

Electrodeposition of Conducting Polymer Fibers

by

Angela Y. Chen

Submitted to the Department of Mechanical Engineering in
Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering

at the

Massachusetts Institute of Technology

June 2004

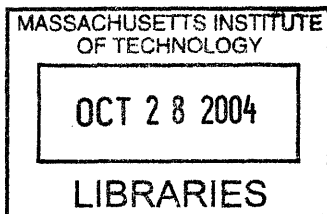
© 2004 Angela Y. Chen. All rights reserved.

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part.

Signature of Author.....
Department of Mechanical Engineering
May 7, 2004

Certified by.....
Ian W. Hunter
Professor of Mechanical Engineering and Professor of BioEngineering
Thesis Supervisor

Accepted by.....
Ernest G. Cravalho
Professor of Mechanical Engineering
Chairman, Undergraduate Thesis Committee



ARCHIVES

Electrodeposition of Conducting Polymer Fibers

by

Angela Y. Chen

Submitted to the Department of Mechanical Engineering
on May 7, 2004 in Partial Fulfillment of the Requirements for the
Degree of Bachelor of Science in Mechanical Engineering

ABSTRACT

Conducting polymers are materials that possess the electrical conductivity of metals while still retaining the mechanical properties such as flexibility of traditional polymers. Polypyrrole (PPy) is one of the more commonly studied electrically conducting polymers due to its high conductivity and stability in ambient conditions.

A one step electrochemical process for growing macroscopic conducting polymer fibers previously described in Li *et al*'s article (*Science, 1993*) was used to grow PPy fibers. Based on a schematic of the electrochemical flow cell used in the electrodeposition process, a physical electrochemical flow cell was constructed. Several trials were carried out in an attempt to repeatedly grow polymer fibers. The fibers grown from successful trials were analyzed and characterized by qualities such as length, diameter, surface texture, conductivity, and elasticity.

There is room for further study involving optimization of parameters such as temperature, monomer concentration, and flow velocity of the monomer solution.

Thesis Supervisor: Ian W. Hunter

Title: Professor of Mechanical Engineering and Professor of BioEngineering

Table of Contents

ACKNOWLEDGEMENTS	7
1 INTRODUCTION.....	9
1.1 CONDUCTING POLYMER.....	9
1.2 POLYPYRROLE	10
1.3 ELECTRODEPOSITION METHOD	10
1.4 ELECTRODEPOSITION OF POLYPYRROLE	11
2 DESIGN OF THE FIBER ELECTRODEPOSITION APPARATUS	11
2.1 ELECTROCHEMICAL FLOW CELL.....	13
2.2 ELECTRODES.....	15
2.3 MONOMER/SALT SOLUTION.....	16
2.4 PUMPING SYSTEM	17
2.4.1 <i>Monomer/Salt Solution Reservoir</i>	18
2.4.2 <i>Tubing</i>	18
2.4.3 <i>Pump</i>	19
2.5 INSTRUMENTATION	20
2.5.1 <i>Power Source</i>	20
2.5.2 <i>Measurement</i>	21
3 CHARACTERIZATION	22
3.1 EXPERIMENTAL PROCEDURE.....	22
3.1.1 <i>Priming the System with Monomer/Salt Solution</i>	23
3.1.2 <i>Running a Fiber Deposition Trial</i>	23
3.1.3 <i>Emptying the Monomer/Salt Solution from the System</i>	24
3.2 CHARACTERIZATION OF FIBERS	24
3.3 SYSTEM PARAMETERS	25
3.3.1 <i>Flow Rate</i>	25
3.3.2 <i>Monomer concentration</i>	26
3.3.3 <i>Salt concentration</i>	26
3.3.4 <i>Current density</i>	27
4 EXPERIMENTAL RESULTS AND DISCUSSION	28
5 DISCUSSION	32
6 CONCLUSION	34
7 FUTURE WORK.....	34
8 REFERENCES.....	35
9 APPENDIX A - SYNTHESIS OF PPY.....	36

Table of Figures

Figure 1: The chemical structure of polypyrrole (taken from Madden, 2000).	10
Figure 2: Experimental design of electrodeposition flow cell.	12
Figure 3: Electrochemical flow cell.	13
Figure 4: Top (left picture) and bottom (right picture) bulbs.	14
Figure 5: Electrodes (anode top, cathode bottom).	16
Figure 6: Pump system setup.	17
Figure 7: Masterflex peristaltic pump.	19
Figure 8: Configuration of instrumentation.	20
Figure 9: Full experimental setup.	22
Figure 10: Fiber grown from trial 1 (top) with SEM pictures (18× magnification) of three sections of the fiber (bottom).	29
Figure 11: Stress-strain curve of PPy fiber.	30
Figure 12: SEM pictures of results from trials 2 to 4.	31
Figure 13: Experimental Setup with the addition of temperature control.	33

Acknowledgements

I would like to take this opportunity to thank Patrick Anquetil for his help, support, advice, encouragement, and time. Thank you for being such a great supervisor. Thanks to Professor Ian W. Hunter for giving me the wonderful opportunity to work in the Bioinstrumentation Lab. Thanks to the rest of the people in the BiLab for helping me find everything in the lab, showing me how different machines worked, and for welcoming me to the lab with open arms. You have all been truly inspirational. Thank you.

1 Introduction

Conducting polymers are unique materials that possess the electrical conductivity of metals while still retaining the mechanical properties such as flexibility of traditional polymers. Research in this area is relatively new and the potential applications of these polymers are varied and very desirable. Such applications include batteries, light emitting diodes, antistatic layers, biosensors, and muscle-like actuators. One of the more commonly studied electrically conducting polymers, Polypyrrole (PPy), has high conductivity and stability in ambient conditions. Because PPy is not soluble in water, traditional methods of forming polymers such as extrusion are not applicable. Instead, an electrodeposition method is used to deposit PPy monomers on a surface. In the Bioinstrumentation Lab at MIT (MIT BiLab), an electrodeposition method of PPy films on cylindrical glassy carbon crucibles has been optimized to repeatedly produce high quality materials. However, there has not been any investigation into the deposition of PPy fibers. The purpose of this project was to design and build a physical setup of an electrochemical flow cell as described by Li *et al* (1993), which would be able to grow PPy fibers. Afterwards, depositions were run with varied system parameters which had different effects on the growth patterns of the PPy. This research attempts to: 1.) describe the physical experimental design of the electrochemical flow cell, 2.) explain the procedure of running a deposition, 3.) characterize the mechanical and electrical properties of the successful fibers that were grown, and 4.) characterize the parameters of the system and how they affect fiber growth.

1.1 Conducting Polymer

Conducting polymers, also referred to as conjugated polymers, are characterized by their conjugated backbone structure. They are constructed from many small monomer units, which

are linked together to form a polymer. The bonds between the carbon atoms of the backbone alternate between single and double bonds, which results in delocalized electrons moving along the chain. As the electrons move around, double bonds become single bonds and vice versa. Upon doping, the electrons on the backbone are even more displaced, thus reducing the electronic bandgap of the material. As a result, conducting polymers are highly conductive semiconductor material.

1.2 Polypyrrole

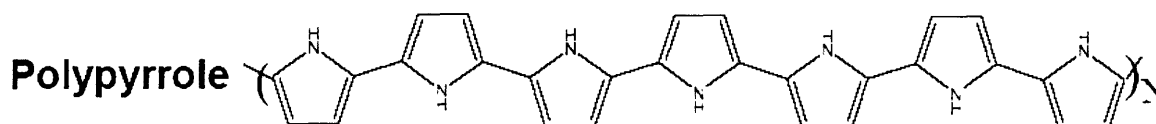


Figure 1: The chemical structure of polypyrrole (taken from Madden, 2000).

Figure 1 shows the chemical structure of the individual monomer units of pyrrole, which are linked together to form Polypyrrole (PPy) polymer¹. Notice the alternating band structure of Figure 1, also called conjugation.

