Continuous Production of Conducting Polymer

by

Terry A. Gaige

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

Bachelor of Science in Mechanical Engineering
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June 2004

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Abstract

A device to continuously produce polypyrrole was designed, manufactured, and tested. Polypyrrole is a conducting polymer which has potential artificial muscle applications. The objective of continuous production was to produce both larger films and films with more consistent properties than the films produced by the current batch-production method. The mechanical properties of polymers produced by batch synthesis are known to be highly dependent on reaction parameters such as temperature, and reactant and electrolyte concentrations. A system of peltier thermoelectric coolers and refrigerated-circulator held the deposition chamber at -10 °C. The polypyrrole film deposited onto the surface of a rotating glassy carbon crucible was peeled off using a blade and spring force mechanism. The temperature, current, and voltage of the electrodeposition were recorded. Several successful, but short, continuous deposition trials were run at a current density of 0.5 A/m^2 and a film 50 mm long and 0.246 mm thick was produced and tested. High rate depositions were also attempted at 150 A/m^2 but failed due to over-oxidation. In this thesis, it is demonstrated that continuous production appears feasible. A second prototype of the device is proposed with several improvements, the most important of which are a larger torque applied to the rotating crucible and a more effective and efficient cooling mechanism.

Thesis Supervisor: Ian W. Hunter

Title: Professor of Mechanical Engineering and Bioengineering

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1.0 Introduction and Background

Polymers are long molecules composed of repeated subunits. There are natural polymers such as DNA, proteins and cellulose and many synthetic polymers such as plastics. Polymers are generally considered insulators and are widely used for that property; however, scientists discovered a class of polymers that has a high electrical conductivity due to its specific molecular structure. In order for a polymer to conduct electricity, the electrons need to be free to move. In a conducting polymer, the electrons can flow down a backbone of alternating single and double bonds, called conjugated double bonds. Another requirement before the electrons are free to move is a disturbance of the basic material structure by the addition or subtraction of electrons, a process known as doping. Some conducting polymers have unique properties such as photoluminescence and contractibility. The material can be both power-efficient and chemically inert so it could prove very useful for medical applications. Other potential applications of conducting polymers include batteries, biosensors, antistatic clothing[1], photovoltaic devices[2], wine-tasting sensors[3], robotic actuators, visual displays and more.

Polypyrrole is one of several different conducting polymers whose properties are being studied and practical applications as engineering materials being explored. Currently, the Conducting Polymer Group in the BioInstrumentation Laboratory at the Massachusetts Institute of Technology (MIT BiLab) has been optimizing current technology by finding ways to maximize the stress and strain capabilities of polypyrrole and improve strain rate, efficiency and conductivity. MIT BiLab has also been experimenting with novel molecular designs and new manufacturing techniques. The subject of this thesis is the development of a method to continuously produce polypyrrole.

Two common methods to produce polypyrrole are by galvanostatic (constant current) or potentiostatic (constant voltage) deposition onto a surface. In a solution containing pyrrole monomer, a small current is run from a copper cathode to a glassy carbon

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[1] Yamato, H., Kai, K., Ohwa, M., Asakura, T., Koshiba, T., Wernet, W., *Sythetic Metals* 83 (1996) 125-130.

[2] Lu, S.L., Yang, M.J., Luo, J., Cao, Y., *Sythnthetic Metals* 140 (2-3): 199-202 FEB 27 2004

[3] Riul, A., de Sousa, H.C., Malmegrim, R.R., dos Santos, D.S., Carvalho, A.C.P.L.F., Fonseca, F.J., Oliveira, O.N., Mattoso, L.H.C. *Sensors and Actuators B-Chemical* 98 (1): 77-82 MAR 1 2004

crucible anode. After about 24 hours (depending on the current), a thin film will have been deposited on the surface of the crucible. This film is then delicately peeled off by hand using a razor blade. The electrical and mechanical properties of the polymers synthesized by this method are dependent on the precise concentrations of reactants, the pH of the solution, and the temperature of the solution. As a deposition progresses, the monomer concentration decreases and pH changes which result in films with varying characteristics throughout.

In this research project, a machine to continuously produce polypyrrole was designed, built, and tested. The advantage of continuously producing conducting polymer is not only to have larger pieces, but also to better monitor its production and get greater consistency, repeatability, and quality. The pH, temperature and monomer concentration had to be continually monitored and controlled and the polymer had to be automatically peeled, treated, and stored as it was produced. Chapter 2 covers previous production methods and also previous attempts at continuous production, none of which succeeded in becoming viable options for continuous production commercially or in a lab. In Chapter 3, the design and theoretical analysis of the first prototype are explained. Chapter 4 describes the system characterizations and trials performed. The final Chapter 5 comments on the partly successful results and makes suggestions for a second prototype.

2.0 Previous Methods and Limitations

The MIT BiLab has been researching the properties of polypyrrole since the early 90's. Several methods of production have been explored but the main method is a batch production.[4]

2.1 Characteristics of batch-produced polypyrrole

Polypyrolle films are grown in a propylene carbonate solution with 0.05 M pyrrole monomer, 0.05 M tetraethylammonium hexaflourophosphate (TEAP) and 1% vol. distilled water. The method is described in detail in Appendix A. The solution is poured into a large beaker containing a glassy carbon crucible surrounded by a copper sheet,

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[4] Madden, J., Conducting Polymer Actuators, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, September 2000; p. 34.

which serves as the counter electrode. The electrodepositions are run at -40 °C with galvanostatic control. During the deposition, measurements of temperature, current and voltage are taken, but no control is implemented. Depositions are typically run at a 1.25 A/m^2 for 16 hours and produce films 28 μm thick. Films have been produced up to 2 m in length using a spiral coil geometry on the crucible. The maximum active stress tested was 40 MPa and the greatest active strain was 2%. The highest conductivity to date is 5×10^4 S/m.

2.2 Previous attempts at continuous production

2.2.1 Outside of MIT BioInstrumentation Lab

The continuous production of conducting polymers has been attempted by many groups. Most often the method of a rotating cyclindrical working electrode was implemented. Groups, such as the International Research Laboratories in Japan and the Intelligent Polymer Research Laboratory in Australia, have succeeded in continuously producing and peeling a polymer film. The films produced had consistently repeatable conductivities, but were poor. They reported conductivities on the order of 3.104 S/m and inferior elasticities.

2.2.2 Within the MIT BioInstrumentation Lab

Several years prior to this research the MIT BiLab realized the potential usefulness of a machine to continuously produce conducting polymer and an attempt was made. The rotating cylindrical working electrode method was employed. Difficulty was encountered because the method required large volumes of the solution. Also, no peeling mechanism was used and no temperature control implemented.

3.0 Theory, Design and Manufacture of First Prototype

There are multiple methods to continuously produce a polymer such as solution drawing and fiber deposition. The rotating drum method was chosen for this project because the MIT BiLab has extensive experience with the deposition of polypyrrole onto cylindrical crucibles. Also, the sheet form produced is useful for bilayer or trimorph actuators[5] and in biomimetic applications such as the fish fin - both subjects being researched over a

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[5] Schmid, B., Device Design and Mechanical Modeling of Conducting Polymer Actuators, B.S. Thesis, Massachusetts Institute of Technology, Cambridge, MA, June 2003; pp. 23-37.

long period of time in the MIT BiLab. A machine to continuously produce polypyrrole requires continued monitoring and precision control of temperature, pH, reactant concentration, and, in the case of the rotating drum method, a device for peeling and storing the film. Figure 1 shows a schematic for the continuous production method that was employed. A computer receives signals from sensors and sends commands to reactant injection devices, the reaction-driving current generator, the crucible stepping motor, and the peltier thermoelectric heat pumps.

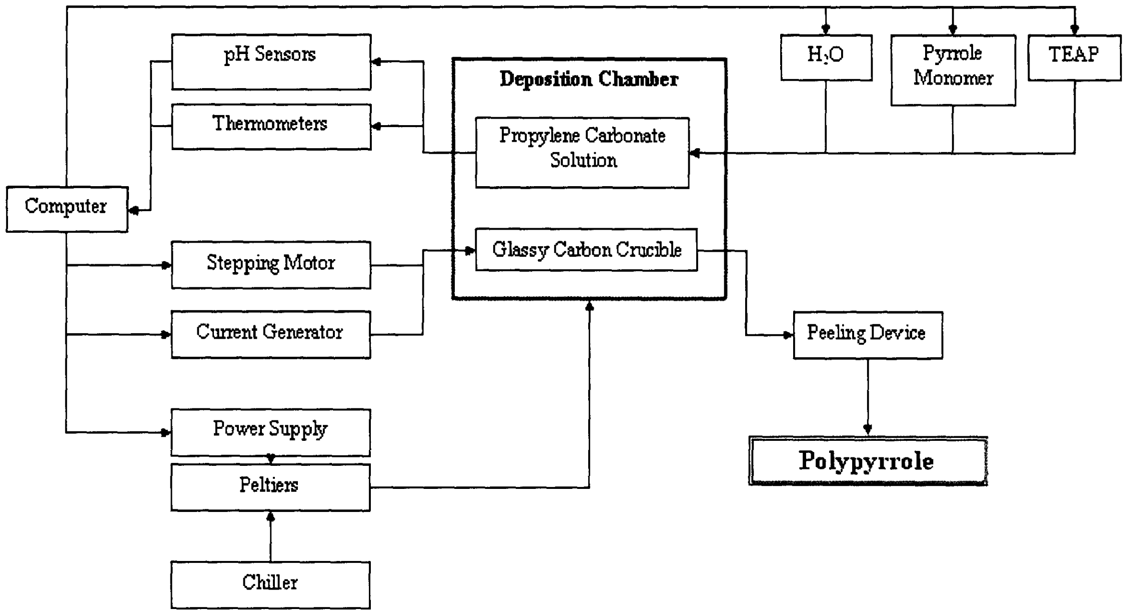

Figure 1: Completed schematic for the continuous production of polypyrrole.

Another possible design was considered in which the propylene carbonate solution would be externally circulated through a chiller, through a mixing/sensing device, then through the deposition chamber; but this design was rejected because it required much larger volumes of the costly chemicals. The design shown in Figure 2 was chosen because the crucial variables such as temperature and reactant concentrations could be readily and precisely controlled within the deposition chamber.

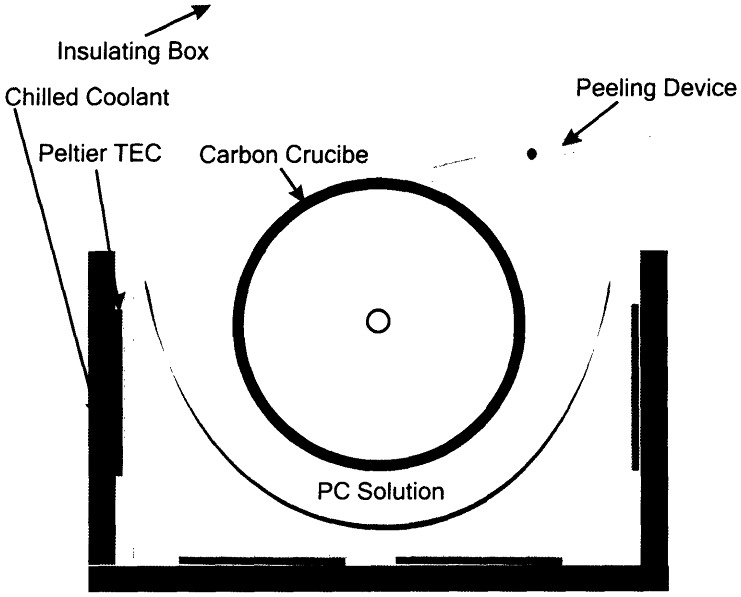

Figure 2: Diagram of deposition chamber.

3.1 Cooling of Deposition Chamber

In order to maintain the propylene carbonate solution at the required -40 °C, a system with a refrigerated-circulator and peltier thermoelectric coolers (peltiers) was used. This system combined the large cooling power of a refrigerated-circulator with the precise, quick-response controllability of peltiers.

3.1.1 Peltier Thermoelectric Coolers

The selection of peltier thermoelectric coolers is a difficult process because the design equations are either very complex or overly simple to be usefully approximate. Figure 3 shows a diagram of a peltier.

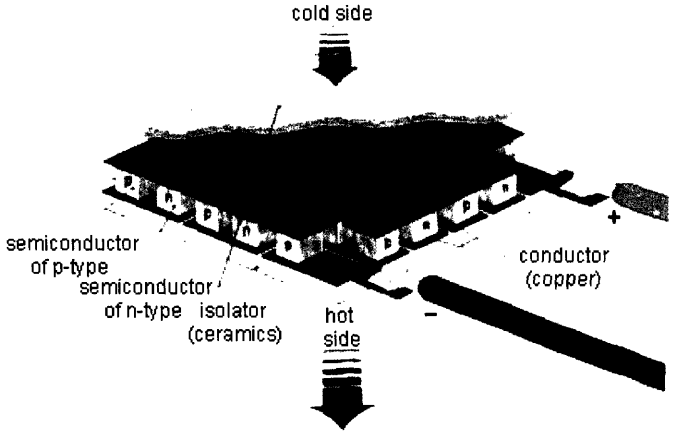

Figure 3: Diagram of a peltier thermoelectric cooler[6].

Heat flows into the cold side from a thermal load and out the hot side into some type of heat sink. The thermal load is a combination of active load and passive load. All loads have a passive component because it is impossible to perfectly thermally isolate anything from conductive, convective and radiative heat. Some sources have an active component, such as computer chips which produce a certain amount of electrical heat or solutions in which an exothermic reaction is taking place. In this project's application, the thermal load is completely passive, meaning that there is no internal heat source and that the thermal load results entirely from the radiation, conduction and convection from the environment as shown in Figure 4.

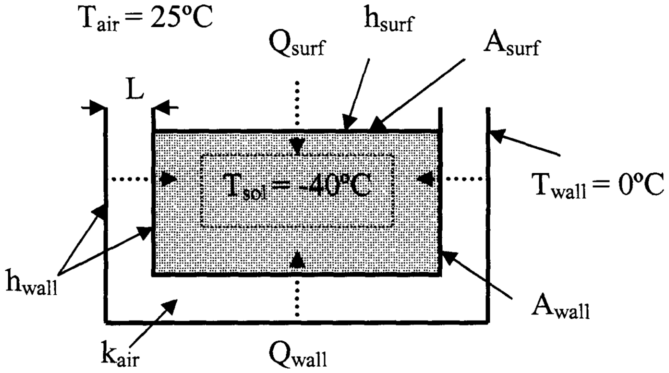

Figure 4: Diagram of the passive heat load due to conductive and convective heat transfer to the solution from the environment.

