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A new PEDOT synthesis method and its application in energy storage

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A New PEDOT Synthesis Method and its Application in Energy Storage

By

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Abstract

A New PEDOT Synthesis Method and its Application in Energy Storage

By

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Master of Science in material science and engineering

Washington University in St. Louis, 2019

Research Advisor: Julio M. D'Arcy

Conducting polymer is a common electrode material in supercapacitors, people usually create nano-structure on electrode surface to enhance the performance of supercapacitors. Synthetic nanostructured polymers have been implemented in many ways, most of them are template-based synthesis, which is time consuming and expensive, people are pursuing an easier way to synthesize nanostructured conducting polymers. Combining ferric chloride solution hydrolysis and EDOT polymerization to get PEDOT nano fiber in one step has been achieved. We develop a new method to synthesis PEDOT nano fiber from solid-state iron in one step. Our process takes place in a single step inside a sealed hydrothermal reactor when monomer vapor contacts a rust coating undergoing dissolution – this approach is scalable requiring only a rusted steel surface, acid vapor and monomer vapor. Freestanding nanofibrillar PEDOT films delaminate from a steel substrate characterized by an electronic conductivity of 323 S cm-1 and high electrochemical stability.

Chapter 1: Introduction

1.1 Background and Motivation

With the development of science and technology around world and the acceleration of urbanization, people's demand for energy is getting higher and higher. As of 2017, the world's per capita electricity consumption has reached 3,127 kWh per year, which is three times that of 1970. Most of the energy consumed by people is provided by fossil fuels such as coal, petroleum and gas, but in terms of the speed at which people now consume energy, fossil fuel resources are expected to be exhausted within 200 years. In addition, the massive use of fossil fuels has led to a series of problems such as global warming and air pollution. Due to concerns about the growing problem of global warming, pollution and unsustainable development due to the increasing cost of fossil fuels, greener and renewable energy resources application such as solar energy and wind energy are being pursued by scientists to deal with those environment problems. In Germany, renewable energy generation accounted for about 3.1% of total power generation in 1990, and developed to 17% at the end of 2010, of which 36.5% were wind power, 33.5% were biomass power generation, and 19.7% were water power. In China, installed capacity of solar energy generation has reached 130.25GW in 2015. Although great improvements of greener renewable energy generation have been achieved by scientists, poor energy harvest and storage technologies become a constraint to the developments of greener energy utilization. The energy generated by wind, solar and water power cannot be transported to a great distance, and many powers are wasted because they cannot be consumed locally. Developing a device which can store these unusable energy sources and apply them to energy-poor regions is meaningful. Such greener renewable energy storage technologies should be able

to store high amounts of energy, and these devices should also be cheap, light and reliable. As a result, high power and high energy density storage systems have attracted people's attention.

Although there are traditional energy storage devices with good performance such as Li-ion batteries and fuel cells, their drawbacks make them incompetent the demands of wide utilize. Li-ion batteries show a relativity low power performance due to its energy storage mechanism. These batteries store energy through reversible reduction and oxidation process, which is quite slow. Furthermore, heating generated by charge and discharge process will damage battery materials, which lead to a short lifetime.

In fuel cell technology, noble metals such as platinum and platinum-based composites are loaded onto high surface area supports and used as electrodes because they exhibit high electrocatalytic activity towards the oxygen reduction reaction, hydrogen oxidation and small organic molecule oxidation which are typically the reactions of choice [1], However, there are downsides for using fuel cells due to high cost and poor stability.

A new energy storage system with high efficiency and new materials can overcome above problems are the key to meet the needs of contemporary developments.

1.2: Supercapacitor: Meeting Present and Future Global Energy Needs

A capacitor is a passive two-terminal electronic component that stores electrical energy in an electric field. In recent years, people have developed a new type of capacitor that is tens of times larger than the capacity of conventional capacitors, which is called supercapacitor.

Supercapacitors are devices capable to managing higher power density compared to batteries and higher energy density compare traditional capacitors [2]. They fill the gap between batteries and capacitors (Fig 1.1). Recently, supercapacitors have been developed to give capacitance with hundreds to thousands Farad, which is 10 times higher than traditional electrolytic capacitors in the same value. Although their capacity is still not comparable to the battery, supercapacitors can reach about 10kW kg^{-1} output, which is much higher than batteries. These properties make supercapacitors play important roles in applications which power bursts are needed but high energy storage capacities are not needed.

Traditionally, capacitors have been constructed using a set of parallel conducting plates separated by an insulator, supercapacitors have the similar design [3]. Depending on the storage mechanism or cell configuration, electric double-layer capacitors (EDLCs) and pseudo capacitors can be distinguished [4].

1.2.1 EDLC

The current ubiquitous commercial electrochemical capacitor is the electric double-layer capacitor (EDLC). EDLCs store charge electrostatically, similar to a traditional electrolytic capacitor, in a double Helmholtz layer at the interface between its electrodes and electrolyte [5]. EDLC has the similar device structure with batteries: two electrodes separated by an electrical insulator (separator) in an electrolyte [6]. However, their storage mechanisms are different. Unlike batteries which store energy through reversable redox reaction, EDLCs store energy by adsorption large amount Electric charges on their high specific surface area under a polarized

electric field between two electrodes, so nanoporous materials such as nanocarbons are widely used in EDLCs due to their high surface area.
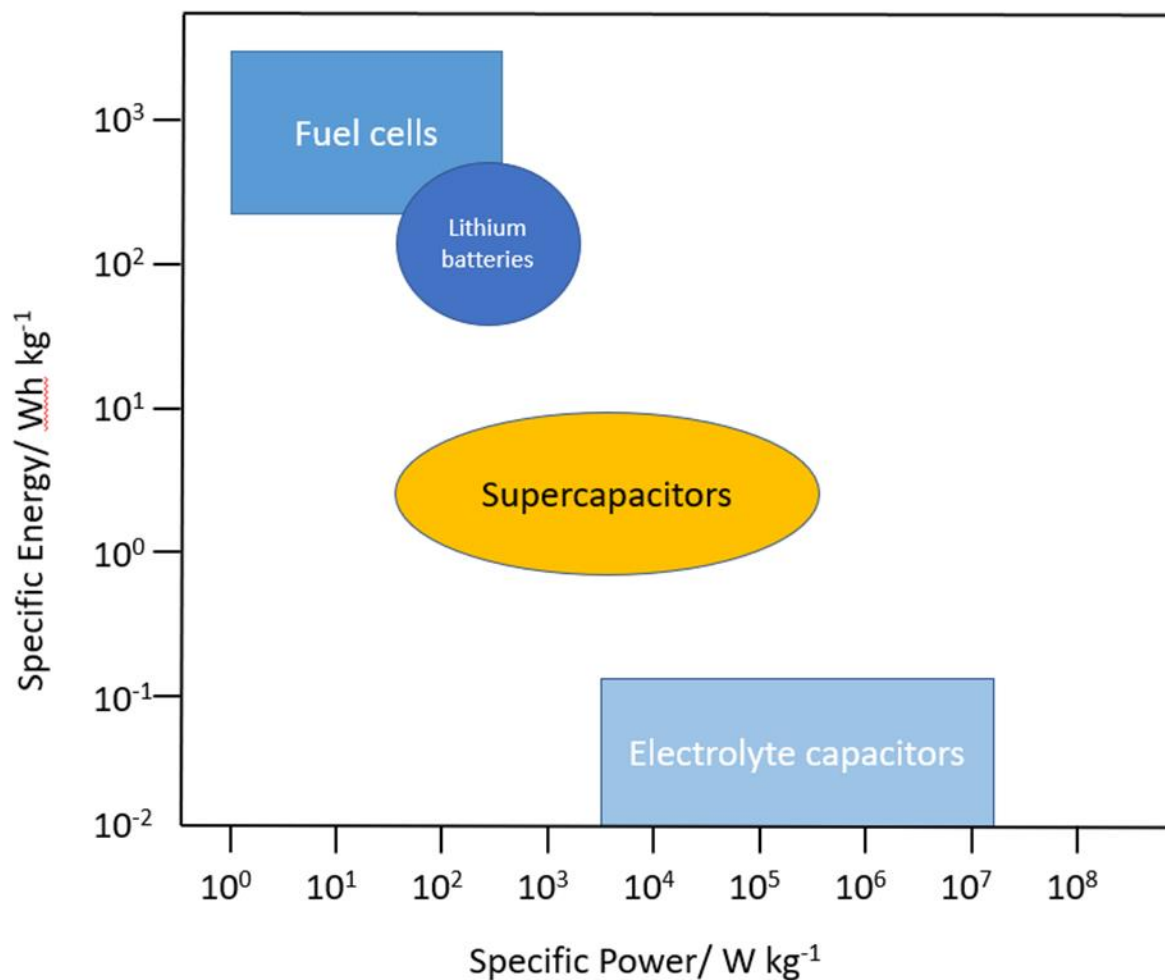
Figure 1.1 Ragone plot illustrates different types of energy-storage devices as a function of specific power and energy.

