

2012

Optimisation of the layer-by-layer synthesis method for polypyrrole actuators

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Recommended Citation

Sangian, Danial, Optimisation of the layer-by-layer synthesis method for polypyrrole actuators, Master of Engineering - Research thesis, School of Mechanical, Materials and Mechatronics Engineering, University of Wollongong, 2012. <http://ro.uow.edu.au/theses/3660>

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Optimisation of The Layer-by-layer Synthesis Method For Polypyrrole Actuators

A thesis submitted in fulfilment of the requirements

for the award of the degree

of

Master of Engineering, by research

From

University of Wollongong



by

Danial Sangian

B.Sc. (Polym.Eng)

School of Mechanical, Materials and Mechatronic Engineering

2012

Declaration

I, Danial Sangian, declare that this thesis, submitted in fulfilment of the requirement for the award of Master of Engineering, in the Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Danial Sangian

June, 2012

This thesis is presented in honour of the ancient waters of
my homeland, the **Persian Gulf**

Acknowledgment

First off, I am indebted to my mate and supervisor *Professor Geoffrey Spinks*, who has supported me and my research while providing me with the opportunity of which many people can only dream. I am especially grateful for his unyielding patience and openness, always willing to give a helping hand at any time.

Secondly, I owe many thanks to *Dr. Wen Zheng*, who paved the way for my research and without whom it would be an insurmountable task, working with me and enriching my experience. Additionally, I would like to thank *Ryan Sullivan* for his friendly aid in the crafting of my thesis. I would also like to acknowledge all the kind staff and students at the Intelligent Polymer Research Institute.

In particular, from bottom of my heart I would like to thank my parents in Iran, *Sima* and *Hossien*, and my sisters *Dayana* and *Diba*, who suffered a lot for me during my study.

ABBRAVATIONS

| | |
|-----------------|-----------------------------------------|
| CV | cyclic voltammograms |
| CPs | conducting polymers |
| Li.TFSI | bis-trifluoromethanesulfonimide lithium |
| PPy | polypyrrole |
| ε | strain |
| σ | stress |
| PF_6^- | hexafluorophosphate |
| Q | charge |
| Ag Ag + | silver silver ion reference electrode |
| PC | propylene carbonate |
| LBL | layer by layer |
| Cont | Continuous |

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Abstract:

Electrochemical actuators based on conducting polymers are being developed for many applications because of their significant advantages such as low voltage operation, relatively easy synthesis process. Polypyrrole actuators are important and popular because of their similarity to natural muscles are often called “artificial muscles”. It is always important and challenging to find an efficient electropolymerization method to modify and develop polypyrrole actuators. A new electropolymerization method, which involves preparing the PPy free-standing film as a sequential series of electrodeposited layers with ethanol washing in between each deposited layer. This method, known as layer by layer electropolymerization, has been shown to be more efficient when compared to the other electropolymerization methods. Here we attempt to compare the mechanical properties and electrical conductivity of PPy free-standing films polymerized at different current densities via the layer by layer (LBL) and continuous electropolymerization methods.

Chapter One: Literature Review

1.1 Thesis motivation

Electrochemical actuators based on conducting polymers are being developed for many applications because of their significant advantages such as low voltage operation, relatively easy synthesis process and comparatively large strokes as well as their ability to operate against high mechanical loads [1]. It is always important and challenging to find an efficient electropolymerization method to modify and develop polypyrrole actuators. A new electropolymerization method, which involves preparing the PPy free-standing film as a series of electrodeposited layers with ethanol washing in between each deposited layer has been reported by Zheng et al [2]. This method, known as layer by layer electropolymerization, has been shown to be more efficient when compared to the other electropolymerization methods. In fact, the washing steps between the sequentially polymerized layers generated non-porous films due to the reduction of the concentration of oligomeric species within the diffuse layer near the electrode, which prevents the three-dimensional growth mechanism that occurs by deposition of secondary particles from solution.

Only very limited studies have been conducted using the layer-by-layer polymerization method. One key variable that requires further study is the applied current density used during the galvanostatic LBL method. The deposition rate, which is directly dependant on the applied current density, of PPy on the substrate also is one of the important parameters that can affect the final properties and morphology of PPy free standing film. Thus, applied current density can and should be carefully controlled in the preparation of PPy actuators.

This thesis aims to compare the mechanical properties and electrical conductivity of PPy free-standing films polymerized at different current densities via the layer by

layer and continuous electropolymerization methods. The results will provide a better understanding of how these properties affect the performance of PPy actuators.

1.2 History of conducting Polymers

Before mid 1970s, polymers were known as insulators. The idea that plastics could transfer electricity was considered to be absurd. In fact, plastics continue to be widely used for electronics purpose because of their high resistance to the transfer of electricity. As such, many conventional polymers are widely used as inactive packaging and insulating material. This old idea is rapidly changing as a new class of polymers introduced as intrinsically conductive polymer (CP) or electroactive polymers became known over the past few decades [3].

Polyacetylene was synthesized by Natta et al. as a black powder in 1958 [4]. This material was found as a semi-conductor with electrical conductivity between 7×10^{-11} to 7×10^{-3} S/m, depending on the polymerization process. Polyaniline was likely the first conducting polymer and was discovered in the mid-19th century [5]. However, the ability of charge transfer was not understood at that time. Early in 1963 three Australian researchers, synthesized a conductive polypyrrole (PPy) which had conductivity around 1 S/cm [6]. Eventually, in 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa achieved high conductivity in oxidized iodine-doped polyacetylene. Because of this research they were awarded the Nobel Prize of Chemistry "For the discovery and development of conductive polymers" in 2000. Their materials were called 'organic metals' and have shown conductivity around 10^3 S/cm which is 10^9 times more conductive when compared with its undoped state.

Conductivity in CPs has been associated with the conjugated backbone with the formation [7] of polarons and bipolarons as charge carriers when the polymer is doped.

Furthermore, the movement of bipolarons transfers the charge under the electrical field is due to the delocalization of π electrons and the high degree of π bond conjugation. The generation of polarons and bipolarons occurs during polymer doping where electrons are added to or removed electrons from the π bonds. As a result of the poor stability of polyacetylene $(CH)_x$ stable CPs such as polypyrrole (PPy), polyaniline (PANi) and polythiophene (Pth) are more popular to use for most of applications. The chemical structures of these polymers are shown in Fig1.1.

Figure1.1 Chemical structure of three famous conducting polymers, Top to bottom: Polyaniline (PANi); Polypyrrole (PPy) and Polythiophene (PTh) (undoped forms shown).

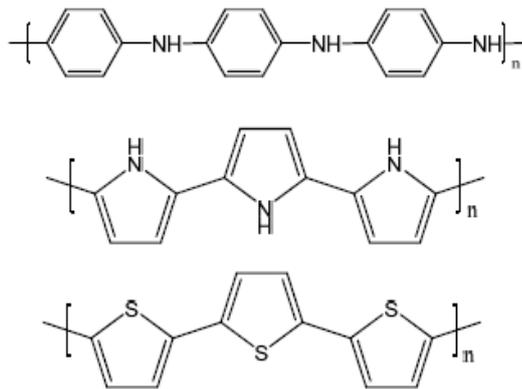
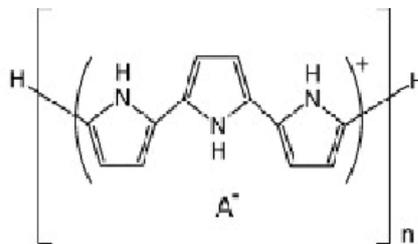


Figure1.2 Chemical structure of oxidized or doped PPy



Successful synthesis of the three major CPs shown in Figure 1.1 can be achieved via electrochemical methods reported by Diaz et al [8-10]. In the case of these CPs, electrons are removed from the polymer bulk via an oxidizing process and ions transfer

in to the polymer to balance the charge. The oxidized, or doped, form of PPy with its associated counterion (A^-) is shown in Fig 1.2. Approximately one positive charge (and one associated dopant counterion) is spread over three pyrrole units in the fully doped PPy. The dopant counterion can be almost any negatively charged molecule, although the properties of the doped polymer depend strongly on the type of dopant used.

1.3 Conducting Polymer actuators

So many applications such as electronics, batteries, electrochromic devices, bionics, solar cells, drug delivery systems, corrosion protection, electrochemical sensors and actuators are identified for conducting polymers [10-19]. Polypyrrole (PPy) is one of the widely used members of conducting polymers which can be synthesized via electrochemical or chemical polymerization process [20, 21]. Polypyrrole is important because of its stability in a wide range of solvents, reasonable mechanical properties, biocompatibility, electrical conductivity and large actuation strain. These useful properties makes PPy a candidate for specific technologies such as antistatic coating, electromagnetic shielding, microwave absorbers, rechargeable batteries, membranes and artificial muscles [20]. Its convenient electrochemical and chemical preparation affords a variety of anionically doped materials possessing a high electrical conductivity [21, 22]. Furthermore, it was already shown that chemical and physical properties of polypyrrole could be strongly affected by electropolymerization parameters such as solvent, electrodeposition rate or current, supporting salt, pH, temperature and pyrrole concentration [23].

1.4 Polypyrrole actuators

Polypyrrole actuators are important and popular because of their similarity to natural muscles are often called “artificial muscles”. Conducting polymers are known to mechanically respond to electrochemical stimuli and have been utilized as linear actuators. For linear actuator, work is performed against an external load on a single axis and principally characterized by stress, strain and strain rate. For most of the conducting polymers, actuation is obtained via ingress and egress of ions contained in an electrolyte bath. The actuation mechanism requires an electromechanical cell with a polymer as working electrode and suitable non-reactive counter electrode, both in contact with an electrolyte.