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[6] http://www.digit-life.com/articles/peltiercoolers/?50859

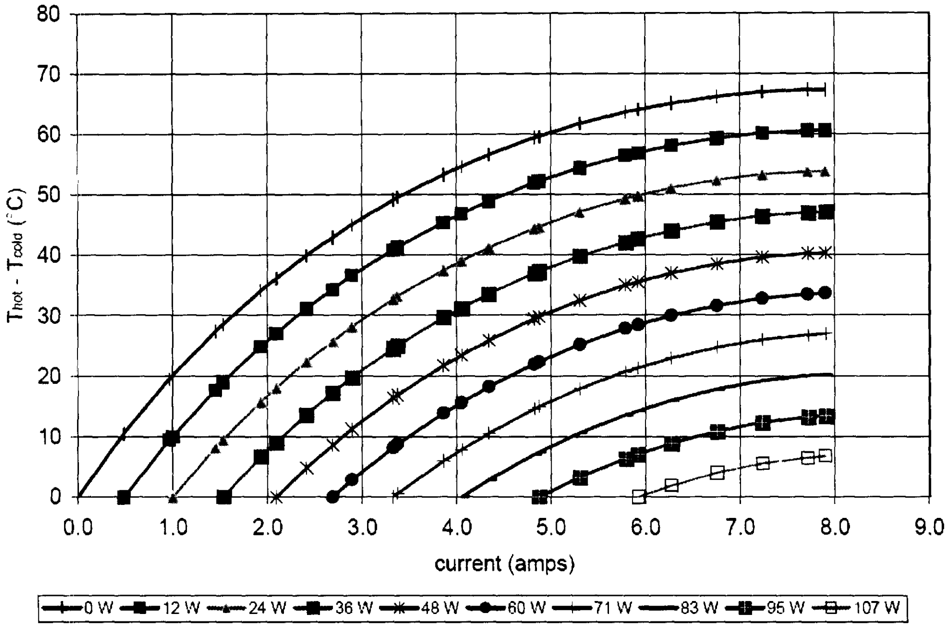

Figure 5: Characteristic curves for the HP-199-1.4-1.15 peltier – temperature difference vs. current.[8]

It is known that $\dot{Q}_{load}$ is around 33.5 W. Twelve peltiers were used to uniformly surround the solution, therefore the thermal load on each was 2.8 W. Figure 5 shows that, for a $\dot{Q}_{load}$ between 0 W and 12 W and temperature difference of 40 °C, the current draw by the peltier will be about 2.5 A. Figure 6 is another graph provided by the manufacturers and can be used to estimate the voltage.

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[8] Taken from http://www.tetech.com/modules/graphs/HP-199-1.4-1.15.pdf

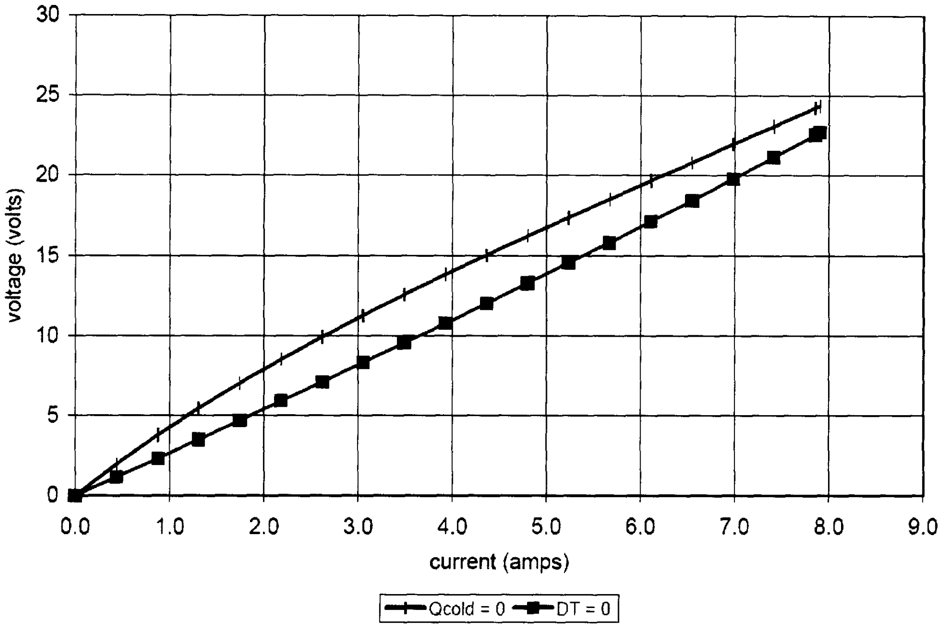

Figure 6: Characteristic curve for the HP-199-1.4-1.15 peltier – voltage vs. current[9]

The upper line in Figure 6 represents the voltage-current relationship for the ideal case of zero thermal load; the lower line represents the voltage-current relationship for when the ΔT is equal to zero. Since the thermal load is small, the upper line should be used. The voltage corresponding to a current draw of 2.5 A is 10 V.

The heat that exits the hot side of a peltier is equal to the sum of the heat pumped out of the load plus the joule heating due to the current running through the peltier,

$$\dot{Q}_{hot} = \dot{Q}_{load} + V_{peltier} \cdot I_{peltier}, \tag{5}$$

where $\dot{Q}_{hot}$ is the total heat exiting the peltier which needs to be removed by a heat sink, $\dot{Q}_{load}$ is the thermal load as calculated by Equation 1, $V_{peltier}$ is the supplied voltage and $I_{peltier}$ is the supplied current. So, using the above estimations for a voltage and current draw of 10 V and 2.5 A, the twelve peltiers will create 300 W of internal joule heating. The total heat expelled out the hot side of the peltiers, which has to be removed by the refrigerator/circulator, is 333.5 W; of which, 33.5 W is from the thermal load.

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[9] Taken from http://www.tetech.com/modules/graphs/HP-199-1.4-1.15.pdf

The total thermal load is equal to the sum of loads due to each mechanism of heat transfer. The heat flow due to radiation can be ignored because it is clearly much smaller than that from conduction and convection. Therefore, the total thermal load is equal to the sum of the conductive and convective heat from all sides:

$$\dot{Q}_{load} = \sum_{i}^{n} Q_i = \dot{Q}_{surf} + \dot{Q}_{wall} \quad . \tag{1}$$

The contributions from each mechanism of heat transfer can be estimated by using the material properties, temperature differences, and geometries and Equation 1,

$$\dot{Q}_i = \Delta T_i \cdot U_i \cdot A_i , \tag{2}$$

where $\dot{Q}_i$ is the heat flow through some area, ΔT_i is the temperature difference between the two surfaces, U_i is the equivalent overall heat transfer coefficient per area, and A_i is the area. The equivalent overall heat transfer coefficient for the walls can be written,

$$U_{wall} = \frac{k_{air}}{L} , \tag{3}$$

where U_{wall} is the equivalent overall heat transfer coefficient for the wall, k_{air} is the conductivity of air, and L is the distance between the inner wall and outer wall. The equivalent overall heat transfer coefficient for the upper surface can be written,

$$U_{surf} = h_{surf} , \tag{4}$$

where U_{surf} is the equivalent overall heat transfer coefficient for the upper surface and h_{surf} is the convection heat transfer coefficient between propylene carbonate and still air. h_{surf} was estimated to be less than 25 W/(m^2·K) from common values for convection coefficients of horizontal plates. By entering the values and material properties in Table 1 and steady state temperatures shown in figure 4 into Equations 3 and 4, the total thermal load, $\dot{Q}_{load}$, is found to be 33.5 W.

Table 1: Values and material properties used to calculate the thermal load.

		Value
Area of walls.	A_{wall}	0.056 m^2
Area of upper surface.	A_{surf}	0.012 m^2
Natural convection heat transfer coefficient for air on horizontal plate.	h_{surf}	25 $W/(m^2{\cdot}K)$
Temperature difference between inner and outer wall.	ΔT_{wall}	40 °C
Temperature difference between solution surface and ambient air.	ΔT_{surf}	65 °C
Conduction heat transfer coefficient for air.	k_{air}	0.025 $W/(m^2{\cdot}K)$

The amount of heat flow that a certain manufactured peltier TEC can produce ranges from less that 0.5 W to over 200 W. This maximum heat flow is called $\dot{Q}_{\max}$ and occurs when the peltier is driven at maximum current and voltage, I_{max} and V_{max} and when the temperature difference is zero. $\Delta T_{\max}$ is the temperature difference between the hot and cold sides of the peltier at which the reverse, conductive heat flow through the peltier is in equilibrium with the pumped heat flow out when the peltier is driven at maximum current and voltage.. These characteristic values, $\dot{Q}_{\max}$, I_{max}, V_{max} and $\Delta T_{\max}$, can usually be found on the specification sheets for a particular peltier.

The peltier specification graphs provided by the manufacturers can be very useful in determining which peltier to use for a particular application. A desired ΔT can be estimated by assuming that the hot side of the peltier will be held at a constant 0 °C by a liquid refrigerated-circulator and knowing the desired temperature is -40 °C. The TE Tech[7] HP-199-1.4-1.15 was chosen because a ΔT of 40 °C is right in the middle of its range as Figure 5 shows. (see Appendix B for more peltier specifications)

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[7] http://www.tetech.com/

The twelve-peltier thermoelectric cooler system is capable of cooling a solution down to -40 °C, but the system is very inefficient because the peltiers produce an extra 300 W of joule heating. The advantage of the peltier system is the ability for quick response time and very accurate holding of temperature.

3.1.2 Serpentine Channel Heat Dissipater

The hot sides of the peltiers were kept cool by contact with aluminum plates containing serpentine channels with coolant flow. Aluminum was chosen because of its machinability and high thermal conductivity. The coolant, circulated by a refrigerated-circulator, entered into one face of the box, split into three, flowed through the channels, rejoined and exited out the opposite face. A CAD model of the heat dissipater, shown in Figure 7, was created using Solid Edge V14[10]. Then, using FeatureCAM 2004 toolpaths were created that guided a HAAS VF-0E to mill channels, o-ring grooves and screw holes into the aluminum plates. To connect the channels from one face to the next, coaxial holes were drilled and o-rings installed at the interface. There could have been an uneven flow distribution between the three faces due to the Coanda effect so a large chamber was milled at the coolant entrance and exit. It this way, a pressure pocket was created which caused the coolant to flow through the somewhat restrictive interface holes at even rates. To cover the channels, 10mm thick acrylic was cut to fit with a lasercutter and sealed with Buna-N o-ring cord stock. Then, for the coolant entrance and exit, brass pipe-to-hose, barbed adapters were threaded into the acrylic.

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[10] http://www.eds.com

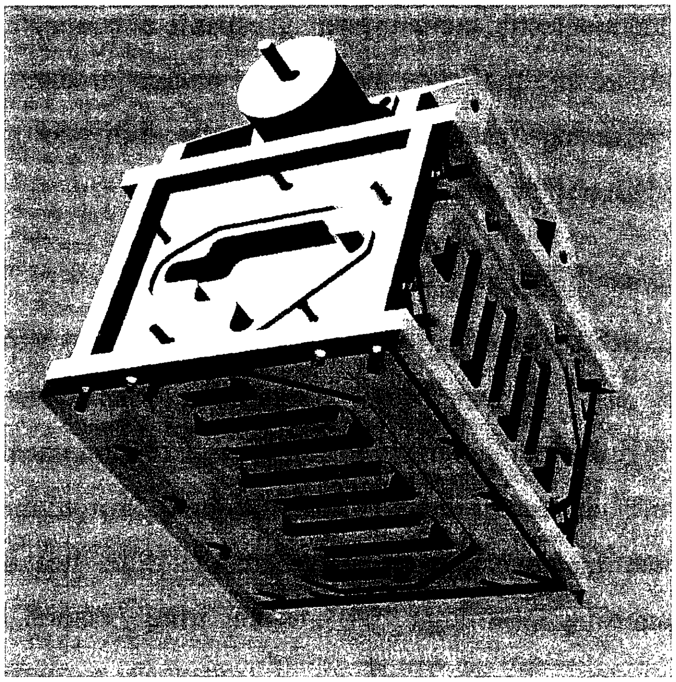

Figure 7: CAD model showing the design of the serpentine channel heat dissipater on the bottom and sides of the cooling chamber.

3.1.3 Refrigerated-circulator

The requirements of the refrigerated-circulator were to pump the coolant through the serpentine channels and to maintain the coolant at less than 0 °C. It was found that 333.5 W of heat would flow out of the hot sides of the peltiers and into the aluminum plates (See Section 3.1.1 for detail). Therefore, the refrigerated-circulator had to remove that thermal load as well as the additional thermal load from ambient air conducting into the supply lines.

The only refrigerated-circulator available for use was VWR Signature Heated/Refrigerated Circulator, Model 1166, with a two-speed pump. The refrigerated-circulator had a 6 L bath and cooling capacity of 200 W at 20 °C and 140 W at 0 °C, which was far below the 333.5 W thermal load, not to mention inadvertent loss to ambient air through the tubing. See Section 4.1.1 for a characterization of the systems ability to cool the solution. Although the system was not capable of keeping the solution at -40 °C, it was able to hold a relatively constant -10 °C which was satisfactory enough to continue with experimentation.

3.2 Crucible and Counter-Electrode

The same type of glassy carbon crucible as was used in batch-production (see Section 2.1) was used for continuous production, a Sigradur 285 mL G-crucible[11]. The bottom face was cut out using an abrasive waterjet machining center to allow for a continuous solid axle. A crucible support as shown in Figure 8 was printed on a Viper stereo lithography machine. Parts produced in the stereo lithography machine were very useful because the hardened resin was completely resistant to the propylene carbonate solution, unlike many other plastics (see Appendix C for a table of several plastics' resistance to propylene carbonate). The crucible support was given a slight taper to fit with crucibles that did not have perfectly circular cross-sections. A stainless steel axle mounted with two ABEC 5 bearings allowed the crucible to spin freely. A 0.4 mm thick copper sheet 100 mm by 200 mm was used as a counter-electrode. It could be flattened when cleaned and then recurved to match the crucible curvature with approximately a 10 mm separation distance.

