [24].

2.6.1 Electrochemical Properties of Conducting Polymers

Physical and electrochemical properties of CPs vary from each other. The chemical structures of commonly used CPs and derivatives are shown in Fig 2-9.



Fig 2-9 Chemical structures of commonly used CPs

After doping, conductivity of CPs can be enhanced by several orders of magnitudes, which is dictated by doping level, mobility of charge carriers, chemical environment (bulk or solution) and doping temperature [58]. Among common CPs in application of ESs, PAni and PPy can only be p-doped because their n-doping potentials are much lower than the reduction potentials of commonly used electrolytes. All CPs have certain working potential window. If potential is beyond the strict potential window, CPs may be degraded at more positive potentials and may turn to an insulating state at more negative potentials [24].

2.6.2 Synthesis of PPy

2.6.2.1 Chemical Synthesis

The product of chemical synthesis of PPy is black powders and its advantages include

high production rate, easy and stable synthesis process. The method allowed for controllable mass loading of electrodes and capability to modify of PPy polymer morphology.



Fig 2-10 Mechanism of synthesis of PPy

The mechanism of chemical synthesis of PPy involves monomer oxidation, which results in the formation of free cation radical species. Then, those free cation radicals combine with each other to form dimer. The dimer will continue to join other free radicals and eventually, long PPy chain will form. However, during the process, when cation radicals join each other, some will not fully discharge, which makes PPy to be positive charged [59]. From the mechanism of chemical synthesis of PPy, it is obvious that oxidants are needed, and it is also known that oxidants also have a great influence on the morphology of PPy. Therefore, choice of oxidants is very important for chemical synthesis of PPy. Commonly used oxidants are peroxydisulfate anions ($S_2O_8^-$), ferric cations (Fe^{3+}), and copper cations (Cu^{2+}) [60]. Under acidic conditions, oxidants such

as ferrous cations (Fe²⁺) [61], permanganate (MnO₄⁻) [62], dichromate (Cr₂O₇²⁻) [63] can also be used for synthesis of CPs. From table 2-2, we can clearly see that with the utilization of oxidants containing iron cations, a high conductivity can be achieved. It may be because that a part of iron cations contributes to conductivity of PPy powders. Ammonium persulfate is another promising candidate for chemical synthesis and was utilized in this research.

| Oxidant (mol dm ⁻²) | Additive (mol dm ⁻²) | Yield (g) | Conductivity (S cm ⁻¹) |
|--|----------------------------------|-----------|------------------------------------|
| (NH4)2S2O8 (0.1) | | 1.36 | 4.42 |
| (NH4)2S2O8 (0.1) | NaDBS (0.0225) | 2.01 | 0.570 |
| (NH4)2S2O8 (0.1) | NaANS (0.024) | 1.91 | 0.221 |
| Fe2(SO4)3 (0.1) | | 1.28 | 1.33 |
| Fe ₂ (SO ₄) ₃ (0.05) | NaDBS (0.0225) | 2.46 | 20.4 |
| (NH4)2S2O8 (0.05) | | | |
| Fe2(SO4)3 (0.1) | NaDBS (0.0225) | 2.44 | 26.1 |
| Fe2(SO4)3 (0.1) | NaANS (0.024) | 2.65 | 15.7 |
| Fe2(SO4)3 (0.1) | NaAS (0.022) | 2.24 | 40.7 |

 Table 2-2 Various oxidants for PPy chemical polymerization [60]

2.6.2.2 Electrochemical polymerization

Electrochemical polymerization has been widely used for PPy thin film sample making

and has been under intense investigation. It has a lot of advantages, including in-situ simultaneous polymerization at substrate surface, easy to control film thickness and composition by modifying parameters such as deposit current density and concentrations of composition.

Unlike chemical synthesis, it is not necessary to add oxidants in solutions to start synthesis because the reaction is initiated by electric current. There are various ways for deposition, such as potentiostatic deposition (with constant potential) [64], galvanostatic deposition (with constant current) [65], potentiodynamic deposition [66] and pulse electro-deposition [66,67]. Usually we choose the constant current density power source for deposition over the constant potential deposition, because with the increase in the film thickness, resistance of the deposit increases, which leads to more difficulties in ions attraction to the substrate and deposition. Among these four methods, pulse electro deposition is considered the best way to deposit uniform PPy thin films.



Figure 2-11 (Left) Schematic diagram of mechanism of fabrication of PPy film via pulse electro-deposition. ton – deposition time; toff – rest time. (Right) SEM images of (A) pulse electro deposited PPy and (B) galvanostatic deposited PPy

[55]

The structure of deposited PPy thin film depends strongly on applied current density [69]. For electrochemical synthesis, Py monomers and additives are dissolved in a solution and consumed on electrode surface. At the interface of electrode and electrolyte, a concentration gradient exists, which is the driving force for attracting monomers and additives to the substrate surface. However, the speed of diffusion is much slower than the speed of polymerization, which leads to defects in thin films [70]. Pulse electrochemical deposition method can solve this problem. When rest time begins, sufficient time is given for monomers to diffuse from the solution to electrode surface. In the end, uniform PPy thin films can be obtained, which can be clearly seen from SEM comparisons between the two samples (Fig 2-11). However, there are several challenges to prevent further application of PPy thin films for practical applications. First, unlike the product of black PPy powders by chemical synthesis, thin films are difficult to remove from substrates for further testing. If deposited PPy films on substrate are directly used, the capacitance would be low because of non-contributing components. Second, other reactions like substrate dissolution or reactions between substrate and other components in electrolyte may affect polymerization and ultimate capacitive performance. Third, conductivity of PPy film decreases along with the increase of film thickness, which makes it difficult to obtain thick films and high mass loading on substrate at the same time. Last, PPy thin films on substrate show adhesion problem during cycling due to film swelling and shrinkage, which leads to increased impedance and shorter cycle life.

2.6.3 Functions of Dopants

Anionic dopants are very important for the synthesis of PPy, and they will also affect the properties of final products.

For electrochemical synthesis, problems are the dissolution of substrate and poor adhesion of PPy films, since it is very easy for steel substrate to get oxidized. The steel substrate will form a layer of non-capacitive iron oxalate [71] which increases the resistance of charge transfer and reduces the total capacitance of PPy films. Adding aromatic anionic dopants with chelating properties can potentially solve this problem. Those dopants will be attracted to steel substrate and have reaction with iron. As a result, dopants bond on iron and restrict the further dissolution of iron substrate. Py will be oxidized at the surface of iron substrate and connect with dopants through electrostatic force, which drastically increase the adhesion between PPy films and substrates. Dopants function as mediators facilitating charge transfer, which is beneficial for decreasing the polymerization potential for PPy. The usage of aromatic dopants induce preferred orientation of PPy ring parallel to the electrode or growth surface, which can lead to increased conductivity [72].

For the chemical synthesis, anionic aromatic dopants are used [73]. Addition of those dopants can boost PPy powders capacitive performance, since they can decrease PPy particle size, reduce agglomeration, increase conductivity and increase cyclic ability [74]. There are four criteria to judge whether a dopant is an ideal candidate, which are large molecule size, multiple charges, high charge to mass ratio and redox active side groups. Large size of dopants can help to decrease PPy molecule size because of steric effect. Multiple charges can make dopants connect with several PPy chain at the same time, and dopants can function as bridges between multiple PPy chains to facilitate charge transfer, which can increase the conductivity of PPy. High charge to mass ratio of dopants can not only reduce agglomeration by strong electrostatic repulsion, but also can increase the capacitance of PPy at high scan rate due to their high mobility. When

a dopant possesses redox active side groups, it will also involve some redox reactions during charging and discharging process, which can increase the PPy's capacitance.

2.6.4 Dispersants for MWCNTs

For PPy based electrodes for supercapacitors, they have two biggest problems which limit further applications, which are low retention at high scan rate and low cyclic ability. Even though PPy is highly conductive, its conductivity is still not high enough when the scan rate is over 20 mv/s. Slow electron transfer speed can not catch high scan rate, which results in less charge storage. What's more, the swelling of PPy electrode will occur during charging and discharging process after several cycles, which will cause severe damage to the cyclic ability. In order to solve this problem, MWCNTs are added to system to prepare PPy/MWCNTs composite. First, MWCNTs can increase conductivity of whole composite drastically. Therefore, electrons transfer speed can be fast enough to match fast scan rate. Second, MWCNTs can form a network, which will restrict the mobility of PPy. As a result, the cyclic ability can increase a lot due to decrease of swelling [75].