As stated previously, PPy is commonly studied because of its high conductivity and stability in ambient conditions. In addition, it is also biocompatible and has been used for studies in areas such as tissue engineering and nerve regeneration (Schmidt, 1997).

1.3 Electrodeposition Method

Electrodeposition is the process used to grow the conducting PPy fibers. It can be described as the deposition of a substance on an electrode by passing electric current through an

¹ Appendix A details the synthesis of PPy.

electrolyte solution². The shape of the electrodes can vary from plates or cylinders to wires. An anode, a cathode, an electrolyte, and a voltage/current source are required for electrodeposition to occur. As a voltage is applied at the electrodes, current flows from the anode to the cathode. The electrolyte is usually a salt which has dissociated into its ions in solution. The ions act to reduce the resistance between the anode and the cathode so that the flow of electrons is possible. As electrons are removed at the anode, the substance to be deposited is plated onto the electrode.

1.4 Electrodeposition of Polypyrrole

In the case of depositing PPy fibers, the working and counter electrodes are Pt wires. Platinum is chosen because it is an inert metal and does not corrode during the process of electrodeposition. The two electrodes are positioned opposite of each other in the PPy monomer/salt solution. For every two electrons removed from the anode, one pyrrole monomer is attached at the anode. As PPy is synthesized, a third of the monomer units are positively oxidized. The negative ions from the solution position themselves near the charged monomers to satisfy electronegativity (doping) (Appendix A). Once PPy has deposited on the anode, the Pt wire is no longer exposed to the solution. The PPy becomes the working electrode, and subsequent pyrrole monomers continue to attach themselves to the PPy.

2 Design of the Fiber Electrodeposition Apparatus

The complete system utilized to grow conducting PPy fibers included an electrochemical flow cell, two platinum wire electrodes, a monomer/salt solution reservoir, flexible tubing, a peristaltic pump, a power source, a multimeter, and a data acquisition device. A cooling system with corresponding measurement devices was added to the system later on.

² <http://www13.brinkster.com/justinmc/glossary/glossary.asp?letter=E>

Figure 2 shows the physical setup of the experiment.

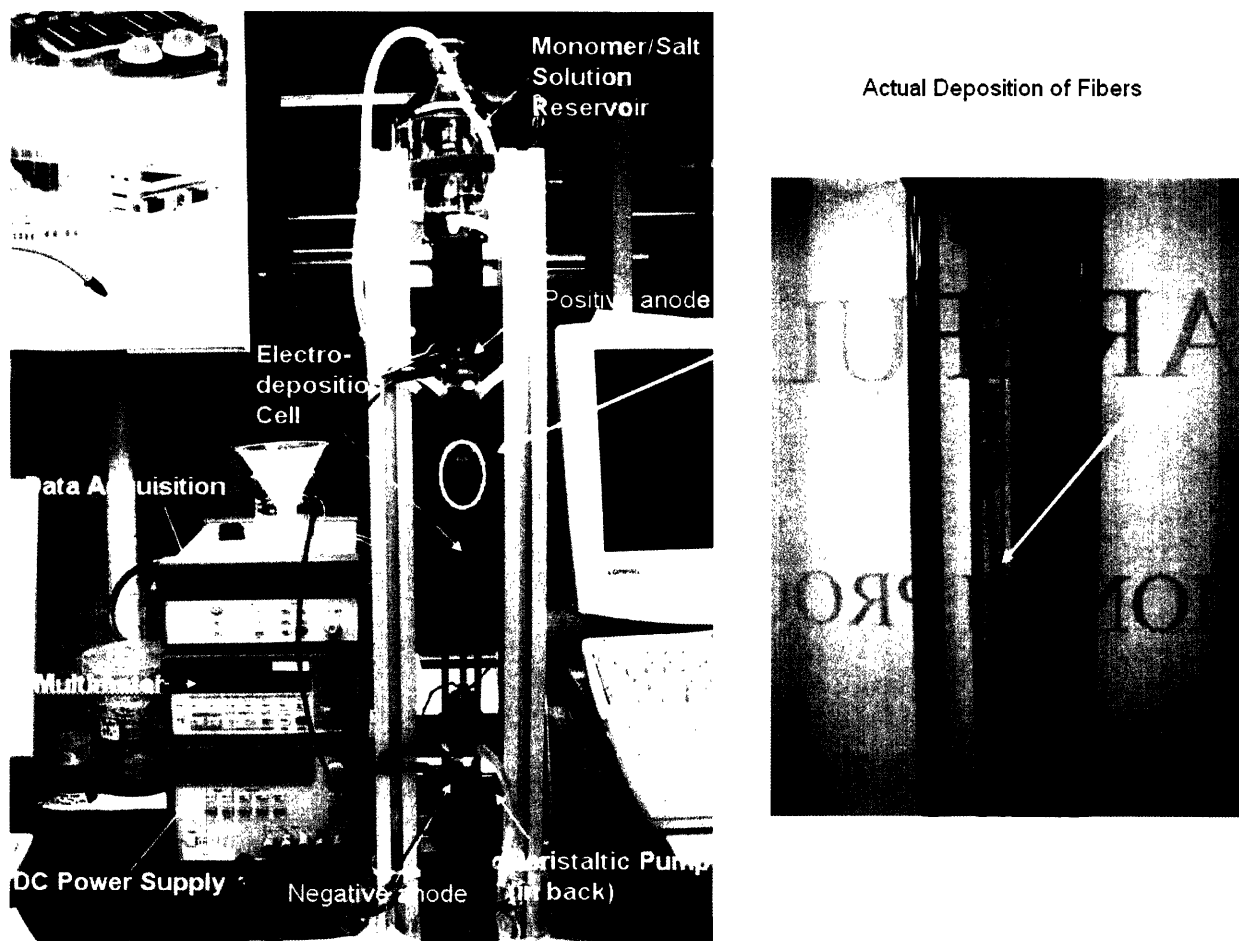


Figure 2: Experimental design of electrodeposition flow cell.

2.1 Electrochemical Flow Cell

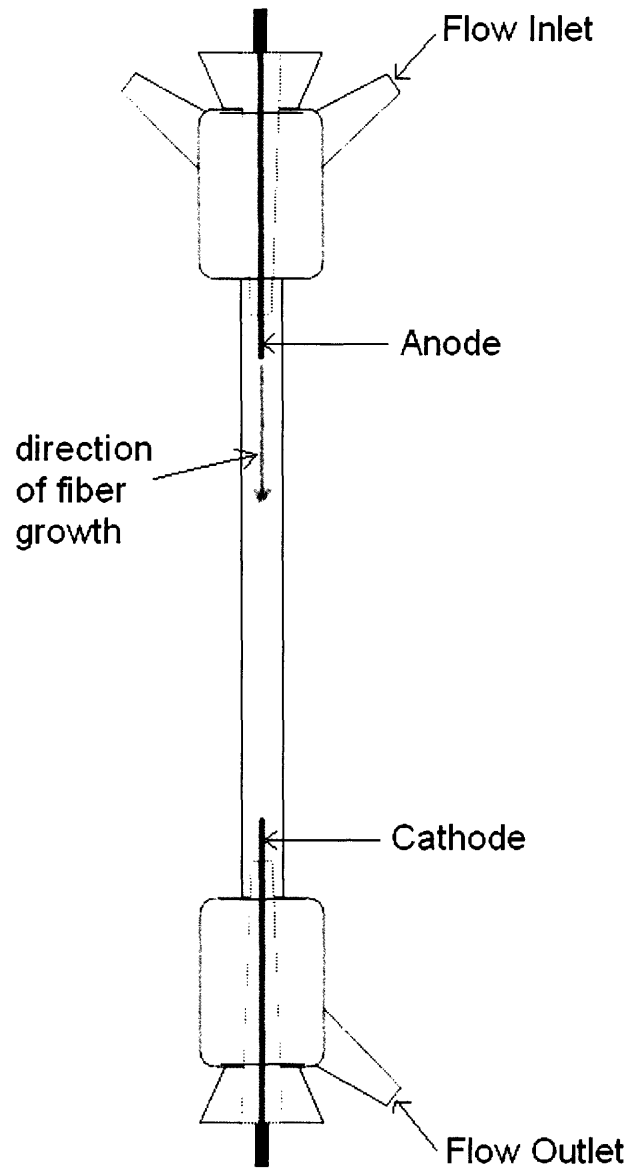


Figure 3: Electrochemical flow cell.