Compared to batteries, EDLCs have a low energy density, the capacitances are delivered in mF and µF quantities [6]. However, EDLCs show a long life time and good cycle efficiency as there is not redox reaction during charge and discharge procession, which can lead to overheating and electrode materials breakdown.

1.2.2 Pseudocapacitor

Pseudocapacitor, another kind of electrochemical capacitor, is different from electric double-layer capacitors. Pseudocapacitors store energy through highly reversible oxidation and reduction reactions in the bulk of redox materials. Although pseudocapacitors have the similar charging mechanism with batteries, pseudocapacitors have a better power performance due to their faster redox reaction. On the other hand, the capacitance of pseudocapacitors can be 10-100 times higher than that of EDLCs as in pseudocapacitors there are redox reactions at bulk materials instead of only adsorption charges on the surface.

Figure 1.2 Capacitor schematic diagram.

Chapter2: Common Electrode Material for Supercapacitors

2.1 Introduction

A typical supercapacitor consists of three essential components, namely the electrodes, the

electrolyte, and the separator [7]. The performance of supercapacitors depends on both electrode

and electrolyte properties.   Nevertheless, the electrode is the most important component for

charge storage/delivery and plays a crucial role in determining the energy and power densities of

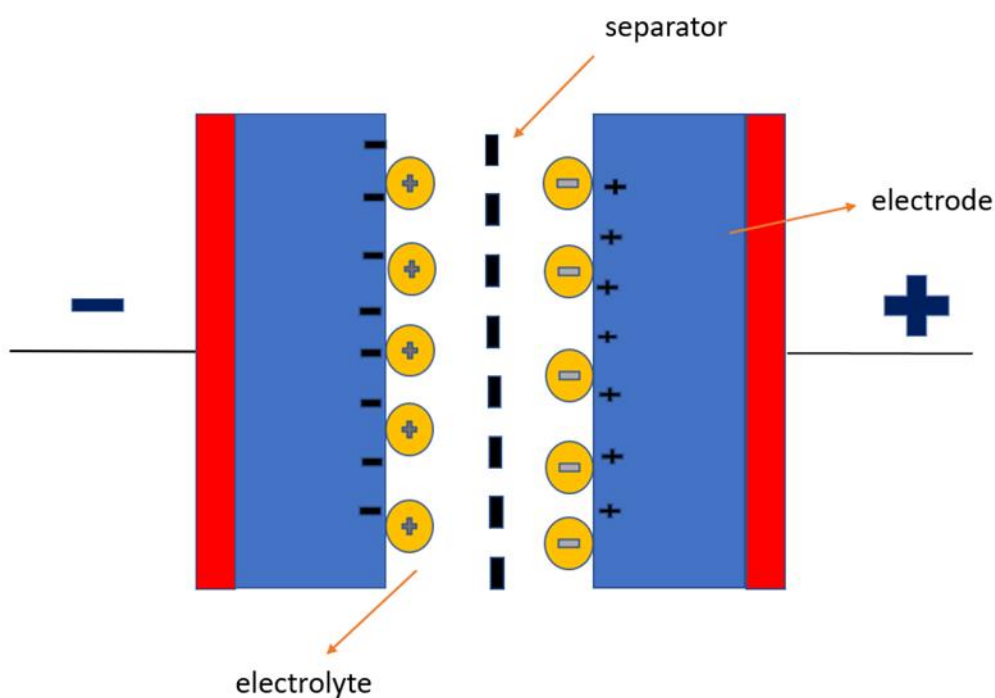a supercapacitor [8]. One of the big challenges of supercapacitor technologies is finding a

property electrode material. Electrode materials should be cheap, stable and environment

friendly. Most importantly, high conductivity of the electrode materials is necessary for allowing

supercapacitors' fast charge/discharge performance.

EDLC store energy through adsorption charges on electrode surface, and capacitance depends on

the surface area of electrodes, which higher electrode surface area leading to a higher

capacitance. Thus, carbon materials and some conducting polymers are commonly used as

electrode materials thanks to their highly porosity and conductivity. Pseudocapacitors store

energy mainly via reversible redox reaction to redox materials on the surface of electrode,

therefore, conducting polymers and some metal oxide with good reversible redox performance

are widely used. However, in practical supercapacitors, the two storage mechanisms often work

simultaneously, therefore, electrode materials with high surface area play a key role in both two

types of supercapacitor. Figure 2.1 shows different types of capacitors.
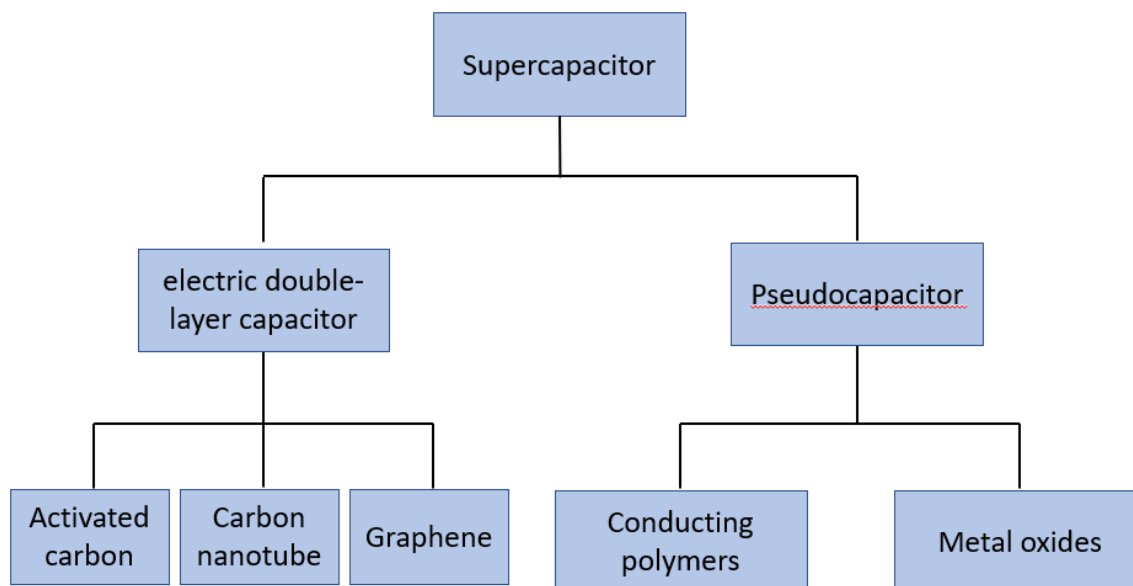
Figure 2.1 Classification of different supercapacitors.

2.2 Carbon

Carbons are the most commonly used electrode materials for electrochemical capacitors, because they are cheap and commercially available, and they can be produced with large specific surface area [9].

Versatile existing forms of carbon have been applied in electrochemical capacitors such as powders, fibers and mats, especially high-surface-area mesoporous carbon and activated carbons are widely used in commercial supercapacitor electrodes due to their low price and extremely high surface area. Supercapacitors with electrode made by activated carbon obtain a relatively good performance. However, Non-uniform pores sizes and distribution limit the electrolyte accessibility in electrode material, combine with their poor electrical conductivity,

supercapacitors electrodes made by activated carbon cannot reach the theoretic capacitance, though they have huge theoretic surface area.