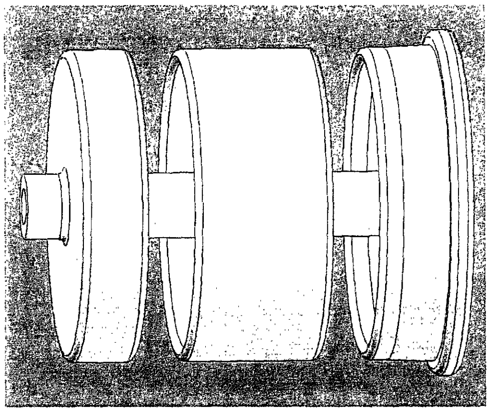

Figure 8: CAD Model of the crucible support which was printed on a Viper stereo lithography machine.

3.2.1 Rotating

To get the desired quality of polypyrrole and 25 μm thickness, a typical batch-deposition was carried out over 16 hours with a 10 mA reaction-driving current. For the equivalent continuous-deposition, where only half the crucible is submerged in solution at any particular time, the crucible must rotate at approximately one revolution every 32 hours to get the same film thickness. The analysis in Section 3.2.2 shows that the crucible must be rotated with at least 0.8 Nm of torque. A stepper motor can meet such requirements for extremely slow speeds and moderate torque. The Zeta 57-83M stepper motor was

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[11] Purchased from – Hochtemperatur-Werkstoffe GmbH, Gemeindewald 41, D-86672 Thierhaupten

used in conjunction with a Parker Compumotor 6104 indexer drive. The stepper motor had 0.8 Nm maximum holding torque and was capable of 50,000 microsteps per revolution which allowed for very smooth control at slow speeds. A 70 mm pitch circle diameter aluminum gear with 128 teeth was mounted to the face of the crucible support so that it could be driven by the stepper motor.

3.2.2 Peeling

It was possible to peel the polypyrrole film off of the glassy carbon crucible by hand using a razor blade. With the acquirement of a small amount of technique, the razor blade could be slightly rocked back and forth and the film would come away from the surface intact. Because of the difficulty of mechanizing the rocking technique, it was hypothesized that the same results could be obtained by applying a larger inward radial force with the blade. The device shown in Figure 9 was designed to hold a razor against the surface of the crucible as it was turned by the stepper motor. The blade angle was adjustable between about 20 ° and 30 ° from the tangent to the crucible surface. The inward radial force could be adjusted by replacing the springs with springs of a different spring constant.

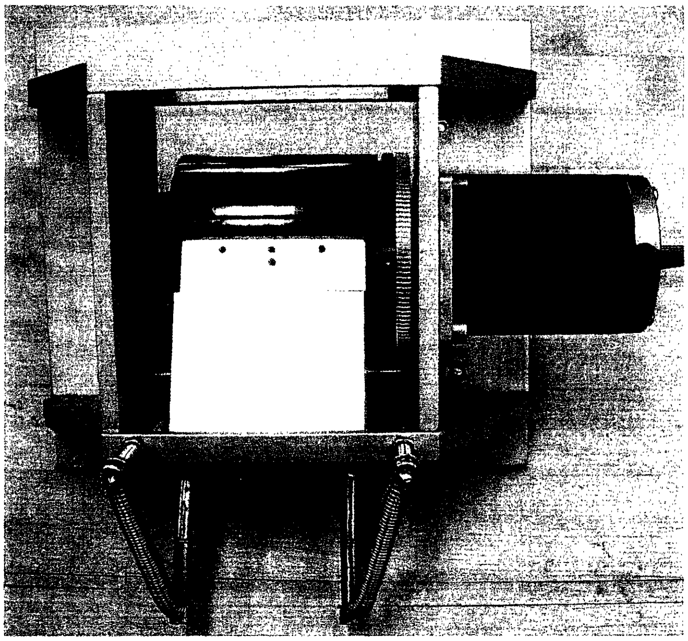

Figure 9: Photo of crucible, stepper motor, and peeling mechanism.

The motor which turns the crucible must have enough torque for the blade to peel the polypyrrole film away from the surface. Figure 10 shows a force diagram of the blade and crucible. In the upcoming analysis, the force required to lift the polypyrrole film will be ignored and simply approximated by a coefficient of friction between the blade and crucible. The minimum torque required by the motor is a function of θ (the angle of the blade to the surface of the crucible) and μ (the coefficient of friction).

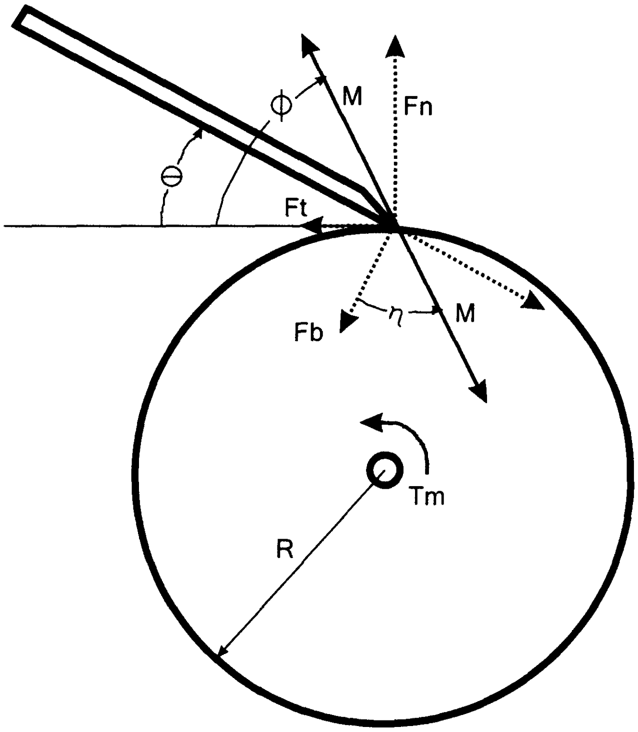

Figure 10: Force diagram of peeling mechanism.

The following expression can be derived by equating the applied and reactionary force magnitudes.

$$F_n = \left[\frac{F_b}{\cos(90 + \theta - \phi)} \right] \cdot \sin(\phi), \tag{6}$$

where F_n is the normal force between the blade and the crucible, F_b is the force applied by the blade to the crucible which depends on the spring tension and length of blade and is determined experimentally, θ is angle of the blade to the surface of the crucible, and ϕ depends on μ,

$$\phi = \cot^{-1}(\mu), \tag{7}$$

where μ is the simplified coefficient of friction between the blade and the crucible surface. The coefficient of friction varies with each deposition. Sometimes, very thick film depositions have already started to self-separate from the crucible, and other times, the film is particularly well adhered to surface. It can be assumed that μ does not go below the coefficient of static friction of dry steel on plexiglass, 0.4, or be larger than that of rubber on aluminum, 1.0.[12] F_b was found experimentally to be about 10 N. Figure 11 shows a plot of minimum motor torque,

$$T_m = \mu \cdot F_n \cdot R, \tag{8}$$

where T_m is the minimum required motor torque to overcome friction, and R is the radius of the crucible. For higher blade angles, the required motor torque increases. For a blade incidence angle of 25°, the motor should have a torque greater than 0.8 N*m or be geared down to provide that amount of torque to the crucible.

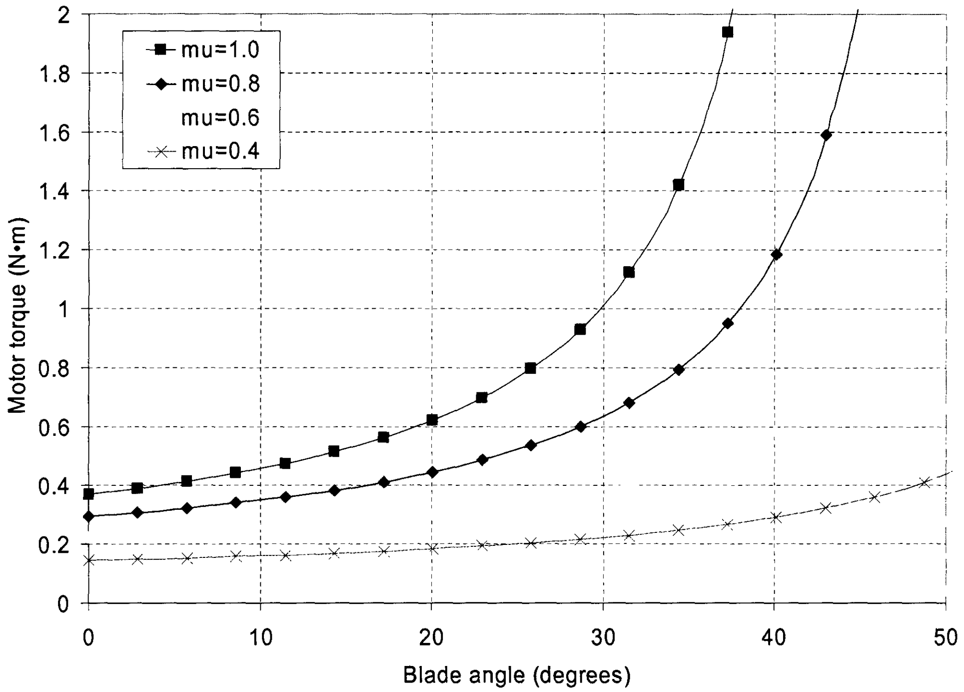

Figure 11: Plot of minimum required motor torque for varying peeling blade angle and coefficient of friction.

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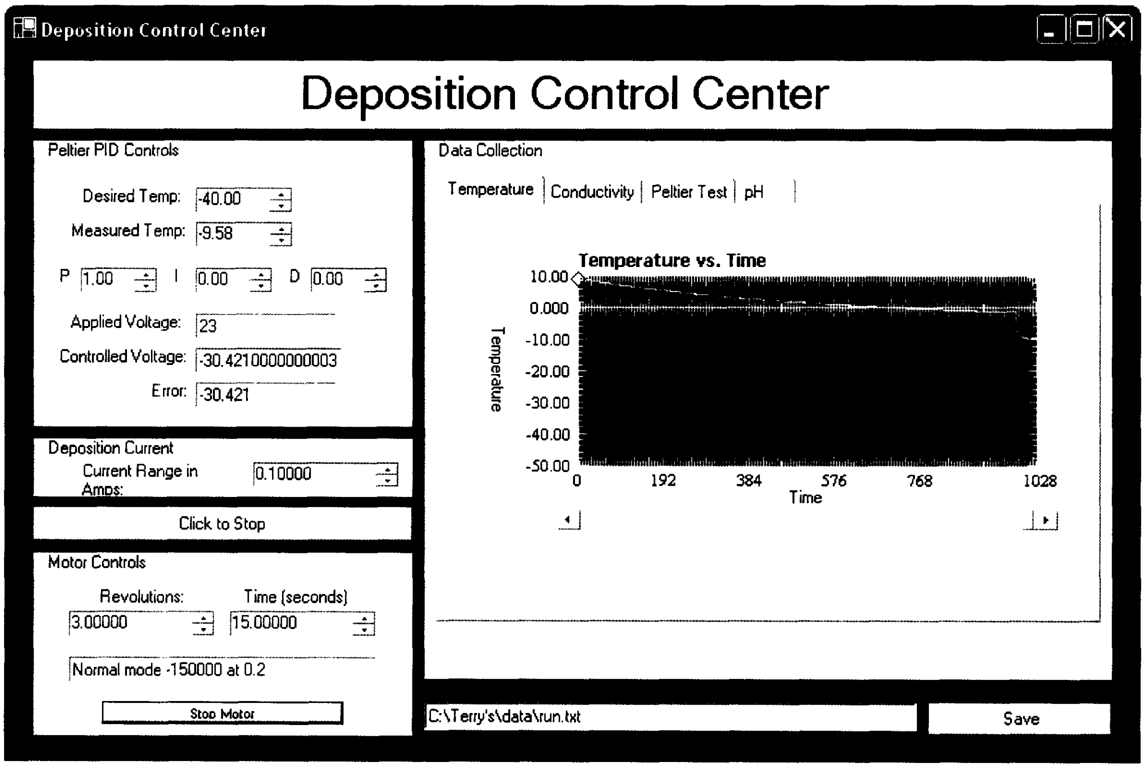
[12] http://www.engineersedge.com/coeffients_of_friction.htm

3.3 Deposition Control Center Instrumentation and Software

The most important aspect of the continuous deposition experiment is the continuous recording of temperature, voltage, and current data which was accomplished using a Visual Basic .NET program (see Appendix D for the code). The program, called the Deposition Control Center, recorded the measured data and plotted it real time in a graphic user interface shown in Figure 12. The Deposition Control Center also contained adjustable parameters for the control of the peltiers and the stepper motor.



Desired Temp: -40.00
Measured Temp: -9.58
P 1.00 I 0.00 D 0.00
Applied Voltage: 23
Controlled Voltage: -30.421000000000003
Error: -30.421
Current Range in Amps: 0.10000
Revolutions: 3.00000
Time (seconds) 15.00000
Normal mode -150000 at 0.2
C:\Terry's\data\run.txt

Figure 12: Screen shot of graphic user interface for the Visual Basic .NET program used to control and record parameters during a deposition.

3.3.1 Measurements

Temperature measurements were made using Omega precision fine wire thermocouples: Teflon insulated, Type E calibration. Figure 13 shows the locations of the four thermocouples. One thermocouple was placed within the propylene carbonate solution, one on the cold side of a particular peltier, one on the corresponding hot side, and one in the air surrounding the machine within the insulated box.

The thermocouples were connected to an Agilent[13] 20 Channel Multiplexer Card 34901A in an Agilent Data Acquisition/Switch Unit 34970A. Also connected to the 20 channel multiplexer were two channels containing signals from the AMEL Instruments Power Supply Model 2053 which was used to drive the deposition. One channel described the voltage and the other described the current. The data acquisition unit collected the measurements of voltage for each of the four thermocouples and also recorded the voltage from the current and voltage signals from the power supply.

The measurements were then transferred using a GPIB to USB adapter from the data acquisition unit to a standard PC and recorded by the Microsoft Visual Basic .NET program. The channel which described the current of the AMEL power supply was multiplied by some power of ten depending on the current range which then had to be divided out in the Visual Basic .NET program. That is why there is a field to input current range in the graphic user interface shown in Figure 12.

3.3.2 Controls

A basic proportional integral derivative (PID) control was implemented to control the temperature of the solution. The temperature of the solution was sensed using a thermocouple (see Section 3.3.1). Using .NET, the temperature's present value, present slope, and previous history was evaluated and compared to the desired temperature of -40 °C then a command was sent to voltage supplies for the peltier heat pumps. Theoretically the temperature of the solution could be cooled to the desired temperature very quickly with no overshoot, but problems arose with the systems ability to cool the solution (see Section 3.1.1). There was a point when increasing the voltage to the peltier heat pumps would begin to warm the solution instead of cool it. The complexity of the system made the PID control go unstable so it was discarded in favor of basic open loop control.