Even though CNTs possess many good properties, it's hard for them to display those properties in the PPy/CNTs composites, since dispersion of CNTs is a challenge. Due to their nano-scale dimensions and resulting high surface areas of particles, the attractive forces between CNTs are high. Besides, high aspect ratio and high flexibilities also increase the possibility of intertube entanglement and close packing. Therefore, CNTs usually assemble into bundles containing hundreds of close-packed CNT tightly bound by van der waals attraction energy [76].

Using surfactant to decrease surface energy to disperse CNTs is particularly attractive because the delocalized π -electrons of carbon nanotubes is beneficial for adsorption of various dispersants on the surface via π - π stacking interactions without any damage. Therefore, in the past 10 years, surfactants have been widely used to prepare welldispersed CNTs solutions [74].

The procedure of non-covalent surface treatment by surfactants is following: first, using ultrasonication to mechanically exfoliate the bundles. Then, adding surfactants and make them absorbed on the nanotubes. Last, ultrasonicating again in order to obtain individual carbon nanotubes. A mechanism of this procedure was proposed (figure 2-12). Ultrasonic treatment can provide high local shear to separate nanotubes from bundle ends. Once gaps at the bundle ends are formed, surfactants will adsorb on the bundle ends to facilitate further separation. Eventually individual nanotubes will separate from the bundle [78]. Generally, ionic surfactants are more suitable for CNT water solutions, and nonionic surfactants are preferable when organic solvents are used.



Fig 2-12 Mechanism of nanotube isolation from bundle obtained by ultrasonication and surfactant stabilization

Surfactants are good at dispersing CNTs, but CNTs wrapped by surfactants can not contact with polymer matrix tightly. Therefore, using surfactants will decrease the interfacial adhesion between CNTs and polymer matrix, which eventually undermine whole composites performance. Recently, small molecules (Fig 2-13) with several benzene rings (number of rings is usually under 5) and charge groups are utilized to disperse carbon nanotubes. The mechanism to dispersing CNTs for those small molecules is similar to that for surfactants. However, since π -stacking interactions of the benzene rings onto the CNT surface are much stronger than hydrophobic attraction between the CNT surface and surfactant's hydrophobic tail, those small molecules have higher dispersive efficiency. Besides, those molecules won't reduce the interfacial adhesion owing to their much smaller size. If the polymer matrix are some conjugated

polymers, those molecules will increase the interfacial adhesion by π - π interaction between CNTs and Conjugated polymers instead [79].



Fig 2-13 Structures of different kinds of small molecules which can disperse

CNTs

3. Problem Statements and Objectives

PPy has many advanced properties, like high specific capacitance, low cost, flexiblility, and easy to process. However, PPy is not perfect, and its some problems limit its further applications. In order to improve PPy's performance as supercapacitor's electrodes, first, advanced dopants are necessary to synthesis PPy. Dopants with high charge to mass ratio, large molecular size and polyaromatic structures have great positive influences on morphology and capacitive properties of PPy and can drastically improve PPy's capacitance. Therefore, the selection of advanced dopants is very important in my research. Second, adding MWCNTs can solve PPy's problems of low retention and low cyclic ability, since they are highly conductive and can form a network in the system. However, the dispersion of MWCNT is a challenging step because it has high aspect ratio that enhances the possibility of agglomeration, which makes the selection of dispersing agent of vital importance. As a result, problems that have been encountered in this research include selection of advanced dopants, dispersion of MWCNT and procedure to prepare PPy/MWCNTs composites.

The overall objective of my thesis work is to develop advanced electrode materials for electrochemical supercapacitors and it includes the following:

• Optimizing selection of advanced anionic dopants for PPy thin films and powders and investigate the influence of dopant structure on PPy properties.

• Developing novel dispersing agents for MWCNT to synthesize composite materials and multifunctional dopants that can act as dispersant and dopant at the same time.

• Fabrication of electrodes and electrochemical testing

4 Approaches and Methodology

4.1 Approaches

PPy powders are synthesized by chemical polymerization process with the presence of various anionic dopants and ammonium persulfate ((NH₄)₂S₂O₈, APS) as an oxidant. Multi-walled carbon nanotubes (MWCNTs) are incorporated into PPy matrix to enhance mechanical and electrical properties. The product morphology then studied and electrodes were fabricated for capacitive tests.

4.2 Methodology

4.2.1 Selection of organic molecules for PPy doping

Dopants' structures have a strong influence on capacitive behaviors of electrode materials. It was found that dopants with large molecular size, high charge-mass ratio and aromatic rings are preferred. Aerosol 22, 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate, potassium benzene-1,2-disofulnate, Ponceau S, Trypan blue, Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt solution and Poly (acrylic acid-co-maleic acid) solution are dopants tried in this research.

4.2.2 Dispersants for CNTs

Addition of CNTs to PPy can bring a lot of benefits, which are higher conductivity, higher retention, better cyclic ability. However, uniform dispersion of CNTs is very

important for the realization of their functions. Multifunctional dopants can solve this problem by utilizing the advantages of their multiple aromatic rings and charges. However, for the small dopants which can not disperse CNTs, using dispersants specially for CNTs becomes necessary. Pyrocatechol violet is the dispersing agent studied in this research

5. Experimental Procedure

5.1 Materials Preparation

All materials involved in this research are listed in Table 5-1.

| Category | Chemical Name | Source |
|------------------|---|---------------|
| Monomer | Pyrrole (>98%) | Sigma Aldrich |
| Oxidant | Ammonium Persulfate | |
| Dopants | 4,4'-Diazido-2,2'-stilbenedisulfonic acid | |
| | disodium salt tetrahydrate | |
| | Poly (acrylic acid-co-maleic acid) solution | |
| | Trypan blue | |
| | Ponceau S | |
| | Potassium benzene-1,2-disulfonate | |
| | Aerosol S | |
| | Poly (4-styrenesulfonic acid-co-maleic | |
| | acid) sodium salt solution | |
| Dispersants | Pyrocatechol violet | Sigma Aldrich |
| Additive | Multi-walled carbon nanotubes | Bayer Inc. |
| Electrolyte salt | Sodium sulfate (Na ₂ SO ₄) | Sigma Aldrich |
| | Aluminium potassium sulfate | |
| | dodecahydrate | |
| | Aluminum sulfate | |

| Other chemicals | Poly (vinyl butyral-co-vinyl alcohole-co- | Aldrich |
|-----------------|---|-------------|
| | vinyl acetate) | Chemical |
| | Ethanol | Greenfield |
| | | Alcohol Inc |
| Current | Nickel foam (porosity ~95%) | Vale (CA) |
| collectors | | |

5.2. Chemical synthesis of PPy/MWCNT composite materials

5.2.1 Procedure for multifunctional dopants

Multifunctional dopants were developed in this investigation. Such dopants are added first to disperse MWCNTs and then Py monomer are added. After that, mix solutions containing APS and Py monomer and dopant together. Reaction begins after mixing and should be kept at low temperature around 4 °C. Reactions take at least four hours to complete and for the first two hours, the solution should be processed with ultrasonication or magnetic stirring. After the final suspension with PPy powders is obtained, vacuum filtration with filter paper are used to separate powders and excess dopants and oxidants. The powders should be kept in oven for at least 24 hours at 60 °C to dry out.

5.2.2 Procedure for non-multifunctional dopants

If dopants are not multifunctional, PPy powders must be synthesized first and then mix together with MWCNTs powders using dispersants. To synthesize PPy powders, the first step is to dissolve Py monomer with dopants in deionized water and to stir continuously during experiment in ice bath (about4 °C). After that, mix solutions containing APS and Py monomer and dopant together. Reaction begins after mixing and should be kept at low temperature around 4 °C. Reactions take at least four hours to complete and for the first two hours, the solution should be processed with ultrasonication or magnetic stirring. After the final suspension with PPy powders is obtained, vacuum filtration with filter paper are used to separate powders and excess dopants and oxidants. The powders should be kept in oven for at least 24 hours at 60 °C to dry out.