With the advancement of technology in recent years, some fancy carbon materials are catching people's eye. Owing to their large surface area, high mesoporosity, good electrolyte accessibility and good electrical properties, carbon nanomaterials, especially graphene and carbon nanotubes (CNTs), are very promising candidates to replace activated carbons as the electrode materials in high-performance supercapacitors [10]. Carbon nanomaterials have been applied to supercapacitors and have achieved very good performance in recent years, but the difficulty of mass production of carbon nanomaterials limits its application.

2.3 Metal Oxide

Metal oxides have high specific capacitance and conductivity, making them suitable for electrode fabrication focused on high energy and high-power supercapacitors. There are several different metal oxide materials used for electrode fabrication such as RuO_2, IrO_2, MnO_2, NiO, Co_2O_3, SnO_2, V_2O_5 or MoO_x. The most studied ones are ruthenium and manganese oxides [11].

Ruthenium oxide (RuO_2) store energy mainly through redox reaction

$$RuO_2 + xH^+ + xe^- \leftrightarrow 2RuO_{2-x}(OH)_x$$
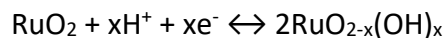
Although Ruthenium oxides can reach the highest capacitance among pseudocapa- citive materials around 1000F g^{-1} (Fig 2.1), their high coast, toxicity and unstable limit their

application. Moreover, Ruthenium oxides have the lowest conductivity compare to carbon and

conducting polymers (fig 2.2), which lead to a relatively low energy density.

Similar to Ruthenium oxides, Manganese oxide (MnO_2) shows a high capacitance through redox

reaction. However, Manganese oxides face the same problem with Ruthenium oxide.
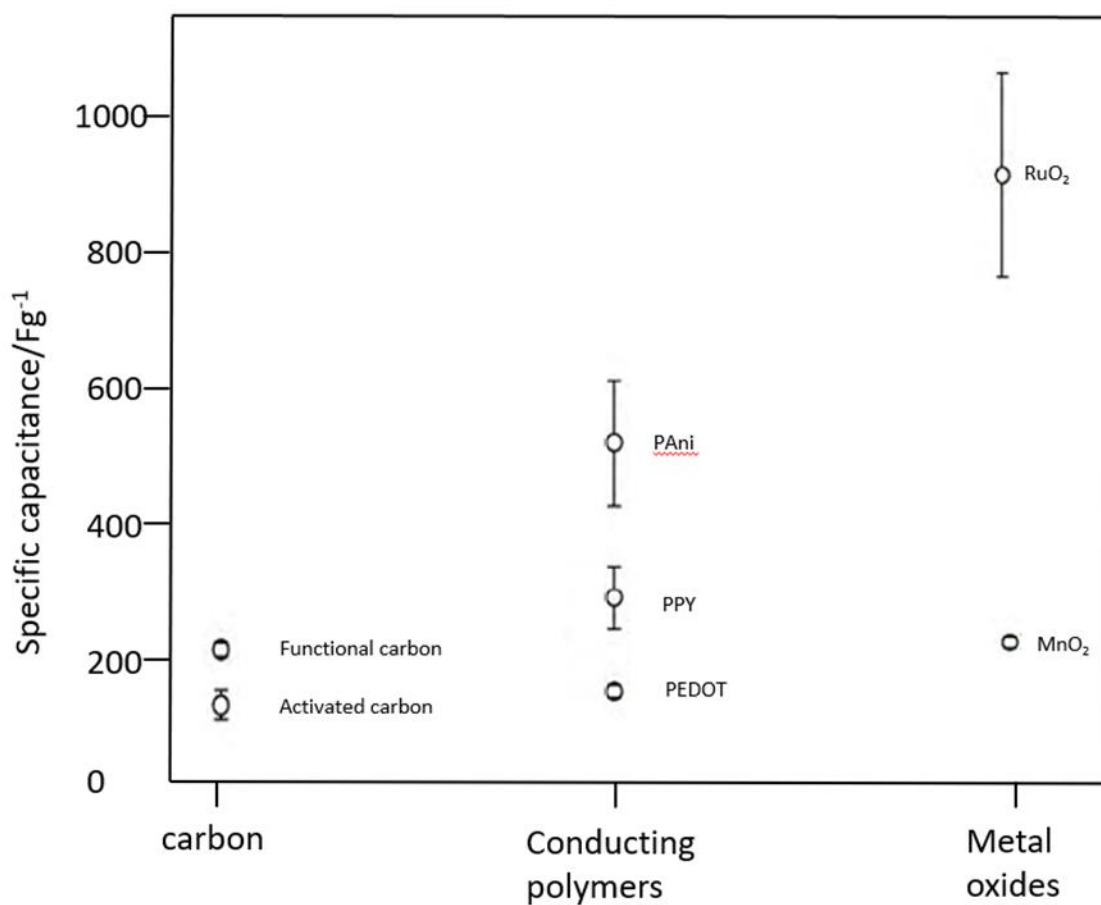
Figure

Figure 2.2 Typical specific capacitances for different supercapacitor materials.

2.4 Conducting Polymer

Conducting polymer is another kind of widely used electrode materials. Polymers used to be considered as insulator, however, doped Polyacetylene showed semiconducting properties was discovered by Shirakawa and co-workers in 1970s. Since then, conducting polymers have been studied for years and many different types conducting polymers have been synthesized. One of the most studied CPs is polyaniline (PANi) as well as polythiophenes, polypyrrole, and polyphenylene vinylene [12]. All of them are conjugated and have a backbone of adjoining sp2 hybridised orbitals, hence, delocalised p electrons are formed along their backbone [13].

Conducting polymers can serve as electrode materials in both EDLC and pseudocapacitors, conducting polymers with good reversible redox performances such as PANI shows relative high capacitance through dope/de-dope reaction during charge/discharge process. However, conducting polymers which cannot under reversible redox reactions such as PEDOT also show a good performance, especially the high charge/discharge rates which are achieved by high conductivity. Moreover, conducting Polymers have good flexibility, which is not available in metal oxides and carbon materials, so conductive polymers have a wider range of applications, such as medical and biological field. Due to the excellent conductivity, capacity and unique flexibility, the conducting polymers become promising electrode materials for supercapacitor.

Usually, conductivities of conducting polymers depend on molecular weight and crystallinity, the polymers have higher molecular weight and higher crystallinity with less defects always

show a higher conductivity. Fortunately, we can control the quality of polymers through

different synthesis methods and reaction conditions.

Typically, polymerization has three steps: radical-cation production, oligomer formation and

polymer growth. The monomers are oxidized to radical cation at the beginning, radicals

coupling to dimers, low molecular weight oligomers formation, and then polymer chain