3.3.3 Actuators

The Zeta 57-83M stepper motor was driven by a Parker Compumotor 6104 indexer drive which was controlled through a standard RS-232 port on a PC. The ultra slow revolution

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[13] http://we.home.agilent.com/USeng/home.html

rates required for a deposition meant that the motor would be sent a command to turn a single microstep and wait an interval of a second or two.

The peltiers were driven by open loop control because of the complexity of the system and the tendency for closed loop control to go unstable (see Section 3.1.1 for an evaluation of the thermal system).

No other actuators were used in this project, but if the concentrations of reactants were to be actively controlled, a computer controlled injection device would have to be implemented.

4.0 Experimental Procedure

After the machine was constructed and before a deposition was attempted, characterizations of specific functions were performed. After their performance was deemed satisfactory, many full continuous deposition trials were performed with the apparatus and procedure described in Section 4.2.

4.1 System Characterizations

The ability of the peltier/refrigerated-circulator system to cool the solution was analyzed and the accuracy of the stepper motor at ultra slow speeds was examined. It was found that the peltier/ refrigerated-circulator system was not capable of cooling the solution to the desired -40 °C. The stepper motor performed exactly as expected and was able to consistently and accurately rotate at speeds slower than one revolution per day.

4.1.1 Peltier/Refrigerated-Circulator System Test

In order to characterize the cooling ability of the peltier/refrigerated-circulator system, thermocouples recorded the temperature at four crucial locations as shown in Figure 14.

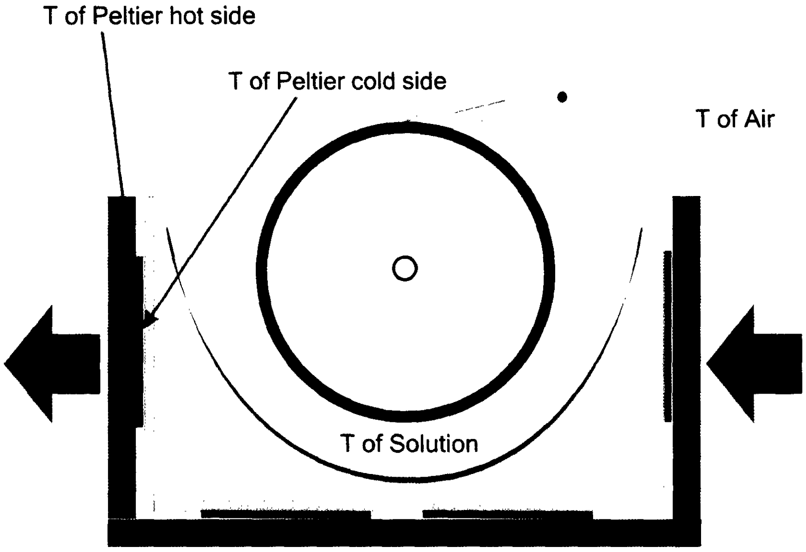


Figure 13: Diagram of the locations of recorded temperatures (T) within deposition chamber.

The refrigerated-circulator was set to hold the coolant at 0 °C and the system was allowed to reach steady state. Because the coolant gained heat from the environment as it flowed from the refrigerated-circulator through the supply tubes and cooling chamber, the coolant would be warmed by several degrees before it returned to the refrigerated-circulator. Therefore the steady state temperature reached by the thermocouples in the deposition chamber was 5 °C. Figure 14 shows a plot of the four temperatures that were recorded. After the system had been steady for about 200 seconds, the power supplies to the peltier TECs were set to 6 V. The system was allowed to reach steady state again before increasing the voltage to 7 V, 8 V, and 9 V. The system obtained the lowest steady state solution temperature of -9 °C at 8 V. At this point, the total current draw of the peltiers was about 23 A which means that 184 W of joule heating was entering the system. The VWR Signature Heated/Refrigerated Circulator, Model 1166 had a rated cooling capacity of 200 W at 20 °C and 140 W at 0 °C so it is logical that the system reached steady state at a coolant temperature of about 5 °C.

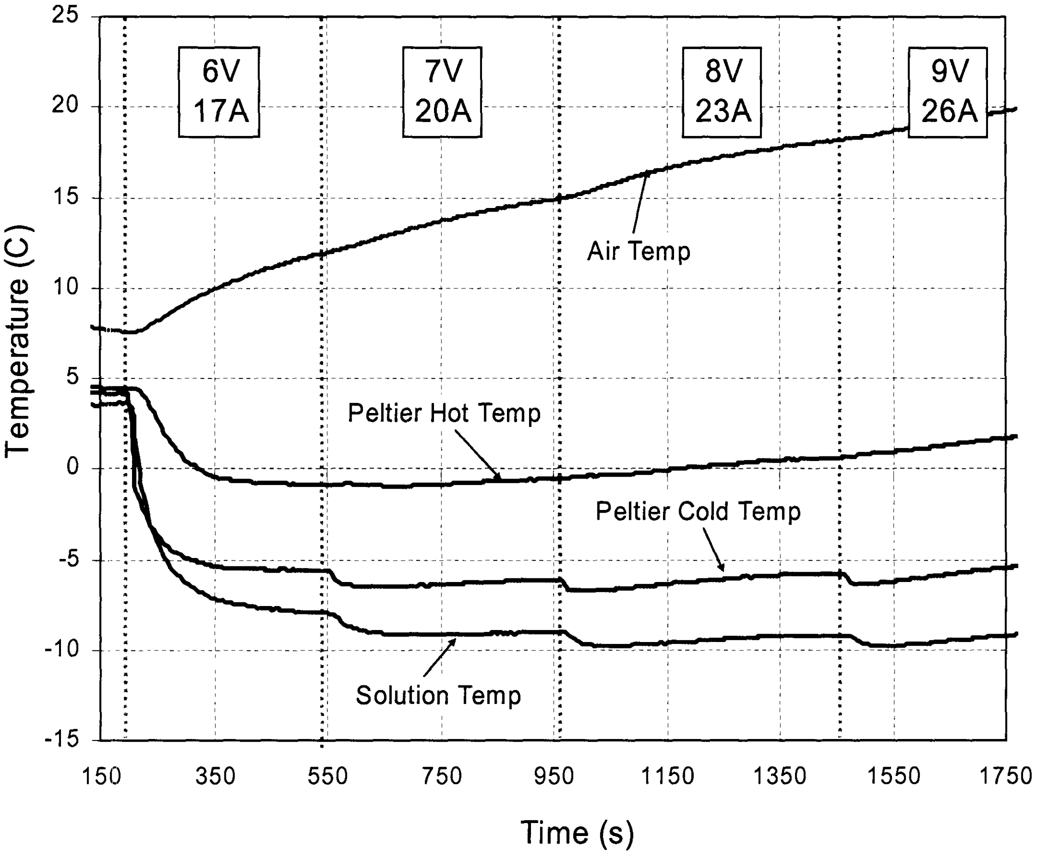


Figure 14: Plot showing temperatures at the four locations when 6V, 7V, 8V and 9V were applied to the twelve peltier TECs in parallel.

A perplexing point about the plot is that the temperature of the hot side of the peltier drops when the voltage is supplied. Theoretically the hot side of all the peltiers should increase above the coolant temperature while the cold sides decrease. The strange effect can be explained by the fact that the coolant entered the right side of the cooling chamber and warmed up as it flowed to the left. The peltiers at the coolant entrance would create a temperature difference of about -15 °C and pass all their heat into the coolant. By the time the coolant got around to the exit, it had warmed up quite a lot. The thermocouples sensed the temperature on a leftmost peltier, as shown in Figure 13, which was kept colder than the coolant by conduction through the internal aluminum box and solution. The peltier TEC still created temperature difference between its hot and cold sides, but just wasn't helping as much as the peltiers near the coolant entrance. Two facts support this conclusion: for one, the recorded temperature for the solution is lower than the recorded temperature for the peltiers, and two, the air temperature within the insulated box rises significantly as time passes. Also, it was verified that all the peltiers were in the correct orientation and connected correctly to the power supplies. Two sets of six peltiers were connected to single power supply in parallel; therefore each particular peltier could draw varying current depending on its temperature and resistance characteristics.

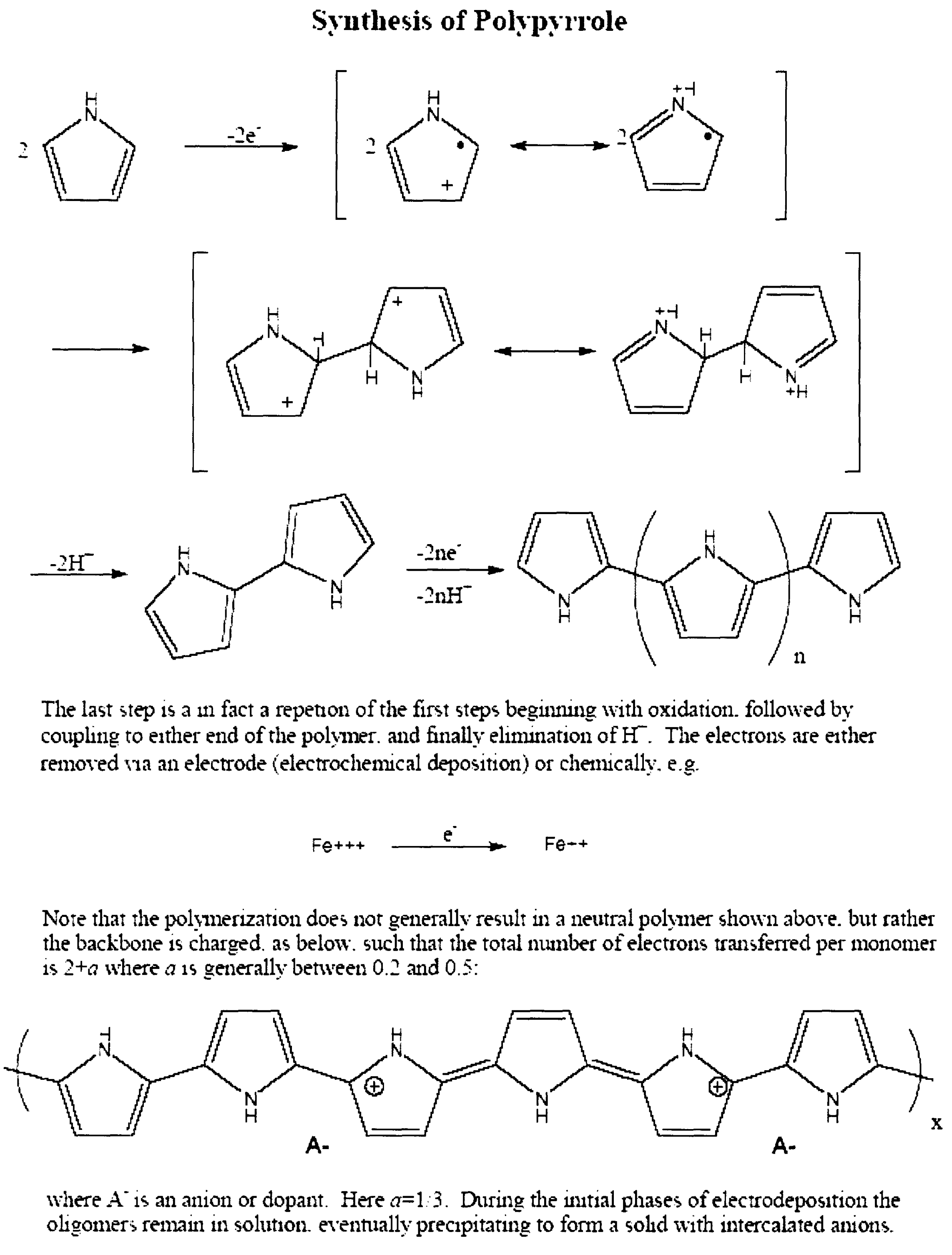
4.1.2 Stepper Motor Test

The stepper motor was tested because at ultra slow speeds the computer had to wait several second between commands to move a microstep. Tiny mistakes may have added up to caus large errors. It was found to perform exactly as expected. The stepper motor was given a command through the Visual Basic .NET program to make 1 revolution in 32 hours. A string was used to keep track of the amount of rotation and after 32 hours, the string had made one complete wind.

4.1.3 Redox Reactions at anode and cathode

The electrodeposition of polypyrrole occurs in an electrolytic cell. A galvanostatic power supply provides the electromotive force. Electrons are pulled away from the pyrrole monomers at the anode creating an oxidized monomer which then connects itself to a polymer chain. Figure 15 shows diagrams of the generally accepted process of polypyrrole synthesis. The reaction at the cathode simply produces OH^- ions and hydrogen gas.

The TEAP in solution serves two purposes. It breaks into ions which increases the conductivity of the solution. Therefore the voltage which drives the reaction does not have to be extremely high. The second purpose of the TEAP is that the PF_6^- negative ions which have migrated to the positively charged anode become part of the polypyrrole as it is deposited. They do this to neutralize the positively charged pyrrole monomer chain. For about every three monomers which attach to the chain, one PF_6^- ion ionically bonds to the chain. The PF_6^- ions serve as a dopant in the polypyrrole and ultimately improve its conductivity.



Synthesis of Polypyrrole

The last step is a in fact a repetion of the first steps beginning with oxidation, followed by coupling to either end of the polymer, and finally elimination of H^+. The electrons are either removed via an electrode (electrochemical deposition) or chemically, e.g.

$$Fe^{+++} \xrightarrow{e^-} Fe^{++}$$

Note that the polymerization does not generally result in a neutral polymer shown above, but rather the backbone is charged, as below, such that the total number of electrons transferred per monomer is $2+a$ where a is generally between 0.2 and 0.5:

where A^- is an anion or dopant. Here $a=1/3$. During the initial phases of electrodeposition the oligomers remain in solution, eventually precipitating to form a solid with intercalated anions.

Figure 15: Mechanisms of polypyrrole polymerization.[14]

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[14] Taken from Madden, J., Conducting Polymer Actuators, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, September 2000; p. 34.

4.1.4 Rate of Deposition

A theoretical high current deposition was simulated using Excel. Various assumptions were used, as shown in Table 2, such as a one to one ratio of pyrrole monomer usage for each electron forced though the circuit by the power supply. In this way, the rate of deposition and decline of reactant concentration could be estimated. The outlined cell boxes were the changeable parameters. Figure 16 and Figure 17 are plots of the estimated number of deposited molecules (proportional to film thickness) and reactant concentrations verses time. Figure 17 shows that the concentration of pyrrole monomer would decrease to 80% of its initial concentration by 600 seconds. This theoretical analysis ignores effects of reactant concentrations on mass transport and diffusion and reaction rates.

