Design, Fabrication and Characterization of Polypyrrole Trilayer Actuators

by

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ABSTRACT
Conducting polymers are currently studied as artificial muscle materials. They are used instead of traditional actuators because they mimic the movements of animal muscles. They can generate larger active stresses than real muscles as well as generate small strains which can be amplified to cause larger motions. Traditionally, conductive polymers are immersed in liquid electrolytes. Utilizing a trilayer configuration by sandwiching the ions between two strips of polypyrrole films can be actuated in air. This thesis compares two methods of constructing polypyrrole trilayers: an electrolyte gel method and a gold coated PVDF membrane method. It will discuss the construction processes as well as properties of resulting trilayers by looking at force production, strain rate, etc.

Thesis Supervisor: Ian W. Hunter
Title: Hatsopoulos Professor of Mechanical Engineering

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1. Introduction

Although it was first discovered in the 1970s, conductive polymers were not studied extensively until decades later. In the nineteen nineties, scientists began to realize the values of theses polymers' properties. Today, these materials continue to demonstrate attractive qualities which deem them to be promising new materials for actuation. Traditional actuators such as motors and hydraulic systems are often bulky, slow, and rigid due to their employment of motors and gears. They lack the degrees of freedom required for rapid motions. These limitations have restricted researchers in developing and improving the designs of certain types of devices. For example, it is difficult for robots to mimic animal movements using traditional actuators. Conducting polymers, on the other hand, are light weight, flexible, and require just a few volts of electricity in order to operate. In addition, conductive polymers themselves demonstrate certain electrochemical properties which make them very attractive to researchers and inventors. The oxidation-reduction reactions which facilitate a volumetric change in the polymers have also inspired many creative usages. With all of these advantages combined, this class of polymers has already been shown to be useful in the constructing of sensors, robotic and surgical tools, batteries, as well as maneuverable surfaces in underwater vehicles.

Experiments have demonstrated conducting polymers' mechanical properties to be comparable to those of skeletal muscles. Recent studies have shown tensile strength to be as high as 100 MPa with maximum strain of up to 40% [1]. Besides these impressive mechanical properties, conducting polymers are biocompatible, relatively easy to make, and need very low voltage to operate. The polymer itself exists in neutral state until an electrochemical change through oxidation-reduction reactions occur under which the polymer undergoes volumetric changes. The biocompatibility aspects of conductive polymers have sparked large amounts of interest in using them as artificial muscles [2]. With more understanding and improvements of their other properties, it can be a useful material for the medical world and beyond.

Although individual tests of conductive polymer actuators mentioned above exhibit high stress and strain levels, these are results obtained from using various deposition and construction methods and from different types of conductive polymers. The current challenge with conducting polymer actuators is being able to construct a trilayer actuator system which gives consistently good performance. Because conductive polymers require an ion source during operation, such a system will allow them to be able to be actuated in air instead of having to be placed under an electrolytic solution. It increases the possibilities of these polymers to be used on a larger scale and for an even wider variety of purposes. The trilayer actuator system must have high stress and strain, a long life cycle, and exhibit high strain rate to convert electrical energy to mechanical energy. This thesis compares two methods of trilayer fabrication to examine which process is simpler and which can produce actuators with better mechanical properties.

1.1 Thesis Outline

Chapter 2 – Gives background information on the electrochemical and mechanical properties of conductive polymers, polypyrrole, and conductive polymer trilayer actuators.

Chpater 3 – Describes manufacturing techniques of electrolytic gel trilayers as well as the new trilayer manufacturing device and procedures to make an actuator out of gold coated PVDF membranes and polypyrrole.

Chapter 4 – Shows the dynamic mechanical analyzer set up and the actuation results collected from the test.

Chapter 5 – Discussion and interpretation of the data given in chapter 4

Chapter 6 – Gives conclusion of the findings and suggests studies that can be done in the future to improve trilayer actuators.

2. Background

2.1 Conductive Polymers

Conducting polymers are grouped as ionic electroactive polymers (EAP) due to the diffusion of ions that causes volumetric change during actuation [2]. They display several common characteristics, but most importantly, their electrical transport characteristics. This is the movement of charges down the polymer chain either by breaking the carbon-carbon double bond or doping. Polyacetylene, the simplest form of conducting polymer displays alternating carbon-carbon double bond structure on as its backbone. More complex structures such as polypyrrole consist of chains of six-member rings to provide the same alternating double bonds. In order for a more complex conductive polymer to be electrically conductive in bulk, a dopant is added. The dopant allows charges to move across the polymer chains making the polymer conductive. Figure 1 shows charges moving down a polycaetylene chain breaking carbon-carbon double bonds

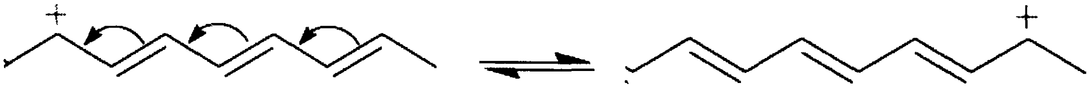


Figure 1: Polycaetylene chain after as the charge moves across the backbone. [3]

2.2 Polypyrrole

The material chosen for this thesis is polypyrrole, a conducting polymer that is advantageous because of its ease to synthesize and material characteristics that mimic animal muscles. Out of all of the conductive polymers, including polyethylenedioxythiophene, poly(p-phenylene vinylene)s, polyaniline and polythiophenes, polypyrrole is the most commonly used as engineering material because of its ease of manufacturing and its mechanical stability. For example, polyacetylene, the most basic polymer shown above, has very high actuation electrical transport rate, but it is not stable enough for actuation [3].

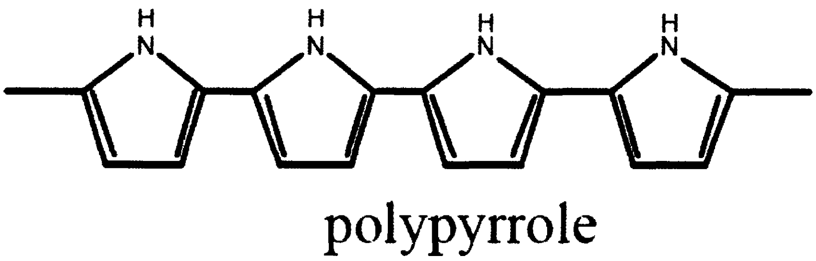


Figure 2: Structure of polypyrrole [4]

In its neutral state, polypyrrole is an insulated material. When voltages are applied, however, delocalization occurs along the chain of polypyrrole. Electrons are introduced to the chain causing double bonds to turn into single bonds and single bonds to double along the length of the chain in order for the polymer to reach its most stable configuration. As the film is being actuated, the external structure of the polypyrrole changes as well. The polymer's film like material curls in a particular direction depending on how the charge moves through it. Because it is non-conductive under normal conditions, the polymer must be oxidized in the presence of an electrolyte.

There are some notable limitations to the material, however. Though it has been deemed the most suitable polymer to experiment with, its properties are largely dependent on its synthesis. Varying temperature, electrolyte, or concentration of solution while making polypyrrole may produce very different active properties. Many different fabrication methods using varying solvents, dopants, salt, electrodes, etc. have produced a wide variety of results. Typical strain for example can range from 0.1% to 28%, while the operating stress has been measured to be as high as 22 MPa but can be as low as 1 MPa [5-7]. Furthermore, the conductive polymer has a relatively slow response time in terms of converting electrical energy to mechanical energy. They also decrease in conductivity across the length of the material as well as across different chains. There has been promising research which show enhanced actuation capabilities. In particular, the trilayer configuration of polymer-electrolyte-polymer can amplify motion to reduce these problems. This thesis will compare two methods of constructing this trilayer system and determine which one produces better, more consistent properties as well as increases the ease of construction.

2.3 Electrochemical Deposition

Polypyrrole films are constructed through deposition using basic electrochemical principles. Depositions require an electrolytic solution which contains metallic salt. Running an electric current through the electrolyte induces reduction of metal ions, causing solid metal to form. A bulk, one directional charge flow goes from one electrode to another, carrying electrons through the solution [8].

Figure 3 demonstrates a simplified version of the electrochemical set up for our polypyrrole deposition. The conducting polymer electrode and the counter electrode are immersed in a solution, in this case, consisting of propylene carbonate and salt tetraethylammonium hexafluorophosphate (TEAP). This process is driven by the motion of the ions. Ions must accumulate onto the electrodes as charge diffuses from the solution to the surface of the film. Part of the solution changes and forms different chemical composition than the rest of the solution. This part is called the electrochemical double layer. Its capacitance affects the electrical response of this setup.