polyacetylene

polypyrrole

Polyphenylene
vinylene

polythiophene

polyaniline

PEDOT
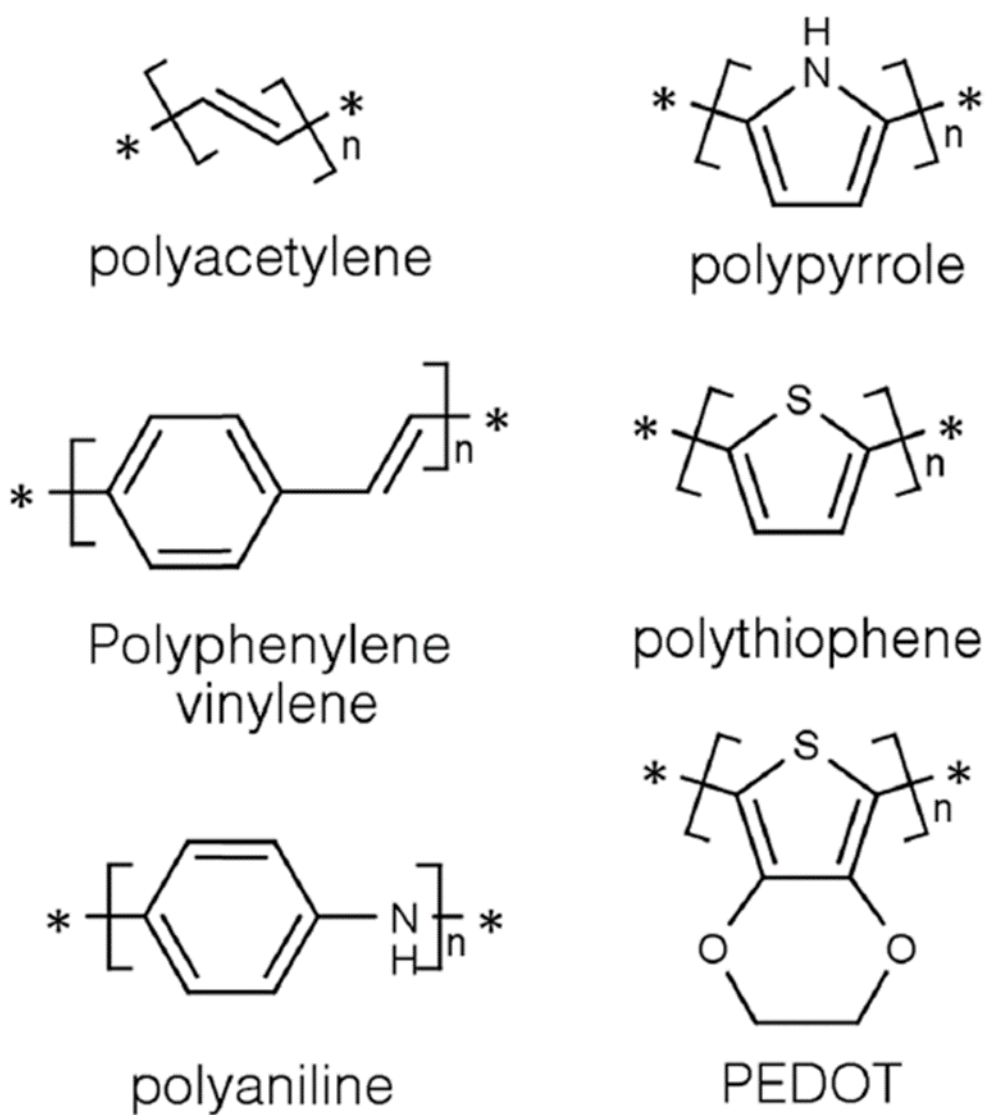
Figure 2.3 Common conductive polymer

propagation because oligomers undergo further oxidation (Fig 2.4). And finally, the polymers

are doped by dopant to provide conductivity (Fig 2.5).

Essentially, there are two conducting polymer synthesis methods, electrochemical oxidation

and chemical oxidation of a monomer [14].

Electrochemical polymerisation is typically achieved by using a three electrodes configuration

(i.e. counter, reference, and working electrodes) [15], polymer is directly deposited onto the

working (Fig 2.5 a).

a)
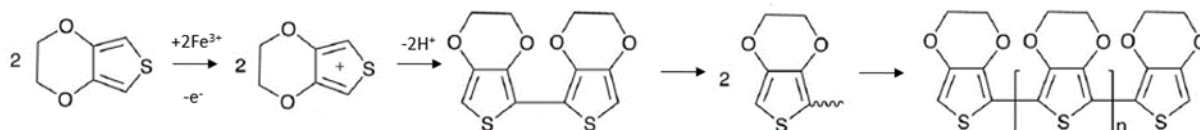
b)
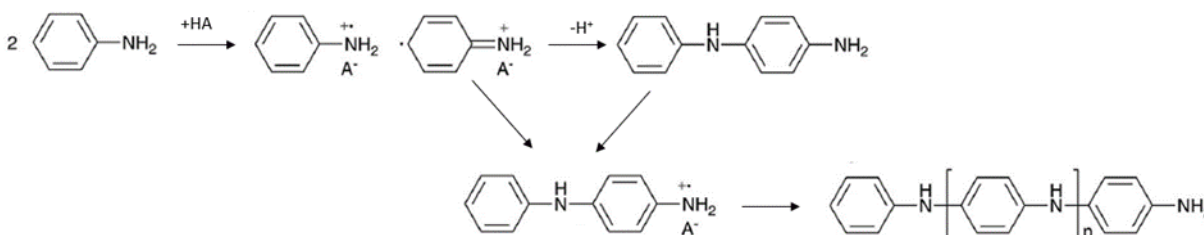
Figure 2.4 Schematic of the proposed polymerization mechanism of a) PEDOT and b)PANi.
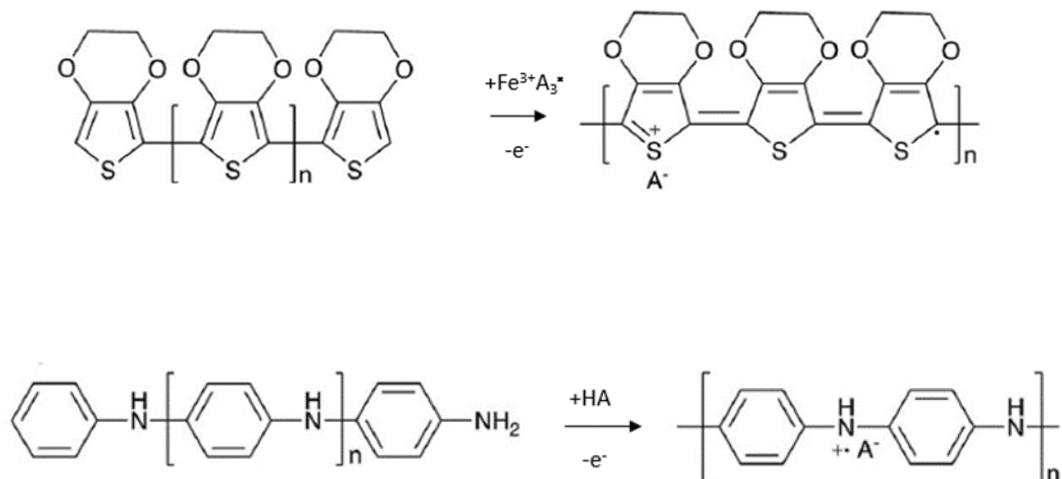
Figure 2.5 Schematic of doping mechanism of a) PEDOT and b) PANi electrode with polymerization process.

However, although synthesis conducting polymers though electrochemical deposition is convenient, only low-quality polymer with relatively low conductivity can be obtained.

In the case of chemical polymerization, monomers are oxidized by oxidizing agents with proper potential. Chemical oxidants such as ammonium persulfate [$(NH_4)_2S_2O_8$] and ferric chloride (FeCl$_3$) which have oxidation potentials of E_0=1.94 V and 0.77 V respectively, are used to polymerize the polymer. The polymerization usually occurs in the solution, the product precipitates out of solution as the reaction proceeds (Fig 2.5b). People also apply vapor phase polymerization technique to produce conducting polymers via chemical polymerization, the monomer vapor contact with the oxidants directly on the substrate, a well-coated substrate with high quality conducting polymers can be derived after reaction (Fig 2.5c).

However, either high capacitance or high charging/discharging rate depends on high surface

area, whatever in EDLC mode or pseudocapacitor mode. Firstly, their high surface area in

contact with the electrolyte, allows for high charge/discharge rates. Secondly,

their short path lengths for ionic transport allows for faster

ionic diffusion within the CP network [16]. Furthermore, high surface area can improve

conducting polymers' tolerance towards to expansion/shrinkage behavior which is leaded by

charge/discharge process, hence decrease the structure breakdown and improve the cycle life.