Table 2: Theoretical analysis of a high current deposition.

Assumptions	
Ppy usage per electron:	0.5
TEAP usage per Ppy:	0.333333333
Ppy mol mass (g/mol):	67.09
Ppy density (g/mL):	0.967
TEAP mol mass (g/mol):	275.22
Geometry	
Surface area of submerged crucible (m^2):	0.0110
Rate of rotation (rot/sec):~	0.002367424
Rate of rotation (rot/min):~	0.142045455
Rate of production (m/min):~	0.016064489
Experimental Conditions	
Applied Current (A)	1.5
Initial Concentration of Ppy (M):	0.05
mL of Ppy added (mL):	1.734488108
Initial Concentration of TEAP (M):	0.05
Grams of TEAP added (g):	6.8805
Volume of Solution (L):	0.5
Calculation Values	
Current density (A/m^2):	136.3636364
Electrons per Coulomb:	6.24E+18
Electron flow rate (e-/s):	9.36E+18
Avagadro's Number	6.02E+23
Initial number of molecules of Ppy:	1.51E+22
Initial number of molecules of TEAP:	1.51E+22

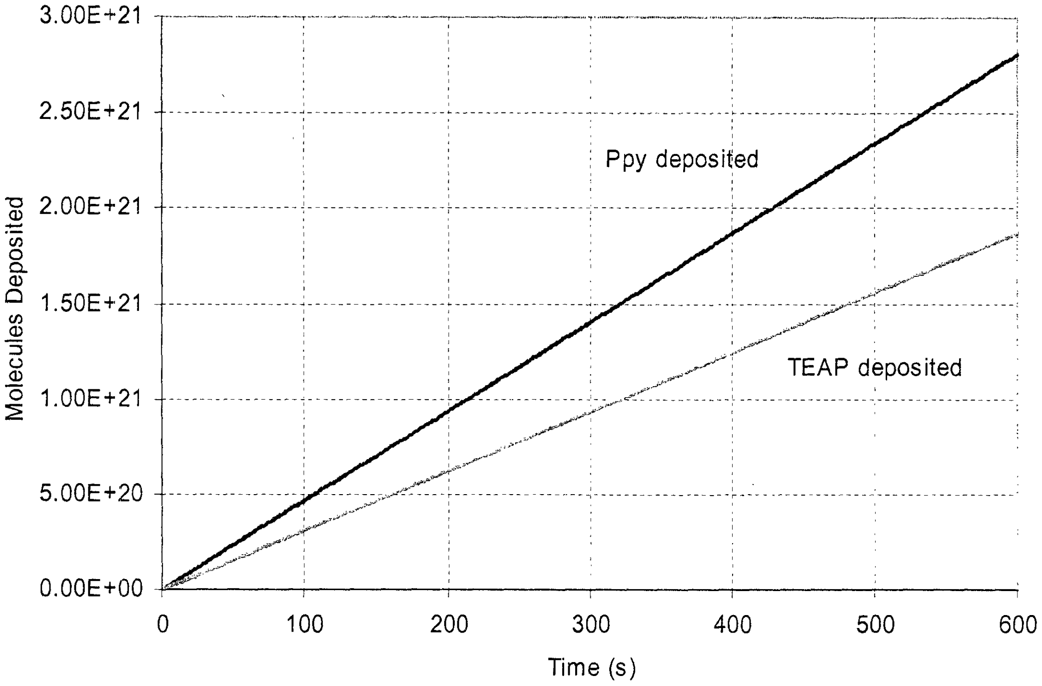

Figure 16: Plot of amount of molecules that would be deposited on surface of crucible with all assumptions for a high current deposition.

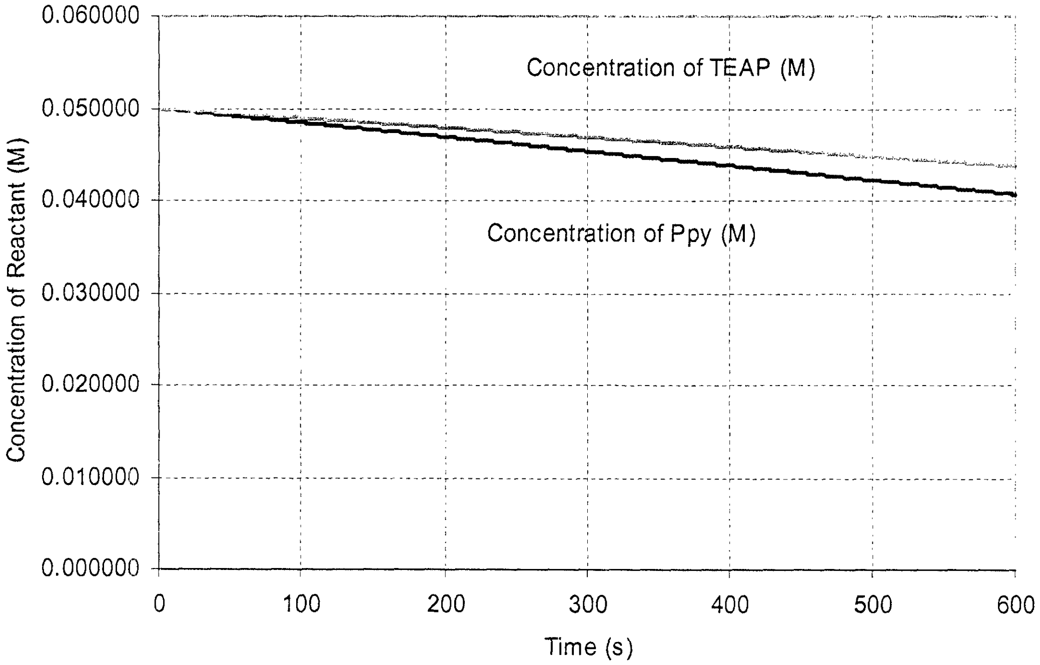

Figure 17: Plot of concentrations of reactants as time passes with all the assumptions for a high current deposition

4.2 Experimental Results

4.2.1 Apparatus

The deposition chamber was an anodized 6061 T6 aluminum open-top box, 120 mm square base, 80 mm tall, with 4 mm thick walls. Twelve TE Tech HP-199-1.4-1.15 120 W peltier thermoelectric coolers surrounded the box and were in contact with anodized aluminum walls with serpentine channels containing coolant of 50% water and 50% Glycol from Alfa Aesar. On top of the cooling chamber rested a lid which held a glassy carbon crucible down inside the deposition chamber. The crucible was supported on an axle on two ABEC 5 bearings and could be rotated by a Zeta 57-83 Stepper Motor driven by a Parker[15] Compumotor 6104 indexer drive. The lid also sported a peeling mechanism which consisted of two standard razor blades pressed against the crucible using spring tension. The deposition chamber and lid with crucible and peeling mechanism are shown in Figure 18.

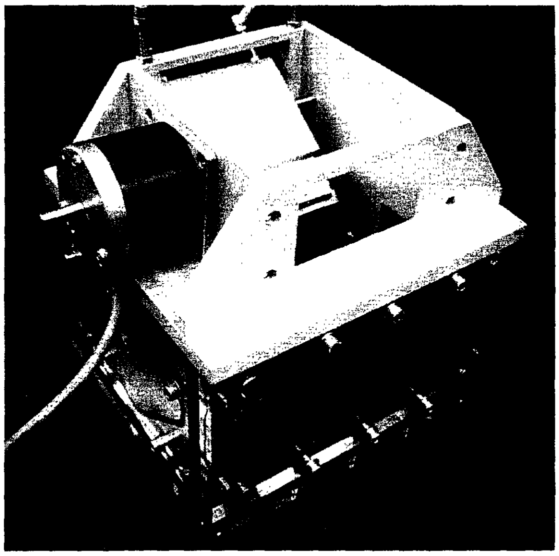

Figure 18: The completed cooling chamber and peeling mechanism.

The deposition chamber sat within a thermally insulating Styrofoam box which is shown in the photo of the entire experimental set-up in Figure 19. A VWR[16] Signature Heated/Refrigerated Circulator Model 1166, with a two-speed pump and 6 L bath cooled the coolant and circulated it through the serpentine channels in the cooling chamber.

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[15] http://www.compumotor.com/

[16] http://www.vwrsp.com/

Two Hewlett Packard[17] System DC Power Supplies, one Model 6653A 0 V to 35 V, 0 A to 15 A and one Model 6652A 0 V to 20 V, 0 A to 25 A, provided the power to the twelve peltier TECs. An AMEL Instruments Power Supply Model 2053 was used to provide current and voltage to drive the reaction

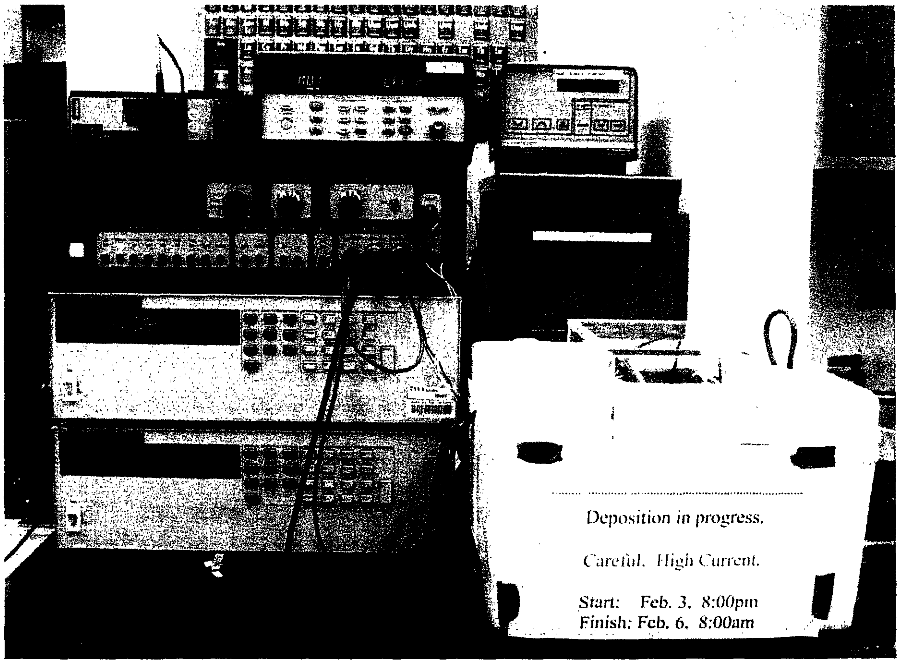

Figure 19: Photo of entire experimental set-up which includes three power supplies, a chiller/circulator, a data-acquisition unit connected to a standard PC, and the deposition chamber within the insulating box.

Temperature measurements were made using Omega precision fine wire thermocouples: Teflon insulated, Type E calibration, 1 m long, and 0.127 mm diameter. The thermocouples were connected to an Agilent 20 Channel Multiplexer Card 34901A in an Agilent Data Acquisition/Switch Unit 34970A. The data acquisition unit also recorded the current and voltage signals from the AMEL Instruments Power Supply. The measurements were then transferred using a GPIB to USB adapter from the data acquisition unit to a standard PC and recorded by the Microsoft Visual Basic .NET program.

4.2.1 Methods

Before beginning a continuous deposition, the crucible was well cleaned with acetone. If the surface was damaged after 3 to 5 repeated uses, it was polished using a Divine Dico

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[17] http://www.hp.com

E-5 emery composition for hard metals rouge stick. The copper counter-electrode sheet was detarnished using Cameo copper, brass and porcelain cleaner.

The propylene carbonate solution was prepared with 0.05 M tetraethylammonium hexaflourophosphate (TEAP) and 0.05 M pyrrole monomer, which were the same concentrations used in batch-productions. 7.5686 grams of TEAP and 1.9793 mL of pyrrole monomer were added to 550 mL of propylene carbonate. The pyrrole monomer must be stored in a nitrogen environment and in a freezer to prevent oxidation and other reactions. After the pyrrole was added to the propylene carbonate solution, nitrogen was bubbled into the solution, and then the beaker was covered with parafilm and placed in a freezer.

The refrigerator/circulator was set to 0 °C and turned on and the system was allowed to reach a steady state temperature. The Deposition Control Center program (Section 3.3) was initiated and began recording data points at 30 second intervals. Then, with the lid and crucible removed, the solution was poured into the deposition chamber and a voltage of 5 V was applied to the peltiers. Figure 20 shows the deposition chamber after the solution has been poured in and the copper counter electrode put into place.

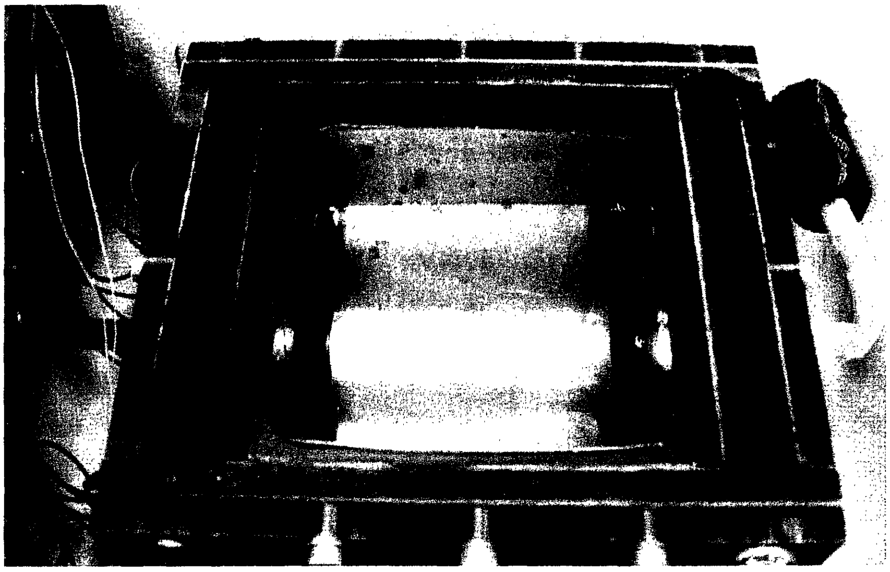


Figure 20: Photo of cooling deposition chamber containing solution and with copper counter-electrode installed.

The lid and crucible were put into place. The positive terminal from the AMEL power supply was clipped to the copper counter-electrode, the negative terminal was clipped to the peeling device which was in contact with the crucible through the blade. The electrodeposition was run under galvanostatic control at a current density of 0.5 A/m^2. The crucible has only 0.011 m^2 of surface area on the bottom half which is below the solution level so the AMEL power supply was set to a constant 5 mA.