The electrochemical flow cell was designed to allow two electrodes to be placed opposite of each other in a glass capillary tube oriented vertically while a monomer/salt solution was circulated through the cell. The PPy fiber inside the glass capillary tube began depositing at the tip of the anode and elongated downwards in the direction of the cathode.

The glass capillary tube was constructed using a 2 mL disposable buret. The tapered end of the buret was cut off using a glass cutter and polished to eliminate sharp edges. The inner diameter of the glass tube measured 3.6 mm in diameter. It was important to use a glass tube that was small in diameter (under 4 mm) to grow fibers of reasonable size. Previous experiments showed that fiber diameters were controlled by the diameter of the capillary in which it was synthesized (Li *et al*, 1993), so larger capillary diameters would produce larger diameter fibers. Smaller capillary diameters lowered the Reynolds number of the solution circulating through so as to ensure a more laminar flow around the electrode and growing fiber.

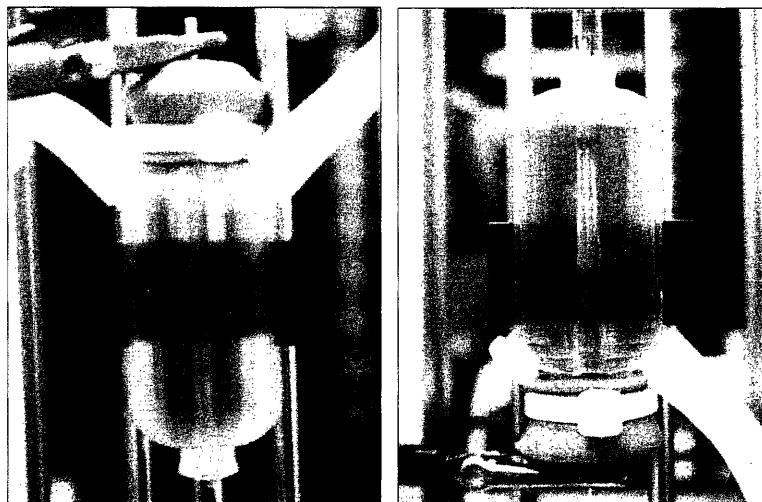


Figure 4: Top (left picture) and bottom (right picture) bulbs.

At both ends of the glass capillary tubes, there were two bulbs (Figure 4). The bulbs serve as a connection point for the flexible tubing that supplied and circulated the monomer/salt

solution. The bulbs also served as small reservoirs to maintain a steady flow of solution through the glass capillary tube. They also helped reduce the effects of entrance and exit flow at the ends of the tube. The top bulb had two ports. One was the input port where solution flowed in. The other was used to introduce ambient pressure when emptying the flow cell after a deposition run. The bottom bulb had one exit port where solution flowed out. Due to the complexity of the shape of these two parts, they were designed in SolidEdge³ and manufactured using the VIPER SLA®, which utilized stereolithography to create 3D parts. A larger opening in the bulb located concentric to the glass tube was for the insertion of the electrode.

2.2 Electrodes

Two Platinum (Pt) wire electrodes were constructed to act as the anode and the cathode in the electrochemical flow cell. A short length of Pt. wire was soldered to electrical wire, which was soldered to a connector pin. The entire entity was housed in a glass pipette, which was cut down to size to fit in the bulbs. The Pt. wire extended a little less than 10 mm from the tapered end of the pipette, and the connector pin protruded at the other end of the pipette. The large end of the pipette was inserted into a rubber cap, which acted as a plug when inserted into the top and bottom bulbs. The anode was the top electrode and the cathode was the bottom electrode. In the primary setup, the Pt wire in both the anode and the cathode were both 0.3 mm in diameter due to the supplies that were available at the time. Later on, these were replaced with the dimensions used in Li's experiments (Li *et al*, 1993). The diameter of the anode was 0.127 mm and the final diameter of the cathode was 1 mm.

³ <http://www.solid-edge.com/>



Figure 5: Electrodes (anode top, cathode bottom).

2.3 Monomer/Salt Solution

The original electrolyte solution circulated through the system consists of 0.05 M pyrrole monomer and 0.05 M tetraethylammonium hexafluorophosphate (TEAP) in propylene carbonate. The concentration of TEAP was later doubled in an attempt to further reduce the resistance between the electrodes in the flow cell.

2.4 Pumping System

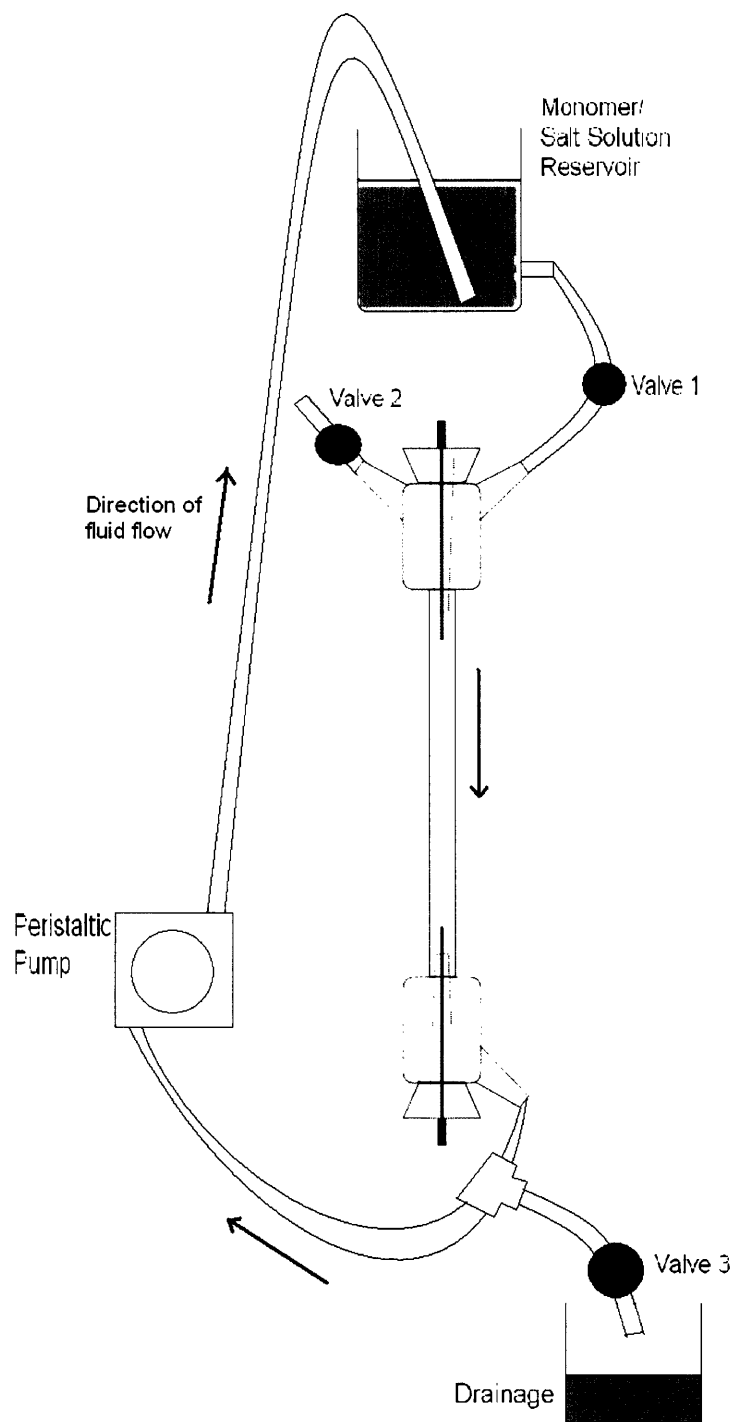


Figure 6: Pump system setup.