Then as-prepared dopants-doped PPy was put into solution containing dispersants and sonicated in an ultrasonic bath for 20 mins in order to form a homogeneous colloidal solution. After that, MWCNT was added and further ultrasonicated for 1 hr. A stable dopants-doped PPy/MWCNT suspension was obtained. A vacuum filtration process was applied to fabricate homogeneous slurry. Excess dispersants in the mixture were removed by the filtration system until the DI-water dropped from the funnel was colorless. The powders should be kept in oven for at least 24 hours at 60 °C to dry out.

5.3 Fabrication of Electrodes

To fabricate electrodes for electrochemical testing, the composite powders were ground in a mortar first. Then, Poly (vinyl butyral-co-vinyl alcohole-co-vinyl acetate) (PVB) binder and ethanol were added to prepare composites' slurry. The reason for use of ethanol is that PVB is better dissolved in ethanol to be fully utilized and ethanol evaporates faster than water. After weighing a clean piece of Ni foam, slurry is pasted onto the nickel foam and the composites penetrated inside the pores of Ni foam. The working area of an electrode is 1 cm² and active material is pasted on both sides. The electrode surface should be full covered with PPy powders without any exposure of Ni, otherwise CV curve will have some noise peaks caused by exposure of Ni. Then, Ni foam pasted by slurry was dried and weighed again to calculate the mass loading of active materials. After that, rolling machine is used to reduce the thickness of the pasted Ni foam to 30% of its original thickness, which helps powders impregnate into the Ni foam.

5.4 Characterization

5.4.1 Morphology Characterization

The morphology of PPy powders from chemical synthesis and PPy-MWCNT composites materials was characterized by JEOL JSM-700F Scanning Electron Microscope (SEM) under magnification from 5,000-50,000X

5.4.2 Electrochemical Characterization

Electrochemical tests include Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The tests were conducted using a PATSTAT 2273 Potentiostat from Princeton Applied Research.

5.4.2.1 Cyclic voltammetry

In a cyclic voltammetry experiment, the potential is varied at a constant linear rate, which means dV/dt is constant, and the current response is measured.

$$I = \frac{dq}{dt} = \frac{Cdv}{dt}$$
 5-1

Where Q is amount of accumulated charge, C is capacitance and V is applied potential (V). For the ideal electrodes for supercapacitors, the capacitance should be a constant. This implies, since voltage is varying linearly with time, that the capacitance is potential independent. Therefore, ideal capacitive behavior will result in a constant current response during a cyclic voltammetry experiment when scan rate is fixed. In the plot, the cyclic voltammogram will be in the shape of an ideal box. A schematic is shown in the fig 5-1 below.



Fig 5-1 Schematic cyclic voltammograms of a supercapacitor electrode (a) at low scan rate (b) at high scan rate

The red curve is characteristic of a low scan rate voltammogram while the black curve is the common shape observed at high scan rates. From the plot, it is much easier for electrodes to keep ideal capacitive behavior when the scan rate is low. When scan rate is high, a strong deviation from the box shape for the CV curve is observed. This can be explained by the resistance of the electrode materials. Relatively slow electron transfer speed and reaction speed can not match high scan rate, which induces different current respond under different potential.

PPy-MWCNT composites were tested in the voltage window -0.5-0.4 V vs SCE at scan rates of 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s. These scan rates were tested sequentially with a 15 second equilibration period between tests at different scan

rates. 2 cycles were performed at 2 mV/s, 3 cycles at 5 mV/s, 5 cycles at 10 mV/s, 10 cycles at 20 mV/s, 10 cycles at 50 mV/s, and 10 cycles at 100 mV/s.

Capacitances under different scan rates can be calculated from CV curves using the following equation,

$$C_m = \frac{A}{2mv(V_{max} - V_{min})}$$
5-2

where A is the integrated area of CV curve, m is mass of active materials on current collector, v is scan rate and $(V_{max}-V_{min})$ is the working potential window of PPy (which is 0.9 V).

5.4.2.2 Impedance Spectroscopy

In an impedance spectroscopy experiment, a small amplitude of 5 mV of sinusoidal alternating voltage (E) is applied in the EIS investigation in the frequency ($\omega/2\pi$) range of 10 mHz to 100 kHz, and the resulting current response (I) is measured. The amplitude (E_o and A) and the phase shift (φ) of the current response with respect to the applied voltage signal yields information on the real (Z') and imaginary (Z'') components of the impedance (Z) of the electrode.

$$E(t) = E_o \cos(\omega t) = E_o \exp(j\omega t)$$
 5-3

$$I(t) = A\cos(\omega t + \varphi) = A\exp(j(\omega t + \varphi))$$
 5-4

$$Z = \frac{E(t)}{I(t)} = \frac{E_0}{A} \exp(-j\varphi) = Z' - iZ''$$
 5-5

If the electrode exhibited purely resistive behavior then the lag in the current response with respect to the voltage signal (quantified by the term φ) would be 0. In all other cases, including capacitive or in complex capacitive circuits, the quantity $\varphi \neq 0$. Pure capacitive behaviour will result in $\varphi = 90^{\circ}$.



Fig 5-2 Schematic Nyquist plot showing general features typically displayed by a

pseudocapacitive electrode

The plot of the imaginary vs real component of the measured impedance shown above in Fig 5-2 is called a Nyquist plot. Each point on the graph corresponds to a different frequency ω of the applied voltage signal and the corresponding measured current signal. The highest frequency points are clustered in the semi-circular feature on the left of the graph while the lowest frequency points are part of the near vertical line of the right of the graph. Nyquist plots can be split into three zones, which are high frequency zone, transition zone and low frequency zone. For the high frequency zone, the semi-circular feature is the result of the resistance to the faradaic reactions governing the pseudocapacitance which can be thought of as existing in parallel with the double layer capacitance. This feature is observed in a wide range of materials that display pseudocapacitance such as MnO₂ and PPy. The medium frequency section of the plot is a transition region. It is a common feature observed in porous materials and arises principally because of the distribution of resistances the porous structure creates. The near-vertical section of the Nyquist plot in the low frequency region corresponds to pure capacitive behavior. The frequency at which pure capacitive behavior is observed is of particular interest because it is informative of the electrodes power capability. Electrodes that have a higher transition frequency will maintain capacitive behavior as well as charge storage capability at higher charge/discharge rates compared to those with a smaller transition frequency. This transition frequency can be readily observed by treating the electrode as a pure capacitance.

The capacitance can be broken down into its real and imaginary components as following

$$C = C' - iC'' \qquad 5-6$$

and can be calculated from the following equations

$$C' = \frac{Z''}{2\pi f |Z|^2}$$
 5-7

$$C'' = \frac{Z'}{2\pi f |Z|^2}$$
 5-8

Where C is the capacitance, c' is real part of capacitance, c'' is the imaginary part of capacitance, f is the testing frequency and Z equals to $\sqrt{(Z')^2 + (Z'')^2}$. The peak in the imaginary capacitance curve corresponds to the transition frequency in the Nyquist plot.

6 Results and Discussion

6.1 Fabrication of PPy/MWCNT composite using Aerosol 22 as dopants

As stated before, ideal dopants should be aromatic molecules with large size, multiple charges, and high charge to mass ratio. However, we don't know whether non-aromatic molecules with such features can also perform well. In this chapter, Aerosol 22 was selected as PPy dopant. Since Aerosol 22 has multiple charge groups and long alkyl group, it can also function as a surfactant to disperse MWCNTs. Therefore, Aerosol 22 can be regarded as multifunctional dopants in this experiment.



6.1.1 Morphology Characterization

Fig 6-2 is the SEM image of PPy/MWCNT composite doped by Aerosol 22. The image shows the formation of PPy coated MWCNT. The coatings were relatively uniform. It is suggested that good dispersion of MWCNT and π - π interaction of MWCNT and



PPy promoted the formation of MWCNT coated by PPy.