As we all know, nano-structured materials have huge surface area, therefore, using nano-

structured conducting polymer in electrode is an efficient strategy to improve supercapacitor

performance. Consequently, synthesis of a highly conductive polymer with nano-structure is a

promising way to achieve a better application in energy store devices.
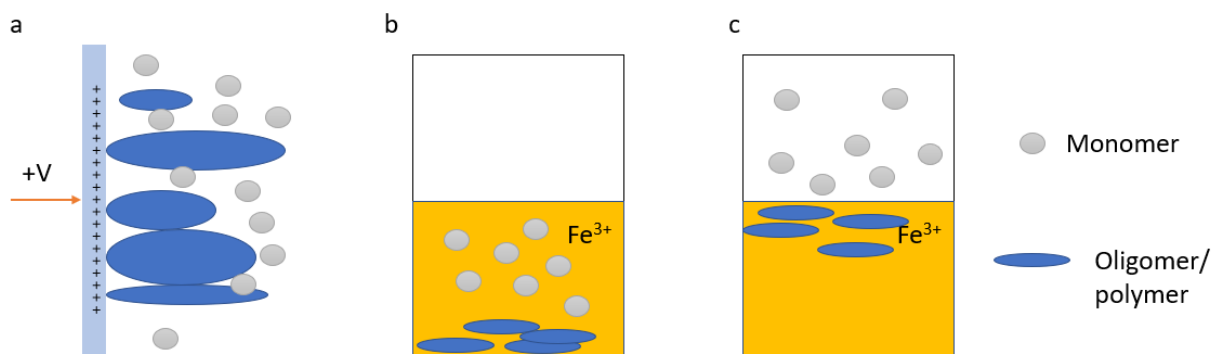

Figure 2.6 Cartoon representation of a) electropolymerization b) solution polymerization c)
vapor phase polymerization.

Chapter3 Nano-structured Poly(3,4-ethylenedioxythiophene) (PEDOT) Synthesis

3.1 Nano-structured Polymer Synthesis

Nano-structured polymers have been achieved for many years, the most common used approach to get nano-structured polymers is through template-based methods, a template is used to direct the polymer to grow into certain shapes and sizes [17]. The template can be made by many different materials, these can be mainly categorized to two types, namely hard template and soft template.

In hard template based nano-structuring, nanoparticles or nano-sized channels are served as molds for directing the growth of polymers. Anodized alumina oxide (AAO) and mesoporous silica–carbon templates are commonly used as hard template; the monomers are polymerized on the surface of or into the gap of templates [18]. In the soft template synthesis, self-assembling surfactants form micelles that confine the polymerization of the CPs into specific shapes and sizes to produce nanomaterials [19].

However, both hard template and soft template based nano-structuring need two steps to get nano-structured polymers, 1) template preparing 2) polymer synthesis/coating. It takes a lot of time and money to prepare template. Hence, an easier and more efficient way to produce highly controlled conducting polymer nano-structure is meaningful.

3.2 Nano-structured PEDOT Synthesis in One Step Through Vapor Phase Polymerization

As we talked above, many metal oxide nano-particles such as ,,, are used to serve as templates when synthesize nano-structured polymers,

When ferric chloride ($FeCl_3$) dissolves in water, the result is a thermodynamically unstable aqueous solution that readily hydrolyzes under standard conditions and at room temperature [20]. A multitude of iron precipitates such as hematite (Fe_2O_3), feroxyhyte (δ-FeOOH) and akaganéite (β-FeOOH) can be yielded through this kinetically controlled reaction. The hydrolysis products, crystal structure and nanostructure morphology with various crystal growth mechanisms are controlled by hydrolysis condition such as PH, reaction temperature and ion concentration of the solution. For example, at high Cl^- concentration (>0.2M) and high temperature (90-100°C), akaganéite (β-FeOOH) is the main product. Those different types of iron compounds nano-crystals can serve as ideal template for synthesizing nano-structured polymer.

Interestingly, ferric chloride is an ideal oxidant for synthesizing a plethora of conjugated polymer due to it's mild oxidation potential (E_0=0.77V) and low coast, yield up to a 200 000 molecular weight polyaniline chain produced by ferric chloride oxidation has been reported. Moreover, ferric chloride plays a role as dopant by providing a Cl^- counter anion that stabilizes charge during polymerization [21]. The monomer such as 3,4-ethylenedioxythiophene (EDOT) can be oxidized by ferric chloride to form oligomers, and final conjugated polymer poly (3,4-ethylenedioxythiophene) (PEDOT) will form though further oxidative polymerization and doping.

Solution and vapor phase polymerization are two commonly used strategies when using ferric chloride as oxidant, though two approaches share the same mechanism, vapor phase polymerization (VPP) usually get better products. Compared to solution polymerization, PEDOT synthesized through vapor phase polymerization has a conformal coating of high chemical and

physical stability and low electrical resistance. Thus, combining vapor phase polymerization with highly controlled hydrolysis of a ferric chloride aqueous solution is a feasible way to generate nano-structured conducting polymers in one step.

An iron oxide-poly(3,4-ethylenedioxythiophene) (PEDOT) hybrid nanofibrillar has been obtained through hydrolysis-assisted vapor-phase polymerization (HVPP) *. HVPP combine the ferric chloride solution hydrolysis and vapor phase polymerization by introducing EDOT monomer vapor phase during controlled ferric chloride solution hydrolysis. The reaction happened in closed CVD reactor with a droplet of ferric chloride water solution on prepared glass slide and EDOT/ chlorobenzene loaded in two separate reservoirs. The reaction temperature controlled by PID controller, ramps from 30 to 130 °C in 10 min and hold holds at 130 °C for 50 min, the uniform core-shell fibrillar PEDOT formed after reaction. Two reactions are carried out simultaneously during HVPP: (1) forced hydrolysis and (2) oxidative radical polymerization, the iron compounds which formed in hydrolysis process serve as a template, and EDOT monomers carried by chlorobenzene penetrate the droplet to form PEDOT under oxidation polymerization. Thus, the product has a core coated by PEDOT, the core composed mainly with β-FeOOH due to high Cl^- concentration and high temperature.

3.3 Synthesis Nanofibrillar PEDOT From Solid-state Iron Source.

Synthesis nano-structured PEDOT by combining the $FeCl_3$ aqueous solution hydrolysis and oxidation polymerization in one step has been proved, however, there are some drawbacks of synthesis PEDOT nano-fibers from Fe^{3+} aqueous solution. Thermodynamically unstable Fe^{3+} aqueous solution readily hydrolyzes to different precipitates, we take advantage of that in

nanofibrillar PEDOT synthesis through HVPP, but as the same time, instability of the Fe^{3+}

aqueous solution becomes a problem in synthesis. There are more than 20 product species are

produced by Fe3+ aqueous solution hydrolysis, tiny changes of solution such as PH,

concentration and even room temperature have great influences on hydrolysis process, so it is

hard to precisely control the hydrolysis process, especially in single droplet. Because the

droplets can hardly maintain their shapes and sizes, even on pretreated hydrophobic glass

substrate the droplet has variety shapes and sizes. And sizes and shapes influence the hydrolysis

process due to different evaporation rates caused by unequal surface area. Thus, hard handling of

the droplet challenges the reproducibility of experiments. However, compared to Fe^{3+} solution,

solid-state iron sources are more stable and controllable. So, it is an easier and more reliable way

if we can produce PEDOT nano-fiber from solid-state iron,

One of the key points for synthesis PEDOT from solid-state iron source is finding a suitable

reagent. The reagent should be rich in ferric ion and stable in solid-state, some ferric ion-

containing salts like ferric chloride are hygroscopic and chemically unstable undergoing

hydrolysis over time which challenges the reproducibility of experiments, iron oxides and

hydroxides such as hematite and feroxyhyte are stable but quite expensive. However, a common

iron rich solid substance is an ideal resource for providing Fe^{3+} in PEDOT synthesis.

Iron corrosion, a byproduct from the chemical reaction between iron and oxygen in the presence

of water, and commonly referred to as rust. Rust is usually considered as a waste in daily life and

represents a major problem for our anthropogenic engineering endeavors. However, rust is a

ferric ion rich resource includes iron oxides, oxyhydroxides and hydroxides such as Hematite (α-

Fe2O3), Maghemite (γ- Fe2O3),

Goethite (α-FeOOH) and Lepidocrocite (γ-FeOOH). Although rust contains many different iron

compounds and phases, it is stable in the room temperature, combining with its low coast, rust is

an ideal reagent for providing Fe^{3+} in PEDOT synthesis.