The effect of electrochemical polymerization (synthesis) conditions such as temperature and deposition rate on the mechanical properties and conductivity of PPy actuator has been widely studied. For example, faster electrodepositions as occurs galvanostatically at higher current densities produce rougher surfaces, porous films and inferior properties. It has been shown that oligomeric species/ low molecular weight chains are trapped in the polymer structure during the electropolymerization and these species promote a “secondary deposition” of polymer via 3-D growth that is both rough and porous [2]. As is well known, the conductivity, mechanical properties and surface roughness of PPy free-standing films are closely related to their microstructures. Strictly speaking, if the density of the material is high (low porosity) the modulus and strength are high as well, because there are fewer defects such as porosity in the microstructure. It is important to note that the microstructure is related to the electrochemical synthesis of the polymer film. Significant improvement in the mechanical properties and conductivity of PPy free-standing film via layer by layer

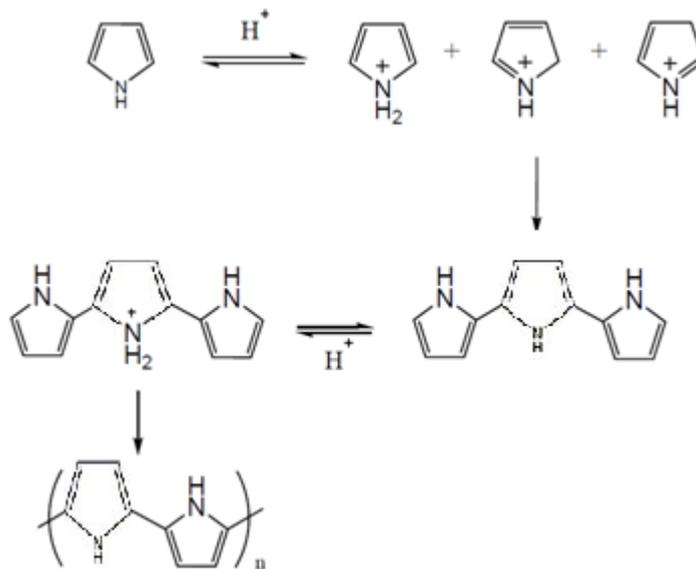
method has been reported by Zheng et al [2]. A layer-by-layer deposition process showed compact deposits while the continuous growth of nuclei in three dimensions produces porous films. It is reported that solvent washing during the electropolymerization of PPy removes oligomeric species from deposited PPy and prevents secondary precipitation of polymer particles. Thus, it has been observed that smooth PPy free-standing film with reasonable mechanical properties and high conductivity can be obtained via layer by layer electropolymerization method due to low porosity and uniform structure of PPy films [2].

1.4.1 Synthesis of Polypyrrole

Chemical polymerization:

Polypyrrole can be synthesised via two main methods, chemically and electrochemically. Chemical polymerization of pyrrole needs an oxidant which is often Fe^{3+} [24]. Other oxidizing agents are acceptable to use as well [25,26]. The typical chemical reaction scheme of PPy is shown in figure 1.3.

Figure 1.3 schematic chemical polymerization of PPy



Poor mechanical properties and low conductivity of chemically polymerized PPy were clarified as the main reasons to make it not suitable for producing actuators [5]. It is important to note that in chemical polymerization method, PPy is obtained as particles or porous coatings instead of a continuous film. The conductivity of chemically polymerized polypyrrole is reported around 10^{-4} S/cm but can approach 100 S/cm when controlled polymerization methods are used [25-27]. Of particular note is the fact that the conductivity of PPy polymerized via chemical methods is significantly lower when compared to the electrochemically obtained PPy due to high porosity [28]. Chemically polymerized PPy is usually used to produce sensors where the high surface area/ porosity can be an advantage [29].

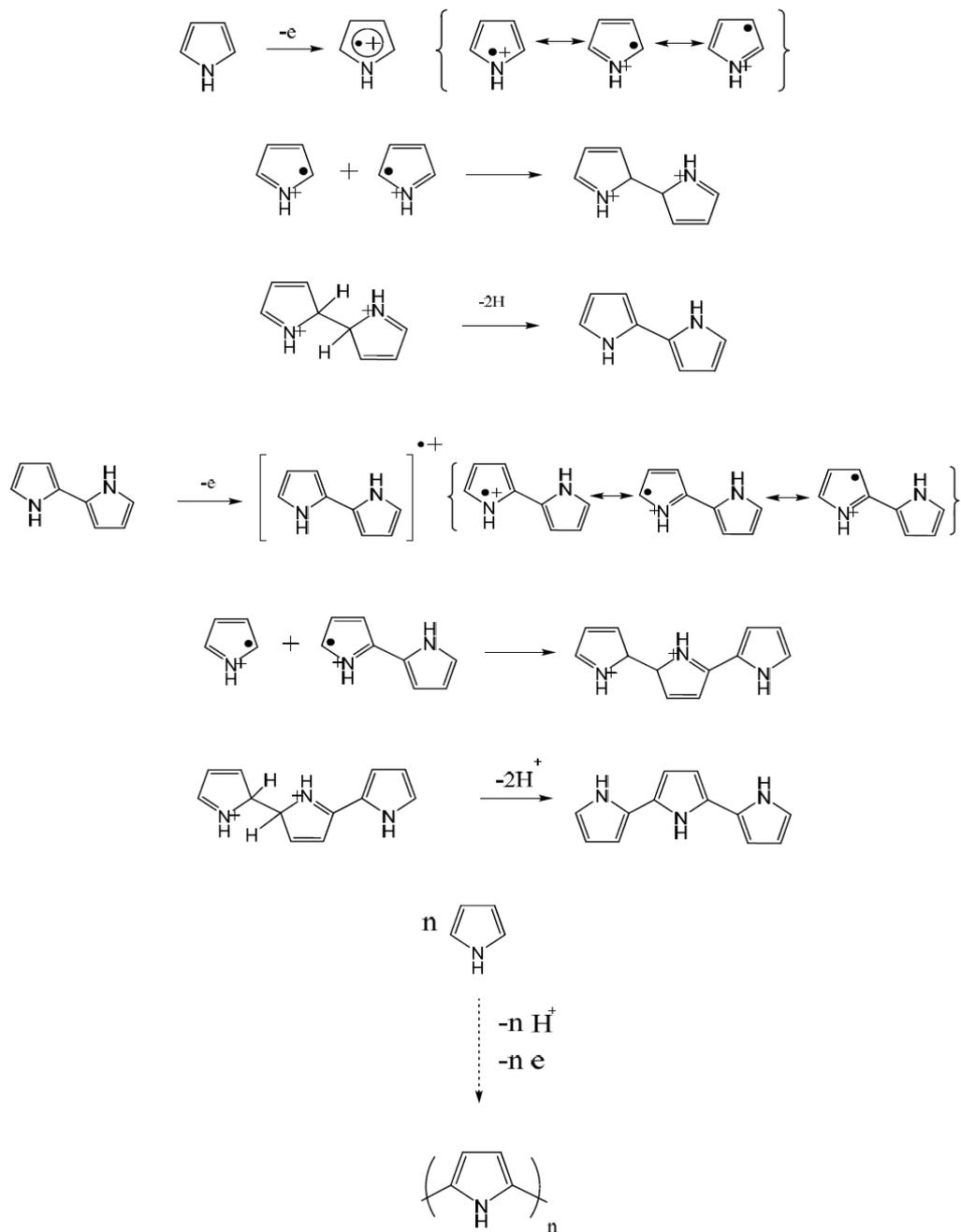
Electropolymerization:

The ability to achieve higher conductivity, controlled film thickness and morphology and reasonable mechanical properties mean that researchers prefer to prepare PPy via the electropolymerization method. In electropolymerization, PPy usually grows on conductive substrates, such as gold, platinum or glassy carbon. It is reported [30] that the final properties of films for each specific substrate can be different. For example PPy films electropolymerized on platinum or glassy carbon have much smoother surfaces when compared with PPy prepared on other electrodes. Electrodeposition of polypyrrole can be achieved using controlled potential or current densities. Temperature of the electropolymerization reaction has a substantial influence on the mechanical properties and electrical conductivity of PPy free-standing films. In general, PPy polymerized at low temperature and low current density shows better properties [31-35]. It is important to note that polymerization at low temperature and low current density avoids any other unpredictable side reactions that can occur at the same time as the polymerization reaction. By eliminating these side reactions and promoting a more ordered molecular structure a higher conductivity result [36].

The first step of pyrrole electropolymerization starts with electrogeneration of radical cation at the anode via oxidation of monomer at the surface of the electrode. The highest charge density resides at the α -position of mentioned radical cation; thus, chain propagation begins by reaction of two radical cations in the first step of polymerization (Fig.1.4). A natural dimer forms by the coupling of two radical cations. Chain propagation continues by oxidation of the dimer into the cation radical with the oxidation potential of the dimer lower than that of the monomer. Consequently, the dimer radical would be more reactive compared with that of the monomer. By coupling another pyrrole monomer with the dimer, a trimer can be generated. Coupling reactions

can occur in several positions such as: α - β , α - α , and β - β . In this stage, there are two ways for chain propagation: linear propagation; and branch propagation. Chain propagation continues via reaction between oligomer radical cations with monomeric radical cations in high concentration close to anode area. By increasing the chain length of polypyrrole, it becomes insoluble in the solution and precipitates out onto electrode (see fig 1.4 for more details).