2.4.1 Monomer/Salt Solution Reservoir

An aspirator bottle, which is a bottle with an outlet port at the base was placed above the electrochemical flow cell and served as the reservoir of solution to be circulated through the system. The position of this reservoir allows potential energy⁴ to be stored and allows gravity to play a role in circulating the solution.

2.4.2 Tubing

Several factors had to be taken into consideration when choosing tubing: flow rate, chemical compatibility, fluid viscosity, and fluid temperature. The tubing had to be able to handle liquids as cold as -40 °C. Viscosity of the solution was not a problem since it was comparable to the viscosity of water. The tubing could not degrade upon contact with the solution primarily comprised of propylene carbonate, which is corrosive to some plastic and rubber materials. Velocities between 100 and 500 mms⁻¹ were desired in the flow cell. Based on these requirements, silicone tubing was selected⁵ with an inner diameter of 6.35 mm and an outer diameter of 9.53 mm. A 25.4 mm length of tubing was placed in a container of propylene carbonate to ensure that there were no corrosive effects.

⁴ Potential energy of the reservoir of solution = ρgh , where ρ is the density of the solution, g is gravity, and h is the height at which it is positioned. The higher the position of the reservoir, the larger the h , the greater the potential energy.

⁵ www.masterflex.com

2.4.3 Pump

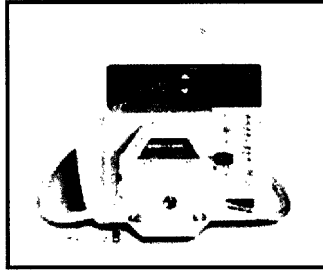


Figure 7: Masterflex peristaltic pump⁶.

A Masterflex L/S[®] Series Peristaltic Pump⁷ was chosen to circulate the solution through the system. The advantage to using peristaltic pumps is that the pump head and drive never come in contact with the propylene carbonate, which can be corrosive to some materials. The tubing is placed between the rotor and the housing of the pump. As the rotor rotates, the rollers on the rotor squeeze pillows of fluid through the tubing. The disadvantage of the peristaltic pump is that it provides pulsing flow instead of continuous flow. On the other hand, this effect is not seen in the deposition chamber due to the use of the aspirator bottle acting as a buffer.

⁶ http://www.visserssales.com/Barnant_LS_StanDigital.htm

⁷ www.masterflex.com

2.5 Instrumentation

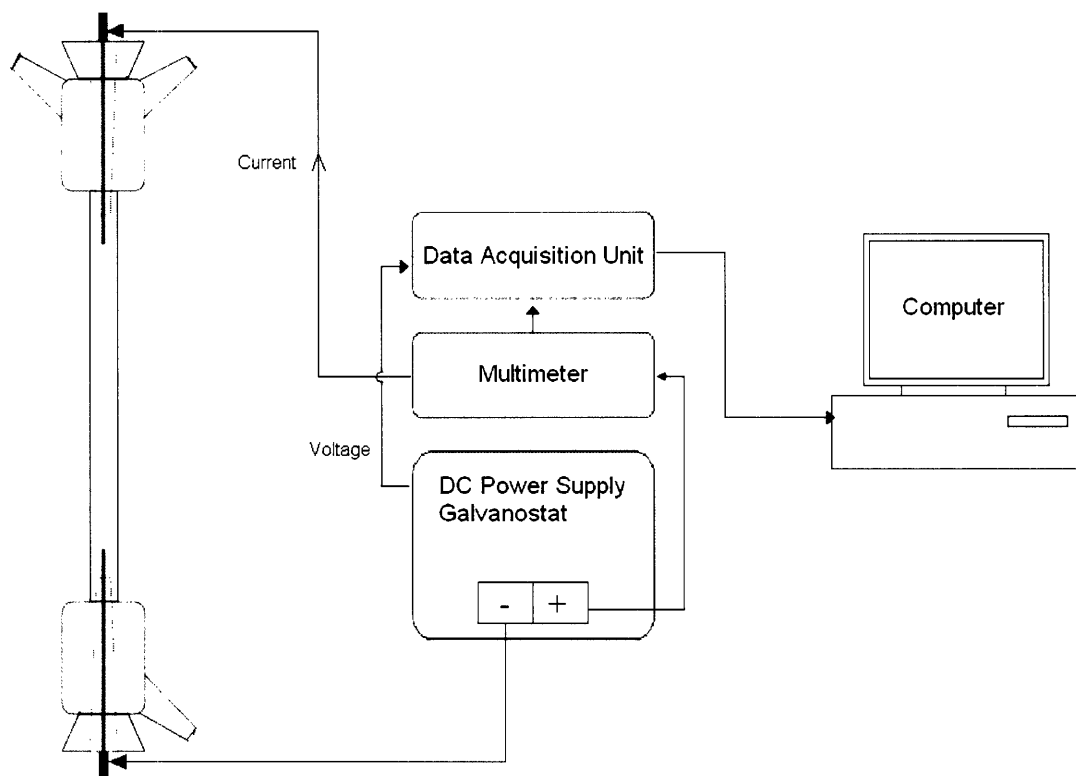


Figure 8: Configuration of instrumentation.

2.5.1 Power Source

A power source was needed to send current through the electrodes. Three different power sources were tested. The first was a HP E3632A DC Power Supply with a range of 0 to 15V, 7A, 0 to 30V, 4A⁸. This current source was successful in the growth of a fiber. However the growth seemed to be very slow. The resistance between the electrodes was extremely high (on the order of M Ω). Therefore the power source was not powerful enough to force a large

⁸ <http://we.home.agilent.com/USeng/home.html>

current through. Even though a current of 1.8 mA was desired (Li *et al*, 1993), only 0.3 mA could be supplied resulting in a slow rate of deposition. It was also difficult to maintain a constant current throughout the entire deposition run. The current drifted and increased during the run which was not desirable because it was meant to be a controllable variable.

In an attempt to send a larger current through the electrochemical flow cell, the first power supply was replaced with second one that was larger, the HP E3612A DC Power Supply with a range of 0 to 60V, 0 to 0.5A/ 0 to 120V, 0 to 0.25A¹⁰. This power source, although larger, was extremely difficult to control. Maintaining a constant current was impossible as the values would continually drift and had to be adjusted by hand.

The final power source used was the most successful at providing a constant current. It was an AMEL Instruments Potentiostat/ Galvanostat Model 2053⁹. In the galvanostat mode, it was very easy to control the amount of current passed through the electrochemical cell.

2.5.2 Measurement

An Agilent 34970A Data Acquisition/Switch Unit¹⁰ was used to take direct measurement of DC voltage, DC current and thermocouple readings. DC voltage was read from the galvanostat, DC current was read from the Agilent 34401A 6½ Digit Multimeter.