Here, we present a robust platform for synthesizing PEDOT nanofibers utilizing solid-state rust

as a reactant and we introduce rust-based vapor-phase polymerization (RVPP) – a versatile

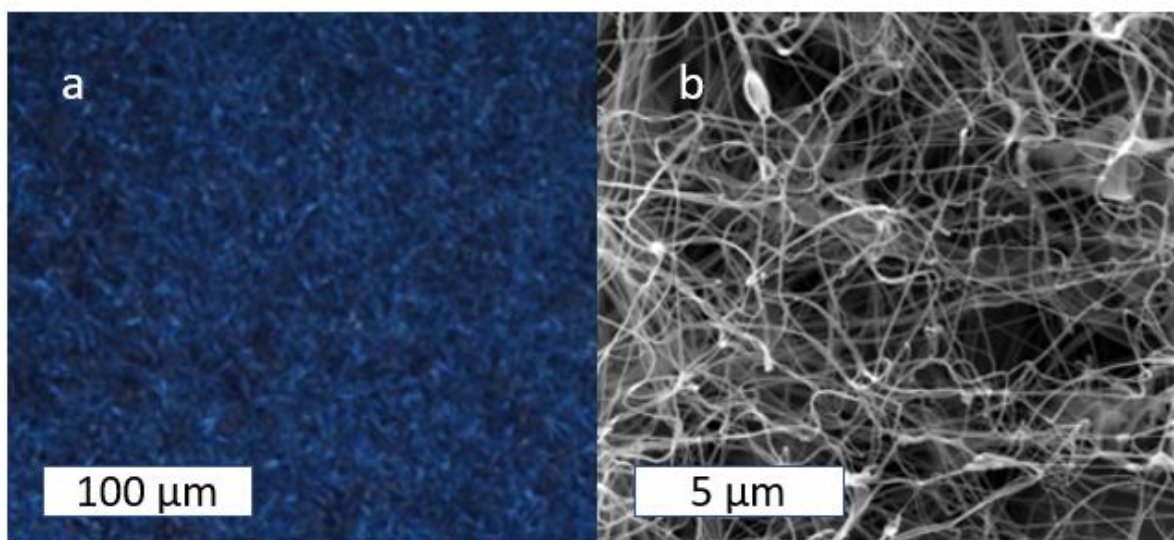alternative to traditional vapor-phase polymerization.

Figure 3.1 Photograph of PEDOT nano fiber a) Optical microscope b) Scanning electron

micrograph

3.4 Results and Discussions

 Rust-based vapor-phase polymerization (RVPP) is a synthetic strategy that utilizes rust to

produce nanofibrillar freestanding films of the conducting polymer PEDOT. Scanning electron

micrograph shows high packing density of high aspect ratio nanofibers formed after synthesis

(Fig 3.1). A 7 mm x 7 mm rusted steel plate was used to vapor deposit a nanofiber PEDOT film,

which was introduced into a sealed container together with 20 μL of concentrated hydrochloric

acid and 200 µL of a 0.0034 M EDOT solution in chlorobenzene, rust layers were produced by immersing a 2.5 cm × 4 cm low carbon steel sheet in 20 mL of a 0.01 M H2SO4 solution for 48 h at 25 oC, and then dried in air. The Powder X-ray diffractogram shows the main components of rust are α-FeOOH, γ-FeOOH, Fe2O3 and FeSO4(Fig 3.3). The reactor was sealed, placed in an oven (150 ° C) for 6 hours, and then cooled in an ice bath for 15 minutes to obtain a blue nanofiber PEDOT film which was easily peeled off from the steel sheet. This mechanism for depositing bulk quantities of PEDOT nanofibers utilizes hydrochloric acid vapor to liberate Fe^{3+} ions from rust; subsequently these aquatic ions initiate the polymerization of PEDOT upon contact with monomer vapor. Polymerization occurs in unison with the hydrolysis of Fe3+ ions leading to the precipitation of one-dimensional inorganic nanostructured colloidal iron species such as FeOOH. The PEDOT film readily delaminates from its substrate by simple immersion in water resulting in a freestanding polymer film, this is because a rust layer lacks chemical coordination to steel.

A core-shell structure of PEDOT fiber has been showed through energy dispersive X-ray spectroscopy maps were collected using a JEOL 7001LVF FE-SEM, the elemental distribution comprised of S and Fe pertaining to a polymer shell and an inorganic core, respectively (Fg3.2).
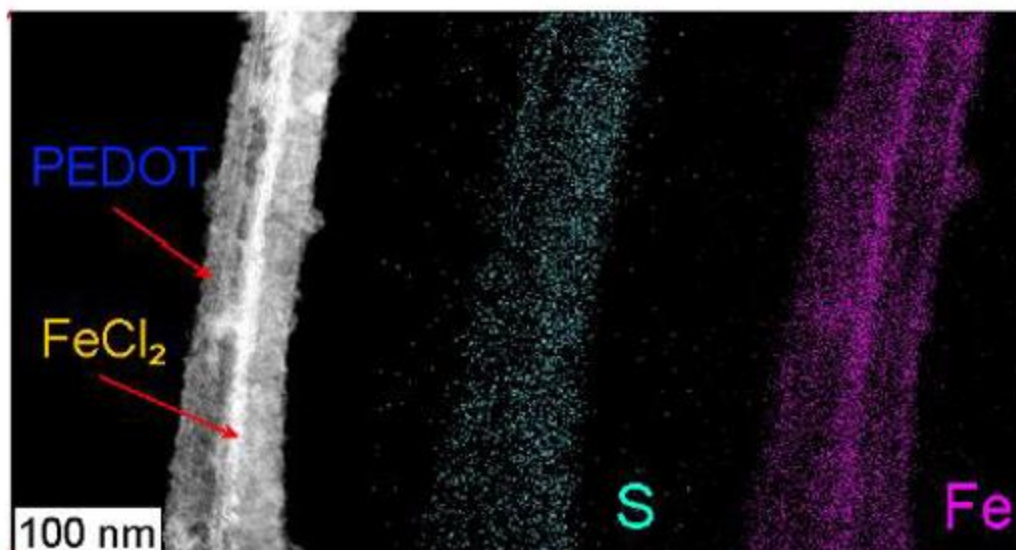
Figure 3.2 A high angle annular dark field scanning transmission electron micrograph for a PEDOT nanofiber shows its core-shell structure and an elemental composition comprised of a sulfur-containing shell and an iron-containing core.

Powder X-ray diffraction confirms the existence of a FeCl2 core (Fig 3.4). The core-shell PEDOT then is purified in 6M HCl to remove this inorganic core, the hollow nanofiber after purification was characterized by Fourier transform infrared spectroscopy, the FTIR spectrum shows an oxidized doped form of PEDOT (Fig3.5).

The electrochemical properties of a freestanding PEDOT film are studied utilizing a current collector-less three-electrode configuration, platinum lead and a polyimide mask that exposes the polymer to the electrolyte. Cyclic voltammograms demonstrate a high electrochemical stability with nearly rectangular shapes after 500 cycles in 1 M H2SO4 at a scan rate of 25 mV s-1 (Figure3.7). Notably, cyclic voltammograms retain their rectangular shape as the scan rate is increased from 25 mV s^{-1} to 100 mV s^{-1}, this is due to a low electrode resistance and the polymer's high electronic conductivity (Figure 3.7). PEDOT-RVPP exhibits a state-of-the-art

capacitance of 181 F g-1 calculated from a discharge curve (Figure 3.8) at a current density of

3.5 A g-1, moreover, triangular-shaped curves at various current densities indicate facile charge
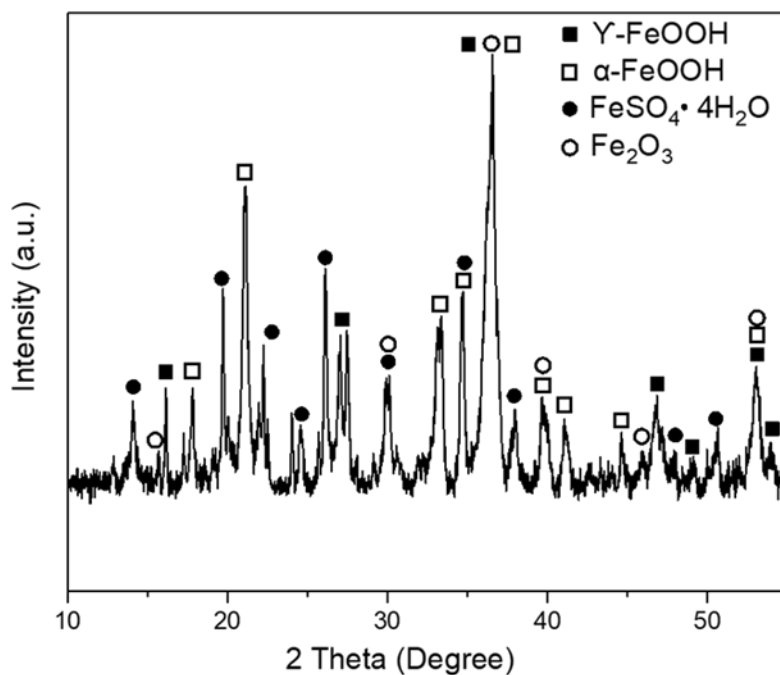
transfer.