Fig 6-2 SEM image of PPy/MWCNT doped by Aerosol 22

6.1.2 CVs and Capacitance



Fig 6-3 CVs for PPy–MWCNT (20 wt%) composite electrodes at scan rates of (A) (a) 2, (b) 5, (c) 10 mV s⁻¹(B) (a) 20, (b) 50, (c) 100 mV s⁻¹, prepared using Aerosol 22 dopant

From the Fig 6-3, we can clearly see that when the scan rate is 2, 5, 10 mV/s, the CV curves of PPy/MWCNT composite is still nearly ideal box shape, which indicates good

capacitive behavior. However, after scan rate increase to 20, 50, 100 mV/s, a strong deviation from ideal box shape is observed.

This trend can be clearly seen on the Fig 6-4. When the scan rate is 2 mV/s, even though the CV curve is closed to box shape, the capacitance calculated from area of CV curve is only 72 F/g, which means less charges were stored in this electrode. When the scan rate increases to 100 mv/s, the capacitance decreases to 32 F/g, corresponding to the narrow area of CV curves at high scan rate. The retention for PPy/MWCNT composite doped by Aerosol S is 44.4%.



Fig 6-4 C_m and C_s versus scan rate for PPy–MWCNT composite electrode doped

by Aerosol 22 dopants
Multiple charges and large molecule size of Aerosol 22 can provide excellent dispersion of CNTs, promote PPy polymerization and facilitate the absorption of PPy to the CNTs' surface. The capacitance retention of this composite electrode at high scan rates is not bad and CV curve is very close to box shape at low scan rate. From this point of view, Aerosol 22 is a decent multifunctional dopant. However, the biggest problem for PPy/MWCNT composite doped by Aerosol 22 is low current response, which results in low capacitance. Considering the structure of Aerosol 22, low current response should be the results of long alkyl groups. Long alkyl groups are hydrophobic and can potentially reduce the diffusion of ions in the electrolyte. As a result, first, it will affect the counter ions to accumulate at the surface of electrode, which elongates the distance between electrode surface and IHP or OHP layer. Second, it will limit ion diffusion inside the electrodes and their contribution to charging and discharging reactions, resulting in less charge produced at the electrodes. Therefore, even though Aerosol 22 can facilitate the formation of good morphology for PPy/MWCNT composite, the current responses of this composite electrode are still low.

6.1.3 Impedance spectroscopy

Impedance data of PPy/MWCNT doped by Aerosol 22 was collected in a wide frequency range and presented in a Nyquist plot in Figure 6-5(A). The Nyquist plot shows relatively low real part of impedance, which means low resistance. Ideal impedance plot for supercapacitors should be straight line parallel to the imaginary impedance Z" axis at low frequency region. The slop of this curve is close to 90° at low frequency region, which indicates good capacitive behavior.

Besides, impedance data provides an alternative way to analyze capacitance of samples. Two parts of complex form of capacitance (C_s) , real capacitance (C_s) and imaginary capacitance (C_S ") (Fig 6-5(B)), also include a lot of useful information about the electrodes. Real capacitance calculated from impedance data is positive related to the capacitance calculated from area of CV curve. As the frequency increases, real capacitances present continuous reduction and eventually remain constant due to the ion diffusion limitation with high external power. Since capacitance of PPy/MWCNT composite doped by Aerosol 22 is relatively low, the real capacitance calculated from impedance data is also not high. In terms of imaginary capacitance, for relaxation type dispersion, it will increase to a peak and then decrease sharply and the peak frequency is also called relaxation frequency. The dependencies of this composite are typical relaxation type dispersion. The relaxation frequency of this composite, corresponding to the maximum of C_s", is higher than 0.1 Hz, which means this electrode can still have good capacitive behavior when the scan rate is high. This result explains why this electrode has good retention.



Fig 6-5 (A) Nyquist plots of complex impedance (B) (a) Cs' and (b) Cs" versus frequency for PPy–MWCNT (20 wt%) composite electrodes, prepared using Aerosol 22 dopants.

6.1.4 Summary

In total, Aerosol S can be used as dopant. Its large molecule size and multiple charge groups provide excellent dispersion of CNTs, promote PPy polymerization and facilitate the absorption of PPy to the CNTs' surface. The retention of this composite electrode is good and CV curve is very close to box shape at low scan rate. However, the electrode material showed low current response caused by long alkyl groups of dopantsr. Multiple charges and high charge to mass ratio of Aerosol S dopant are more important for good capacitive performance of doped PPy electrodes..

6.2 Fabrication of PPy/CNT composite using aromatic dopants

Aromatic dopants have a lot of advantages over non-aromatic dopants. First, such dopants can promote preferred orientation of PPy rings, which can significantly increase

the conductivity of PPy polymer chain. Second, dopants with multiple charged groups can function as charge transfer mediators, which facilitate charge transfers between PPy chains or PPy chain and CNTs. Thus, they can increase charge interchain mobility drastically. From this point of view, aromatic dopants are more promising than nonaromatic dopants for the application in supercapacitors. In this chapter, several aromatic molecules were selected to be used as dopants to fabricate PPy/MWCNT composite electrodes.

6.2.1 Using small aromatic dopants

Small aromatic dopants usually have high charge to mass ratio, which means high mobility. This is beneficial for improving PPy capacitive performance. However, they only have one or two benzene rings. It is hard for small aromatic dopants to be absorbed on the MWCNTs' surface for dispersion. In order to prepare PPy/MWCNTs composites using small dopants, another dispersant must be used for dispersion of CNTs.

4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate and potassium benzene-1,2-disofulnate are small aromatic molecules. Because of small size and multiple charges, they usually have high charge to mass ratio, which is beneficial for boosting capacitance performance. As introduced before, since those molecules only have one or benzene rings, they are not capable of dispersing CNTs. In order to use these two small molecules as dopants to prepare PPy/MWCNTs composite, in this chapter, pyrocatechol violet is used as dispersants to specially disperse CNTs.



Fig 6-6 Chemical structures for small aromatic dopants (A) 4,4'-Diazido-2,2'stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-

disofulnate



Fig 6-7 Chemical structures for pyrocatechol violet

6.2.1.1 Morphology characterization

Fig 6-8 is the SEM image of PPy/MWCNT composite doped by potassium benzene-

1,2-disofulnate, which is fabricated by mixing of the suspensions, followed by a vacuum filtration process. The results indicate that MWCNTs were well dispersed in the PPy matrix. Good dispersion of MWCNTs allowed the fabrication of PPy electrode with improved capacitive performance.



Fig 6-8 SEM image of PPy/MWCNT composite doped by potassium benzene-1,2-

disofulnate

6.2.1.2 CVs and Capacitance

It was found that CVs at scan rates of 2, 5, 10 mv/s (Fig 6-9) have nearly box shapes, which indicate good capacitive behavior at low scan rates. When the scan rate increases over 20 mV/s, deviations from box shapes for CV curves were observed. Unlike the

dopant used before, even though the CV curves are slightly tilted, they still have high current response and large area at high scan rate (Fig 6-10). Fig 6-11 shows the capacitance is 61 g/F at 100 mV/s for 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate and 65 g/F at 100 mV/s for potassium benzene-1,2-disofulnate, which are 80.2% retention and 67.7% retention (much higher than the data from literature for other dopants), respectively. The high retention can be accounted for high charge to mass ratio of dopants. At high scan rate, mobility of these two dopants is high enough to catch up fast scan speed so that charging and discharging reactions can still happen and charges can still be stored to some extent. Therefore, PPy/MWCNT composites doped by small aromatic molecules still can have good capacitive performance at high scan rate. Actually, high capacitance at 100 mV/s is very important, which indicates both electrodes are promising for applications in the future.