Using the Deposition Control Center program, the stepper motor was set to make 2 revolutions in 64 hours and all temperatures and voltage and current data were recorded every 30 seconds. The experiment was checked periodically to make sure no malfunction occurred.

5.0 Results and Discussion

5.1 Typical Deposition

Many full continuous deposition trials were performed; although, since no reactant addition devices were implemented, the maximum length of time for a trial was under 72 hours. Figure 21 shows plots of typical data for a trial. The solution temperature was maintained at a relatively stable -10 °C. The wavelike shape of the temperature plot is a result of room temperature variation throughout a day - one period in 24 hours,

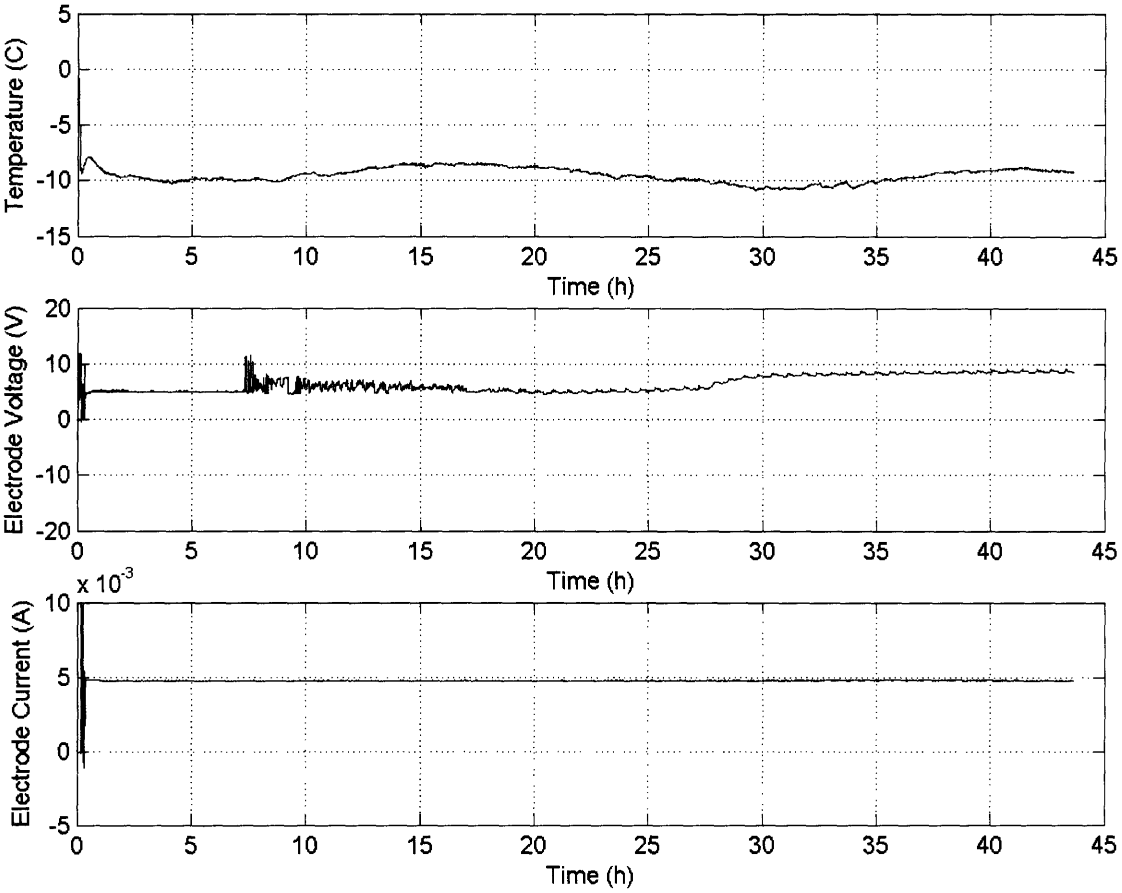


Figure 21: Typical plot of recorded values of solution temperature and the electrode voltage and current for a full continuous deposition trial.

The power supply was set to hold a constant 5 mA and transferred 792 C of charge in 44 hours. The typical, initial 4.5 V potential between the electrodes was several volts higher than expected from batch-deposition with the same current density. The higher potential was caused by higher resistance in the electrodeposition circuit. The spikes in electrode voltage that occurs at about 7.5 hours is associated with the blade beginning to peal the first polypyrrole from the crucible. When the resistance of the circuit changed because of poor blade contact with the crucible, the driving voltage had to adjust. The repetitive small peaks that follow are explained by the fact the stepper motor did not have enough torque to peal the polypyrrole film off of the crucible. The stepper motor would take micro steps until the reverse force was too great and and the stepper motor would be forced to jump one whole step in reverse, then the cycle would repeat. This means that the crucible stayed in the same position from 7.5 hours onwards.

The film deposition that results from a trial during which the stepper motor failed looks like the one shown in Figure 22. A section of the crucible was beneath the surface of the propylene carbonate solution for many hours while the crucible was stationary and the reaction-driving current was still applied. This section of film began to bubble and separate from the crucible. One possible reason for the film separation is the degradation of the polymer by continued application of current while submerged in propylene carbonate – a phenomenon that has been witnessed during the testing of polypyrrole as an actuator. The precise method of polymer attachment to the crucible surface is not completely understood. The polymer strands might form in solution then "settle" onto the surface of the crucible. Varying degrees of peeling difficulty are experienced and could be a function of many variables such as temperature. The crucible and polypyrrole have different coefficients of thermal expansion and so when the section of the crucible in the ambient air has warmed to 25 °C from the -10 °C, the film may have already started to separate from the surface.

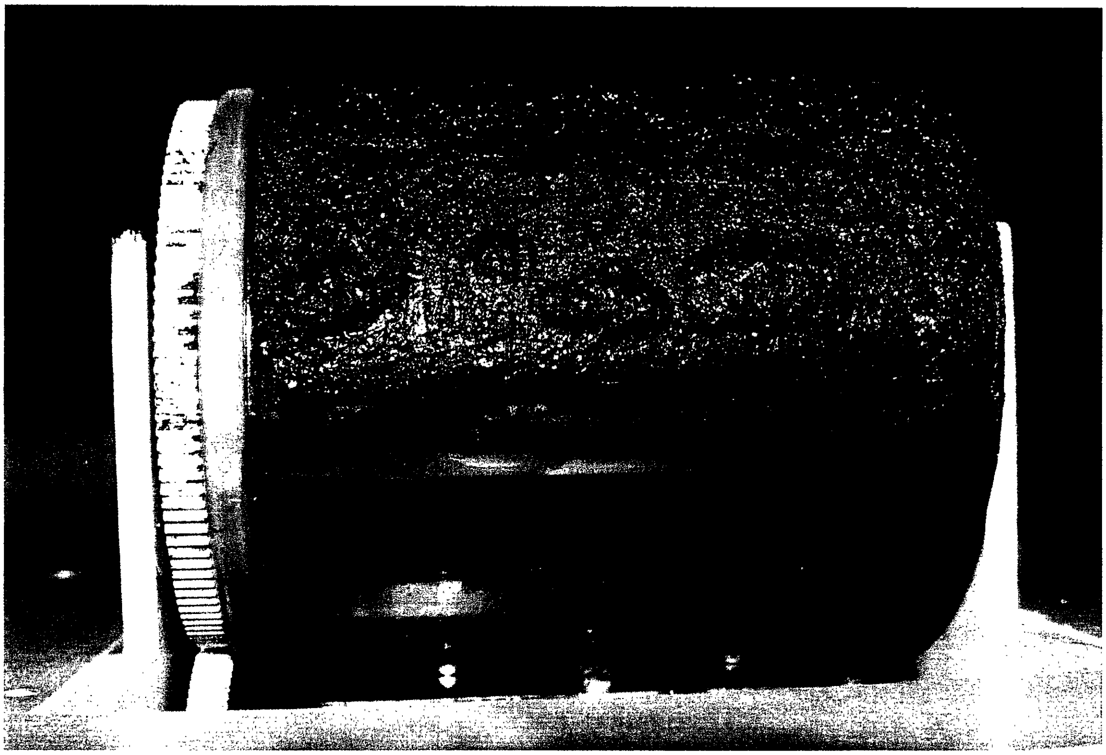


Figure 22: Photo of deposition during which the stepper motor failed to turn. The film on the bottom half of the crucible bubbled and began to separate from the surface.

A deposition was run with manual help to initiate peeling and a piece of polypyrrole almost 50 mm long and 70 mm wide was successfully produced. Figure 23 shows the polypyrrole being peeled off of the crucible. Once the peeling was started by hand, the stepper motor was easily able to perform the rest. Figure 24 shows the piece of polypyrrole that was produced. The side displayed was the side which touched the surface of the crucible and was more glossy than the side formed facing the solution. The piece of film was 0.246 mm in the thickest area – over three times thicker than a typical batch-deposition run for the same length of time and current density. The greater thickness could be a result of the deposition occurring at -10 °C instead of -40 °C because reaction rates increase with temperature.

Figure 23: Photo of a successful deposition. The blade has started peeling the polypyrrole off of the crucible.

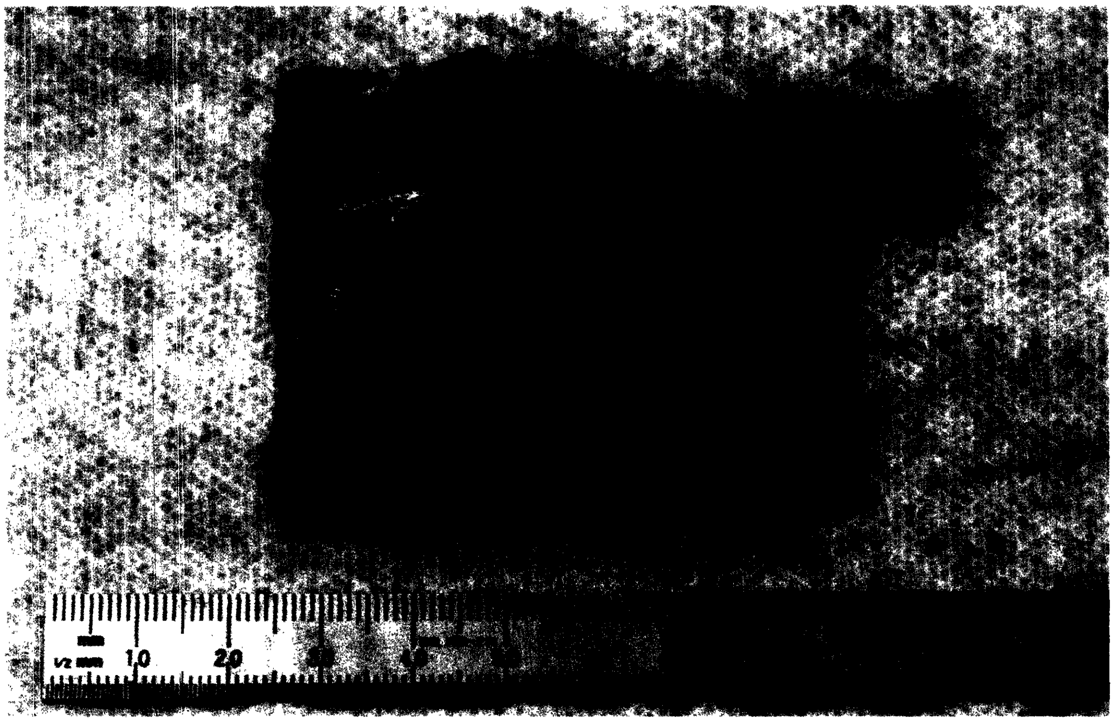
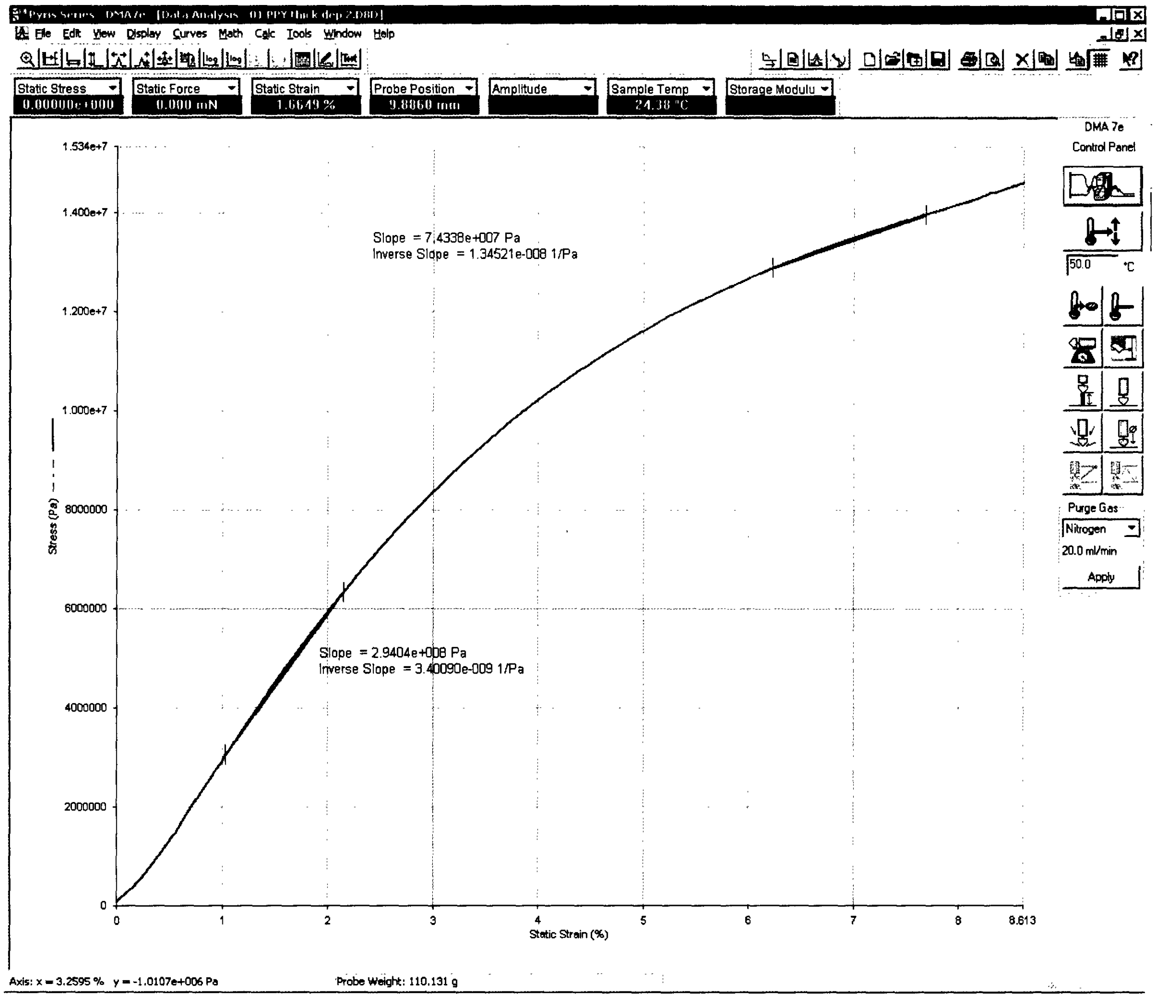


Figure 24: Photo of a piece of produced polypyrrole.