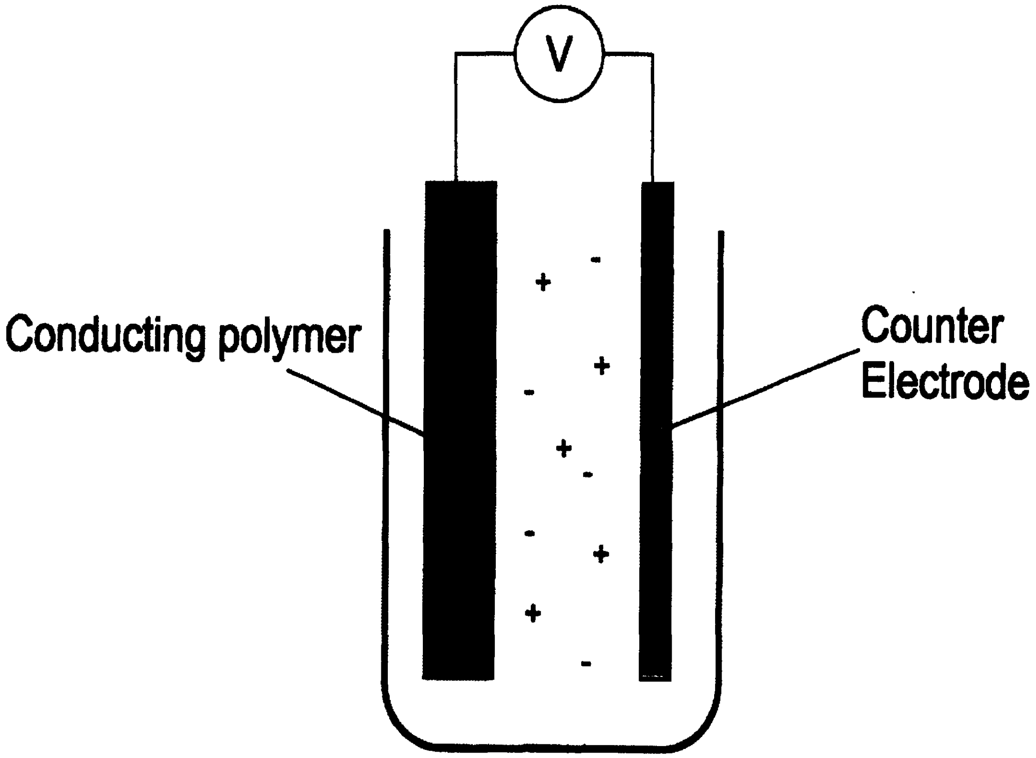


Figure 3: Polypyrrole polymer electrochemical deposition set up. A voltage is applied to the conducting polymer and the counter electrode which are soaked in an electrolytic solution [9].

2.3.1 Polypyrrole Deposition Techniques

The electrochemical deposition process described above is employed in the production of polypyrrole films. 0.05 M TEAP is mixed with propylene carbonate and 1% distilled water to make the electrolyte solution. This solution has to be stored in a -20 °C environment for at least half an hour. However, it can be stored for much longer in this condition if needed.

Right before deposition starts, the solution is removed from the -20 °C chamber. The following step is performed: 0.05 M distilled pyrrole monomer is added to the TEAP-propylene carbonate solution while nitrogen is bubbled through for 10 to 15 minutes to protect the pyrrole from oxidation. Then, the working and counter electrodes are placed in the solution.

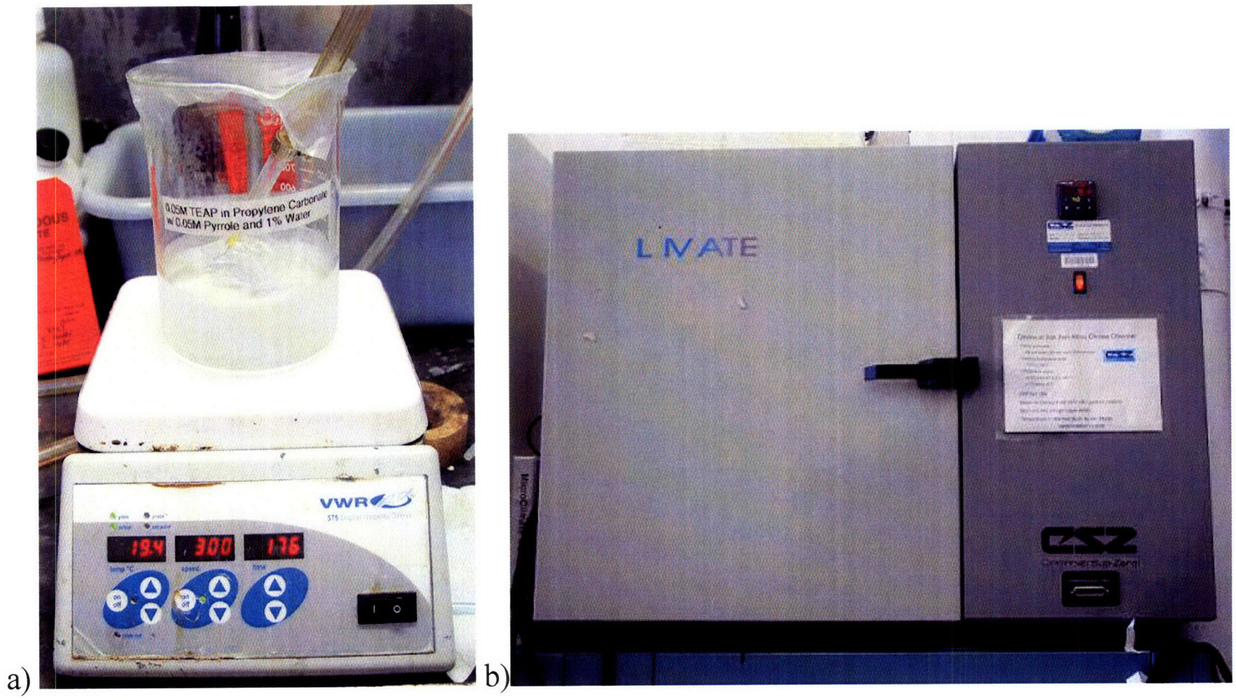


Figure 4: a) Preparation by bubbling nitrogen into TEAP-PC solution with pyrrole monomer added. b) MicroClimate chamber for deposition

The working electrode in this case is a glassy carbon crucible on which the film grows. Kapton tape is placed on top and bottom on the crucible. These tapes should mark the height of the film which is used for calculating the current needed to be applied for the specified film density. Weights are placed in the center of the crucible to prevent it from floating. The counter electrode is a copper sheet about twice the size of the crucible. It is polished and placed around the outside of the glassy carbon crucible in a beaker 22 mm away. The solution made is then poured into the beaker and placed in the MicroClimate Chamber set to -40 °C. The progress of the deposition is controlled by a VMP Multichannel Potentiostat performing the deposition at 1A/m^2 for 10 hours. The finished crucible is removed from the beaker solution. A thin film should form between the top and bottom Kapton tapes. Wash this film with some propylene carbonate to remove any unwanted copper color [4]. Then, the crucible is placed under a fume hood to dry for 6 to 12 hours. The resulting polypyrrole film of about 15 to 20 μm on the crucible is then peeled off using a blade.

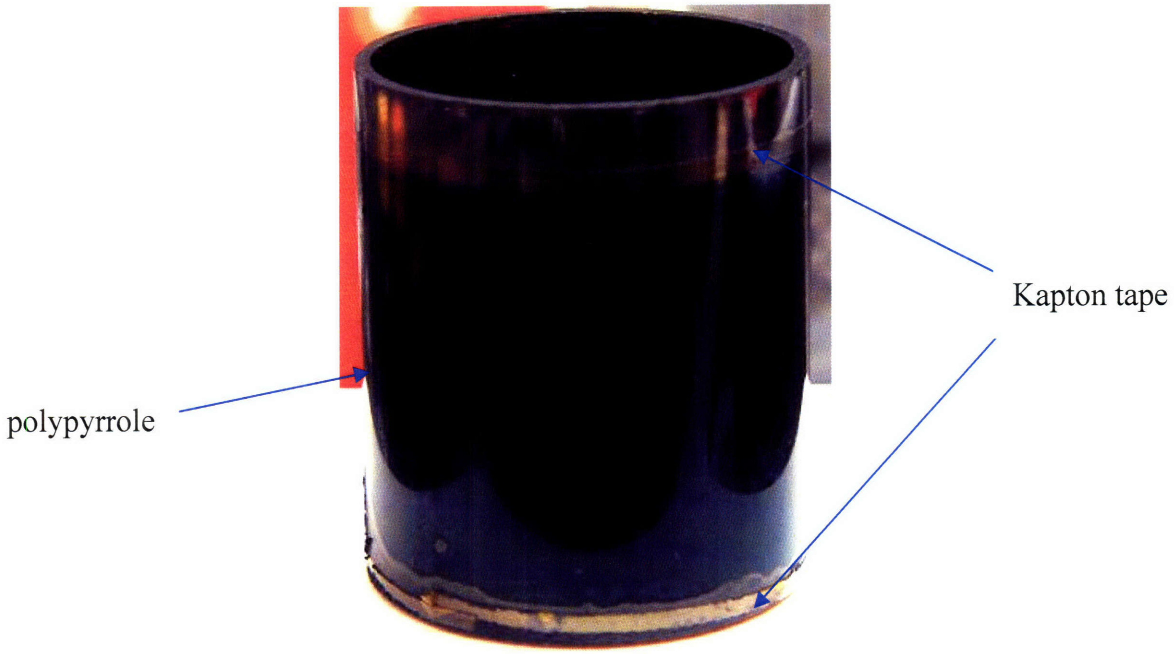


Figure 5: Polypyrrole film deposition on a glassy carbon crucible

Because the entire deposition process is very time consuming, it is more convenient to prepare large batches of TEAP-PC solutions before hand since it can be stored for a long time in the right environment. Steps after the adding of pyrrole monomers must be done quickly to prevent the solution from losing its properties at room temperature. It is very important to clean both the working and counter electrode properly in order to obtain good quality films. The copper counter electrode, especially, can lead to the discoloration of film if not polished well. Check all electrical contacts before deposition; set the temperature to be -20 °C before the start of the deposition so the wires and clips are not frozen by the time the beaker is placed in the chamber. By doing so, one must allow a cooling time of 30 minutes for the chamber to lower the temperature to instead of -40 °C. Moreover, the thickness of the film is affected greatly by both temperature and time, so make sure they are on the right setting.