Fig 6-9 CVs for PPy/MWCNT composite electrodes at scan rates of (a) 2, (b) 5,
(c) 10 mV s⁻¹, prepared using (A) 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-disofulnate



Fig 6-10 CVs for PPy/MWCNT composite electrodes at scan rates of (a) 20 (b) 50 (c) 100 mV4 s⁻¹, prepared using (A) 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-disofulnate



Fig 6-11 Cm and Cs versus scan rate for PPy/MWCNT composite electrodes, prepared using (A) 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-disofulnate

6.2.1.3 Impedance spectroscopy

Fig 6-12 is the Nyquist plot for both composite electrodes. They both have very small diameter for the high frequency Faradaic charge transfer semi-circular feature, which indicate small resistance to Faradaic reactions governing the pseudocapacitors. They both move toward an essentially vertical segment indicative of capacitive behavior as

the frequency decreases. Their slope of the Z" versus Z' was close to 90° at low frequency region, indicating good capacitive properties. The two electrodes show relatively low resistance (R = Z'). At 0.01 Hz, the real part of impedance of composite doped by potassium benzene-1,2-disofulnate is 0.59 Ω , which is a little bit lower than that of composite doped by 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (2.47 Ω). In another plot (fig 6-13), the frequency dependencies of the AC capacitance for both composites show typical relaxation type dispersion, as indicated by the reduction in C' with increase in frequency and a maximum in the frequency dependence of C". At low frequency region, real capacitance calculated from impedance data of PPy/MWCNT composites doped by 4,4'-Diazido-2,2'stilbenedisulfonic acid disodium salt tetrahydrate is lower than that of PPy/MWCNT composites doped by potassium benzene-1,2-disofulnate, which corresponds to the capacitance calculated from areas of CV curves. The relaxation frequency, corresponding to the maximum of Cs", are 0.2 Hz and 0.16 Hz for composite doped by ,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate composite and potassium benzene-1,2-disofulnate, respectively, indicating excellent capacitive performance at high scan rate. In conclusion, the results of impedance spectroscopy testing, in good agreement with the results from CV testing, show that small aromatic dopants can boost capacitive performance of PPy/MWCNT composite at high scan rate drastically.



Fig.6-12 Nyquist plots of complex impedance for PPy/MWCNT composite electrodes, prepared using (A) 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-disofulnate



Fig 6-13. (a) Cs' and (b) Cs" versus frequency for PPy/MWCNT composite electrodes, prepared using (A) 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (B) potassium benzene-1,2-disofulnate

6.2.2 Using large aromatic dopants

Large aromatic dopants have a lot of advantages. First, large size of dopants can reduce PPy particle size, which can increase surface area. Second, since they have at least three or four benzene rings, it is much easier for them to get absorbed at the CNTs surface through π - π interaction. They can help to disperse CNTs through their electrostatic

repulsion. In this sense, large aromatic dopants are multifunctional. Using multifunctional dopants can simplify experimental procedures. All chemicals can be mixed together at first without any afterwards remixing. In this way, PPy can coat MWCNTs to form PPy/MWCNTs composites. There is no doubt this pattern can significantly facilitate charge transfers between PPy and MWCNTs, which increase conductivity and capacitance of whole system, especially at high scan rate.

In this chapter, Ponceau S and trypan blue were investigated as large aromatic dopants. They both have large molecule size, multiple aromatic rings and multiple charges, which potentially can be used as excellent dopants.



Fig 6-14 Chemical structures of (A) trypan blue (B) Ponceau S

6.2.2.1 Trypan blue

6.2.2.1.1 CVs and Capacitance

From Fig 6-15(A), even at low scan rate, there is a strong deviation from ideal box shape and the current is very low, which indicating poor capacitive performance. Fig 6-15(B) is the plot of Cm and Cs versus scan rate. Capacitance is 19.84 F/g at 2 mV/s and 2.54 F/g at 100 mv/s. The retention is only 13%. It is easy to tell trypan blue is not a good dopant from those CVs data. The reasons can be following: first, even though trypan blue has large size and multiple charges, the charge to mass ratio for this dopant is low, which means low mobility of trypan blue. In this sense, it is hard for trypan blue to participate in charging and discharging process, resulting in less charges storage. Second, even though the existence of two NH₂ groups can be beneficial for trypan blue absorption on MWCNTs, NH₂ groups of trypan blue can also be detrimental for Py polymerization. The dissolution of trypan blue in water can result in partial protonation of such groups. In this case, the trypan blue structure includes positively charged protonated NH₂ groups and anionic SO_3^- groups at the same time. As a result, partial charge compensation of the SO₃⁻ groups limits their involvement in the polymerization process.



Fig 6-15 (A) CVs at scan rates of (a) 2, (b) 5, (c) 10 mV s⁻¹ (B) Cm and Cs versus



6.2.2.1.2 Impedance spectroscopy

The Nyquist plot (Fig 6-16 (A)) clearly shows the poor capacitive performance of this PPy/MWCNT composite doped by trypan blue. The resistance (R=Z') is extremely large, which can be attributed to low conductivity of defective PPy chains. The slope of Z'' versus Z' is much smaller than 90°, which indicates bad capacitive behaviors. In another plot (Fig 6-16(B)), the frequency dependencies of the AC capacitance for PPy/MWCNT composites doped by trypan blue do not show typical relaxation type dispersion, since a maximum in the frequency dependence of C'' was not observed within testing frequency region. It is highly possible that relaxation frequency exists, but is much lower than 0.01 Hz, which is in good agreement with results derived from CVs data. At 0.01 Hz, real capacitance calculated from impedance data is only 0.12



 F/cm^2 , which corresponds to low capacitance calculated from areas of CV curves.

Fig 6-16 (A) Nyquist plots of complex impedance (B) (a) Cs' and (b) Cs" versus

frequency for PPy/MWCNT composite electrodes doped by trypan blue

6.2.2.2 Ponceau S

From structures, Ponceau S is a very promising dopant. It has large molecule size, multiple charges, high charge to mass ratio (4 charge groups to 4 benzene rings) and redox active groups (nitrogen double bonds). Therefore, a lot of efforts have been taken to investigate Ponceau S.

6.2.2.2.1 Morphology Characterization

Multifunctional dopants can function as dispersants for MWCNT and promote PPy deposition on MWCNT during chemical synthesis. Fig 6-17 shows PPy-MWCNT composite, prepared using Ponceau S. From the SEM images, MWCNTs were dispersed evenly and coated by a thin layer of PPy. However, PPy particles were also observed.

The reason may be that Ponceau S's large molecule size reduces electrostatic attraction between Py and dopants. Therefore, not all PPy polymerized at the surface of MWCNTs. Small amount of Py monomers polymerized away from the MWCNTs surface and aggregated into large particles. This morphology is not ideal, and will affect the whole systems conductivity, especially the charge transfer between PPy and MWCNTs.



Fig 6-17 SEM image of PPy/MWCNT composite doped by Ponceau S

6.2.2.2 CVs and Capacitance

At low scan rate, the areas of CV curves are large (Fig 6-18), which indicates good

capacitive properties. However, there are obvious peaks between -0.5 V and -0.4 V, which are probably caused by reduction of nitrogen double bonds. When the scan rate is high, the shape of CV curve undergoes strong deviation from box shape, which can be accounted for poor electrolyte access to active material and release of dopants from the electrode to electrolyte solution. The evidence is that transparent colorless electrolyte solution changed to red solution after testing and Ponceau S water solution is red. In this case, a large amount of dopants left electrode during testing, resulting in less dopant staying at electrode to participate in charging and discharging process. As a result, way less charges were accumulated and capacitance was low at high scan rate. From the plot C_m and C_s versus scan rate, specific capacitance at 2 mV/s is 114 F/g and 43.5 F/g at 100 mV/s, which is only 38% retention. This capacitance retention is low in comparison with results obtained using other dopants. However, the redox active Ponceau S contributed to capacitance of PPy.



Fig 6-18 CVs for PPy–MWCNT (20 wt%) composite electrodes at scan rates of (A) (a) 2, (b) 5, (c) 10 mV s⁻¹(B) (a) 20, (b) 50, (c) 100 mV s⁻¹, prepared using Ponceau S



Fig 6-19 Cm and Cs versus scan rate for PPy–MWCNT composite electrode doped

by Ponceau S dopants.