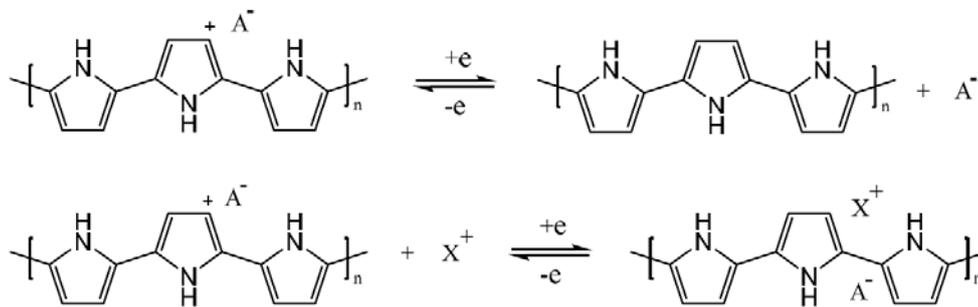
Figure 1.4 schematic electropolymerization of PPy



1.4.2 The switching principles of PPy actuators

Generally, "switching" behaviour can be defined by reversible oxidation and reduction of PPy. Fundamentally, electrons flow in/out of the polymer and create charged or uncharged sites during the reducing/oxidizing process. Simultaneously, ions move in/out of the polymer to balance the total charge number in the system. As a result of the movement of ions the volume of PPy changes during redox cycling. It has been indicated that either anions (A^-) or cations (X^+) also can be moved during the process.

Figure 1.5 The switching property of PPy where A^- represents anion incorporated into the polypyrrole, X^+ represents the cation from the electrolyte.



The changing of PPy redox state is always accompanied by ion exchange between the polymer and the surrounding electrolyte [37]. Gandhi et al [38] has described four general stage of oxidation/reduction process which may happen during actuation. It is also important to note that the following processes:

- 1) Oxidation by cation ejection
- 2) Oxidation by anion incorporation

3) Reduction by anion ejection

4) Reduction by cation incorporation

The size of the counter-ion (A^-) determines which processes take place; large anions follow 1 & 4 only, small anions follow 2 & 3 only, while medium sized anions may utilize a combination of all processes.

It has been noticed that the magnitude of the volume change depends on the size of ions that being exchange between polymer and electrolyte. According to Kaneto and co-workers the actuation strain was observed to be linearly proportional to the size of the cation in poly (styrene sulfonate)-doped PPy [34]. Qi et al [38] has found that a larger strain was achieved for larger anions for anions smaller than Br^- . Furthermore, they summarized that for anions size of $Br^- > Cl^- > F^-$ the strain followed this trend and for anions larger than Br^- , $CF_3SO_3^- > ClO_4^- > BF_4^-$ the largest anion generated the smallest strain. They concluded that larger anions were difficult to penetrate in to the polymer film. Cation-dominated actuation in PPy polymerized with large size dopant anion has been reported in many papers. Those large ions were trapped in to the polymer bulk during the polymerization process [32]. Polypyrrole doped with dodecylbenzenesulfonate (PPy/DBS) and polypyrrole doped with *p*-toluene sulfonic acid salt (PPy/PTS) are two typical cation driven actuators as only small cation like Na^+ can penetrate in to the polymer, pTS and DBS were unable to move [40-42].

1.4.3 The performance of PPy actuators

The performance of the PPy actuators exceeds that of natural muscle in many respects making them applicable to use anywhere where a muscle-like response is desirable. Natural muscles have some particular mechanical properties such as large strain, moderate stress, high efficiency and stability, fast response time, high power/weight ratio, and long lifetime that conventional actuators do not possess. It has been known that the performance of polypyrrole actuators needs to improve and develop to achieve mentioned parameters. For example, PPy actuators show strains around 50% lower than natural muscles [43]. Moreover, it is also necessary to increase the response time and obtain more durable actuators. The performance of polypyrrole actuators is greatly affected by the electrical, mechanical, and electrochemical (switching) properties. For instance, having a material with a high conductivity allows the use of lower applied potentials, both increasing the energy efficiency of the device and avoiding unwanted redox reactions which may lead to degradation of the material. In addition, such contractile materials need to have sufficient mechanical strength so as to be able to apply the needed force during contraction without breaking. The actuation strains as a one the important parameters and is affected by the size of the ions that enter or exit from the polymer bulk. These kinds of behaviour are related to the polymer structure which can be modified via selecting useful electropolymerization method.

1.5 Thesis aims

The main objective of this thesis is to explore further the use of layer-by-layer electropolymerization to prepare PPy free-standing films for actuators. This thesis specifically aims to compare mechanical properties and electrical conductivity of free-standing PPy films polymerized at different applied current densities and to find the most suitable applied current density, and therefore the deposition rate, to create the actuator. In the previous studies using LBL electropolymerization only a very limited number of applied current densities were used to polymerize polypyrrole films. As such, in this study we attempt to polymerized polypyrrole free films at six different applied current densities.

The LBL method has been shown to be more efficient than continuous polymerization for mid to high current densities ($> 0.1\text{mA/cm}^2$), but the case is not so clear cut at lower current densities. In this work, the effects of a lower range of current densities for LBL and continuous electropolymerization methods will be compared, specifically analysing the morphological, mechanical, and electrical properties of samples for use in the future works.

Chapter Two: Experimental

2.1 Introduction

The experimental and technical methods are briefly explained in this chapter, including microscopy characterization, polymer preparation, mechanical testing, and electrochemistry characterization and actuation test.

2.2 Methods used for Polymer preparation

2.2.1 Electrochemical polymerization

Polypyrrole was prepared from LBL and continuous electrochemical polymerization methods. Both methods use a constant current (galvanostatic). The total electropolymerization time was calculated according to the particular current density to ensure that the total charge passed was the same for each sample. The deposited polymer thickness is known to be proportional to the charge passed [30].

Figure 2.1 Typical electrochemical polymerization cell for free standing film preparation.

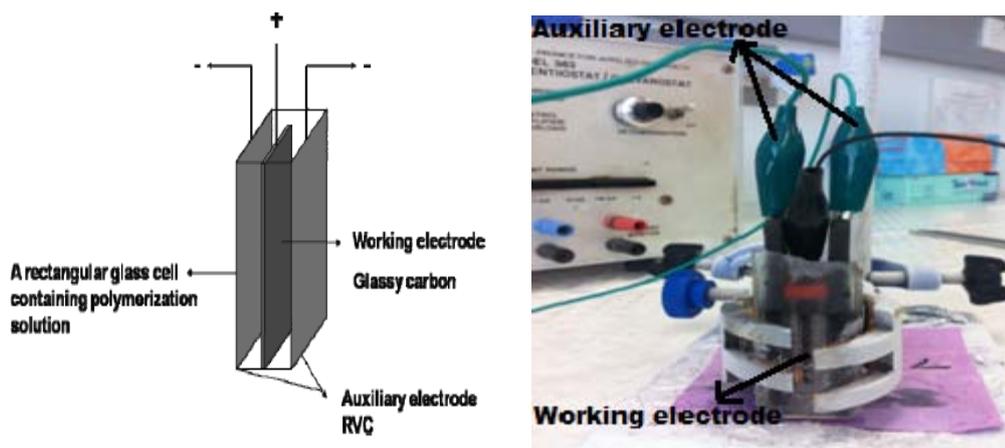


Fig 2.1 shows the electrochemical polymerization cell which was used to prepare PPy free - standing film in our lab. A rectangular glass cell in the fig 2.1 that contains polymerization solution was used as an electropolymerization cell. The two green wires on the top that have been connected to the auxiliary electrode transfer negative charge to the polymerization cell. Additionally, the black wire in the middle that has been connected to the working electrode (substrate) transfers positive charge in to the polymerization cell. Working electrode was placed in the middle of polymerization cell and in the between of auxiliary electrodes that were placed parallel. The above electropolymerization cell was kept in freezer (-31°C) during the polymerization process. The substrate used to prepare PPy-free standing film plays a critical role and can affect on the mechanical properties and actuation performance [44,45]. Materials used as a working electrode for polymerizing CPs must meet criteria of being stable under the polymerization conditions to avoid oxidation of the electrode itself. In this thesis glassy carbon (GC) with 2cm wide, 4cm long and 0.2cm thick was used as a working electrode. Reticulated vitreous carbon (RVC) also was used as counter electrode.

There are typically three different types of electrochemical deposition methods according to the electrical signals provided; namely galvanostatic, potentiostatic and potentiodynamic polymerization. In this thesis, all the samples were polymerized under same total charge by galvanostatic method. The amount of polymer deposited on the substrate can be controlled via varying the charge which depends on current density and polymerization time.

The total charge Q passed through the cell could be calculated as:

$$Q = \int i \cdot dt \quad (2.1)$$

Where i and t are the current and the deposition time respectively. As described in chapter 1, the current density is one of the critical parameters that can affect the conductivity, surface morphology and mechanical properties of PPy [46,47]. The present study involved varying the current density while maintaining a constant Q .

In this thesis, Electropolymerization used a solution of 0.06M pyrrole, 0.05M of TBA.PF₆ (tetrabutylammonium hexafluorophosphate) and 1 wt% H₂O in PC (Propylene carbonate) after bubbling with nitrogen gas. In all cases polymerization was conducted at -31 °C.

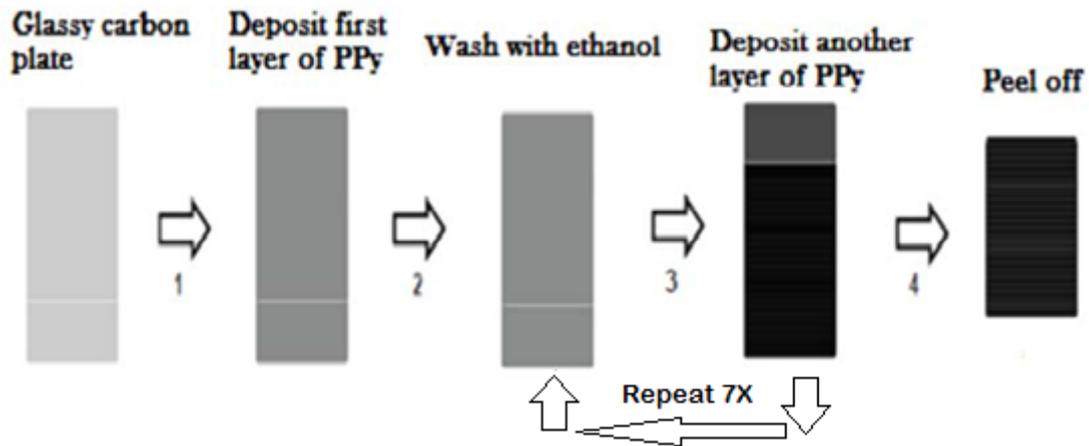
2.2.2 Continuous method

For comparison purposes one sample was polymerized via the continuous method. This continuous sample was polymerized at 0.1 mA/cm² for 8 hours without any interruption or ethanol washing.