⁹ <http://www.amelchem.com/>

¹⁰ <http://we.home.agilent.com/USeng/home.html>

3 Characterization

3.1 Experimental Procedure

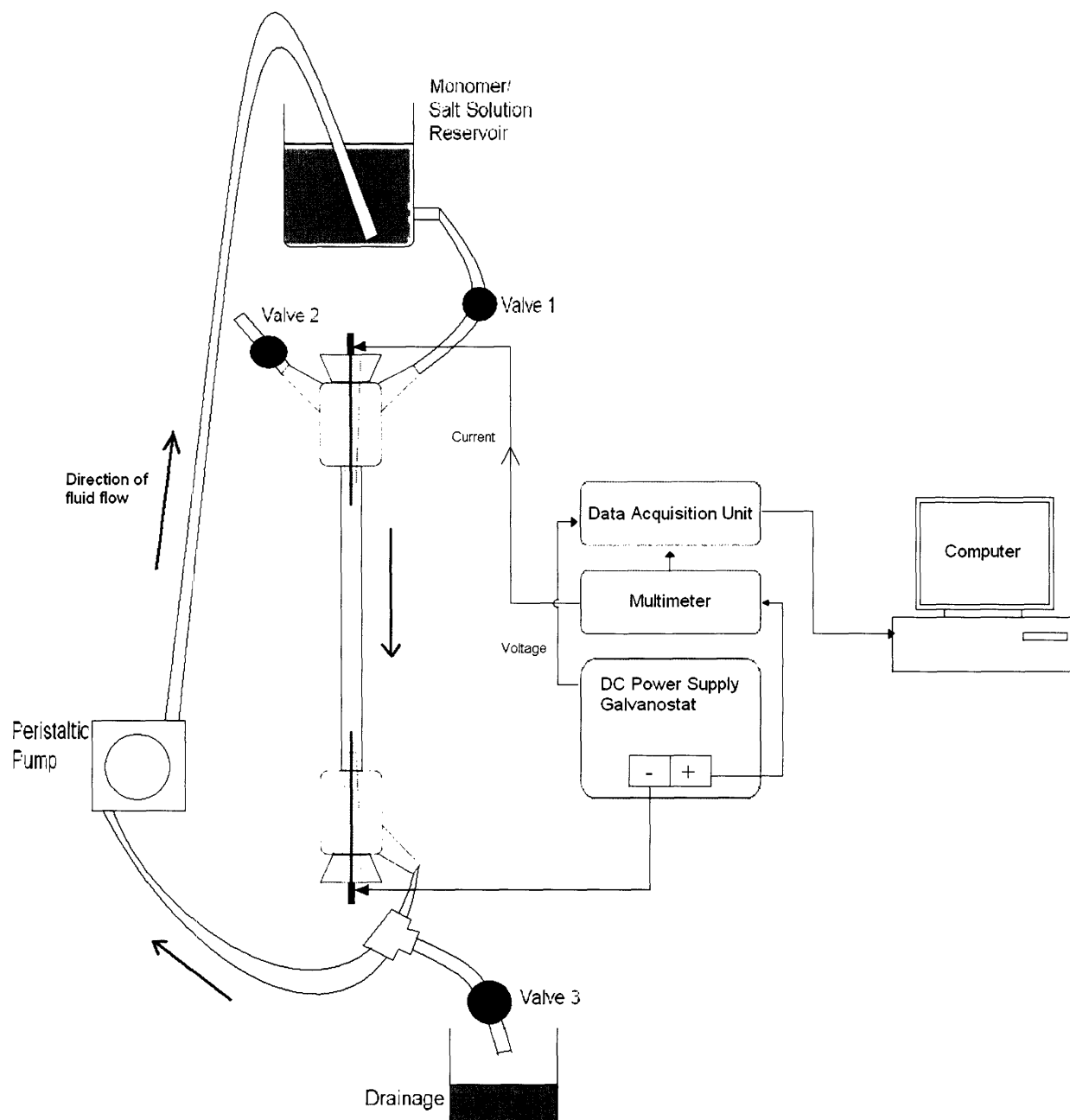


Figure 9: Full experimental setup.

The following sections details the experimental procedure, which includes the priming of the electrochemical cell with the monomer/salt solution before the run, the actual running of the fiber deposition, and the emptying of the electrochemical cell.

3.1.1 Priming the System with Monomer/Salt Solution

1. Make sure all electrodes are in place and sealed in tight.
2. All valves are closed to begin with.
3. Open valve 1.
4. Check to make sure that the end of the tube is submerged in the reservoir of solution.
5. Run peristaltic pump in a direction that allows the fluid to flow from the bottom to the top of the electrochemical cell until there are no more air bubbles present in the cell.
6. Stop the pump.
7. The system is primed to begin continuous circulation of the solution.

3.1.2 Running a Fiber Deposition Trial

Once the system is primed and ready to begin an electrodeposition run, pump the solution in the opposite direction used to prime the system. The solution should flow from the top to the bottom of the electrochemical cell. The leads from the power source should be then be connected to the electrodes. The positive lead is connected to the anode at the top, and the negative lead is connected to the cathode at the bottom. Once the leads are connected, current will be able to flow from the anode, through the monomer/salt solution, to the cathode. Once the power source to the desired current output is set, data acquisition can begin. The duration of a fiber deposition trial depends on the linear growth rate of the fiber and can be determined by the experimenter.

3.1.3 Emptying the Monomer/Salt Solution from the System

1. Stop the pump.
2. Make sure a drainage container is in place to catch any spillage.
3. Close valve 1.
4. Open valve 3.
5. Open valve 2 and let the flow cell drain.
6. Close valve 2.
7. Position the end of the tube so that it is not submerged in the reservoir of solution.
8. Run peristaltic pump in the same direction used to prime the system (opposite of the direction during the run) until the system is drained.
9. Stop the pump.
10. Close all valves.

3.2 Characterization of Fibers

Mechanical and electrical properties of the fibers grown were tested using several different methods.

The Perkin Elmer Dynamic Mechanical Analyzer 7e (DMA) was used to perform tensile testing on the fiber. A known length of the fiber was placed between two clamps. As the fiber was stretched, the force exerted by the DMA and the distance the clamps moved were recorded to produce the stress-strain curve. From the stress-strain curve, mechanical properties such as the Young's Modulus and tensile strength were determined. The Young's Modulus specified the elasticity of the fiber, while the tensile strength was the stress required to break a sample.

The conductivity of the fibers was calculated by taking the resistance, which was measured using the 4 point method. The four point method is used to eliminate the effects of

lead resistance. Two leads are used to circulate a current through the sample. The other two leads are used to measure the potential drop of the sample being tested. This method decouples the tasks of applying a current and measuring the voltage drop of a sample.

3.3 System parameters

Different parameters of the system can be varied to produce different results. Parameters include cell flow rate of the solution, monomer concentration, salt concentration, diameter of electrodes, current density, and deposition voltage. Although the exact effects of these parameters are not known, some general predictions can be made as to how each of these parameters might affect the growth of the fiber.

3.3.1 Flow Rate

Experimental observations in Li's experiment suggested that fiber growth was governed by hydrodynamic flow patterns in the cell and around the electrode. As the monomer solution is circulated through the cell, it forms a concentric sheath between the cell wall and the electrode. As the fluid flows over the electrode, there is a region at the tip of the electrode where the velocity of the fluid is almost zero. This region is where monomer attachment occurs and is responsible for fiber elongation. Li and his colleagues studied the effect of flow rate on diameter of fiber and linear growth rate. As volumetric flow rate increased, the diameter of the fiber decreased linearly while the linear growth rate increased.

In this experimental setup, flow rate was held constant at 2.8 mLs^{-1} , or a linear velocity of 275 mms^{-1} past the electrode. The Reynolds number was on the order of 1500 (Table 1), which is within the laminar flow region, although there are still some entrance effects at the tip of the electrode. In an effort to reduce the entrance region effects, the electrodes were shifted down

further in the glass capillary cell. This should not have a great effect on the growth of the fiber since Li confirmed that fibers could be grown at flow rates that corresponded to both laminar and turbulent flow rates.

3.3.2 Monomer concentration

The monomer concentration is an important parameter that affects the amount of deposition that occurs. Electrochemical oxidation of the monomer, which causes polymerization, occurs at the anode. The rate limiting factor of the electrochemical reaction is mainly the transport of the monomer to the electrode surface. Therefore, the higher the concentration of monomer in the solution, the higher the probability that a monomer will be near the anode to be polymerized and the faster the rate of polymerization. Fiber growth does not occur for concentrations less than a few millimolar because there are not enough monomers near the anode at one time to be polymerized. However, when there is a large concentration of monomers (more than 2 M) in the solution, fiber growth becomes dendritic due to excess polymerization (Kissinger, 2002). The monomer solution used in these experiments was 0.05 M.