6.2.2.3 Impedance spectroscopy

Fig 6-20 is the Nyquist plot for PPy/CNT composites doped by Ponceau S. It has very small diameter for the high frequency Faradaic charge transfer semi-circular feature. As the frequency decreases, it moves toward an essentially vertical segment indicative of capacitive behavior. Their slope of the Z" versus Z' was close to 90° at low frequency region, indicating good capacitive properties. It shows relatively low resistance (R = Z'). At 0.01 Hz, the real part of impedance of composite doped by Ponceau S is 1.5 Ω . Fig 6-21 is the real capacitance and imaginary capacitance versus frequency. The

frequency dependencies of the AC capacitance for PPy/ MWCNT composite doped by Ponceau S show typical relaxation type dispersion, as indicated by the reduction in C' with increase in frequency and a maximum in the frequency dependence of C". At 0.01 Hz, real capacitance calculated from impedance data is 2.2 F/cm², which matches the capacitance calculated from area of CV curve. The relaxation frequency, corresponding to the maximum of C_s", is 0.07 Hz, which is not high. This is in good agreement with relatively low retention derived from CV data.



Fig 6-20 Nyquist plots of complex impedance for PPy/MWCNT composite doped

by Ponceau S



Fig 6-21 (a) Cs' and (b) Cs" versus frequency for PPy/MWCNT composite

electrodes doped by Ponceau S

6.2.3 Summary

In conclusion, aromatic dopants have a lot of advantages over non-aromatic dopants. Molecules having aromatic rings with SO_3^- charge groups are easily attracted to PPy chains to compensate positive charges and promote polymerization. Usually, PPy doped by small aromatic dopants with high charge to mass ratio can have high retention, which even can reach to 80%. Large aromatic dopants can be absorbed by MWCNTs through π - π interaction. Electrostatic repulsion between charges groups of dopants can provide excellent dispersion for CNTs. Furthermore, absorption of dopants on MWCNTs can also facilitate PPy coating on MWCNTs, which can increase conductivity of whole systems drastically by promoting charges transfer between MWCNTs and PPy.

6.3 Fabrication of PPy/MWCNT composite using polymer dopants

Polymer dopants attract a lot of attention due to their large size and multiple charge groups, which can increase interchain charge transfer between PPy macromolecules and improve cyclic ability. Poly (acrylic acid-co-maleic acid) and poly (4-styrenesulfonic acid-co-maleic acid) sodium salt with 4-styrenesulfonic acid: maleic acid mole ratio of 3:1 (PMSS –SR31) were used as polymer dopants in this chapter.



Fig 6-22 Chemical structures for (A) PMSS-SR31 (B) Poly (acrylic acid-co-maleic

acid)

Fig 6-22 shows their chemical structures. The main difference between two polymer dopants is PMSS-SR31 has aromatic rings and Poly (acrylic acid-co-maleic acid)

doesn't. Moreover, PMSS-SR31 has SO₃⁻ groups, which offer an advantage of nearly pH independent charge. Electrochemistry testing was used to judge the effectiveness of these two polymer dopants. Since those polymer dopants can not disperse MWCNTs, another dispersant has to be used. Pyrocatechol violet (PV) was used in this chapter as dispersants to prepare PPy/MWCNTs composite.

6.3.1 Poly (acrylic acid-co-maleic acid) solution

6.3.1.1 CVs and Capacitance



Fig 6-23 CVs for PPy–MWCNT composite electrodes doped by Poly (acrylic

acid-co-maleic acid) solution at scan rates of (a) 2, (b) 5, (c) 10 (d) 20 (e) 50 (f) 100

mV s⁻¹

Fig 6-23 shows CV curves of PPy/MWCNTs doped by Poly (acrylic acid-co-maleic acid) solution. The CV curves all strongly deviate from box shape and have low current. The capacitance is 12 F/g at 2 mV/s, and 0.35 F/g at 100 mV/s. This dopant only has carboxylic groups with a pH dependent charge, which resulted in poor electrochemical performance. By contrast, SO₃⁻ groups of PMSS-SR31 have nearly pH independent charge. It will be shown below that such groups are beneficial for improved capacitive behavior of PPy.

6.3.1.2 Impedance spectroscopy

Fig 6-24(A) is the Nyquist plot of PPy/MWCNT doped by Poly (acrylic acid-co-maleic acid) solution. There is no semicircle part related to Faradaic charge transfer resistance at high frequency region in this plot. The tilted graph indicates significant diffusion limitations. At low frequency region, the resistance (R=Z') is very high, closed to 70 Ω . The slope of Z'' versus Z' is much smaller than 90°, indicating bad capacitive performance. The reason behind that is that un-doped PPy has low conductivity and agglomerates easily, which will affect charge transfer between PPy chains and decrease amounts of pores at surface significantly. Thus, less ions in electrolyte can diffuse inside pores and electrons transfer very slowly in electrode, making the resistance very high. In another plot (Fig 6-24(B)), the frequency dependencies of the AC capacitance for PPy/MWCNT composites doped by Poly (acrylic acid-co-maleic acid) solution do not

show typical relaxation type dispersion, since a maximum in the frequency dependence of C" was not observed within testing frequency region. It is highly possible that relaxation frequency exists, but is much lower than 0.01 Hz, which is in good agreement with results derived from CVs data. At 0.01 Hz, real capacitance calculated from impedance data is only 0.12 F/cm².



Fig 6-24 (A) Nyquist plots of complex impedance (B) (a) Cs' and (b) Cs" versus frequency for PPy/MWCNT composite electrodes doped by Poly (acrylic acid-co-

maleic acid) solution

6.3.2 PMSS-SR31

6.3.2.1 PPy/MWCNT composite doped by PMSS-SR31

6.3.2.1.1 CVs and Capacitance

Fig 6-25 shows the CV curves for PMSS-SR31 doped PPy/MWCNT composite at scan rates of 2, 5, 10 mV/s. Unlike the composite doped by Poly (acrylic acid-co-maleic acid)

solution, the CV curves of this composite are of nearly ideal box shape and have high current at low scan rate, indicating good capacitive behavior. When the scan rate is high, there is a strong deviation from box shape due to poor electrolyte access to active materials, but current response is still high. The capacitance is 118 F/g at 2 mV/s and 54 F/g at 100 mV/s (fig 6-26), and retention is 45.8%, which shows that PMSS-SR31 is a good dopant.



Fig 6-25 CVs for PPy–MWCNT (20 wt%) composite electrodes at scan rates of (A) (a) 2, (b) 5, (c) 10 mV s⁻¹ (B) (a) 20, (b) 50, (c) 100 mV s⁻¹, prepared using PMSS-SR31

The good capacitive performance can be attributed to the benzene ring and its SO₃⁻ side groups (Fig 6-22). Some segments of PMSS-SR31 chains are exactly same as Poly (acrylic acid-co-maleic acid) chains. The biggest difference between these two is PMSS-SR31 has segments with benzene rings and charged groups SO₃⁻ in the structure. Benzene rings with SO₃⁻ groups can facilitate the absorption of dopants onto PPy through electrostatic attraction to compensate positive charges and promote PPy polymerization. That's the reason why those two dopants have such different effect on PPy capacitive performance.



Fig 6-26 C_m and C_s versus scan rate for PPy–MWCNT composite electrode doped

by PMSS-SR31 dopants

6.3.2.1.2 Impedance Data

Fig 6-27 shows the Nyquist plot for PPy/CNT composites doped by PMSS-SR31. It has very small diameter for the high frequency Faradaic charge transfer semi-circular feature. As the frequency decreases, it moves toward an essentially vertical segment indicative of good capacitive behavior. Their slope of the Z'' versus Z' was close to 90° at low frequency region, indicating good capacitive properties. It shows relatively low resistance (R = Z'). At 0.01 Hz, the real part of impedance of composite is 0.44 Ω . Fig 6-28 is the real capacitance and imaginary capacitance versus frequency. The frequency dependencies of the AC capacitance for PPy/ MWCNT composite doped by PMSS-SR31 show typical relaxation type dispersion, as indicated by the reduction in C' with increase in frequency and a maximum in the frequency dependence of C". At 0.01 Hz, real capacitance calculated from impedance data is 2.67 F/cm², which matches the capacitance calculated from area of CV curve at low scan rate. The relaxation frequency, corresponding to the maximum of C_s", is 0.12 Hz, indicating good capacitive behaviors at high scan rate. This is in good agreement with relatively high capacitance retention derived from CV data.