The software E-C lab controls and monitors the voltage, time, and current range during the deposition. The voltage in the technique described above usually ranges between -0.5 V when the chamber cools down and 4 V during the deposition. A typical graph produced during the deposition is shown in Figure 2.6. The voltage drops below zero while the chamber lowers its temperature to -40 °C. Then, it spikes up to around 3.2 V and increases slowly during the actual electrochemical process in order to achieve the current density of $1A/m^2$.

As mentioned earlier, other methods have been investigated, creating polypyrrole actuators with a variety of mechanical properties. Besides TEAP, other commonly used salts include TBAP and NaPF6. LiTFSI and DMPIMe are amount the choices for solvent. Platinum, stainless steel, gold, and silver, wires, tubes, and mesh have all been used as materials for deposition [7]. Even helical depositions have been made [5]. In this wide range of techniques, deposition times can also vary from just a few hours to up to 24 hours.

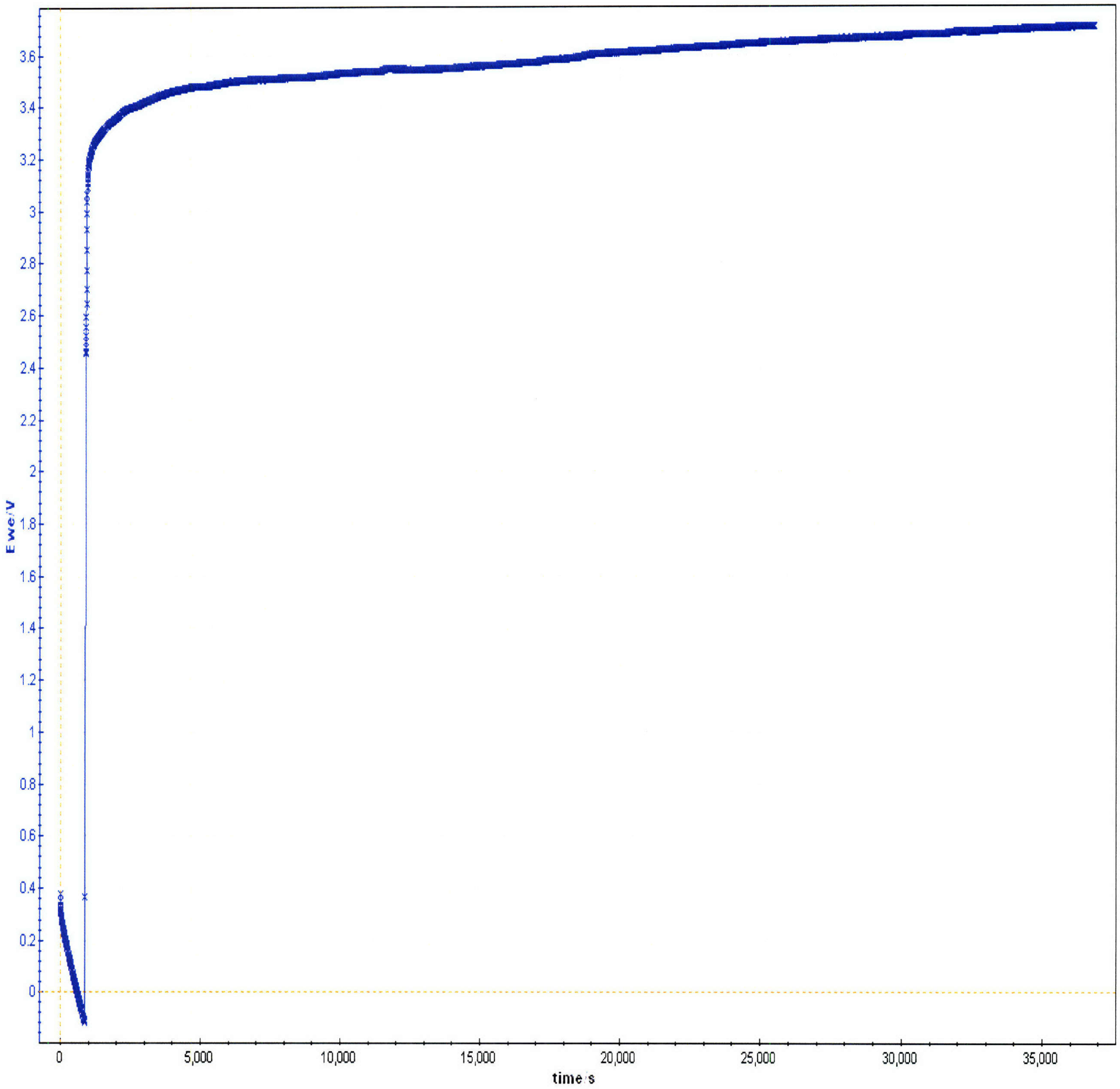


Figure 6: A typical voltage vs. time graph produced from deposition. Voltage drops during cool down and spikes up when deposition starts. The current is set at 220mA to get a current density of $1A/m^2$.

2.3.2 Film Quality

There are several methods in determining the quality of the final polypyrrole film product. The simplest way is to observe the color of the film. The color in high quality films should be black and have evenly distributed texture. The crucible side should be glossy while coloring on the solution side is duller.

Low quality films, on the other hand, tend to have a yellowish or brownish tint. This is often because the copper counter electrode is not polished enough. Sometimes, the solution side of an unsuccessful film will be glossy. In addition, bad films are often flakey and hard to peel off the crucible.

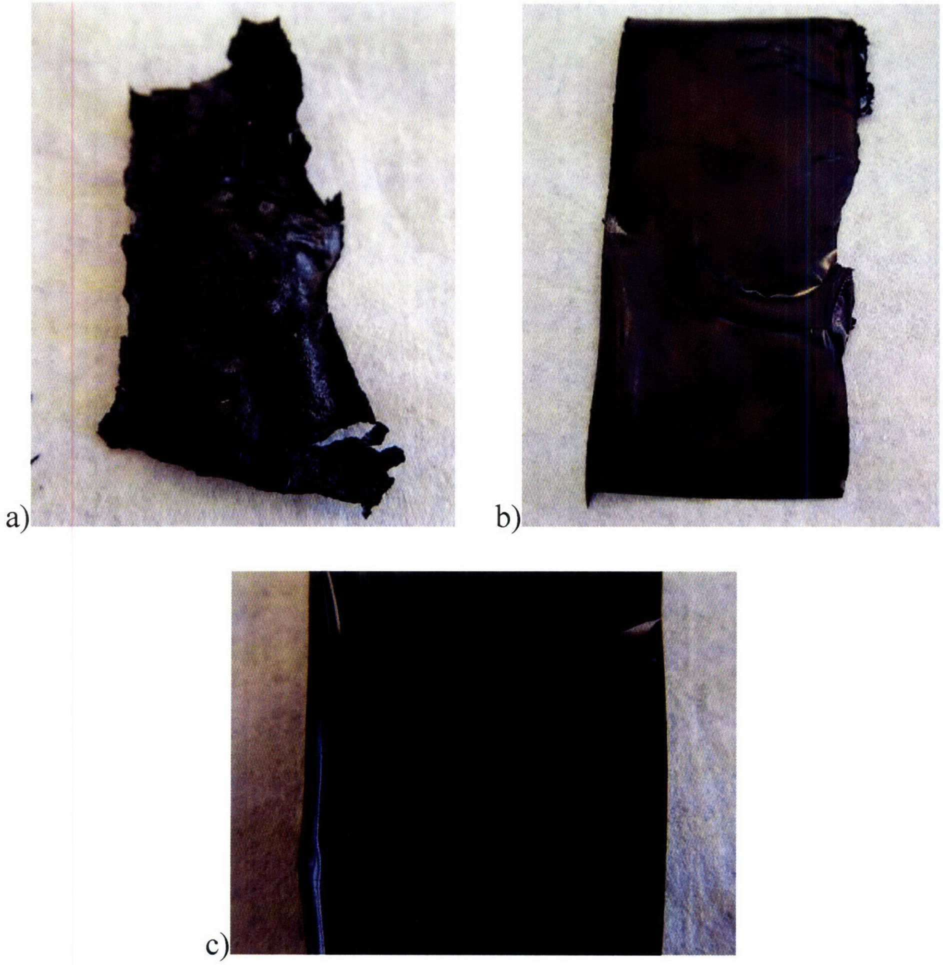


Figure 7: a) An unsuccessful film which came out flakey and hard to peel off of the crucible b) low quality film showing brown discoloration c) successful film

Measurements of the conductivity of the films are also taken for quality control. A four wire measuring method is employed. A small, rectangular piece of film around 10mm × 30mm is used. Its conductivity is calculated using by

$$\sigma = \frac{IS}{VTW}, \tag{2.1}$$

where σ represents the conductivity of the polymer. The spacing between the four measuring points is S. The current applied is given by I while V is the voltage. T and W are thickness and width to give the dimensions of the film. According to Madden, the conductivity of polypyrrole is on the order of 10^4 S/m. The conductivity of polypyrrole with dopant as been measured to be on the same magnitude as copper [10]. It can be affected by both the temperature and the type of dopant used.