3.3.3 Salt concentration

The salt solution in the electrochemical cell serves mainly to close the electrical circuit between the anode and the cathode. Without the salt solution, the resistance between the two electrodes would be too large for current to flow. Ions provide ionic conductivity to the solution. As electrons are removed from the anode, negative ions flow toward it to balance the charge. Positive ions flow towards the cathode to balance the charge as reduction takes place at that end. As salt concentration increases, the resistance between the electrodes should decrease, and the amount of power needed to drive the current through the electrodes also decreases. In latter trial

runs, the salt concentration was increased from 0.05 M to 0.1 M in an attempt to reduce the large resistance between the electrodes.

3.3.4 Current density

The fundamental process occurring during electrodeposition is the removal of electrons from the pyrrole monomer by the surface of the electrode. Current density, which is independent of the surface area of the electrode, is an important factor which plays a role in the rate of polymerization of the pyrrole monomer at the anode. Current density is an important quantity because up to a point, it is essentially a measure of the chemical reaction occurring at the electrode (Kissinger, 2002). If it surpasses the rate of reaction occurring between the monomer and the electrode, other undesired reactions may start to occur. Therefore, large and excess voltages are undesirable since they would lead to high current densities, which would lead to over-oxidization and degradation of the monomer.

4 Experimental Results and Discussion

Table 1: Electrodeposition Parameters

PARAMETERS	TRIAL #			
	1	2	3	4
Pyrrole Monomer Concentration [M]	0.5	0.5	0.5	0.5
TEAP Salt Concentration [M]	0.05	0.05	0.1	0.1
Solvent	Propylene Carbonate	Propylene Carbonate	Propylene Carbonate	Propylene Carbonate
Diameter of flow cell [mm]	3.6	3.6	3.6	3.6
Volumetric flow rate [mL/s]	2.8	2.8	2.8	2.8
Linear flow rate [mm/s]	275	275	275	275
Reynolds number ¹¹ $\rho(D-d)V/\mu$	1500	1500	1500	1500
Electrode type	Platinum	Platinum	Platinum	Platinum
Anode diameter [mm]	0.3	0.127	0.127	0.3
Cathode diameter [mm]	0.3	1	1	1
Distance between electrodes [mm]	175	150	150	150
Current density at anode ⁹ [A/m ²]	4240	15790	51310	3540
Effective current ¹² [mA]	0.3	0.2	0.65	0.25
Voltage [V]	30	20	50	12
Power Supply	HP E3632A DC Power 0 to 15V, 7A/ 0 to 30V, 4A	HP E3632A DC Power 0 to 15V, 7A/ 0 to 30V, 4A	AMEL Instruments Galvanostat Model 2053	AMEL Instruments Galvanostat Model 2053
Power [mW]	9	4	32.5	3
Duration [hrs]	63	25	12	13
Charge [C]	68	18	2.8	1.2
Result	Fiber	Dendritic mass	Dendritic mass	Dendritic mass

¹¹ $\rho(D-d)V/\mu$: $\rho = 1300 \text{ kgm}^{-3}$ for PPy; D (diameter of flow cell) = 3.6 mm; d (diameter of anode) = 0.3 mm
 $V = 2.8 \text{ mm}^{-1}$; μ (assumed viscosity similar to water) = $8 \times 10^{-4} \text{ Nsm}^{-2}$

¹² These are approximate values since the power supply used was difficult to control. Current was controlled and constant in Trials 3 and 4.

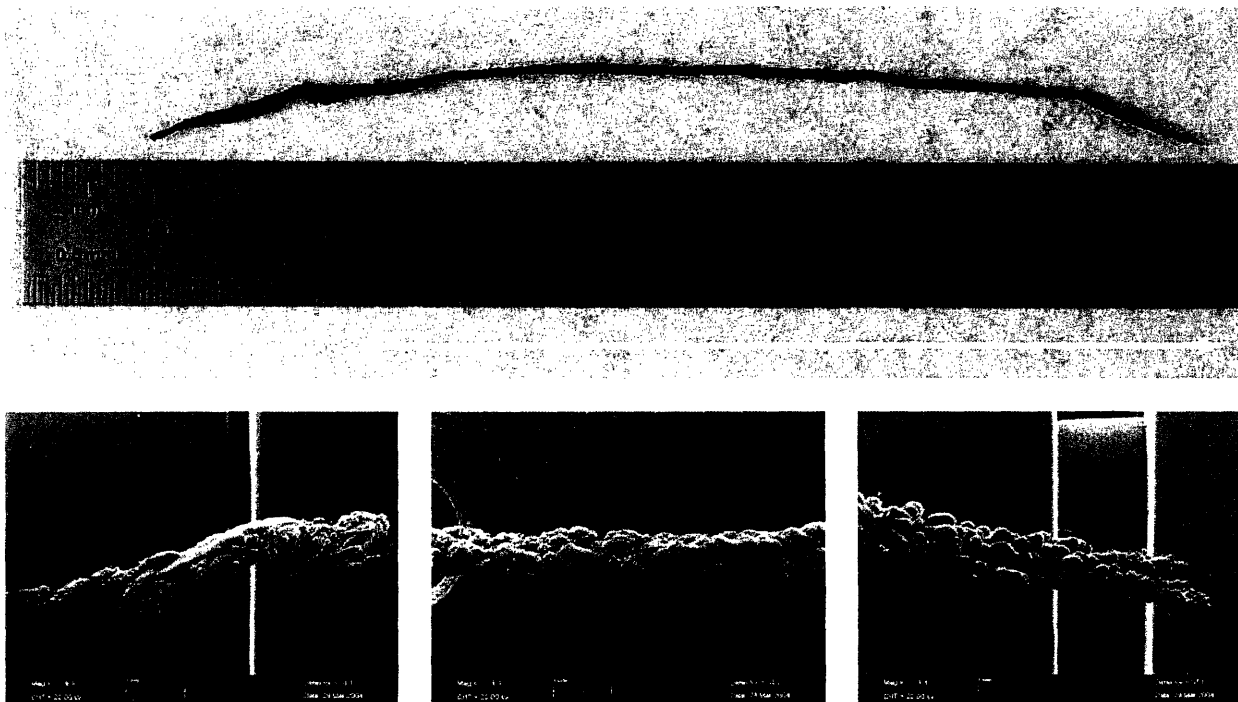


Figure 10: Fiber grown from trial 1 (top) with SEM pictures (18× magnification) of three sections of the fiber (bottom).

The first trial of the experimental setup was a success. After running a deposition for 63 hours, the result was a fiber 83 mm in length and between 0.8 to 1.05 mm in thickness. The initial section of the fiber was not uniform in thickness, but a uniform thickness was reached in the middle section of the fiber after 25 mm. The fiber possessed some flexibility, but for the most part was very brittle.

As evident from the SEM pictures of the beginning, middle, and end sections of the fiber shown in Figure 10, the texture of the beginning of the fiber is quite smooth. Moving along the length of the fiber, the texture becomes bumpier and rougher. The tip of the fiber where the most recent deposition was made is very dendritic. This could be due to the fact that over time, the hydrodynamic flow the solution smoothes out the texture as it flows over the fiber.

Mechanical tests were performed on the fiber using the DMA. Figure 11 shows the stress strain behavior of the fiber. The Young's Modulus of the fiber was 0.155 GPa and the tensile stress was at 3.26 MPa.