2.2.3 Layer by layer (LBL) method

The layer by layer (LBL) electropolymerization method involved preparing the free-standing film as 8 separate polymerized layers with an ethanol wash between layers. The typical electropolymerization process of layer by layer method on glassy carbon substrate is shown clearly in figure 2.2.

Figure 2.2 The electropolymerization process of layer by layer method.



2.3 Technique used for film characterization and property measurement

2.3.1 Film thickness

The thickness measurement of free standing PPy film is an important parameter to measure, since its determination affects the accuracy of the mechanical properties and conductivity values. Previously, thickness of free standing PPy film was measured with micrometer which is not accurate for film thicknesses used here (10 μm).

In this study the PPy free standing-film thickness was measured via micrometer, SEM microscopy and profilometer. The SEM microscopy and profilometer produced accurate and reproducible results. The simple, rapid and convenient operating of the profilometer machine meant that it was used as the main instrument to measure the films thickness in this thesis.

2.3.1.1 Micrometer

Micrometer or micrometer screw gauge is an instrument incorporating a calibrated screw which is widely used for precise measurement of small distances in mechanical engineering and machining as well as most mechanical trades. The thickness of three different particular positions on a PPy free- standing film as a reference was measured and compared by three different instruments to find the most accurate instrument. Table 2.1 shows the thickness measurements result of three different instrument. Micrometer results have shown similar numbers of thickness for each position which indicates high accuracy of measurement while the numbers were not precise because of the limited measurement resolution ($>1 \mu\text{m}$).

Table 2.1 Thickness measurement of PPy free-standing film by three different instruments.

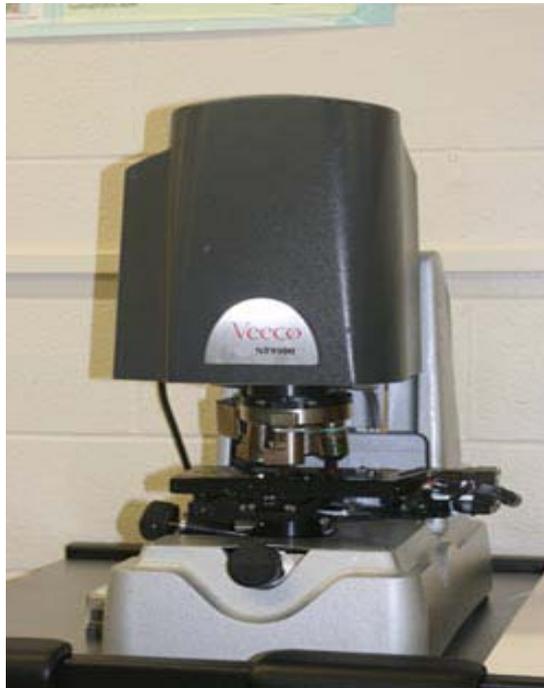
| Instrument | Thickness (μm) | | | Average thickness (μm) |
|--------------|-----------------------------|------------|------------|-------------------------------------|
| | Position 1 | Position 2 | Position 3 | |
| Micrometer | 10 | 10 | 10 | 10 |
| Profilometer | 9.5 | 9.6 | 9.5 | 9.53 |
| SEM | 9.5 | 9.6 | 9.5 | 9.53 |

2.3.2 Profilometer analysis

An optical profilometer machine (Wyko 9100) was investigated as a means to measure a more precise thickness of the PPy films. The average thickness was obtained by measuring the height of a cut edge of the film mounted on a glass slide. The film was first attached to the glass slide by double sided tape to accurately measure the PPy

free -film thickness. In all cases, the average thickness was between 9.5 and 10.2 μm . The image clearly shows the glass substrate, double-sided tape and PPy layers (Fig.3.1). Profilometer measurement has been done for all six different PPy samples to measure the thickness as accurately as possible.

Figure 2.3 Optical profilometer machine.

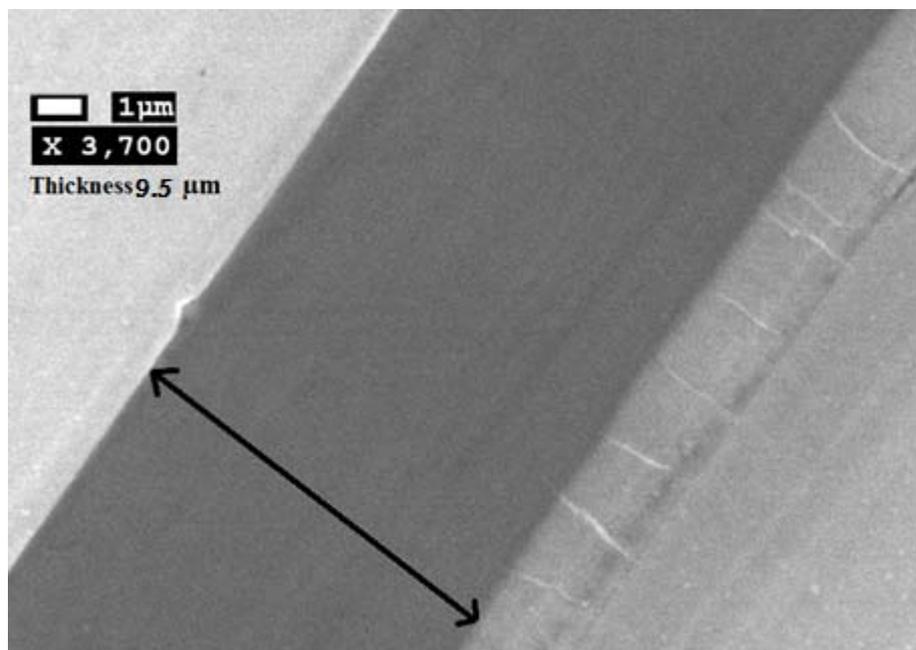


2.3.3 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. SEM is a useful method to measure accurate thickness of polymer films via cross sectional image. The PPy free-standing film was first cut to a small size and then was fixed horizontally in to the resin to hold the sample flat in order to reducing the observation

errors. It has been found that the sample preparation for SEM method takes more time when compared to the profilometer method, while both of the methods were shown similar results which are accurate and correct. Figure 2.4 shows a uniform cross sectional image of PPy free standing film which is obtained via SEM method.

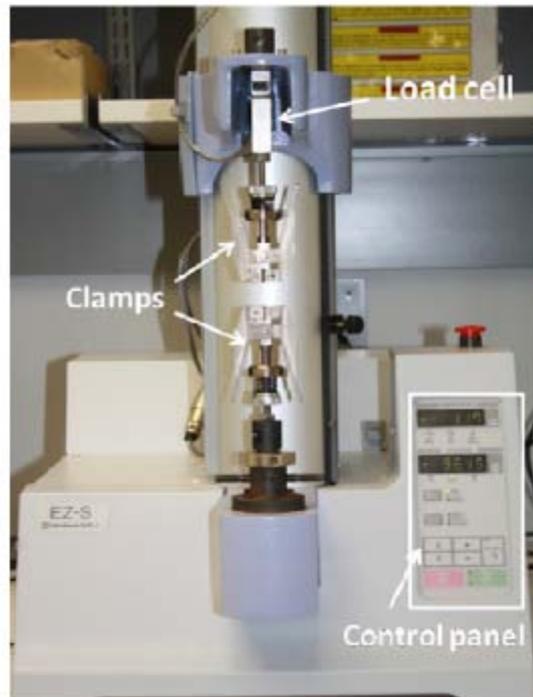
Figure 2.4 the SEM image of a cross-section of a PPy free-standing film



2.3.4 Mechanical properties

The mechanical properties of PPy free-standing films such as elastic (Young's) modulus, elongation at break and tensile strength were obtained using Shimadzu EZ tensile test machine. According to the instrument manual, it has 0.001mm resolution in length measurement and $1/50000$ * load cell capacity resolution in force measurement (2N cell will give $2\text{N}/25000=0.04\text{mN}$ resolution).

Figure 2.5 Shimadzu EZ Tensile test machine.

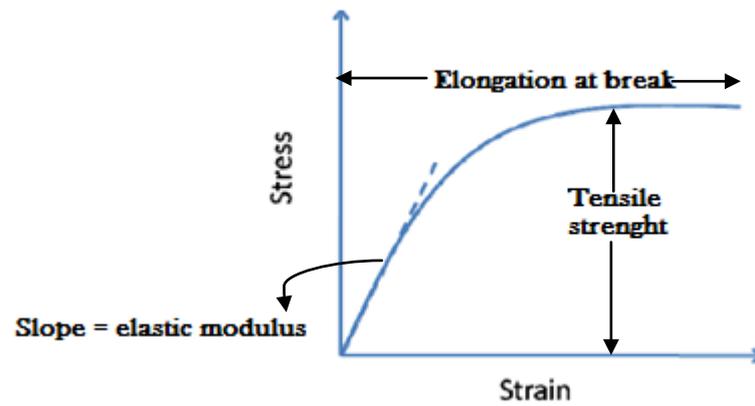


Elastic modulus of PPy free-standing films were determined by fitting the linear region of the strain/strain curve according to the equation:

$$Y = \frac{\sigma}{\varepsilon} \quad (2.2)$$

Where Y is elastic modulus (Young's modulus) σ is applied stress and ε is strain generated by load. CPs typically shows the stress/strain curve like figure 2.6 [48, 49]. The Young's modulus is taken from the slop as shown and the tensile strength and elongation at break are also obtained directly from the stress-strain curve.