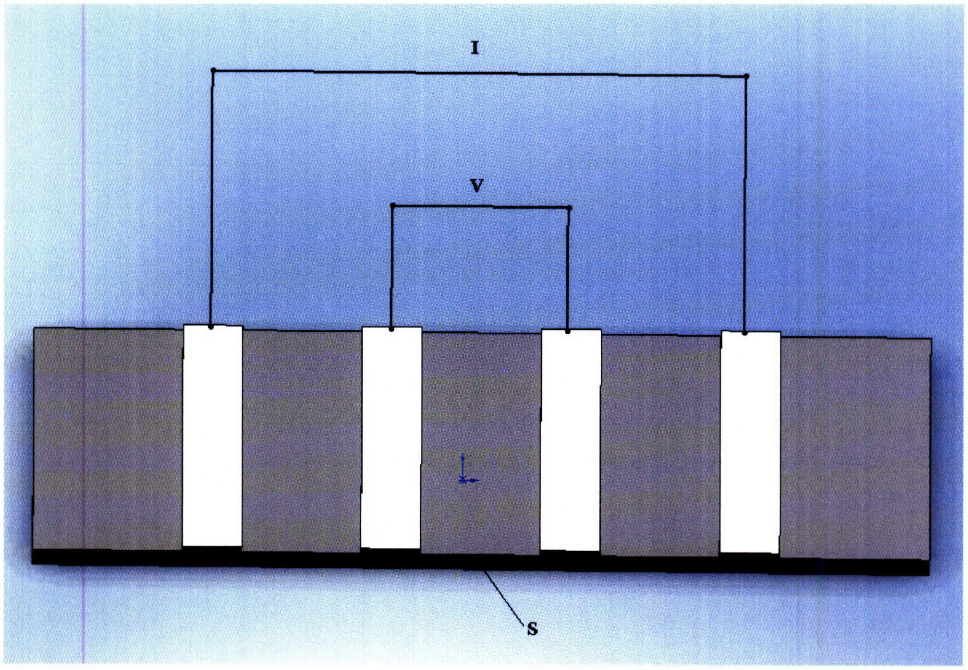


Figure 8: Model of a polypyrrole film (grey) using a four point technique (white) to measure conductivity

2.4 Actuation Theory

A polypyrrole actuator consists of three main parts: the polypyrrole film, an electrolyte, and a counter electrode. During actuation, a voltage is applied to the electrolyte and the polymer is either oxidized or reduced. In reduction, positive ions move towards the surface of the ion and negative ions move away. The reverse happens in oxidation. As the polypyrrole becomes charged, a bulk of ions from the electrolyte diffuses into the polymer to balance out the charges causing expansion of material. The polypyrrole-electrolyte system itself does not create volumetric changes. The ion diffusion driven by the application of voltage is the key element in creating motion in the actuator.

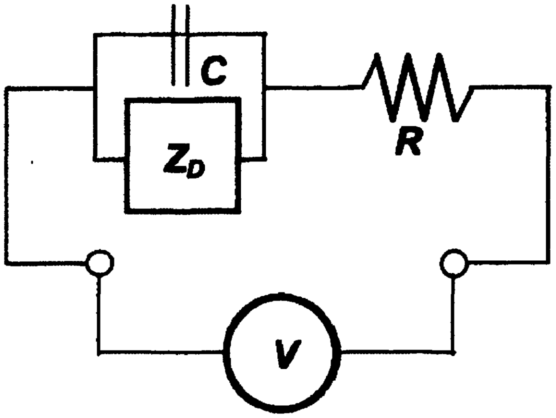


Figure 9: Circuit model of polypyrrole actuator which shows polypyrrole capacitance, resistance, diffusion impedance and voltage source.

When polypyrrole is soaked in an electrolytic solution, a circuit model can be used to describe its actuation as described by J.D. Madden in his PhD thesis [9]. C describes the polypyrrole-electrolyte capacitance while R stands for the resistance of both the electrolyte solution and other contact resistance. Z_D is the diffusion impedance, and V is the external voltage source. Charging the capacitance term of Z_D results in the volumetric expansions mentioned above. It is important to distinguish between the charging of ion density within the polypyrrole film and the charging of the entire actuator since ion density of the polymer is responsible for the volumetric changes, not the whole actuator.

2.5 Polypyrrole Trilayers

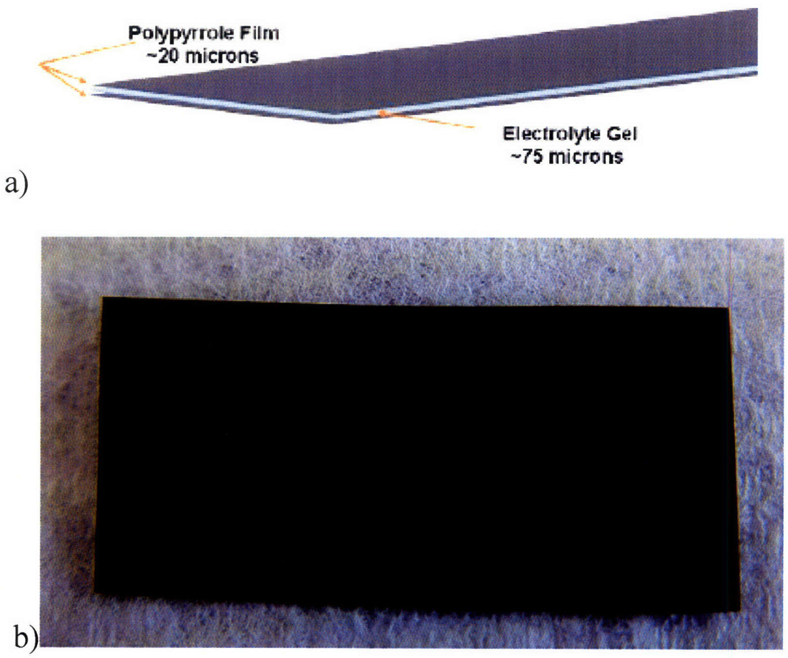


Figure 10: a) A model of polypyrrole trilayer actuator with two polypyrrole films sandwiching a layer of electrolyte gel [4] and b) an actual electrolytic gel trilayer

In order for conductive polymer actuators to be used in a broad variety of applications, it is necessary to eliminate the electrolytic solution and make the material actuate in air. However, electrolyte still needs to be provided in order for the volumetric expansion of the polypyrrole to occur. Since the use of liquid electrolytes prohibits actuation in air, other methods were explored. A popular solution is to construct an electrolytic gel to be sandwiched between two polypyrrole films. One of the films act as the working electrode while the other serve as counter electrode. Sansinena and Olazabal describe the trilayer as "conductive polymer film (CP)//no volumechange film (NVC)//conductive polymer film (CP)"[2]. Reduction of polypyrrole causes contraction and oxidation allows expansion. When one side of the trilayer contracts and the other expands, bending motion is observed. When a negative current is applied to the polypyrrole film, contraction occurs, and when a positive current runs through, the polymer expands. A trilayer actuator bends as both negative and positive charges are applied.

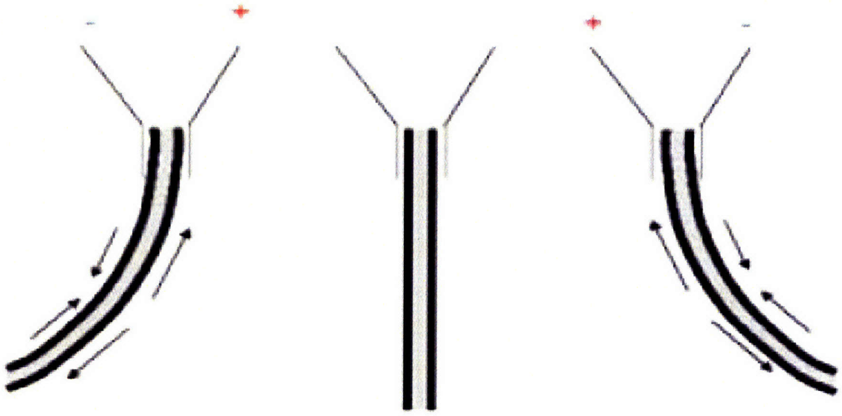


Figure 11: Bending polypyrrole trilayer actuators moving in acting in its oxidation, reduction and neutral states [4]

Three other kinds of polypyrrole trilayer systems have been studied extensively as actuators [2]. The first is one which a plastic film is coated with metal while polypyrrole is deposited on top of the plastic film. Common plastic materials used are polyethylene and polyimide. A problem with this technique is that the polypyrrole tends to peel off not long after the deposition. The second type of trilayer system deposits the polypyrrole onto a metallic electrode. After the deposition, the film is peeled off from the electrode using a flexible adhesive polymer film. This technique, however, still requires the presence of a liquid electrolytic solution in order to work. It has been suggested that encapsulation materials can be used for actuation in air. However, it is difficult to find a material that prevents conduction between the counter electrode and the polymer, displays similar mechanical properties so it does not prohibit certain actuator movements, and encapsulates. The last system is one which is described as a "polypyrrole(PPy)//solid polymer electrolyte(SPE)//polypyrrole(PPy)" trilayer. It was first studied in 1997 and had a bending movement of 360 degrees. Though it demonstrates very promising mechanical properties, it often has the problem of low ionic conductivity. The challenge in this case lies in finding a material that is both high in ionic conductivity and low in stiffness. The solid polymer electrolyte must first be treated with metallic salt, then, it is sandwiched between the two polypyrrole films in this technique.