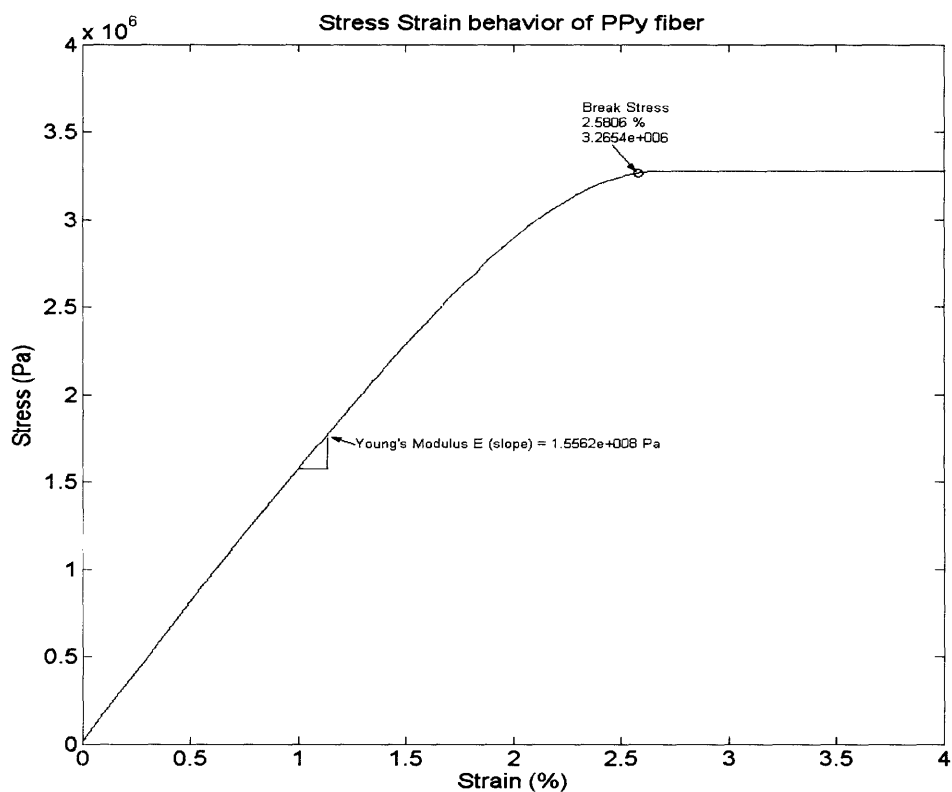


Figure 11: Stress-strain curve of PPy fiber.

The resistivity of the fiber was 7Ω using the four point resistivity test. Using this value, the fiber's conductivity¹³ was calculated to be 850 Sm^{-1} .

¹³ Conductivity = $(1/R_{4R}) \times (1/A_c) \times d$, where R_{4R} is the resistivity measured using the 4 point method, A_c is the cross-sectional area of the fiber (the section of the fiber being tested was 0.8 mm in diameter), and d is the distance between the two probes. In this case, $d = 3\text{mm}$.

Although trial 1 was successful, it was difficult to reproduce the results in subsequent trials due to the different parameters used and the inability to control the current in the first few trials with the power supplies used.

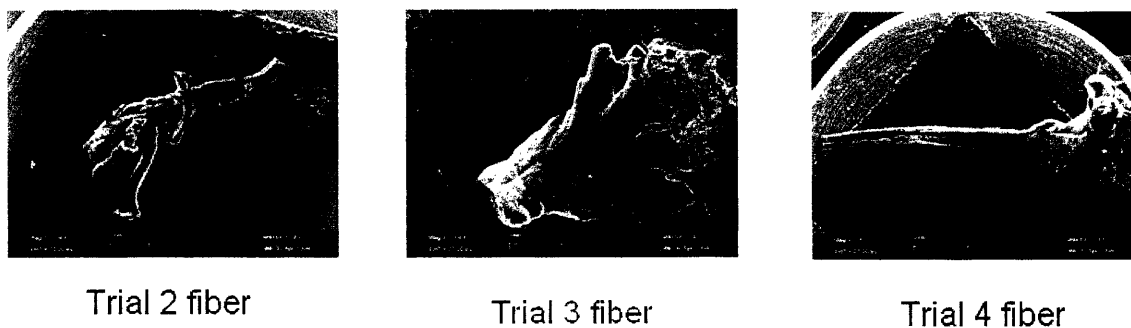


Figure 12: SEM pictures of results from trials 2 to 4.

In an attempt to match the current density of $140 \times 10^3 \text{ A/m}^2$ used in Li's experiments, the current density was raised in trials 2 to 4. This resulted in dendritic growths of PPy. It seems that the desired current density was too large and possibly created excess nucleation sites where pyrrole began to polymerize. This caused the PPy to branch out in different directions. Some of the deposited fibers had hollow centers. The PPy deposited on the sides and spread outward but left a hollow opening in the middle.

Except for Trial 4, there seems to be a trend where large current density leads to dendritic growth. Although the cause is not certain, one could hypothesize that it is a result of over-oxidation and excess nucleation sites occurring at the anode. The current supplied probably surpassed the rate of reaction of the polymerization of the pyrrole. This initially causes the pyrrole to deposit quickly on the anode forming a tiny conglomeration of PPy at the tip of the electrode. Once this bulb forms, it affects the hydrodynamic flow for the rest of the deposition

and causes the pyrrole to deposit in many dendritic configurations. At times, the conglomeration of pyrrole at the tip of the anode is so big that it disrupts the hydrodynamic flow and prevents monomer from being deposited at the tip. This results in the formation of a hollow center.

5 Discussion

From a schematic taken from Li *et al's* experiment, a physical experimental setup of an electrochemical flow cell was built to grow conducting polymer fibers. Several parameters of the systems such as flow rate, cell diameter, current density, deposition voltage, and salt and monomer concentrations, and their effects on the rates and directions of PPy deposition were discussed. A fiber 83mm in length and 0.8 to 1.05 mm in diameter was successfully grown using this electrochemical flow cell. An increase in current density resulted in dendritic growths of PPy. This was probably be due to excess nucleation sites, and over-oxidation and degradation of the PPy. Some of the power sources that were used were difficult to control. The AMEL Instruments Potentiostat/ Galvanostat Model 2053, which was used for latter experiments was successful at supplying a constant current to the cell.

Initial studies were begun to investigate the effects of and optimize the temperature of the monomer/salt solution. Temperature was chosen as a parameter to investigate because it had been shown in previous studies at the MIT BiLab that depositions at low temperatures increased the quality of PPy films (Yamaura *et al*, 1988). A cooling system was added to cool the reservoir of solution down below zero (Figure 13).

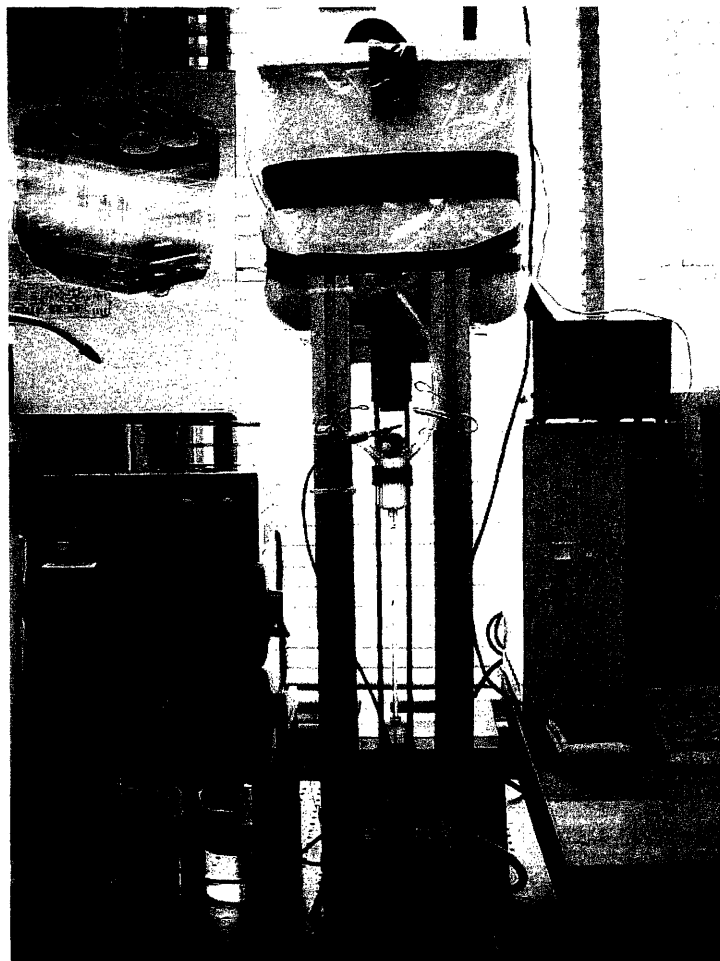


Figure 13: Experimental Setup with the addition of temperature control.