Figure 3.3 The Powder X-ray diffractogram shows the main components of rust are α-FeOOH,

γ-FeOOH, Fe2O3 and FeSO4

3.5 MATERIALS AND METHODS

Materials. 3,4-ethylenedioxythiophene (EDOT, 97%), chlorobenzene (99%), hydrochloric acid

(37%), sulfuric acid (98%), methanol (≥99.8%) were purchased from Sigma Aldrich and used

as received.

Corroding Protocol. α-FeOOH, □-FeOOH and FeSO4 rust layers were produced by immersing a

2.5 cm × 4 cm low carbon steel sheet in 20 mL of a 0.01 M H2SO4 solution for 48 h at 25 oC.

Corroded sheets were then rinsed and dried under ambient conditionss.

Rust-Based Vapor-Phase Polymerization of PEDOT. The Teflon liner of a hydrothermal reactor

is loaded with a 7 mm × 7 mm rusted steel substrate, 20 μL of concentrated hydrochloric acid

and 200 μL of a 0.0674 M EDOT solution (3.37□10-5 mol) in chlorobenzene (4.93□10-3 mol).

Each of these components is contained in a glass vial.

This rector is sealed, heated for 6 h in an oven at 150 °C and then cooled in an ice bath for 15

min. A PEDOT-coated substrate is immersed in water to delaminate the polymer film.
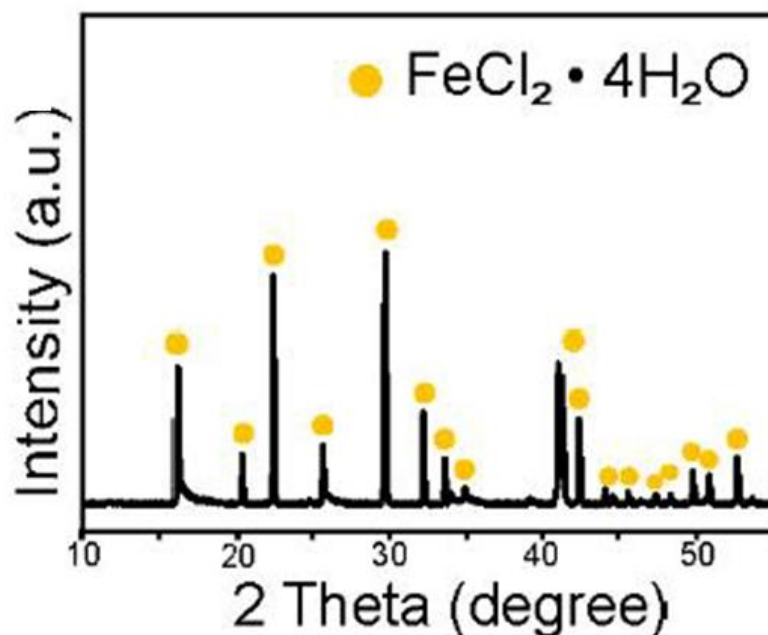

Figure 3.4 Powder X-ray diffractogram confirms that the core is comprised of ferrous chloride –

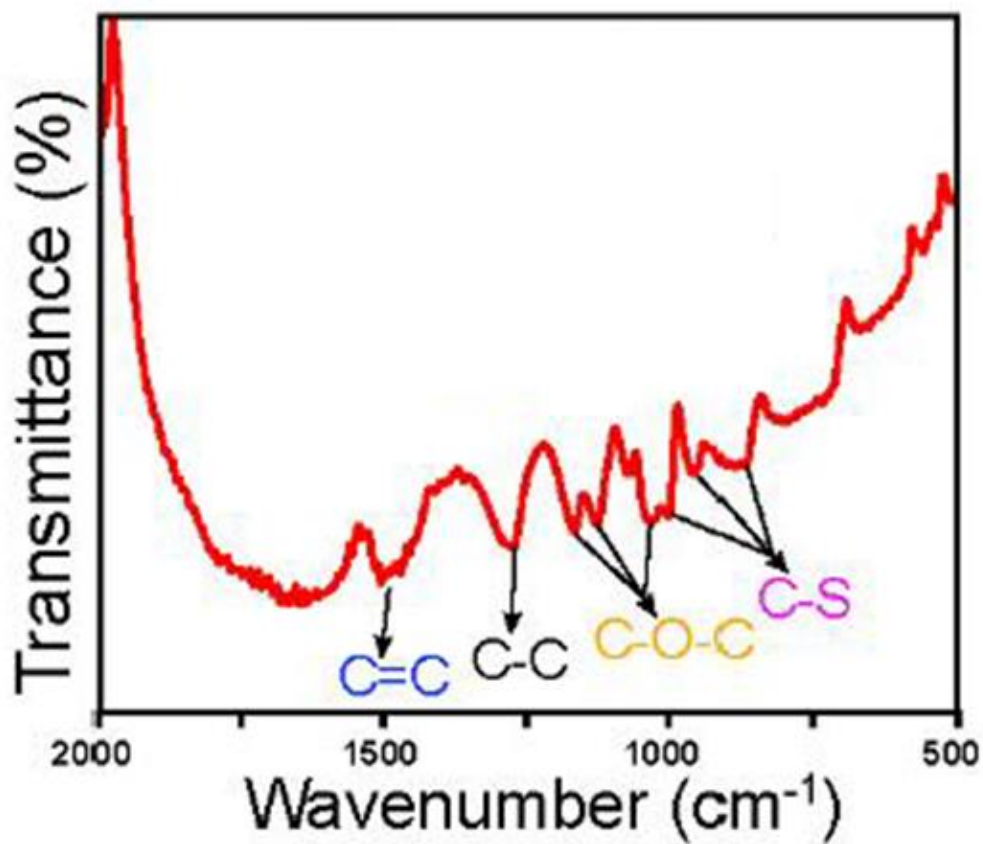this salt is the product of reduced ferric ions.

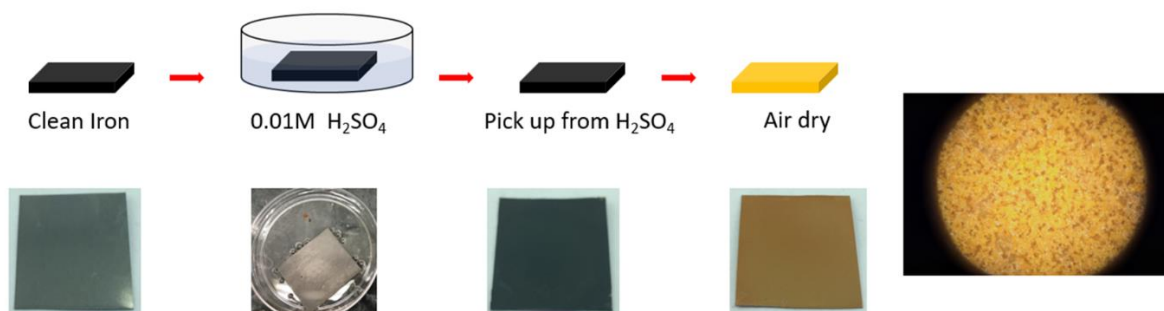Figure 3.5 FT-IR spectrum shows a doped conjugated backbone.