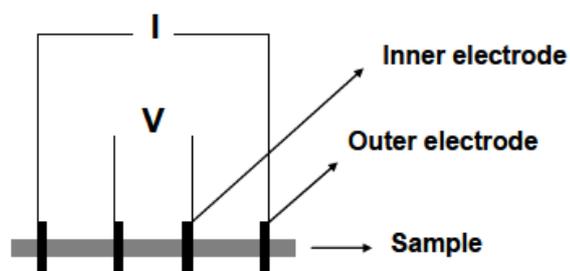
Figure 2.6 Typical stress/strain curve of CPs



2.3.5 The electrical conductivity

The electrical conductivity of materials refers to their ability to pass electricity. The electrical conductivity was obtained by using ASTM (American society for testing and material) 4 point probe instrument. A schematic diagram of the instrument is shown in figure 2.7.

Figure 2.7 a schematic design of four point probe machine.



A known current is applied between the outer electrodes and the potential is measured between the inner electrodes. According to Ohm's law, resistivity can be calculated as:

$$\rho = \frac{whv}{Il} \quad (2.3)$$

Where w is sample width, h is thickness of sample. V is potential drop, I is the applied current, l is the distance between inner electrodes and ρ is surface resistivity or sheet resistivity.

2.3.6 Cyclic Voltammetry (CV)

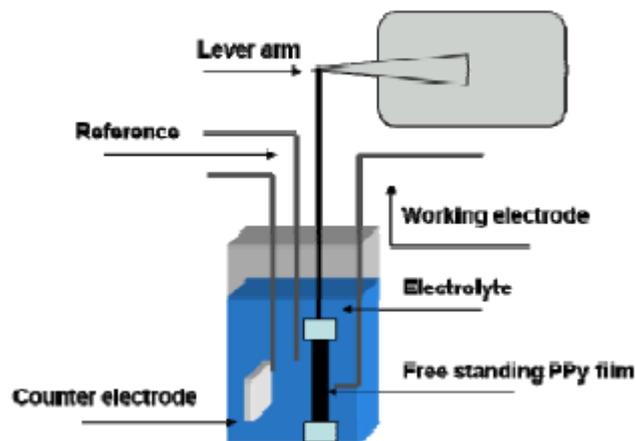
Cyclic voltammetry is a technique for electrochemical studies and is useful in obtaining information for even very complicated electrode reactions. During the CV test, the potential is linearly scanned over a certain range of voltage. Potential will start from an initial value and continuously sweep between an upper and lower limit for a number of cycles at a set linear scan rate then return to the final potential at the end of experiment. In this thesis, cyclic voltammetry (CV) curves were obtained for one continuous and one LBL sample to compare with each other. Ag|Ag⁺ was used as a reference electrode which is suitable for organic electrolyte. A potential scan between 0.9- to 0.7 V and scanning rate 5 mV/s was used.

2.3.7 Actuation test

Electrochemical actuation test was conducted in a three electrode system and deformation changes were recorded by a force/distance transducer (Aurora Scientific Inc). The PPy free-standing film was held under tension while the voltage was scanned

in the particular range. In addition, the tension rate has been kept constant during the length increasing of sample. Alternatively, five different amounts of stresses were applied during the actuation test and three cycles were fixed for each particular applied stress. The actuation strain also was calculated by diving length deformation from initial length of PPy free- standing film. A convenient electrochemical cell was used in this thesis. $\text{Ag}|\text{Ag}^+$ was used as a reference electrode which is suitable for organic electrolyte. A potential scan between - 0.9 to 0.7 V and scanning rate 5 mV/s was used. The experiment set up is shown in figure 2.8

Figure 2.8 Experiment set up for actuation test



Chapter Three: Results and Discussion

3.1 Results

3.1.1 Polymerization condition

The aim of this thesis is to compare the mechanical properties and electrical conductivity of different PPy free-standing films. To achieve this aim, a series of PPy films were prepared and characterized at different current densities via two different electropolymerization methods (LBL and continuous). As described in chapter.1, the current density used during electropolymerization has a major influence on the electrical and mechanical properties of PPy. While the LBL method has been shown to produce high quality PPy films in a short time, no research has been conducted to data on the effect of the current density used in the LBL method on film properties.

Table 3.1 Washing conditions and average thickness of polypyrrole films polymerized at various current densities. (LBL: layer by layer polymerization; Cont: continuous polymerization). “Three separate measurements of thickness were used to determine the average and standard deviation”

| Current Density (mA/cm ²) | Total Electro-polymerization Time | Number of layers | Electro-polymerization time for each layer | washing solvent and temperature(°C) | Average thickness (μm) |
|---------------------------------------|-----------------------------------|------------------|--------------------------------------------|-------------------------------------|------------------------|
| 0.10(Cont) | 8 hr | 1 | 8 hr | None/-31 | 9.65 μm ±0.1 |
| 0.10(LBL) | 8 hr | 8 | Each 1 hr | Ethanol/ -31 | 9.7 μm ±0.1 |
| 0.50 | 96 min | 8 | Each 12 min | Ethanol/ -31 | 9.55 μm±0.1 |
| 1 | 48 min | 8 | Each 6 min | Ethanol/ -31 | 10.1 μm ±0.1 |
| 2 | 24 min | 8 | Each 3 min | Ethanol/ -31 | 10.2 μm ±0.1 |
| 3 | 16 min | 8 | Each 2 min | Ethanol/ -31 | 9.5 μm±0.1 |

Films were polymerized using one of six different selected current densities. Table 3.1 summarizes the conditions used to prepare the polypyrrole free-standing films and their average thickness. The total electropolymerization time was calculated for each current density to ensure that the total charge passed was the same for each sample. Thus, the total electropolymerization time decreased when increased current

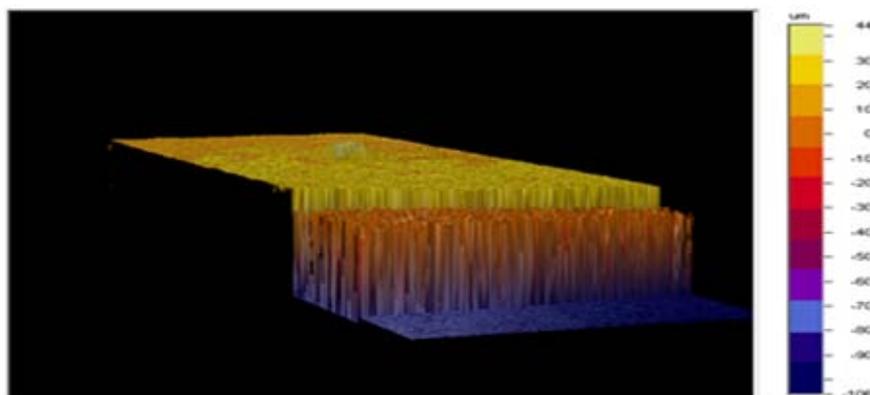
density. The layer by layer electropolymerization method involved preparing the free-standing film as 8 separate polymerized layers with an ethanol wash between layers. Table 1 lists the electropolymerization time used to deposit each PPy layer between washing steps. As a comparison, one film was prepared in one continuous polymerization at 0.1 mA/cm^2 . This sample was not washed with ethanol.

3.1.2 Film characterization

3.1.2.1 Profilometer analysis

The thickness of each polypyrrole free-standing film was measured with a profilometer (Wyko 9100) as thickness is one of the important and sensitive parameters used to calculate conductivity and mechanical properties. The average thickness was determined by measuring the height of a cut edge of the film mounted on a glass slide. In all cases, the average thickness was between $9.5 \mu\text{m} \pm 0.1\text{SD}$ and $10.2 \mu\text{m} \pm 0.1\text{SD}$. Figure 1 shows the 3-Dimensional interactive image of profilometer that was taken from the height of a cut edge of a PPy free-standing film.

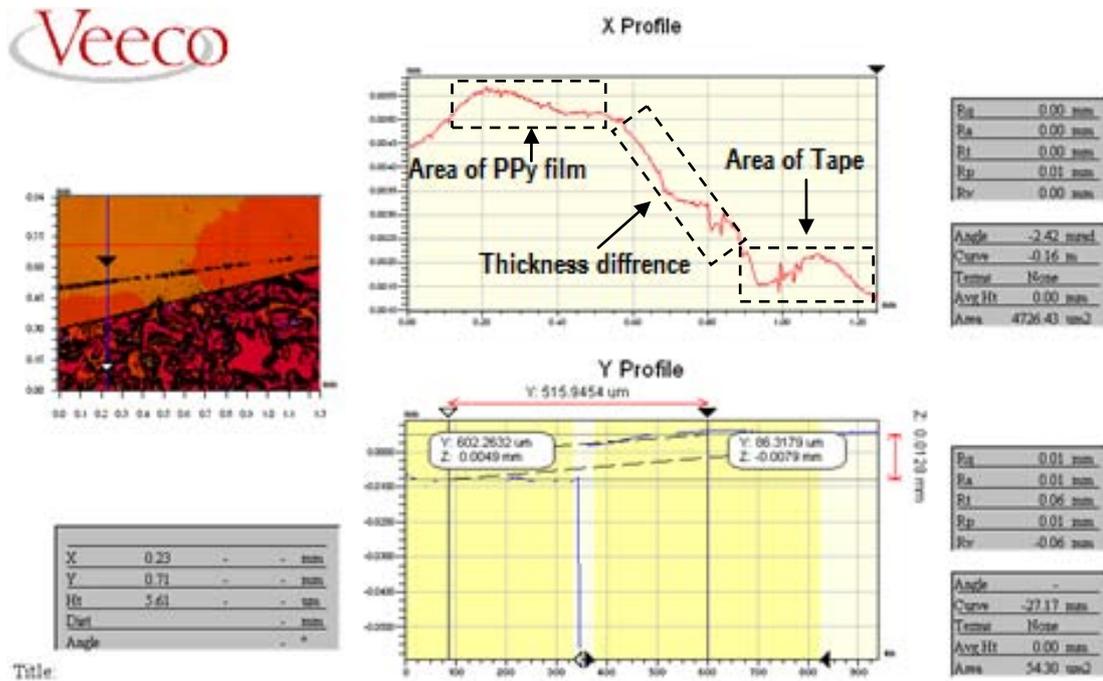
Figure 3.1 The 3-Dimensional interactive image of profilometer.