A section of the polymer was cut 2 mm wide and 60 mm long. It was found to have a conductivity of 1.4×10^4 S/m. Copper has a conductivity on the order of 10^7 S/m and a material with a conductivity below 10^{-8} is considered an insulator. The best conductivity of polypyrrole produced in the MIT BiLab was 5×10^4 S/m. The piece was tested using a Perkin Elmer Dynamic Mechanical Analyzer 7e (DMA). The results shown in Figure 25 show that the Young's modulus was 0.29 GPa for low strain and 74 MPa for high strain. The sample was not taken to the failure point because the DMA reached its maximum force output. At 8% strain the 2 mm wide sample held a load of almost 7 N.



Static Stress: 0.00000e+000
Static Force: 0.000 mN
Static Strain: 1.6649 %
Probe Position: 9.8860 mm
Amplitude:
Sample Temp: 24.38 °C
Storage Modulu:

Slope = 7.4338e+007 Pa
Inverse Slope = 1.34521e-008 1/Pa

Slope = 2.9404e+008 Pa
Inverse Slope = 3.40090e-009 1/Pa

Axis: x = 3.2595 % y = -1.0107e+006 Pa
Probe Weight: 110.131 g

Figure 25: Screenshot of the stress-strain results of DMA test of 2 mm wide sample of polypyrrole.

5.2 High Rate Deposition

Several high rate depositions were performed. The same procedure as described in Section 4.2.1 was followed except 1.5 A instead of 5 mA was used to drive the reaction and the stepper motor was run at 1 revolution per 4 minutes instead of 1 revolution per 32 hours. Higher current would have been used, but the AMEL power supply had reached its maximum power output. The idea for high rate deposition came from a journal article on the industrial polypyrrole deposition on zinc-electroplated steel[18]. The study had shown that 2 μm of polypyrrole could be deposited in 1 s with a current density of 7000 A/m^2.

During all the high rate depositions, the film created on the surface of the crucible was very powdery – not much a film at all – and the propylene carbonate solution turned from clear to black. Both of these observations suggest that the pyrrole monomer was over-oxidized. Side reactions occurred and polymer chains were cut short. The solution turned black because short pyrrole oligomes diffused back into solution after over-oxidation.

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[18] E. Hermelin, J. Petitjean, S. Aeiyach, J.C. Lacroix, P.C. Lacaze, *Journal of Applied Electrochemistry* 31 (2001) 905-911.

6.0 Conclusion

In order to produce conducting polymer in larger quantities and higher quality and repeatability, a prototype for a device was designed, built and tested. The device successfully produced a thick polypyrrole film 50 mm by 70 mm with mechanical properties comparable to typical batch-produced polypyrrole at the MIT BiLab. Longer pieces were not produced because the stepper motor was too weak for the peeling mechanism to work. A few high-rate depositions were attempted, but failed – most likely due to over-oxidation preventing the formation of long polymer strands. More research should be performed on depositions with current densities over 300 times typical batch depositions to explore the possibilities and qualities of quickly produced polymer.

7.0 Future Work

A second prototype of this machine should be designed with improvements based on what was learned from the first prototype.

- Apply more torque to the rotating crucible. The use of a gear box to gear down the stepper motor would both increase the motors resolution and torque so that it was strong enough to initiate peeling of the polypyrrole film from the crucible.
- Use more effective and more efficient cooling device. A liquid to liquid heat exchanger and placing the deposition chamber in heat transfer fluid would eliminate the inefficiencies of multi-stage cooling
- Direct connection to working electrode. The first prototype used the peeling blade to make contact with the rotating working electrode. The blades corroded quickly because of the current running through them. The uncertain contact between blades and crucible surface caused spikes in resistance. A free spinning direct wire attachment would allow the crucible to turn while still providing a non-corroding, direct electrical contact.
- Actively control reactant concentrations. The use of powered syringes or gravity and computer actuated valves to add precise amounts of reactants would make it possible to keep reactant concentrations constant for long depositions.
- Measure hydrogen ion concentration. The propylene carbonate solution is only 1% water so pH does not really apply and typical electronic pH sensors do not work below -5 °C because the impedance of glass gets too high. The hydrogen

ion concentration could be measured using an Oxygen-Reduction Potential (ORP) platinum electrode like the Beckman 511120 12×150 mm. Although the absolute value of $[H^+]$ would not be known, the change could be measured and counteracted.

- Easy to clean. All parts should be simple and designed with thought to how they can be cleaned
- Plastic parts where possible. Using plastic instead of metals whenever possible would eliminate unwanted electric fields and short circuits. It would also help cleanability. Attention must be given to use plastics which resist the chemicals used.
- Beware of hydrogen gas production. Some of the depositions may have failed because of hydrogen gas formed at the counter electrode and rose up through the solution to hit the working electrode. A screen could be installed between the two electrodes which allows the passing of ions, but deflected the hydrogen gas. In a typical batch-deposition, the crucible and counter electrode are vertical so the gas is not a problem.

Figure 26 shows a sketch of a proposed second prototype. The idea uses a smaller glassy carbon crucible so that solution quantities are smaller and also so high current density depositions could be performed with a typical power supply. The gear box tower will give the stepper motor plenty of torque at the crucible. The large volumes in the deposition chamber to the left and right of the crucible give room for reactant concentration measurement and control. The entire chamber will sit in a liquid to liquid chiller bath.

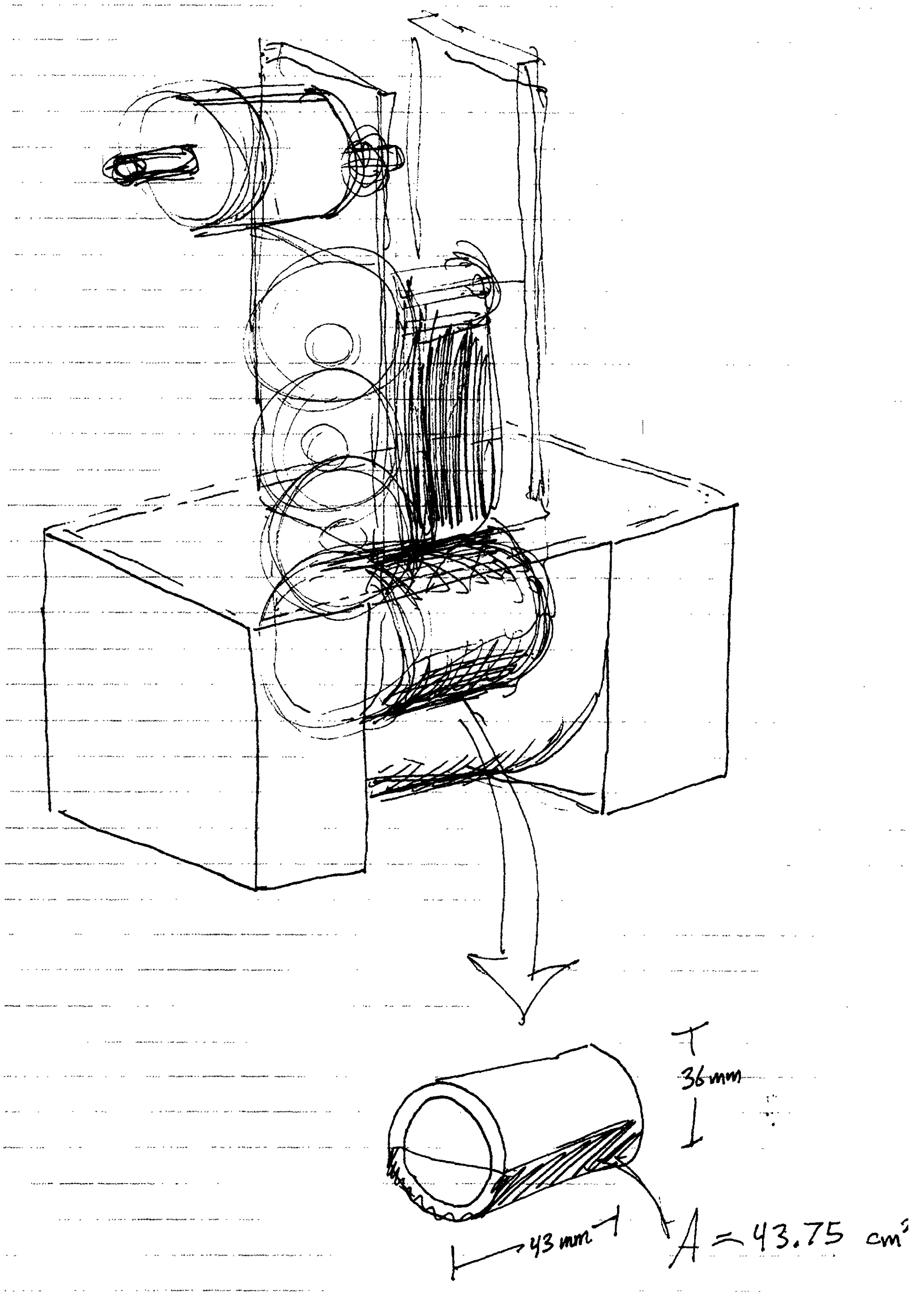

Figure 26: Sketch of proposed second prototype.

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Appendix A – Polypyrrole Batch-deposition Method

Materials:

- Glassy Carbon Crucible
- Peter Madden's Lathe Mount
- Jeweler's Rouge
- Copper Sheet (Counter Electrode)
- Fine Sandpaper
- Plastic Wrap
- Stir Magnet
- Stir Magnet Removal Rod
- Crucible Centering Cap
- Potentiostat
- BNC to dual banana plug converter
- BNC cable
- BNC to alligator clips cable
- -40 °C Refrigeration Unit and Cooler
- 1L Beaker
- Solutions:
    - Propylene Carbonate
    - TEAP (tetra-ethylammonium hexafluorophosphate)
    - Distilled Water
    - Pyrrole Monomer

Method of Preparation:

- Turn on refrigeration unit
- Prepare the first fraction of the pyrrole solution in 1L beaker
    - 0.05 M PC (propylene carbonate)
    - 0.05 M TEAP (tetra-ethylammonium hexafluorophosphate)
    - 1% vol. H_20 (distilled water)
- Cover the beaker with plastic wrap then place it in the refrigeration cooler
- Wash crucible with acetone
- Polish crucible with jeweler's rouge on lathe using lathe mount
- De-tarnish copper counter-electrode with fine sandpaper
- Following steps should be done as quickly as possible to prevent, as much as possible, excessive temperature rise in the solution
    - Remove Pyrrole monomer from its stock tube using a disposable syringe
    - Remove beaker from cooler, allowing the coolant to drip off as much as possible then keeping it ion a paper towel
    - Place a stir magnet in the beaker (carefully! cold glass can crack easily)

  - Place the beaker on the stir plate and turn on the plate
  - Add Pyrrole monomer while it is stirring
  - Once the solution is homogeneous, remove the beaker from the plate and remove the stir magnet using the stir magnet removal rod
  - Place the beaker back in the cooler
- Place copper counter-electrode on the interior periphery of the beaker
- Place the crucible centering cap on the crucible
- Place the crucible in the center of the beaker with a weight inside of it
- Connect the potentiostat (Pstat) leads in the following manner
  - Pstat Counter Electrode connects to the Pstat Working Electrode
  - BNC to dual banana plug converter's positive banana terminal connects to the Pstat Working Electrode
  - GND connects to the Pstat Counter Electrode
  - BNC cable connects to the converter
  - BNC to alligator cable connects to the BNC cable
  - Positive clip connects to the crucible, negative clip connects to the Copper counter electrode
- Set the potentiostat's range to appropriate current
- Deposition should be set to run according to desired film thickness
  - 16hrs at 1.25 A/m^2 yields an approximately 25 μm thick film
- Remove PPy layer from crucible with razor blade and cut to desired size
- Lie flat on Saran wrap and add a small amount of Propylene Carbonate/TEAP/dH20 to help film keep its moisture content
- Seal Saran and label

Appendix B – Peltier specifications

Table 3: Specifications for HP-199-1.4-1.15 peltiers[19]

Product:	*HP-199-1.4-1.15*
Imax (amps)	7.9
Qmax (watts)	120
Vmax (Volts)	24.6
DT max (Th=300K)	69
Width	40
Length	40
Thickness	3.6

---

[19] http://www.tetech.com/

Appendix C – Corrosion Resistance of Plastics to Propylene Carbonate Solution

Corrosions tests were run on the various plastics and rubbers to see which ones were possible materials for construction. The materials were submerged in propylene carbonate for over 24 hours.

Table 4: The corrosion resistance of plastics and rubbers to propylene carbonate.[20]

Materialt:	*Resistance:*
PTFE	Resistant
Nylon	Resistant
Lexan	-Degraded-
Acrylic	Resistant
Polyester (PET)	Resistant
Accura S140 Stereolithography Resin	Resistant
Silicon seal	Resistant
Viton seal	Resistant
Buna-N seal	-Degraded-

---

[20] Rinderknecht, D., Design of a Dynamic Mechanical Analyzer for the Active Characterization of Conducting Polymer Actuators, Cambridge, MA, June 2002; p. 61.