The reservoir was encased in a Styrofoam box, which acted as an insulator. Inside the Styrofoam box and around the container holding the solution, a low range heat transfer fluid was cooled using a chiller (located on the right in Figure 13) to the desired temperature. Temperature readings were taken using Omega Precision Fine Wire Thermocouples, type E¹⁴. Four thermocouples were placed in the system. One was in the heat transfer liquid, one was in the reservoir of monomer solution, and two were placed at the inlet and outlet of the electrochemical flow cell. Difficulties arose with cooling the entire system since the chilled solution was exposed to ambient temperature when it exited the box and circulated through the system. The

¹⁴ <http://www.omegaprecision.com/>

entire electrodeposition apparatus needs to be insulated or placed in a chiller in order to better get an understanding of the effects of temperature.

6 Conclusion

From a schematic taken from Li *et al's* experiment, a physical experimental setup of an electrochemical flow cell was built to grow conducting polymer fibers. Several parameters of the systems such as flow rate, cell diameter, current density, deposition voltage, and salt and monomer concentrations, and their effects on the rates and directions of PPy deposition were discussed. A fiber 83mm in length and 0.8 to 1.05 mm in diameter was successfully grown using this electrochemical flow cell. An increase in current density resulted in dendritic growths of PPy. Temperature optimization test were begun. Now that the task of growing conducting polymer fibers has been proven to be feasible, this topic merits further investigation.

7 Future Work

With a reliable current source, more controlled experiments can be carried out. Reproduction of the results of trial 1 would be desirable. Different parameters of the system could be optimized. Parameters could include current density, deposition voltage, flow rate, monomer concentration, and temperature.

8 References

Bard, A. J. and L. R. Faulkner. *Electrochemical Methods: Fundamentals and Applications* 2nd ed. New York: Wiley, 2001.

<http://electrochem.cwru.edu/ed/encycl/art-e01-electroplat.htm>

<http://we.home.agilent.com/USeng/home.html>

<http://www.amelchem.com/>

<http://www.omegaprecision.com/>

<http://www.solid-edge.com/>

http://www.visserssales.com/Barnant_LS_StanDigital.htm

<http://www.wam.umd.edu/%7Esmela/actuators.htm>

Kissinger, P. T. *Electrochemistry for the Non-Electrochemist. Current Separations* vol 20: pp. 2. 2002.

Li, S., C. W. Macosko, and H. S. White. *Electrochemical Processing of Conducting Polymer Fibers. Science* vol. 259, pp.957-960, 1993.

Madden, J. D. W. *Conducting Polymer Actuators. MIT Mechanical Engineering Ph. D Thesis.* Cambridge, MA, 2000.

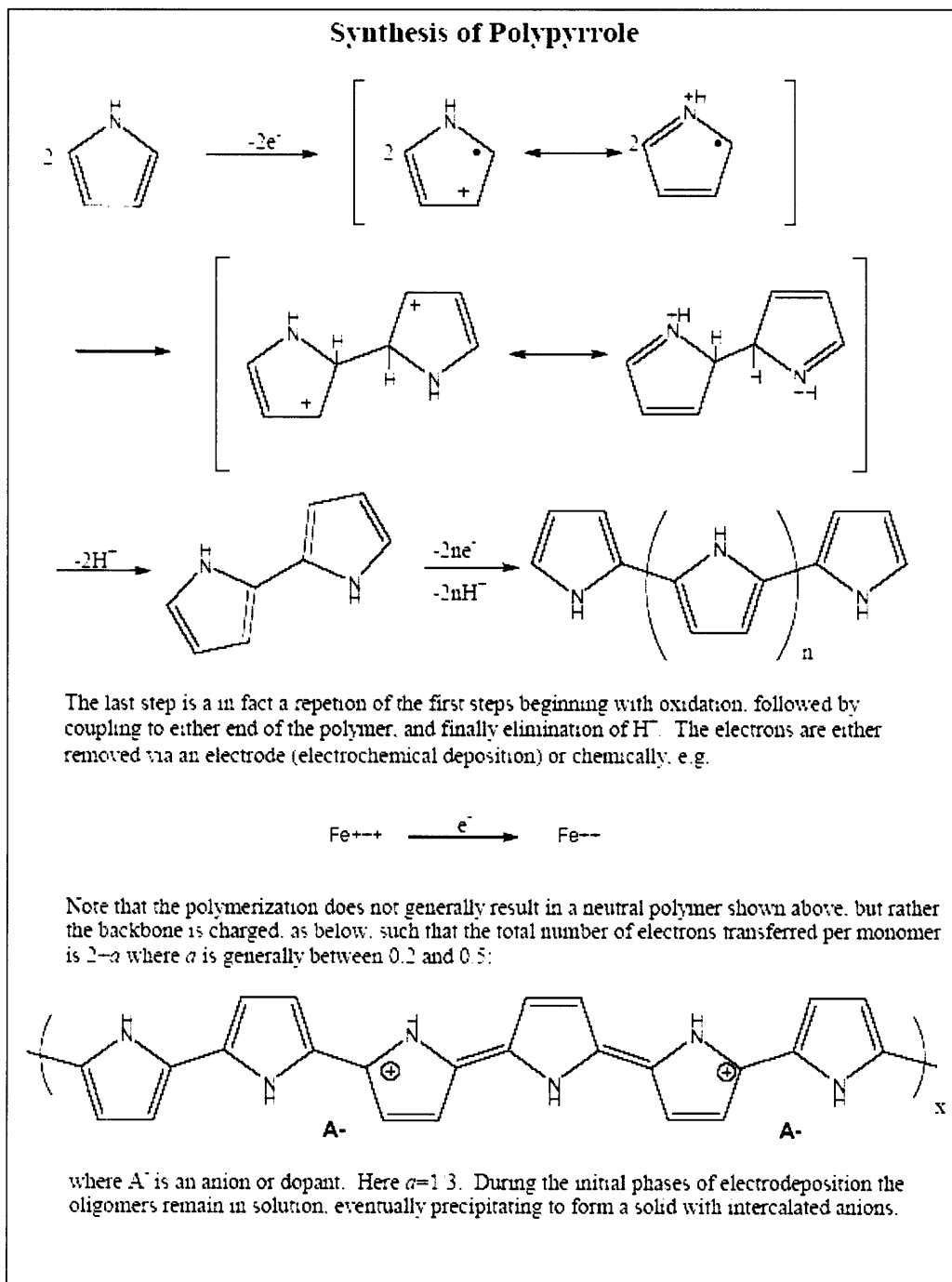
Schmidt, C.E., V.R. Shastri, J. P. Vacanti, and R. Langer. *Stimulation of neurite outgrowth using an electrically conducting polymer. Proceedings of the National Academy of Science. USA* vol. 94: pp. 8948-8953, 1997.

www.alfa.com

www.masterflex.com

Yamaura, M., Hagiwara, T. and Iwata, K. *Enhancement of Electrical Conductivity of Polypyrrole Film by Stretching: Counter Ion Effect. Synthetic Metals*, vol. 26, pp. 209-224, 1988.

9 Appendix A¹⁵ - Synthesis of PPy



¹⁵ Taken from Madden, 2000