Besides the major problems mentioned above, other great challenges of making a successful polypyrrole trilayer polymer includes the lowering the difficulties of construction, the timescale of fabrication, and elongate the lifetime of the trilayer. The CP//NVC//CP method lacks all three. It tends to create a wide range of trilayers with large quality discrepancies. Many of the steps contain variables that may affect the functions of the trilayers greatly. For example, it takes several tries to get consistent polypyrrole film depositions in the first place. The amount of time the trilayer is left in the oven, whether air bubbles are eliminated, and how tight the clamps were set can also affect trilayer performance. Furthermore, electrolyte gel cross linking makes it decrease in quality over time. Quality of trilayers decrease significantly when left in temperature even after a week. The response rate of the actuator becomes much lower due to this. The new way of constructing trilayers is a hybrid of the PPy//NVC//PPy mehtod and the deposition of polypyrrole onto a metal sputtered plastic technique. It attempts to resolve the problems mentioned above while producing a trilayer with reasonable active properties.

3 Manufacturing

3.1 Electrolytic Gel Trilayers

In her research in 2006, Angela Chen, describes a method of fabricating trilayers as bending actuators [4]. As mentioned earlier, her technique includes making polypyrrole films and electrolytic gels separately before sandwiching the gel between two polypyrrole films to construct a trilayer. The resulting actuator is usually around 115 μm in thickness. Chen demonstrated three major steps in this fabrication process: polypyrrole deposition, electrolytic gel fabrication, and finally, trilayer construction.

3.1.1 Electrolytic Gel Fabrication

Ingredients	Molarity %	Molar Mass (g/mol)	Desired Mass (g)
BMIMBF4	40%	226.03	10.00
2-Hydroxyethyl methacrylate	58.4%	130.14	8.41
Ethylene glycol dimethacrylate	0.8%	198.22	0.175
Azobisisobutyronitrile	0.8%	164.21	0.145

Table 1: Amount of ingredients needed to make a batch of electrolytic gel.

The first step of polypyrrole trilayer fabrication, polypyrrole deposition, is already described in detail in Chapter 2. In order to eliminate an electrolytic bath for polypyrrole actuation, Chen writes about the fabrication of an electrolytic gel serving as an ion source for the polypyrrole films. 40% liquid salt 1-butyl-3-methyl-imidazolium tetrafluoroborate, or $BMIMBF_4$ is mixed with 58.4% 2-hydroxyethyl methacrylate, 0.8% ethylene glycol dimethacrylate, and 0.8% azobisisobutyroniterile. Ethylene glycol dimethacrylate is a gel linking agent that when added to

2-hydroxyethyl methacrylate, a gel polymer, along with azobisisobutyroniterile, a crosslinking initiator, crosslink the gel in order for it to work. Chen's recipe, shown in Table 1 above, calls for a total of 18.73 g of chemicals. The resulting gel can be placed in a small vial. Once combined and mixed well, the gel is stored at -20 °C so premature crosslinking does not occur. Crosslinking can cause a decline in the performance of the gel. Even when it is stored at such a low temperature, however, crosslinking still occurs overtime. After about one month of sitting in the -20 °C temperature, crosslinking becomes visible in gel. Since each trilayer only requires a few dabs of the gel, make small amounts of it each time.

Figure 12: White fiber-like lines indicate crosslinking of the electrolytic gel occurred one month after it was made

3.1.2 Trilayer Construction

The side of the polypyrrole that was previously touching the crucible is placed face up on a Teflon sheet. On top of the polypyrrole film, two sheets of Kodak lens cleaning paper are placed. These thin, porous papers are to serve as separators in order to isolate the two conducting polymer layers electrically. Then, the electrolyte gel is laid on top of the paper. The layers of Kodak lens papers can change according to the amount of force the actuator needs to exert. Adding lens papers makes the actuator stiffer but also decreases the rate of actuation. Finally, the second layer of polypyrrole is put on top of the gel with the crucible side facing down while another Teflon sheet is placed on top of it. Two plates and clamps secure the structure and the trilayer is cured in an oven set at 85 °C for less than 20 minutes. The trilayer needs to be left in the oven for at least another hour or two before being taken out. It should, however, be stored in the oven until used.

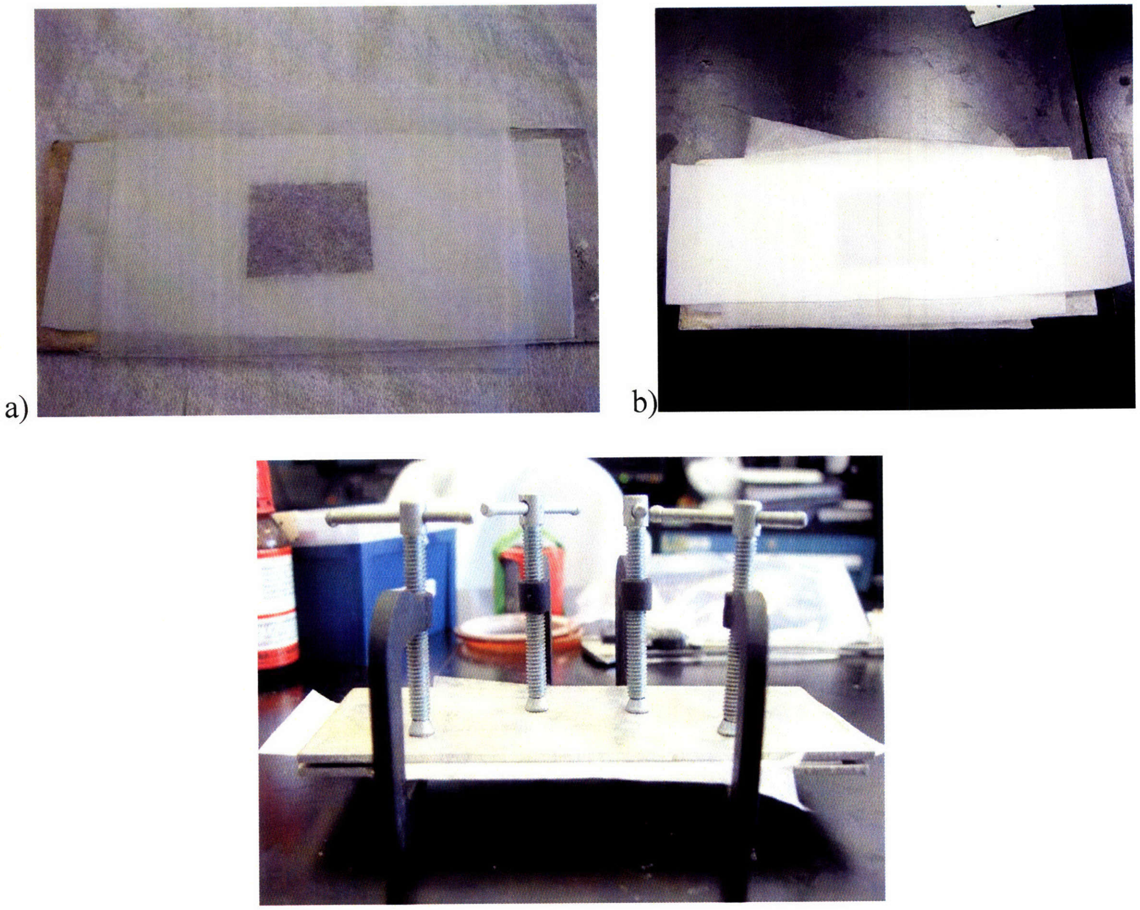


Figure 13: a) Two sheets of Kodak lens papers are placed on top of the crucible side of the polypyrrole film b) another film is placed on top of the lens papers along with a sheet of Teflon c) the whole structure is securely clamped together and placed in the oven.

In order to make a successful trilayer, it is extremely important to make sure to flatten both polypyrrole films during construction. Placing the films under heavy objects such as text books immediately after peeling them off the crucible is highly recommended. Bubbles might form when the electrolytic gel is applied to the lens papers. Use a rod to even out the gel and get rid of these bubbles. The clamps must be tightened all the way to prevent separation of the polypyrrole films from the gel soaked lens papers. Spread the clamps out evenly so equal forces are applied on the trilayer. In addition, it is best to leave the film in the oven for a few hours longer than the proposed one to two hours.

A simple test is done to see whether the trilayer functions using the device shown in Figure 4.3. Two nine volt batteries are inserted in this device. Opposite charges are applied on the two sides, causing the trilayer actuator to bend left and right. The tester can observe the rate of response when the currents are applied. A setup that acquires numerical force, position, current and potential data is described in Chapter 4.