PPy films were fixed to a glass slide using double-sided adhesive tape. In Figure 3.1, the yellow layer on the top refers to the PPy free standing film surface and the red layer in the middle refers to the double sided tape and the blue layer on the bottom is the surface of the glass slide. Profilometer measurement has been done for all six different PPy samples to measure the thickness as accurately as possible. In all cases, the average thickness was between $9.5 \mu\text{m} \pm 0.1\text{SD}$ and $10.2 \mu\text{m} \pm 0.1\text{SD}$. It is important to note that the software of machine is able to calculate the average thickness of a specific area of PPy film. In this thesis, an average thickness of wide range of area of each sample was obtained automatically by the software. (See Figure. 3.2 for more details)

Figure 3.2 shows the calculation procedure for data obtained from the profilometer machine. The top left panel shows an image of the profilometer analysis with different colours representing different height. A line was drawn manually on the image parallel to the vertical axis (X-axis) so that line crosses the edge of the PPy film. The height profile along this line is shown in the top middle panel of Figure 3.2. Dashed rectangles drawn on this profile identify the PPy film, the adhesive tape and PPy film edge. The PPy film thickness was determined from the height difference as illustrated in the Figure. The line profile analysis was repeated three times for each film to give the average thickness and variation.

Figure 3.2 Calculation method of profilometer machine.



3.1.2.2 Scanning electron microscope (SEM)

The scanning electron microscope is a powerful and accurate instrument to use for surface analysis, thickness measurement and morphology/structure analysis. Figure 3.3 shows the cross-section SEM images of a PPy free-standing film that was obtained via the layer by layer electropolymerization method. Over the image region the film was uniform in thickness and free of internal porosity. The interfaces of several separate polymerized layers are clearly visible in the images.

Figure 3.3 The SEM images of a cross-section of a PPy free-standing film (Polymerized layer by layer).

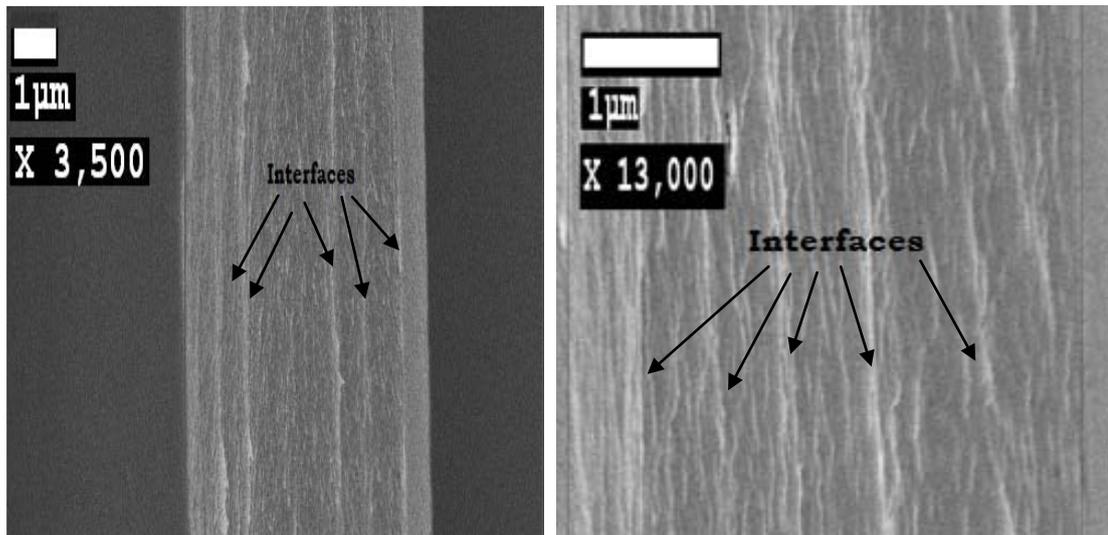
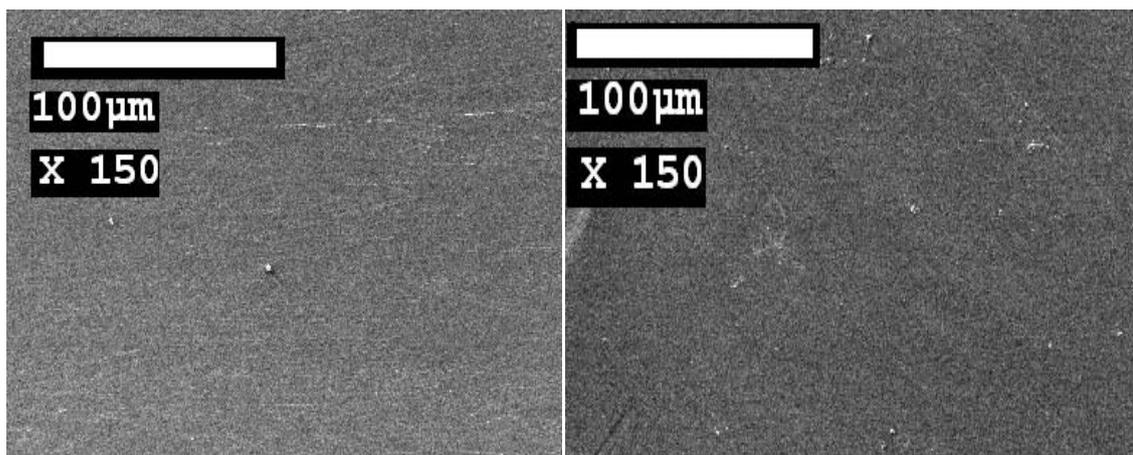


Figure 3.4 shows the surface microscopy images of the solution side of a PPy free-standing film. The sample was obtained via the layer by layer electropolymerization method. The surface was quite smooth and continuous.

Figure 3.4 The surface microscopy images of a solution side of PPy free-standing film.



3.1.3 Mechanical properties

Mechanical properties such as elastic (Young's) modulus, tensile strength and elongation at break are important in determining the use of polypyrrole free-standing films. Table 3.2 shows the elastic (Young's) modulus of the six different samples of polypyrrole free-standing films that have been prepared as described in Table 1.

Table 3.2 Elastic (Young's) modulus of polypyrrole films polymerized at various current densities. "Three separate measurements of thickness were used to determine the average and standard deviation"

| Current density (mA/cm ²) | Modulus(GPa) | | | Average | ST dev (mA/cm ²) |
|---------------------------------------|--------------|--------|--------|---------|------------------------------|
| | Test 1 | Test 2 | Test 3 | | |
| 0.10(Cont) | 0.57 | 0.54 | 0.65 | 0.58 | 0.05 |
| 0.10(LBL) | 1.21 | 1.35 | 1.15 | 1.23 | 0.10 |
| 0.50 | 0.75 | 0.72 | 0.80 | 0.75 | 0.04 |
| 1 | 0.95 | 0.91 | 0.99 | 0.95 | 0.04 |
| 2 | 0.81 | 0.97 | 0.72 | 0.83 | 0.12 |
| 3 | 1.54 | 1.48 | 1.58 | 1.53 | 0.05 |

Three different samples were tested by tensile testing for each different polymerization condition used to prepare the PPy films. Samples were tested dry at ambient conditions. From the resultant stress-strain curves the average modulus and standard deviation for each current density indicate that accurate measurements were achieved. The percentage measurement error for the modulus ranged from 3% to 14%.

Figure 3.5 Elastic (Young's) modulus of dry samples with sample details given in Table 2

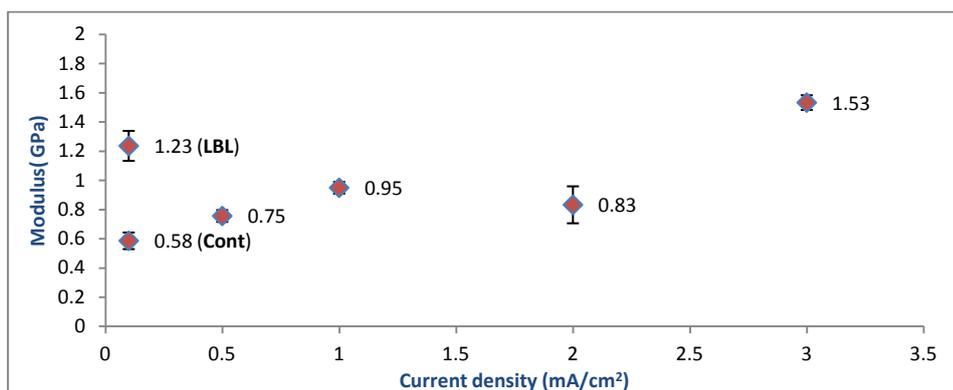


Figure 3.5 shows the relationship between the elastic (Young's) modulus and different selected current densities used for electropolymerization. It is identified that the samples polymerized at 3 and 0.1 mA/cm² have the highest elastic modulus of between 1.2- 1.5 GPa. The samples polymerized at 2, 1 and 0.5 mA/cm² have similar elastic moduli in the range 0.7- 0.9 GPa. Of particular note is that the continuously polymerized sample (0.1 mA/cm²) that showed the lowest elastic modulus of 0.58 GPa. It is also important to note that total polymerization time of sample 3 mA/cm² was only 16 minutes while it has even higher elastic modulus when compared to the LBL sample at 0.1 mA/cm² that was polymerized for 8 hours. All samples appeared to be uniform are likely to be free of significant internal porosity, since slow deposition of PPy is known to promote the formation of fully-dense films [1, 2]. The differences in modulus for the samples prepared in this study are, therefore, not related to differences in porosity. Instead, it is possible that the films retained different amount of plasticising solvent (propylene carbonate) after polymerization, with higher retained PC decreasing the modulus. Alternatively, the films may also be generated with different crosslink densities with higher crosslinking resulting in a higher modulus.