Fig 6-27 Nyquist plots of complex impedance for PPy/MWCNT composite

electrodes doped by PMSS-SR31



Fig 6-28 (a) Cs' and (b) Cs" versus frequency for PPy/MWCNT composite electrodes doped by PMSS-SR31

6.3.2.2 PPy/FeOOH/MWCNT composite doped by PMSS-SR31

Since PPy working voltage window is -0.5-0.4 V and PPy can only be p-doped, PPy is commonly used as positive electrode. Shifting the working voltage window to more negative direction is a good way to make PPy used as negative electrode. FeOOH has outstanding capacitive behavior at very negative working voltage range and is usually used as negative electrode. In this sense, adding FeOOH to PPy to prepare PPy-FeOOH composite is a potentially promising way to shift PPy working voltage to more negative direction and facilitate utilization of PPy as a negative electrode. PMSS-SR31 is an ideal dopant for PPy. PPy/MWCNT composite doped by PMSS-SR31 has capacitance of 118 F/g at 2 mV/s. Furthermore, chelating maleic acid group of PMSS-SR31 can react with FeOOH (Fig 6-29), which can facilitate PPy coating on FeOOH. This is beneficial for charge transfer between PPy and FeOOH. Therefore, PMSS-SR31 is an ideal dopant to fabricate PPy/FeOOH/MWCNT composite electrodes.



Fig 6-29 Adsorption involves chelation of Fe atoms on FeOOH surface

6.3.2.2.1 Morphology characterization

Fig 6-30 shows SEM image of PPy/FeOOH/MWCNT composite. PV was used as codispersant for MWCNTs, PPy and FeOOH. PV is a good dispersant for MWCNTs and PPy, because π - π interactions facilitated PV adsorption. It was suggested that catecholate type bonding also can facilitate PV adsorption on FeOOH, which was beneficial for dispersion.



Fig 6-30 SEM image of PPy/FeOOH/MWCNT

6.3.2.2.2 CVs and Capacitance

Fig 6-31(A) shows CV curves for FeOOH/MWCNT composite at scan rate of 2, 5, 10 mV/s from -0.8 V to 0.1 V. The active mass loading of this electrode is 34 mg/cm². It shows good capacitive performance at very negative voltage range from -0.8 V to -0.3 V. When voltage is above -0.3 V, the current responses decrease drastically and CV curves become very narrow. The capacitance at 2 mV/s is 134.8 F/g. Fig 6-31(B) shows the CV curves for PPy/MWCNT composite at scan rate of 2, 5, 10 mV/s from -0.8 V to

0.1 V. The active mass loading of this electrode is 30 mg/cm². The CV curves for PPy/MWCNT composite showed different behavior, compared to FeOOH/MWCNT composite. It presents poor capacitive behavior when the voltage is lower than -0.5 V and huge capacitance improvement above -0.5 V. The capacitance at 2 mV/s is 92.4 F/g. In conclusion, FeOOH/MWCNT has much higher capacitance than PPy/MWCNT in the negative voltage range, and PPy and FeOOH can complement with each other in terms of their CV shapes. Their composite is supposed to have nearly box shape CV curve and high capacitance from -0.8 V to 0.1 V.



Fig 6-31 CVs for (A) FeOOH/MWCNT composite electrodes (B) PPy/MWCNT composite electrodes at scan rates of (a) 2, (b) 5, (c) 10 mV s⁻¹



Fig 6-32 CVs for (A) PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/2) (B) PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/3) at scan rates of (a) 2, (b) 5, (c) 10 mV s⁻¹

Fig 6-32 shows the CV curves for PPy/FeOOH/CNT composite. PPy and FeOOH have different mass ratios in these two plots, which are 7/2 and 7/3. Fig 6-32(A) shows good capacitive behaviors, since CV curves are nearly box shape. The active mass loading for this electrode is 31.6 mg. The capacitance at 2 mV/s is 118 mV/s, which increases drastically from 92.4 F/g after adding FeOOH to PPy/MWCNT composite. This is a 27.7% boost. The CV curves in Fig 6-32(B) are not as good as Fig 6-32(A). The peak occurs at -0.8 V and when the voltage is over -0.3 V, CV curves begin to shrink, which is similar to CV curves of pure FeOOH/MWCNT composite. The active mass loading for this electrode is 31.6 mg. The capacitance at 2 mV/s is only 92.8 mV/s. The capacitance increases slightly compared to pure PPy/MWCNT composite. Therefore, 7/2 mass ratio between PPy and FeOOH is the optimal mass ratio to fabricate PPy/FeOOH/MWCNT composites.

Another comparison can also be made between CV curves of PPy/MWCNT composite at normal -0.5 - +0.4 V voltage range and CV curves of PPy/FeOOH/CNT composites (mass ration between PPy and FeOOH is 7/2) at -0.8-0.1 V voltage range. At scan rate is 2 mV/s, both electrodes have capacitance of nearly 118 F/g and ideal box shape, which indicates roughly same capacitive performance for these two electrodes. Therefore, adding FeOOH to PPy according to 7/2 mass ratio can shift PPy working voltage window 0.3 V to negative direction without sacrificing any capacitive performance. -0.8-0.1 V voltage window for PPy was never recorded in the past



literature, which facilitates the utilization of PPy as negative electrodes in the future

Fig 6-33 C_m and C_s versus scan rate for (a) PPy–MWCNT composite (b) PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/2) (c) PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/3)

For the PPy/FeOOH/MWCNT composite (mass ratio between PPy/FeOOH is 7/2), a strong deviation from ideal box shape is observed as the scan rate increases above 20 mV/s, which can be account for poor electrolyte access to active material. Fig 6-33 is the Cm and Cs versus frequency for PPy/FeOOH/CNT composite (7/2 and 7/3 mass ratio of PPy and FeOOH) and PPy/CNT composite. PPy/FeOOH/CNT composite (7/2 ratio of PPy and FeOOH) has highest capacitance not only at low scan rate (2 mV/s),

but also at high scan rate (100 mV/s), which are 118 F/g and 42 F/g, respectively. By contrast, pure PPy only has capacitance of 92 F/g at 2 mV/s and 31 F/g at 100 mV/s.

6.3.2.2.3 Impedance Data

Fig 6-34(A) is the Nyquist plot for PPy/MWCNT composite and PPy/FeOOH/CNT composite (7/2 and 7/3 ratio of PPy and FeOOH). The slope of Z" versus Z' for PPy/FeOOH/CNT composite (7/2 between PPy and FeOOH) is closest to 90°, which indicating best capacitive behavior. For PPy/FeOOH/CNT composite (7/2 between PPy and FeOOH), it also has the lowest resistance (R=Z') compared to other two composites, which is only 1.36 Ω at 0.01 Hz. However, FeOOH has low conductivity than doped PPy, but adding FeOOH to the PPy/MWCNT system does decrease the resistance when testing voltage window is between -0.8 V and 0.1 V. The reason is that when voltage is lower than -0.5 V, almost all oxidized PPy chains are reduced, resulting in that PPy turns to insulating state. As a result, almost no reaction occurs and few charges accumulate beyond -0.5 V. Therefore, resistance for PPy/MWCNT composite at -0.8-0.1 V voltage range is much larger than that at -0.5 - +0.4 V voltage range. FeOOH is highly conductive from -0.8 V to -0.3 V. Therefore, adding FeOOH to PPy/MWCNT system actually can decrease resistance. Fig 6-34(B) and Fig 6-34(C) are the real and imaginary capacitances versus frequency for PPy/MWCNT composite and PPy/FeOOH/MWCNT composite (7/2 and 7/3 ratio of PPy and FeOOH). Real capacitance of PPy/FeOOH/MWCNT composite (7/2 ratio of PPy and FeOOH) calculated from impedance data is the highest, corresponding to the capacitance calculated from CV area. No matter what ratio between PPy and FeOOH, the PPy/FeOOH/MWCNT composites have similar relaxation frequency. PPy/MWCNT composite doesn't show typical relaxation type dispersion, since the peak is very small.