Figure 3.6 Rust layers were produced by immersing a 2.5 cm × 4 cm low carbon steel sheet in 20 mL of a 0.01 M H2SO4 solution for 48 h at 25℃. Corroded sheets were then rinsed and dried under ambient conditions.
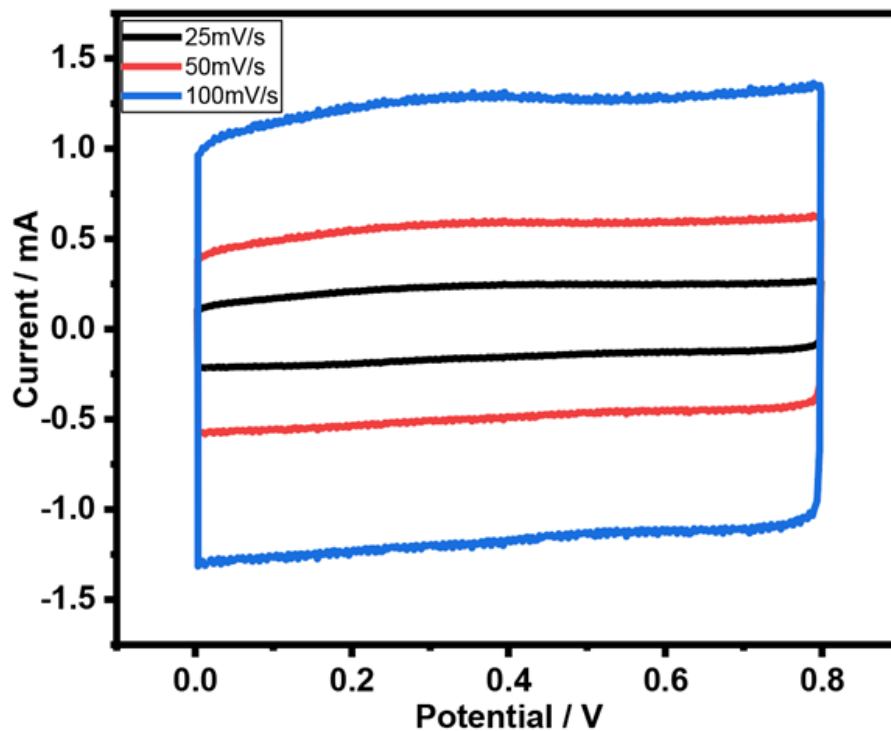
Figure 3.7 A rectangular-shaped curve and stable capacitive behavior is exhibited as the scan rate increases from 25 to 100 mV s-1
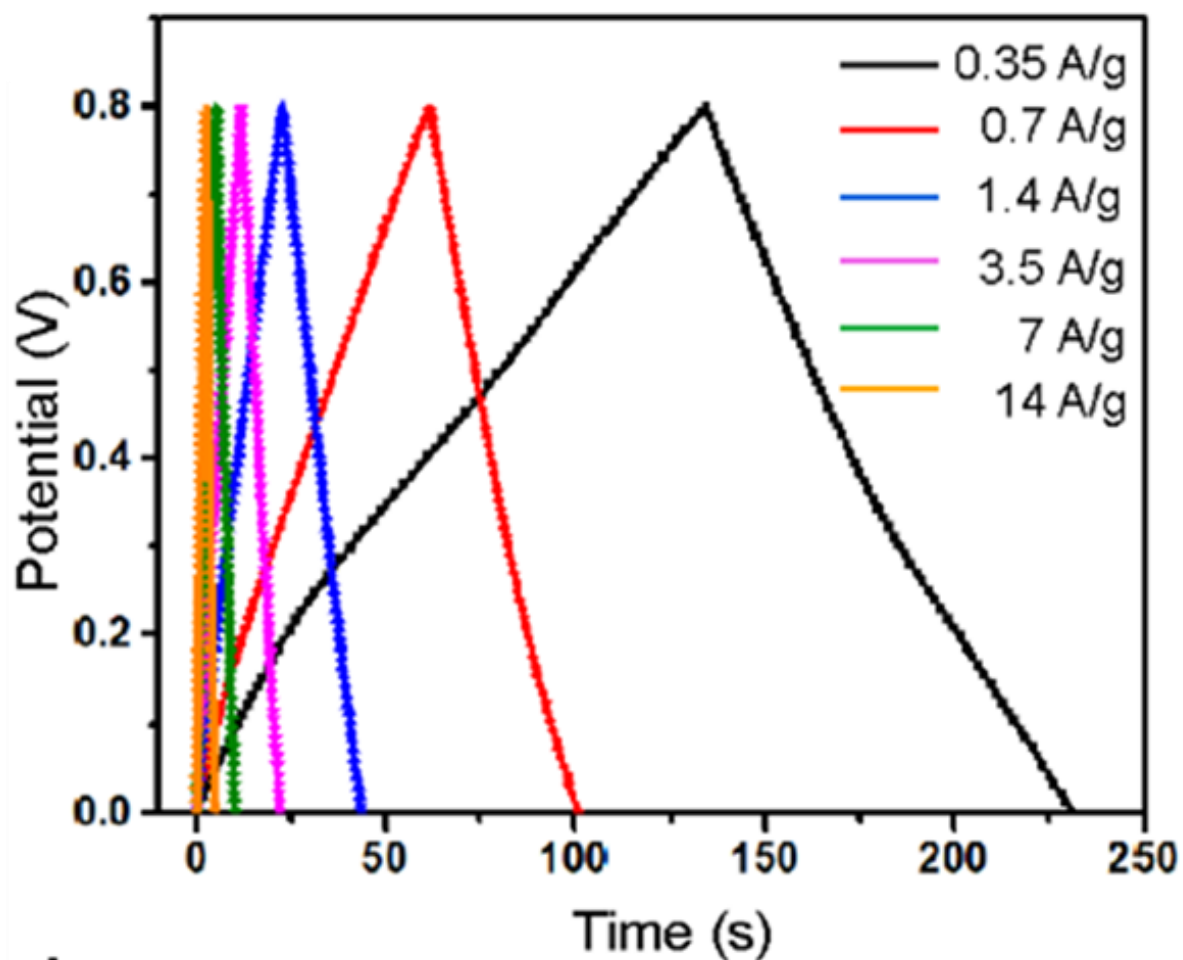
Figure 3.8 PEDOT-RVPP exhibits a state-of-the-art capacitance of 181 F g-1 calculated from a discharge curve at a current density of 3.5 A g-1

Table 3.1: Capacitances at different current density

Current density A/g	0.35	0.7	1.4	3.5	7	14
Capacitance F/g	152	165	174	181	176	154

Chapter 4 Summary

Supercapacitors have become a promising energy storage device with superior performance such as high energy density and power density. The electrode material of the supercapacitor has a great influence on its performance. The conductive polymer has high conductivity and flexibility and is therefore often used as an electrode material for supercapacitors. PEDOT has excellent electrical conductivity, making it ideal for making electrode materials for high power density supercapacitors. However, conventional PEDOT synthesis methods such as chemical oxidation and electrochemical oxidation are unable to synthesize PEDOT with high surface area, which results in insufficient surface area to adsorb charge, thereby limiting the performance of the supercapacitor. People usually increase the surface area by creating nanostructures on conductive polymers. The traditional method is template based nano-structuring, which is expensive and time consuming. Combining ferric chloride aquatic solution hydrolysis and polymerization to obtain PEDOT nano-fiber in one step has been confirmed, however, more controllable synthesis should be proposed.

Rust contains many types of iron oxides and iron hydroxides, it will liberate Fe^{3+} when meet with acid. So rust is a good solid source for providing Fe^{3+} as oxidant in PEDOT polymerization. We introduce HCl vapor to release Fe^{3+} from rust and introduce EDOT monomer as the same time. The polymerization of PEDOT combine with Fe^{3+} hydrolysis lead to a core-shell structure PEDOT nano-fiber formed. The electrochemical properties of a freestanding PEDOT film are

studied utilizing a current collector-less three-electrode configuration, platinum lead and a polyimide mask that exposes the polymer to the electrolyte. The PEDOT nano-fiber film shows good cycle life, and high capacitance of 181 F g-1 at a current density of 3.5 A g-1. In this approach, we advance the fields of conducting polymer synthesis, vapor-phase chemical deposition and energy storage through a facile scalable and patternable process that enables deposition of electroactive high surface area electrodes for fabricating state-of-the-art electrochemical capacitors.

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