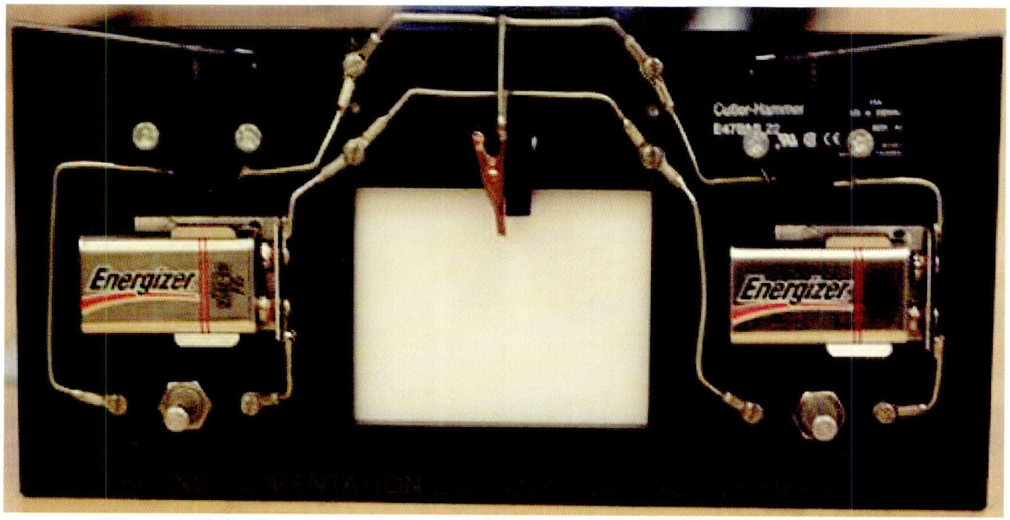


Figure 14: Device used to test actuator made by Angela Chen.

3.2 Gold-Coated PVDF Trilayers

3.2.1 Theory and Method

The method describe above is not only time consuming and contains too many variables during production, it also produces films with short lifetimes. A different technique is needed to build trilayers for actuation that will also perform well mechanically. The combination of PPy//SPE//PPy and the metal coated plastic trilayer techniques is proposed. The polypyrrole will be directly deposited onto the metal-coated SPE to reduce both timescale and inconsistency. The SPE chosen for this study is polyvinylidene fluoride (PVDF). It is a piezoelectric polymer used in western blotting, making of sensors, piping, and paint coating, to name a few. It is chosen because it is both inert and porous and improves ionic conductivity [11]. Furthermore, PVDF is resistant to most solvents and is relatively low cost compared to similar materials. Like all middle layers, the PVDF membrane will be utilized as an ion reservoir and separator for the polypyrrole layers electrochemically. The coating of gold onto the PVDF requires a sputter coater. The gold will increase the conductivity of the membrane, allowing deposition of polypyrrole to take place directly onto the membrane. The same electrochemical principles described for regular polypyrrole film deposition apply. Another advantage to this technique is that very little has to be changed in terms of deposition. The same solutes and solvents with the same concentrations can be applied. This time though, instead of having a glassy carbon crucible as the working electrode, the gold coating with the help of some pieces of stainless steel will serve as the working electrode. Copper will remain as the counter electrode.

To make sure that this deposition technique is valid, a trial deposition was done on a PVDF membrane with gold coating on just one side. A short twenty minute deposition gives a thin layer of polypyrrole on top of the PVDF while the non-deposited areas due to the lack of gold coating turned from an off-white color to transparent.

Figure 15: Trial gold-sputtered PVFD membrane with polypyrrole deposition on the left. The gold streak in the middle was due to a plastic piece of the deposition device floating because it was not secured correctly.

3.2.3 Deposition Device Design

With the new method of trilayer construction in mind, a device is built to facilitate the deposition of polypyrrole onto the gold coated PVDF membrane. The device contains two major parts: a bath and a polyethylene frame. The former is used to hold the TEAP-PC-pyrrole solution during the deposition. Teflon is chosen as the material because it does not dissolve in this particular solution. Other plastics that are easier to machine such as acrylic and ABS tend to dissolve in TEAP-PC solutions. The bath's inner dimension is 71 mm × 92 mm × 95.5 mm. It has to be wide enough so the two pieces of counter electrodes are not too close to the Au-PVDF membrane, which may prevent the exchange of ions. It is also designed to minimize the amount of solutions used while making a two sided deposition possible in order to reduce the timescale for trilayer fabrication. The polyethylene frame is designed to support the gold-coated membrane during

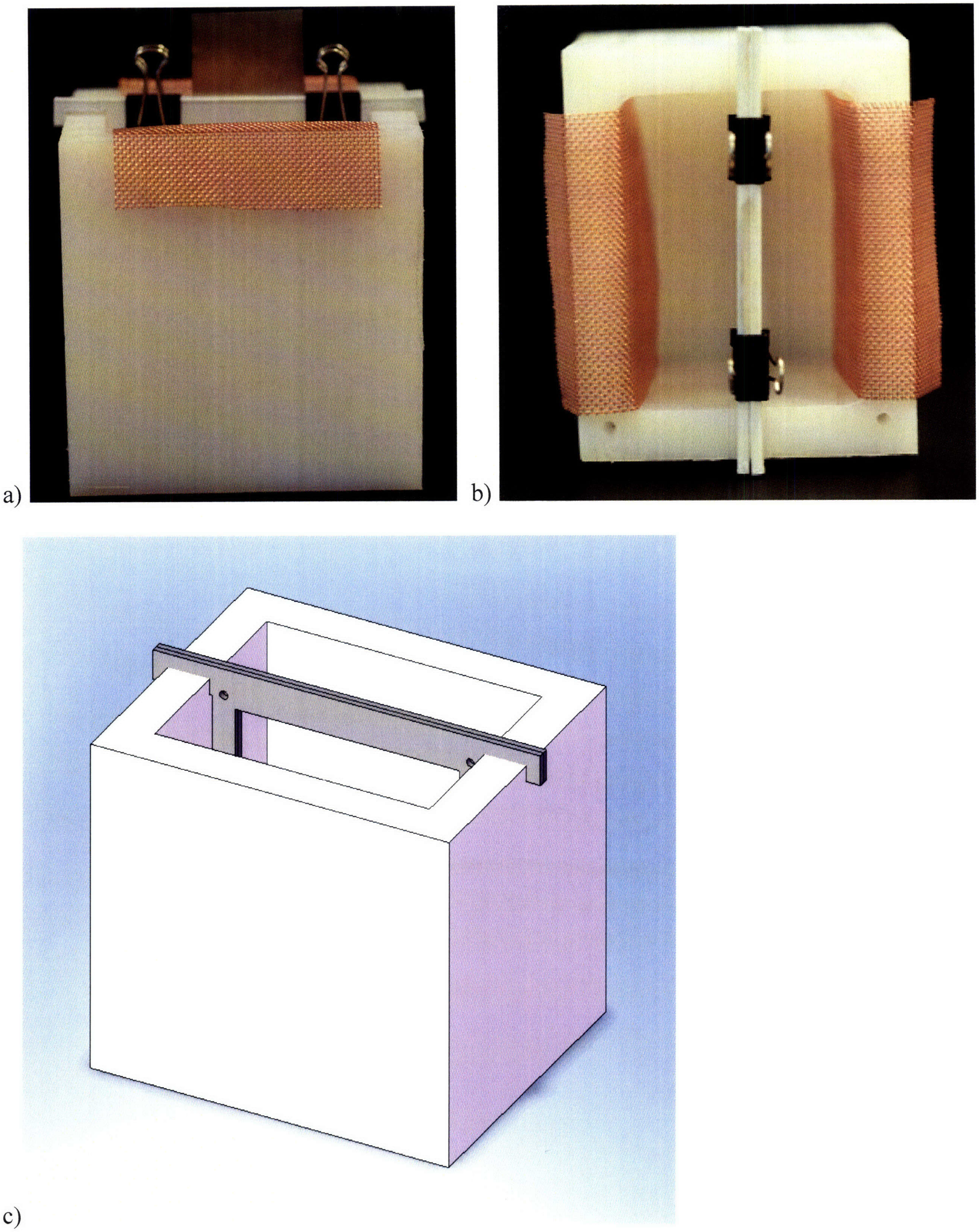


Figure 16: a) Front view of the device shows the copper mesh, large clips holding the frames together and a strip of stainless steel for electrical contact. b) top view and c) solid model.

deposition. The frame consists of two identical pieces that sandwiches the membrane tightly in the middle to make sure that the flexible surface stays flat. It is held together on top with two large clips and on the bottom with two pieces of delrin. The part is designed to hold a 90 mm × 95 mm piece of Au-PVDF to give a 75 mm × 80 mm trilayer after deposition. The top section of the frame has a dent on each side, designed to fit over the bath to hold the frame in place. Furthermore, a copper mesh counter electrode is placed on each side of the device parallel to the sputtered membrane. It ensures an evenly distributed electrical field during the deposition. Copper mesh is used instead of solid copper sheets due to its higher surface area in order to get higher quality trilayers. In addition, two 6 mm delrin pieces were placed on the bottom to secure both the frame and the copper mesh pieces. The weight of the delrin prohibits them from floating and the height is similar to the inner and bottom of the frame that it will not disturb the deposition. Electrical contacts are made with the working electrode by adding stainless steel pieces on top.