Table 3.3 Elongation at break of Polypyrrole films polymerized with various current densities.
 “Three separate measurements of thickness were used to determine the average and standard deviation”

| Current density (mA/cm ²) | Elongation at break | | | Average | ST dev |
|---------------------------------------|---------------------|--------|--------|---------|--------|
| | Test 1 | Test 2 | Test 3 | | |
| 0.10(Cont) | 33% | 21% | 34% | 29% | 7.23% |
| 0.10(LBL) | 14% | 13% | 14% | 14% | 0.57% |
| 0.50 | 80% | 77% | 73% | 77% | 3.51% |
| 1 | 6% | 14% | 6% | 9% | 4.61% |
| 2 | 13% | 11% | 12% | 12% | 1% |
| 3 | 55% | 50% | 52% | 52% | 2.51% |

Figure 3.6 Elongation at break of dry samples prepared at different current densities .

(For some samples, the error bars are too small to be seen in this chart)

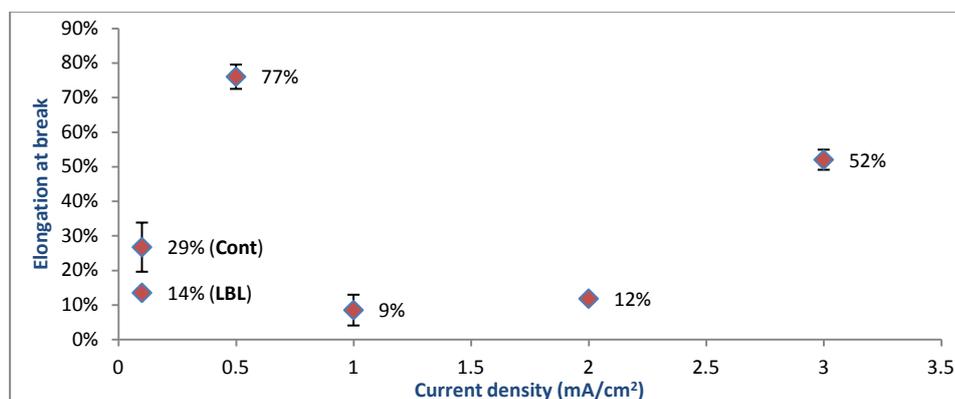


Figure 3.6 and Table 3.3 shows the elongation at break (%) for the six different polypyrrole samples. The small standard deviation values obtained from the 3 repeat tests indicate that the measurements were accurate. It is clear that the samples polymerised at 3 and 0.5 mA/cm² have the highest elongation at break, being around 50%-70%. The sample polymerised by the continuous method at a current density of 0.1 mA/cm² shows 29% and the samples polymerized via LBL at 1, 2 and 0.1mA/cm² show almost the same elongation at break, around 9%-14%. Again, it should be noted that while the total polymerization time for the sample at 3 mA/cm² was only 16 minutes, it showed similar elongation at break to that of the sample polymerized at 0.5

mA/cm², which had been polymerized for 96 minutes. The differences in elongation at break between samples may again be related to plasticisation crosslinking. However, no strong correlation between modulus and elongation at break was noted.

Table 3.4 Tensile strength of Polypyrrole films polymerized with various current densities.
 “Three separate measurements of thickness were used to determine the average and standard deviation”

| Current density (mA/cm ²) | Tensile strength (MPa) | | | Average | ST dev (MPa) |
|---------------------------------------|------------------------|--------|--------|---------|--------------|
| | Test 1 | Test 2 | Test 3 | | |
| 0.10(Cont) | 33 | 38 | 32 | 34 | 3.21 |
| 0.10(LBL) | 37 | 59 | 44 | 47 | 11.23 |
| 0.50 | 50 | 46 | 52 | 50 | 3.05 |
| 1 | 66 | 62 | 66 | 65 | 2.3 |
| 2 | 45 | 45 | 41 | 44 | 2.3 |
| 3 | 38 | 40 | 37 | 38 | 1.52 |

Figure 3.7 Tensile strength of dry samples with sample details given in Table 4

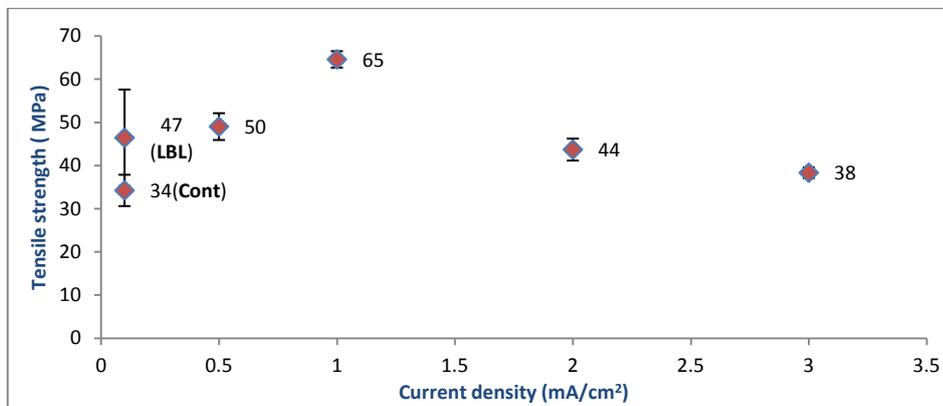


Figure 3.7 and Table 3.4 shows the relationship between tensile strength (MPa) for the six different polypyrrole samples. The small standard deviation values obtained from the 3 repeat tests indicate that the measurements were again accurate. It is obvious that the sample polymerized at 1 mA/cm² has the highest tensile strength,

being around 65 MPa. The samples polymerized via LBL at 3, 2, 0.5 and 0.1mA/cm² have shown almost the same tensile strength, around 40-50 MPa and The sample polymerized by the continuous method at a current density of 0.1 mA/cm² shows tensile strength of 34 MPa.

3.1.4 Electrical conductivity

Electrical conductivity is known as a basic requirement for many applications for polypyrrole including actuators. Actuation performance is improved when the polymer has higher conductivity [49] that can be modified by varying polymerization parameters such as current density, temperature and dopant.

Table 3.5 Conductivity of polypyrrole films polymerized with various current densities.
 “Three separate measurements of thickness were used to determine the average and standard deviation”

| Current density (mA/cm ²) | Conductivity(S/cm) | | | Average | ST dev (S/cm) |
|---------------------------------------|--------------------|--------|--------|---------|---------------|
| | Test 1 | Test 2 | Test 2 | | |
| 0.10(Cont) | 310 | 309 | 308 | 309 | 0.80 |
| 0.10(LBL) | 505 | 506 | 506 | 506 | 0.77 |
| 0.50 | 250 | 251 | 251 | 251 | 0.48 |
| 1 | 185 | 185 | 186 | 185 | 0.80 |
| 2 | 190 | 192 | 191 | 191 | 1.008 |
| 3 | 181 | 180 | 181 | 181 | 0.80 |

Figure 3.8 Conductivity of dry samples with sample details given in Table 5.

(For all samples the error bars are too small to be seen in this chart)

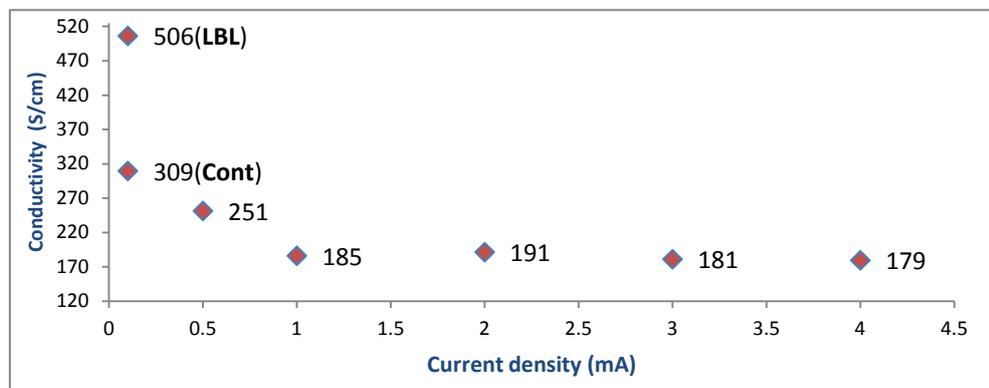
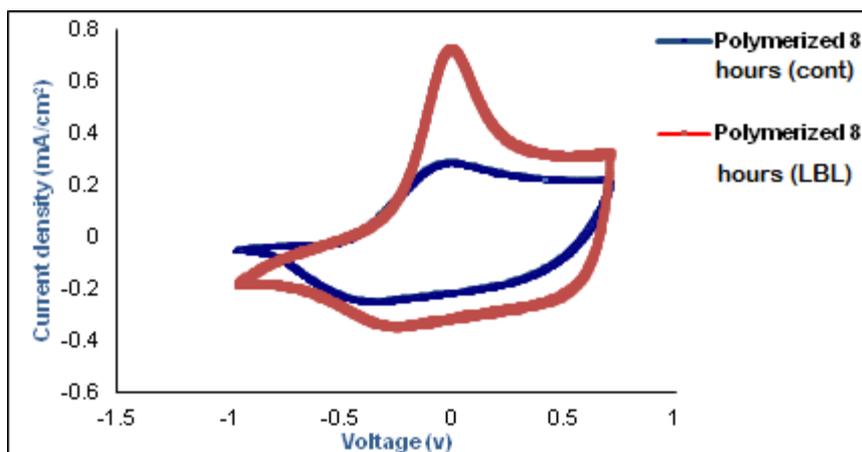