Fig 6-34 (A) Nyquist plots of complex impedance (B) Cs' versus frequency

(C) Cs" versus frequency for (a) PPy–MWCNT composite (b)
PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/2) (c)
PPy/FeOOH/MWCNT composite electrodes (PPy/FeOOH is 7/3)

6.3.2.3 PPy/FeOOH/MWCNT – MnO₂/MWCNT device

PPy/FeOOH/MWCNT composite doped by PMSS-SR31 has good capacitive behavior at negative voltage range between -0.8 V and 0.1 V. It should be noted that capacitances for the negative electrodes, reported in the literature, are typically significantly lower, than capacitances of positive electrodes. The important task is to develop efficient negative electrodes and improve performance of asymmetric devices. Such devices offer the advantage of large voltage window and enhanced power-energy characteristics. Therefore, advanced PPy/FeOOH/MWCNT composites, developed in this work were utilized for the fabrication of asymmetric devices. MnO₂/MWCNT composite prepared using PV as a dispersant for MWCNTs has high capacitance of 170 F/g at 2 mV/s in a window from 0 V to 0.9 V, which is an excellent material for positive electrode. Asymmetric device composing of PPy/FeOOH/CNT composite as negative electrode and MnO₂ composite as positive electrode showed good performance in different voltage windows (Fig 6-35).



Fig 6-35 CVs for PPy-FeOOH-MWCNT and MnO₂ -MWCNT at scan rate of 10 mV s⁻¹

6.3.2.3.1 CVs and Impedance spectroscopy

Fig 6-36 shows the CV data for asymmetrical device in a voltage window of 1.6 V. The active ass loading for negative electrode is 63.5 mg and for positive electrode is 34 mg. This device showed nearly box shape of CVs at low scan rates, and capacitance are 27.6, 24.5, 21.5 F/g at scan rate of 2, 5, 10 mV/s, respectively. As the scan rate increased over 10 mV/s, a deviation from box shape was observed, which is due to poor electrolyte access to active material.



Fig 6-36 CV curves for PPy-FeOOH-MWCNT/ MnO₂-MWCNT asymmetrical

device at scan rates of (a) 2, (b) 5, (c) 10 mV s⁻¹

Fig 6-37(A) shows the Nyquist plot for the device. The device shows relatively low resistance (low real part of impedance). The slope of the Z" versus Z' graph was close
to 90°, indicating good capacitive properties. However, the asymmetric cell has larger internal resistance, compared to the resistance of individual electrodes. The AC capacitance of the device was obtained from the impedance data and presented in Fig 6-37(B, C) in the form of frequency dependences of real C' and imaginary C'' components. Similar to the corresponding dependencies for individual electrodes, the frequency dependencies of the AC capacitance for the device showed relaxation type dispersion, as indicated by the reduction in C' with increase in frequency and a maximum in the frequency dependence of C''. The observed relaxation frequency of 0.02 Hz for the device, corresponding to the C'' maximum, was lower than the relaxation frequencies for the individual PPy/FeOOH/MWCNT (0.11 Hz) and MnO₂– MWCNT (0.1 Hz) electrodes. The difference in the relaxation frequencies can result from larger internal resistance of the cell.



Fig 6-37 (A) Nyquist plots of complex impedance (B) Cs' versus frequency (C) Cs" versus frequency for PPy-FeOOH-MWCNT/MnO₂-MWCNT asymmetrical

device

6.3.2.3.2 Charging and discharging testing and Ragone plot

The galvanostatic charge–discharge curves at different charging and discharging rates were shown in Fig 6-38 for a voltage window of 1.6 V. The charge–discharge curves were of nearly triangular symmetrical shape, indicating good capacitive behavior. This also means that PPy/FeOOH/MWCNT can be utilized as an efficient negative electrode. In contrast with this asymmetrical device, the symmetrical device, containing two PPy–MWCNT can be charged and discharged in the voltage window of 0.9 V. The energy densities of the capacitors are proportional to the U², where U is operating voltage. As a result, the asymmetric device showed improved energy characteristics, compared to the symmetric device. The Ragone plots for asymmetric devices are presented in Fig 6-39. The highest energy density of 11.15 Wh/kg was obtained for the asymmetric device at a current of 3 mA. The energy density of the symmetric device at the same discharge current was only 4.25Wh/kg. The difference is attributed to larger voltage window of the asymmetric device.



Fig 6-38 Charging and discharging curves for PPy-FeOOH-MWCNT/MnO2-

MWCNT asymmetrical device



Fig 6-39 Ragone plots for PPy-FeOOH-MWCNT/MnO₂-MWCNT asymmetrical

device

6.3.3 Summary

Polymer dopants with aromatic ring structures and SO₃⁻ charge groups can increase interchain charge transfer between PPy macromolecules and improve capacitance retention. PMSS –SR31 with chelating maleic acid groups can function not only as a good dopant for PPy, but also as a dispersant for FeOOH and for the fabrication of the PPy/FeOOH/MWCNT composite. Adding FeOOH to PPy/MWCNT system according to 7/2 mass ratio between PPy and FeOOH can shift working voltage window to -0.8 -+0.1 V, which facilitates the utilization of PPy--FeOOH-MWCNT as a negative electrode. The charge–discharge curves for PPy-FeOOH-MWCNT/ MnO₂-MWCNT asymmetrical device were of nearly triangular symmetrical shape. The highest energy density of 11.15 Wh/kg was obtained for the asymmetric device at a current of 3 mA.

7. Conclusions

The chemical synthesis of PPy/MWCNT composite with different dopants, such as Aerosol 22, 4,4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate, potassium benzene-1,2-disofulnate, Ponceau S, Trypan blue, PMSS-SR31 and Poly (acrylic acid-co-maleic acid) solution was studied in this research. Morphology analysis and electrochemical tests, including cyclic voltammetry and impedance were carried out for characterization in terms of capacitive properties.

The results showed that potassium benzene-1,2-disofulnate, Ponceau S and PMSS-SR31 gave the best results. Common features between these three ideal dopants are possession of aromatic rings, multiple pH independent charge groups like SO₃⁻, high charge to mass ratio. Dopants with these features can have a lot of good influence on PPy capacitive properties. First, they can be easily absorbed by PPy chains to involve the polymerization and compensate positive charges. Second, strong electrostatic repulsion between dopants can help to reduce agglomeration of PPy particles, which can increase the numbers of pores at the surface of electrode. In this sense, the resistance of diffusion of electrolyte ions will decrease a lot. Third, they can function as charge transfer mediator to facilitate charge transfer between PPy chain or between PPy chain and MWCNTs, which can drastically increase the conductivity of whole system. Last, the high charge to mass ratio of the dopants allowed the fabrication of electrodes with enhanced performance at high charge-discharge rates. These features provide a guide for the search of more ideal dopants in future. The size of dopants here will not affect too much on PPy capacitive performance. Large size of dopants can facilitate PPy coating on MWCNTs. By contrast, another dispersant has to be used if dopants for PPy have small size. Among all the dopants I studied in the research, the highest SC of 118.26 F/g was achieved at 2mV/s by using PMSS-SR31 doped PPy-MWCNT electrodes. The highest SC of 65.09 F/g at 100mv/s was achieved by using Potassium Benzene doped PPy-MWCNT electrodes. The highest retention of 80.2% was achieved by using 4'-Diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate doped PPy-MWCNT electrodes.

PMSS –SR31 was also used to fabricate PPy/FeOOH/MWCNT composite. Adding FeOOH to PPy/MWCNT system according to 7/2 mass ratio between PPy and FeOOH can shift working voltage window to -0.8 -0.1 V without sacrificing any capacitive performance, which facilitates the utilization of PPy as negative electrode. The charge– discharge curves for PPy-FeOOH-MWCNT/ MnO₂-MWCNT asymmetrical device were of nearly triangular symmetrical shape in a voltage window of 1.6 V. The highest energy density of 11.15 Wh/kg was obtained for the asymmetric device at a current of 3 mA.

8. Future work

The development of PPy/FeOOH/MWCNT composite is a very promising field. In my study, dispersion of FeOOH is a challenge. The ideal solution for this problem is that finding a multifunctional dopant with maleic acid groups, which can react with FeOOH for dispersion and can also facilitate PPy coating FeOOH. PMSS-SR31 satisfies this requirement, but PMSS-SR31 is not that effective. I suggest that large size of polymer molecules restricts the chemical reactivity of maleic acid. Therefore, I think I should focus my attention more on small aromatic dopants with maleic acid groups and other chelating polymers.

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