The procedure of using this device should be as follows: gold coating is applied using a desk II sputter coater set at 45 mA for 100 seconds. The resulting coating is between 30 to 40 nm. The membrane must be cut to size and carefully placed between two frames. Put a 30 mm × 30 mm stainless steel piece inside the frame but in contact with the gold coating on each side. Place the two clips on the frame on either side of the stainless steel. Next, secure the two pieces of copper mesh on each side of the bath so they will be parallel to the Au-PVDF. Position the delrin pieces tight against the meshes to secure them on the bath wall, and then insert the frame between the delrin. Pour 450 mL of TEAP-PC-pyrrole solution into the bath. The preparation of the solution is the same as described in section 2.3. Attach the working electrode wire to both stainless steel pieces and attached the counter and reference electrode wires to both copper pieces. The deposition procedures should also be the same as the one in section 2.3 except the current applied should be 6.0 mA. Wipe both sides of the trilayer with propylene carbonate and let it dry before testing.

Figure 17: Trilayer deposition using the gold-coated PVDF technique. Polypyrrole is directly deposited onto the gold coating on both sides of the PVDF membrane.

4. Actuation

4.1 Testing Setup

An electrochemical dynamic mechanical analyzer (DMA) is used to collect data on actuation. DMA's, in general, test mechanical properties as a result of changes in force, strain, temperature, time, and frequency [12]. It is used to test polymers because polymers demonstrate viscoelastic characteristics. The inputs of our DMA, though, are voltage and current through a potentiostat. A more detailed description of the electrochemical DMA can be found in Nathan Vandesteeg's Ph.D thesis [3]. This particular test performed is isometric, meaning that it occurs at a constant length. The property that this thesis is most interested in is force, though it is also important to be able to record the current through the trilayer.

This test setup is simple and easy to construct. It uses the same principles as the handheld trilayer tester shown in Chapter 3. Voltages are applied through working, counter and reference electrodes on top and bottom of the same side of the trilayer prompting actuation through oxidation and reduction. The initial design of the setup consists of a Mitutoyo magnetic stand, a piece of acrylic that has a rectangular part which fits over the magnetic stand and two extruded parts. Attached to this acrylic piece are two metal clips and a Futek LSB200 (L2357) JR S-Beam 1 Newton load cell force sensor (Appendix A). The short extruded part is designed for the placement of two gold clips, one serving as the working electrode and the other as the counter and reference electrode during actuation. Pieces of Kapton electrical tape are placed on opposing sides of the gold clips. The force sensor is attached to the end of the long extruded part of the acrylic piece. This allows the 30 mm trilayer sample's tip to push onto the sensor. A signal condition amplifier is connected to the sensor and an oscilloscope. This makes the output of the sensor visible on the oscilloscope so adjustments can be made for test performed. In order for the trilayer to be able to push in the direction of the sensor, the wires for counter and reference electrodes are placed on the top clip while the working electrode is placed on the bottom. The wires are connected to the Amel Instruments 2053 potentiostat which monitors the voltage and current going into the clips. The Aerotech DMA program on the computer, in turns, controls the parameters of the potentiostat and records the data as MATLAB m files for the ease of analyzing.

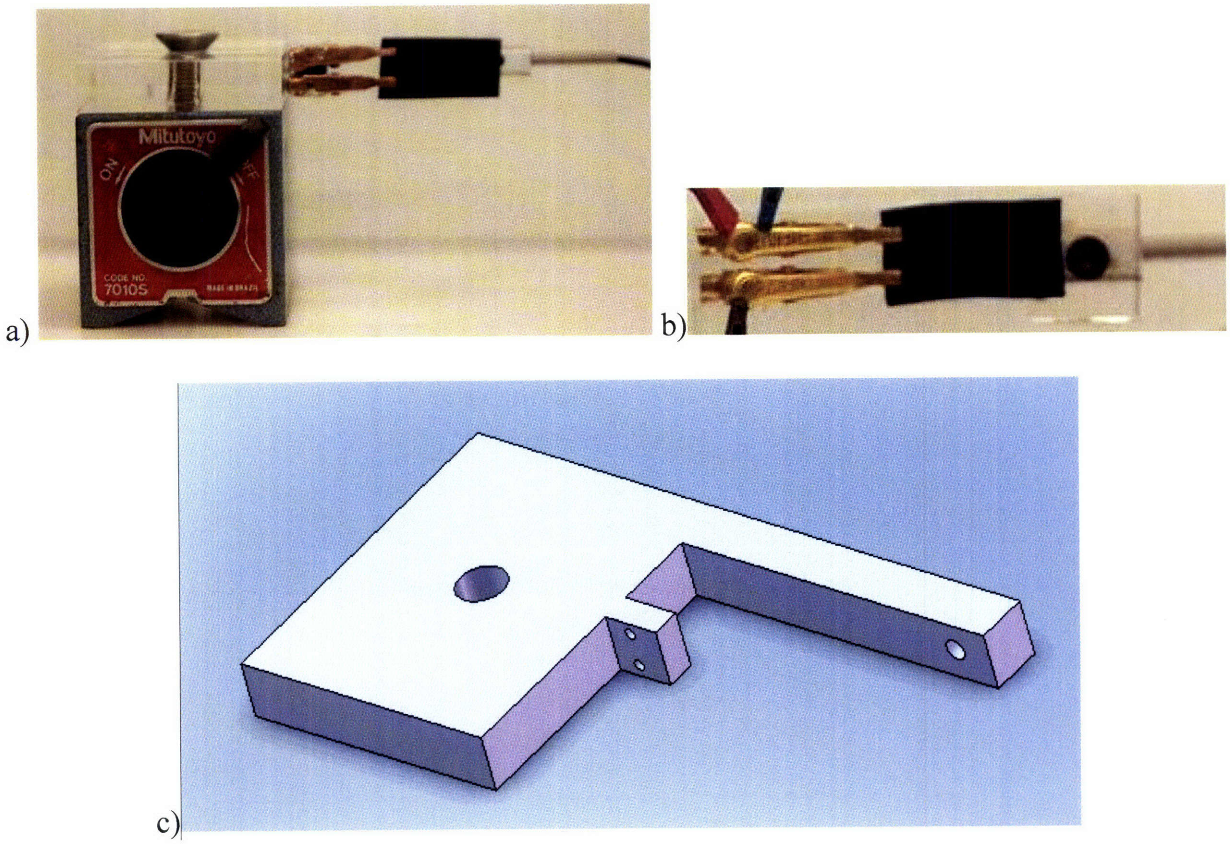


Figure 18: a) the original DMA testing setup designed for actuation. b) a small plate attachment on the sensor to maximize force sensing. c) solid model of the modified acrylic piece.

However, after several actuation tests, it is discovered that the PPy//NVC//PPy trilayers tend to curl around the sensor, making it difficult for measurements of position and force data. A small 19 mm × 16 mm × 3 mm acrylic plate is attached to the sensor to ensure that the tip of the trilayer is pushing onto the plate instead of an empty space in case the trilayer curls. The smaller extrusion holding the gold clips are moved up 3 mm to account for the thickness of the plate. The trilayers are cut to be 10 mm × 25 mm. One end of it must stay within the electrical tape areas on the clip while the other end of the trilayer should reach right before where the screw on the sensor plate is located. This way, the trilayer does not curl around the screw, causing the same problem as mentioned earlier. Higher and more consistent forces were detected after the addition of the acrylic plate.

4.2 Electrolytic Gel Trilayer Testing Results and Discussion

Five samples of electrolytic gel trilayers are cut to 10 mm × 25 mm and placed on the metal clips for testing. Two samples consist of trilayers made one week before the test, and one sample was made ten days before. The rest are cured immediately prior to data collection. The isometric setting on the Aerotech DMA program is chosen and actuation is done through applying square waves for ten cycles. Each cycle is run at 4 V for 45 seconds and than 0 V for 15 seconds at a frequency of 100 Hz. This allows the trilayers to move back and forth in both directions, though focus will be on the force applied onto the sensor in compression. During each cycle, four properties are recorded: potential, current, force, and position. Each sample is tested for three runs under the same setup. An additional run is done for each sample after they are soaked in $BMIMBF_4$, the liquid salt used in gel making. Data is collected with three important goals in mind: comparison between old and newly made trilayers, how $BMIMBF_4$ will affect the qualities of the trilayer, and lastly comparison with trilayers made using the new Au-PVDF membrane deposition method.

Actuation active force for freshly made trilayers can be as high as 4×10^{-3} N and as low as 1.5×10^{-3} N. Its current is between positive and negative 4 mA. Trilayers that had been made a week prior to testing yield active forces between 3×10^{-3} N and a little less than 1×10^{-3} N.

Because actuation of conductive polymer trilayers is due to the volumetric changes caused by electrochemical changes, there is a close relationship between the force applied onto the sensor and the current going through the trilayer, which is shown in Figure 19.