Figure 3.8 and Table 3.5 shows the relationship between conductivity (S/cm) for the 7 different polypyrrole samples. In these tests it was possible to measure the conductivity of the brittle 4 mA/cm² sample. The small standard deviation values obtained from the 3 repeat tests indicate that the measurements were accurate. It is clear that the sample polymerized via LBL at 0.1 mA/cm² has the highest conductivity of around 506 S/cm. The sample polymerized by the continuous method at a current density of 0.1 mA/cm² also has shown reasonable conductivity around 309 S/cm and the samples polymerized via LBL at 0.5 mA/cm² has shown conductivity of 251 S/cm. The samples polymerized via LBL at 1,2,3 have shown almost the same conductivity, around 180-185 S/cm. The higher conductivity of the 0.1 mA/cm² LBL sample suggests that this material has a higher doping level or enhanced conjugation length, as these features are known to improve the conductivity of conducting polymers [51].

3.1.5 Cyclic Voltammetry

Cyclic voltammetry is a type of potentiodynamic electrochemical measurement widely used to study the electrochemical properties of materials. Figure 3.9 shows the cyclic voltammogram (CV) for two different PPy free-standing films in 0.1 M LiTFSI PC solution, using a scan range of -0.9 to 0.7 V (vs. Ag | Ag +) and scanning speed of 5 mV/s.

Figure 3.9 The CV voltammogram diagram for two different PPy free-standing films.

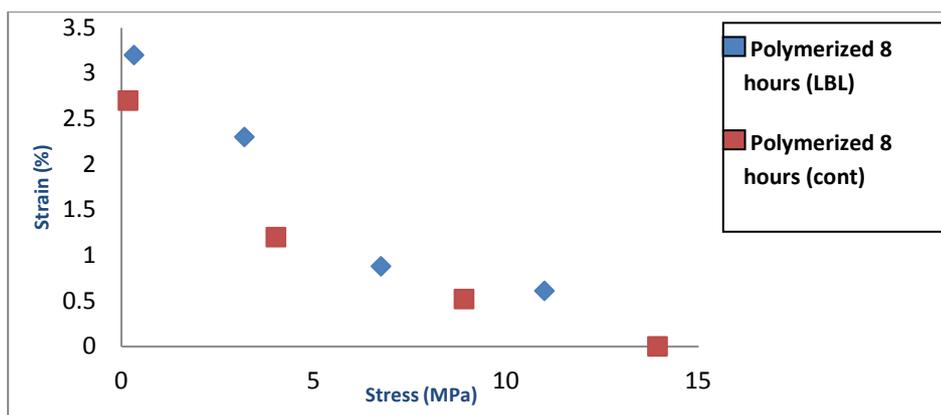


The CVs of films polymerized via two different electropolymerization methods (LBL & continuous) at 0.1 mA/cm^2 for 8 hours were compared. For the sample polymerized via LBL method it is identified that the oxidation peak occurred at -0.02 V and the reduction peak was centred at -0.25 V . For the sample polymerized via the continuous method, the oxidation peak occurred at -0.01 V but reduction occurred at -0.40 V . The most significant different in these CVs is the oxidation peaks of both samples showed different current densities. The maximum current density of the sample polymerized via LBL method ($\sim 0.7 \text{ mA/cm}^2$) was significantly higher than the maximum current density obtained for the sample polymerized via the continuous method ($\sim 0.3 \text{ mA/cm}^2$). However, maximum reduction current densities of both samples appeared almost the same, around $-0.25 \sim -0.35 \text{ mA/cm}^2$. The improved oxidation response of the LBL film compared to the continuous film may be related to the higher conductivity of the former-allowing easier electrochemical charge injection and higher currents.

3.1.6 Actuation test

Figure 3.10 shows the actuation stroke (percent strain) obtained during constant stress (isotonic) testing. The measured strain versus applied stress for two different PPy free-standing films in 0.1 M LiTFSI PC solution is shown. A potential scan between 0.9- to 0.7 V (vs. Ag | Ag +) and scanning speed of 5 mV/s was used for all actuation tests.

Figure 3.10 The Actuation stroke versus applied stress.



PPy free-standing films were polymerized via two different electropolymerization method (LBL & continuous) at 0.1 mA/cm^2 for 8 hours. It is identified that the isotonic actuation strain decreases almost with the similar rate for both samples as the applied stress increases. The results of the present study show that the sample polymerized via LBL method showed a slightly higher electrochemical strain around 3.2% when compared to the continuous sample when tested at small applied stresses.

3.2 Discussion

In this thesis, it has been indicated that layer by layer (LBL) electropolymerization method at low current density (0.1 mA/cm^2) and low temperature produce polypyrrole films of significantly high conductivity and reasonable mechanical properties when compared with films made by the conventional continuous polymerization method. From previous work it is known that PPy polymerized at low temperature and low current density shows better quality with a regular structure [31-35]. However, the slow electropolymerization is a major encumbrance with 8 hours or more needed to generate practical film thickness [52,53]. The LBL method enables films to be prepared much faster.

Preparing the PPy free-standing film as series of electrodeposited layers with ethanol washing in between is reported by Zheng et al [2] and has shown better properties when compared to films produced by the continuous method. The present thesis extends the work of Zheng et al. by considering the effect of polymerization current density on the properties of the LBL PPy films. It is identified that the sample polymerized at 0.1 mA/cm^2 via LBL method shows an elastic modulus around 1.2 GPa which is two times higher than the sample polymerized continually at 0.1 mA/cm^2 ($\sim 0.5 \text{ GPa}$). The LBL sample shows 27% increases in tensile strength when compared to the continuous sample (Table 3.4). Similarly, the electrical conductivity of LBL film polymerized at 0.1 mA/cm^2 (506 S/cm) was significantly higher than the continuous film polymerized at same current density (309 S/cm). Furthermore, both of the samples produced a positive actuation strain when the applied electrochemical potential was between -0.1 V and $+0.8 \text{ V}$ (Fig 3.9). The LBL sample showed higher strain at low applied stress of 3.5% which is 1% higher than continuous sample (Fig

3.10). It is also important to note that, polymer may swell or contract when an external stress is applied will also be affected by the mechanical properties [50]. Accordingly, the improved redox activity of LBL film (perhaps due to its higher conductivity) allows for more charge injection and higher actuation strain.

According to this study; it has been found that layer by layer polymerization method is a useful way to grow PPy actuator because of the modified film properties. In fact, the washing step between the sequentially polymerized layers altered the deposition mechanism, eliminating the typical dendritic growth and generating non porous deposits. Scanning electron microscopy (SEM) images from cross sectional area of PPy free-standing films also proved the low porosity and compact nature of LBL film when compared to the continuous one (Fig 3.3 & 3.4).

Chapter Four: Conclusion and future work

4.1 General Conclusion

In summary, after some experimentation it was found that the Layer by Layer (LBL) method has been shown to be more developed in terms of mechanical properties, conductivity and morphology as compared to continuous polymerization at current density 0.1 mA/cm^2 . The performance of polypyrrole actuators also is greatly affected by the electrical, mechanical, and electrochemical (switching) properties. The morphology, mechanical properties and electrical conductivity of the PPy samples polymerized via LBL method have shown more applicable for artificial muscles as a result of their improved mechanical and electrical performance.

The deposition rate, which is directly dependant on the applied current density and polymerization time, of PPy on the substrate also, is one of the important parameters that can affect the final properties and morphology of PPy free standing film. In this study it has been found that polymerization at low current densities which takes more time is most suitable for creating the actuator as a result of avoiding other unpredictable side reactions that can occur at the same time as the polymerization reaction. However, layer by layer method shows more efficiency in terms of time as this method enables films to be prepared much faster with reasonable properties in the higher current densities when compared to the continuous one.

Finally in this thesis, the Layer by layer electropolymerization method at low current densities was found to be the best condition to grow PPy with high applicability in terms of mechanical and electrical properties. While the LBL method at 3 mA/cm^2 has been previously shown to produce films of equivalent performance to continuously grow films at 0.1 mA/cm^2 , it has been shown in this thesis that further improvements in

properties can be achieved by LBL polymerization at low current density ($0.1\text{mA}/\text{cm}^2$). At this low current density the LBL method no longer is more time-efficient than the continuous polymerization. However, the improved properties derived from films prepared by the slow LBL method can be important in certain applications.

4.1 Future Work

Some key variables that are suggested for further study can be the number of layers, dopant type and washing solvent. In this thesis, the number of deposition layers has been fixed to eight layers while the effect of this important parameter was not investigated and can be considered in the future works. The number of layers and the polymerization time used for each layer will affect film thickness and, possibly, film properties.

The type of dopant can also play a vital role in the performance of PPy actuator. This variable was also not investigated for the LBL method as the dopant performance may also affect by ethanol during the washing process between deposition layers. In this thesis, ethanol is the only solvent that has been used as a washing solvent between deposition layers, the effect of another type of solvents (strong /weak) such as Acetone, Methanol and MEK can be considered in the future works.

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