Appendix D – Visual Basic .NET code

```
Imports Agilent.TMFramework
Imports Agilent.TMFramework.DataAnalysis
Imports Agilent.TMFramework.DataVisualization
Imports Agilent.TMFramework.InstrumentIO

Public Class Form1
    Inherits System.Windows.Forms.Form

#Region " Windows Form Designer generated code "
----"this section is omitted, unimportant, see CD"----


    'for voltage output
    'Dim myDirectIO As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::3::INSTR", False,
2000)
    'Dim HPpwrRT As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::3::INSTR", False,
2000)

    'for temperature measurement, and Kepco control
    Dim AgilentDAQ As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::9::INSTR", False,
2000)
    'Dim electrode_power As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::2::INSTR", False,
2000)

    'peltier testing multimeters
    'voltage
    'Dim multimeter1 As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::22::INSTR", False,
2000)
    'current
    'Dim multimeter2 As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::23::INSTR", False,
2000)


    'large HP power supplies
    ' Dim HPpwrUP As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::7::INSTR", False,
2000)
    'Dim HPpwrDN As New
Agilent.TMFramework.InstrumentIO.DirectIO("GPIB0::1::INSTR", False,
2000)



#Region "peltier/PID globals"

    Dim PID As New PID_object()

    'Basic Parameters
    Public counter1 As Long
    Public counter2 As Long
```

```
    Dim TempReadout As Double
    'Dim TempReadout2 As Double
    Dim err As Double
    Dim controlvoltage As Double
    Dim applyvoltage As Double
    Dim cutoff As Double
    Dim Data(3600000, 3) As Double
    'Dim oldval As Double = 999

#End Region

#Region "pH and conductivity Globals"

    Public pH_meter As New ExtechThing()
    Public Conductivity_meter As New ExtechThing()

    Public pH_readout As Double
    Public conductivity_readout As Double

#End Region

#Region "Motor globals"

    'make a compumotor object
    Public cm1 As New Compumotor()

    '# of Revolutions
    Private varRevs As Integer

    '# of seconds to run
    Private varVel As Double


#End Region

#Region "Other globals, arrays for data"

    Dim temppeltiercold() As String = New String(999999) {}
    Dim volt_readings() As String = New String(999999) {}
    Dim pH_readings() As String = New String(999999) {}
    Dim conductivity_readings() As String = New String(999999) {}

    Dim electrode_volts() As Double = New Double(999999) {}
    Dim electrode_currs() As Double = New Double(999999) {}
    Dim temppeltierhot() As Double = New Double(999999) {}
    Dim tempsolution() As Double = New Double(999999) {}
    Dim tempair() As Double = New Double(999999) {}

    'Dim volt_readings2() As String = New String(999999) {}
    Dim count As Integer = 0

    Dim peltcount As Integer = 0
    Dim peltstring As String = New String("")

#End Region

    Private Sub Form1_Load(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles MyBase.Load

        'Peltier/PID load routines
```

```
        err = 0.0#
        counter1 = 1.0#
        counter2 = 1.0#
        'TempReadout = measuredTemp.Value

        PID.Reset()
        PID.T = 1 / 10
        PID.ARWupGain = 1
        cutoff = 23.0#
        PIDTimer.Enabled = False
        PIDTimer.Interval = 5000   '30000

        'pH and conductivity meter Routine
        'pH_meter.Open(6)
        'Conductivity_meter.Open(7)
        pH_meter.Open(5)
        Conductivity_meter.Open(6)

        'Motor loading routine
        'Open the compumotor connection
        cm1.Open(1) 'COM1
        'cm1.Open(2) 'COM2
        cm1.set_res(50000) '50000 clicks per turn

        'Assign default values
        varRevs = 1
        varVel = 1

    End Sub

#Region "PID and Temperature Graph"


    Private Sub Form1_Close(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles MyBase.Closed
        PIDTimer.Enabled = False
        'myDirectIO.Close()
        AgilentDAQ.Close()
        '   HPpwrRT.Close()
        pH_meter.Close()
        cm1.Close()
    End Sub

    'do_PID
    'Does PID stuff
    'Gets Data (Temp, voltage)
    Private Sub do_PID()

        PID.SetPoint = SetTemp.Value     ' set reference point
        PID.P = Pgain.Value
        PID.D = Dgain.Value
        PID.i = Igain.Value

        'get temperature
        'AgilentDAQ.WriteLine("MEAS:TEMP? (@101)")
        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@101)")
        measuredTemp.Value = AgilentDAQ.Read()

        ' Controls calculations part
        TempReadout = measuredTemp.Value
```

```
        err = PID.SetPoint - TempReadout
        errortext.Text = err
        controlvoltage = PID.Control(err)

        If controlvoltage >= 0 Then
            'applyvoltage = cutoff
            applyvoltage = 0
            PID.i = 0
        ElseIf controlvoltage <= -cutoff Then
            'applyvoltage = -cutoff
            applyvoltage = cutoff
            PID.i = 0
        Else
            applyvoltage = -controlvoltage
        End If

        controlvoltage = PID.Control(err)

        PID.ARWupDiff = applyvoltage - controlvoltage


        'myDirectIO.WriteLine("SOUR:VOLT " & applyvoltage)
        '  HPpwrRT.WriteLine("SOUR:VOLT " & applyvoltage)
        ' AgilentDAQ.WriteLine("SOUR:VOLT " & (applyvoltage / 5.0) & ",
(@205)")
        'HPpwrUP.WriteLine("VOLT " & applyvoltage)
        'response = myDirectIO.Read()


        applyvolt.Text = applyvoltage
        ctrlvolt.Text = controlvoltage



    End Sub

    Public Sub update_graphs()

        'Plot and record the data

        '-- Set the data
        TemperatureChart.Traces(0).SetData(TempReadout)
        phChart.Traces(0).SetData(pH_readout)
        conductivity_chart.Traces(0).SetData(conductivity_readout)

        '-- Plot the data
        TemperatureChart.PlotAll()
        phChart.PlotAll()
        conductivity_chart.PlotAll()

        '-- record data
        temppeltiercold(count) = TempReadout
        pH_readings(count) = pH_readout
        conductivity_readings(count) = conductivity_readout

        ' myDirectIO.WriteLine("MEAS:VOLT?")
        ' volt_readings(count) = myDirectIO.Read()

        'AgilentDAQ.WriteLine("SOUR:VOLT? (@205)")
        'volt_readings(count) = AgilentDAQ.Read()
```

```
        'volt_readings(count) *= 5 '34970A to Kepco conversion

        AgilentDAQ.WriteLine("MEAS:VOLT? (@107)")
        electrode_volts(count) = -AgilentDAQ.Read()

        AgilentDAQ.WriteLine("MEAS:VOLT? (@108)")
        electrode_currs(count) = (-AgilentDAQ.Read())*
CurrentRange.Value

        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@102)")
        temppeltierhot(count) = AgilentDAQ.Read()

        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@103)")
        tempsolution(count) = AgilentDAQ.Read()

        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@104)")
        tempair(count) = AgilentDAQ.Read()


        ' HPpwrRT.WriteLine("MEAS:VOLT?")
        ' volt_readings2(count) += HPpwrRT.Read()

        'Get electrode data
        '   electrode_power.WriteLine("MEAS:VOLT?")
        '  electrode_volts(count) = electrode_power.Read()

        ' electrode_power.WriteLine("MEAS:CURR?")
        'electrode_currs(count) = electrode_power.Read()

        count += 1

    End Sub


    Private Sub PIDTimer_Tick(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles PIDTimer.Tick
        do_PID()
        do_pH()
        do_conductivity()
        update_graphs()
    End Sub

    Private Sub PIDswitch_Click(ByVal sender As System.Object, ByVal e
As System.EventArgs) Handles PIDswitch.Click
        PIDTimer.Enabled = Not PIDTimer.Enabled
        If (PIDTimer.Enabled = True) Then
            PIDswitch.Text = "Click to Stop"
        Else
            PIDswitch.Text = "Click to Start"
        End If
    End Sub


    Private Sub savebutton_Click(ByVal sender As System.Object, ByVal e
As System.EventArgs) Handles savebutton.Click
        FileOpen(1, strPath.Text, OpenMode.Output)
```

```
        PrintLine(1, "Created " &
System.DateTime.Now.Date.ToLongDateString & " " &
System.DateTime.Now.Date.ToLongTimeString)
        PrintLine(1, " ")
        PrintLine(1, "Time(Sec)", "Peltier(V)", "pH(-log[H])",
"Conductivity", "Volts", "Amps", "TempPCold(C)", "TempPHot(C)",
"TempAir(C)", "TempSol(C)")

        Dim x = 0
        For x = 0 To count
            Try
                PrintLine(1, x * PIDTimer.Interval / 1000,
volt_readings(x), pH_readings(x), conductivity_readings(x),
electrode_volts(x), electrode_currs(x), temppeltiercold(x),
temppeltierhot(x), tempair(x), tempsolution(x))
            Catch
                MsgBox("Alert, invalid input: " & x)
            End Try
        Next

        FileClose(1)
    End Sub
#End Region

#Region "pH and Conductivity Graph"

    Private Sub do_pH()

        'Note: Timer/graphing routine is stuck in with PID/temp graph
group

        Dim temp As New String("")
        Try
            ' As long as there is information, read one byte at a time
and
            '   output it.
            While (pH_meter.Read(1) <> -1)
                ' Write the output to the screen.
                temp += Chr(pH_meter.oCP.InputStream(0))
            End While
        Catch exc As Exception
            ' An exception is raised when there is no information to
read.
            '   Don't do anything here, just let the exception go
        End Try
        Try
            phString.Text = temp.Substring(temp.Length - 5, 4)
            pHvalue.Value = (phString.Text) / 100
            pH_readout = pHvalue.Value
        Catch exc As Exception
            'do nothing
        End Try
    End Sub

    Private Sub do_conductivity()

        'Note: Timer/graphing routine is stuck in with PID/temp graph
group

        Dim temp As New String("")
```

```
        Try
            ' As long as there is information, read one byte at a time
and
            '   output it.
            While (Conductivity_meter.Read(1) <> -1)
                ' Write the output to the screen.
                temp += Chr(Conductivity_meter.oCP.InputStream(0))
            End While
        Catch exc As Exception
            ' An exception is raised when there is no information to
read.
            '   Don't do anything here, just let the exception go
        End Try
        Try
            constring.Text = temp.Substring(temp.Length - 5, 4)
            convalue.Value = (constring.Text) / 1000
            conductivity_readout = convalue.Value
        Catch exc As Exception
            'do nothing
        End Try
    End Sub


#End Region

#Region "Motor Stuff"
    Private Sub btnGo_Click(ByVal sender As System.Object, ByVal e As
System.EventArgs)

        'Set DV
        'TAG - now DV_Set includes the GO command
        DV_Set()
        'Write "GO"
        'Write to port
        'cm1.Write("GO" & Chr(13))

        'display
        tempview.Text = "running " & varRevs & " at " & varVel

    End Sub



    Private Sub btnStop_Click(ByVal sender As System.Object, ByVal e As
System.EventArgs)
        cm1.kill()
        tempview.Text = "Stopped."
    End Sub

    Public Sub DV_Set()
        'Change Distance to 25000*numrevs
        'TAG - I think what he means here is that you find total clicks
to travel by multipying number of revs by the clicks per rev.
        'TAG - The numRevs value is written as negative so that the
motor will turn in the correct direction.

        varRevs = cm1.clicks_per_revolution * -numRevs.Value

        cm1.Write("D" & varRevs & Chr(13))
```

```
        'calculate time and set appropriate velocity
(Revolutions/Second)
        varVel = numRevs.Value / numTime.Value

        'for exceedingly slow times, lets use steps
        If varVel < 0.0001 Then
            'Find the length of time to wait between steps in
miliseconds
            MotorTimer.Interval() = -1 * numTime.Value * 1000 / varRevs
            tempview.Text = "Step mode " & varRevs & " at " & varVel
            'tempview.Text = "low value: " & varVel & ", V set to
.0001"
            'cm1.Write("V" & 0.0001 & Chr(13))
            Exit Sub
        End If

        tempview.Text = varVel & ", " & varRevs

        cm1.Write("V" & varVel & Chr(13))
        tempview.Text = "Normal mode " & varRevs & " at " & varVel

        cm1.Write("GO" & Chr(13))

    End Sub

    Private Sub Motor_Tick(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles MotorTimer.Tick
        cm1.Write("GO" & Chr(13))
    End Sub

    Private Sub Button1_Click(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles Button1.Click

        DV_Set()

        If (MotorTimer.Enabled = False) Then

            'tempview.Text = "running program"
            cm1.Write("D -1" & Chr(13))
            cm1.Write("V 1" & Chr(13))
            'btnStop.Enabled = False
            'btnGo.Enabled = False
            Button1.Text = "Stop Motor"


        Else

            tempview.Text = "Motor Stopped"
            cm1.kill()
            'btnStop.Enabled = True
            'btnGo.Enabled = True
            Button1.Text = "Start Motor"

        End If

        MotorTimer.Enabled = Not MotorTimer.Enabled

    End Sub

#End Region
```

```
#Region "Peltier Test"

    Private Sub peltier_test_Tick(ByVal sender As System.Object, ByVal
e As System.EventArgs) Handles peltier_test.Tick

        'Read Multimeter
        'multimeter1.WriteLine("MEAS:VOLT:DC? 100, 0.001")
        'multimeter1_readout.Text = multimeter1.Read()

        'multimeter2.WriteLine("MEAS:CURR?")
        'multimeter2_readout.Text = multimeter2.Read()

        'Read both temperatures
        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@101)")
        temperature101.Value = AgilentDAQ.Read()

        AgilentDAQ.WriteLine("MEAS:TEMP? TC, E, (@102)")
        temperature102.Value = AgilentDAQ.Read()

        peltcount = peltcount + 1
        peltstring = peltstring & peltcount & Chr(9) &
multimeter1_readout.Text & Chr(9) & multimeter2_readout.text & Chr(9) &
temperature101.Value & Chr(9) & temperature102.Value & vbCrLf

    End Sub

    Private Sub btnPeltier_Click(ByVal sender As System.Object, ByVal e
As System.EventArgs) Handles btnPeltier.Click

        peltier_test.Enabled = Not peltier_test.Enabled

        If (peltier_test.Enabled = True) Then
            btnPeltier.Text = "Stop Test"
        Else
            btnPeltier.Text = "reStart Test"
            save_peltier_data()
        End If

    End Sub

    Private Sub save_peltier_data()
        'print to file

        FileOpen(2, strPathPelt.Text, OpenMode.Output)

        PrintLine(2, "Peltier Test started " &
System.DateTime.Now.Date.ToLongDateString & " " &
System.DateTime.Now.ToLongTimeString & vbCrLf)
        PrintLine(2, " ", "voltage", "current", "T1", "T2", vbCrLf)
        PrintLine(2, peltstring)

        FileClose(2)

        'reset variables
        peltstring = ""
        peltcount = 0

    End Sub
```

```
#End Region

    Private Sub Label1_Click(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles Label1.Click

    End Sub

    Private Sub GroupBox2_Enter(ByVal sender As System.Object, ByVal e
As System.EventArgs) Handles GroupBox2.Enter

    End Sub
End Class
```