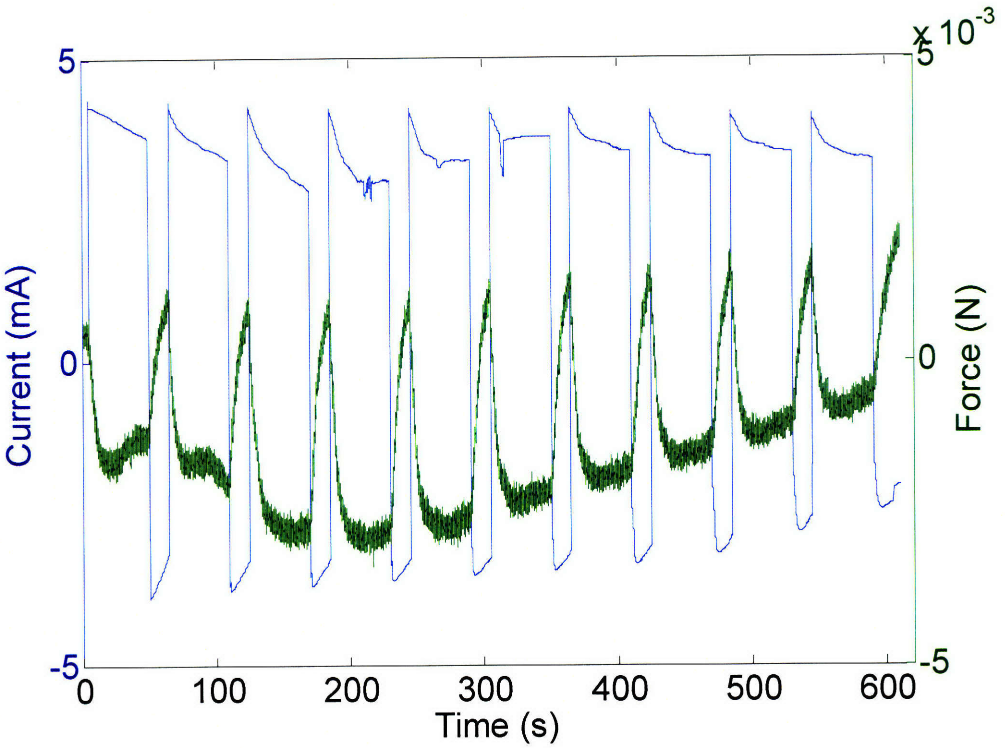


Figure 19: Current and force relationship during actuation. As the current (blue) increases, the force applied (green) in the negative direction increases, and as current decreases, so does the force.

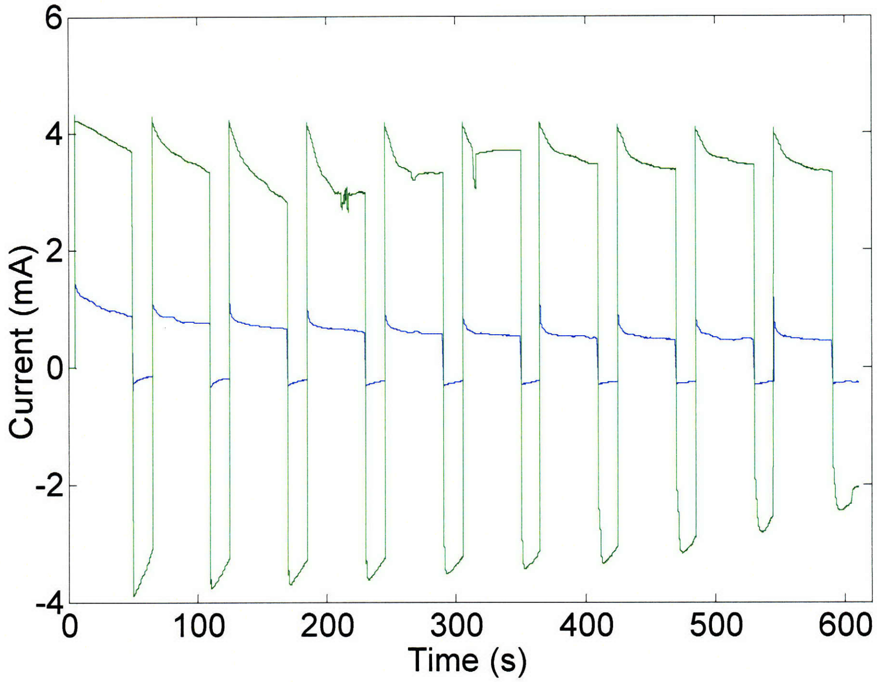


Figure 20: A plot showing the difference in current between the week old trilayer sample (blue) and the newly made sample (green).

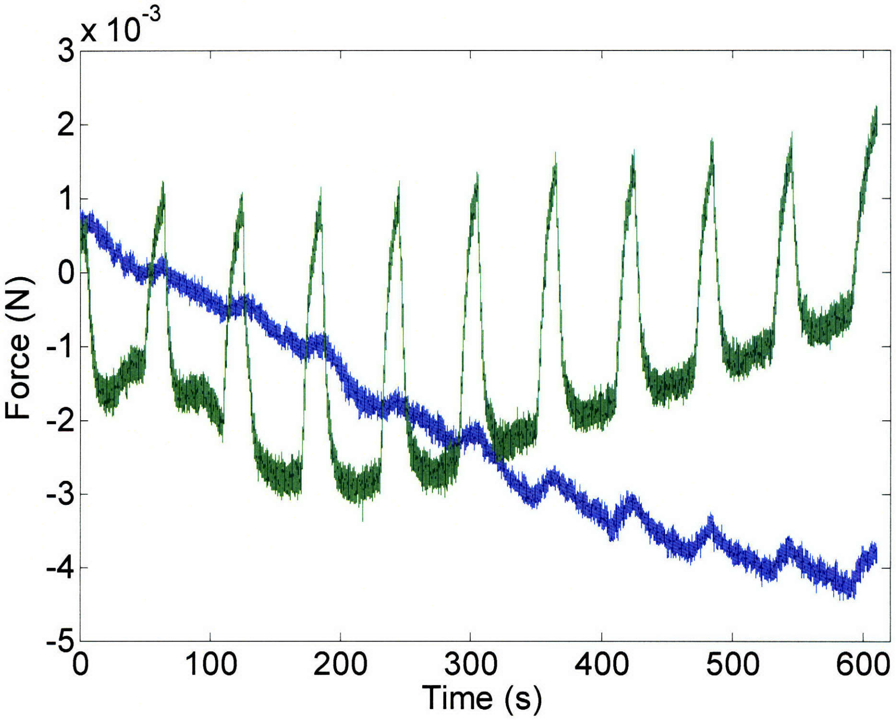


Figure 21: Force exerted during actuation of the sample made the week before (blue) and the sample made immediately prior to testing are compared.

Force and current comparisons are made between trilayers fabricated days before actuation and, and new trilayers that has just been out of the oven in Figures 20 and 21 above. This is to determine the lifetime that actuators made out of electrolytic gel trilayers can have. Figure 19 indicates that the force applied by the newly made sample will be much higher because current is higher. Figure 21 gives the force vs. time graph of the same test, showing that the force output of the trilayer made immediately before the test is clearly superior with the maximum active force measured at 4×10^{-3} N compared to 1×10^{-3} N for the week old. In addition, the negative slope downward given by the week old trilayer suggests that it recovers poorly when no voltage is applied. This causes the sample to push farther inward onto the sensor instead of actuating back in the other direction before pushing against the sensor again. The degradation of the trilayer over time can be seen very clearly. Crosslinking of the electrolytic gel is most likely the source of this diminishing quality.

It has been suggested that storing or soaking trilayers in liquid salt $BMIMBF_4$ can increase their mechanical properties. An investigation of this is done as a potential way to make better actuators. After each sample is tested under normal conditions, they are dipped in $BMIMBF_4$ for further testing. The data collected between soaked and non-soaked samples are compared in Figure 22 and 23.

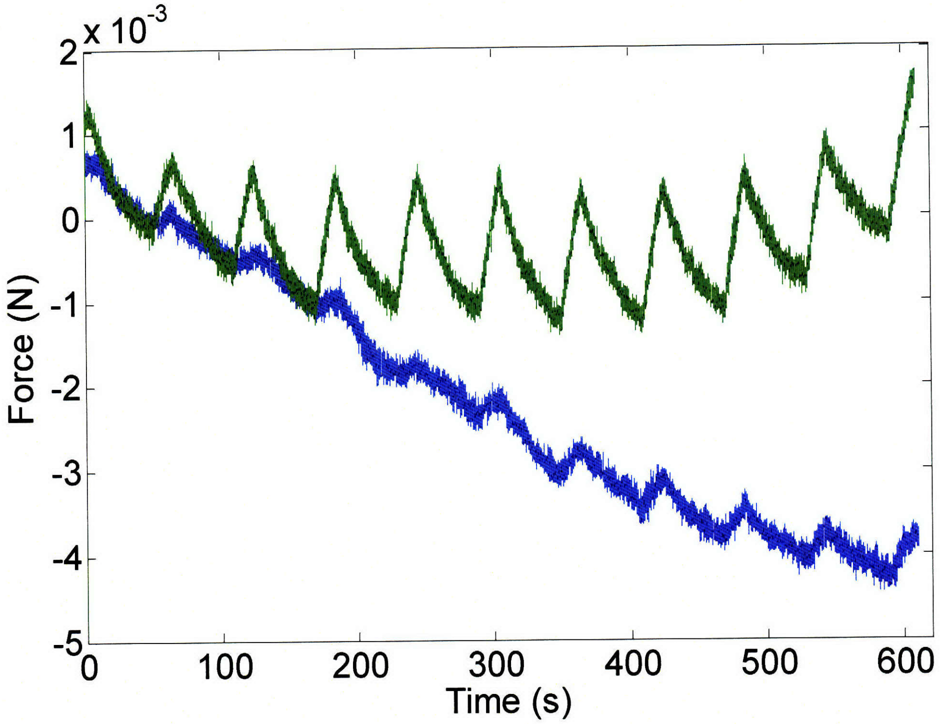


Figure 22: A plot showing the differences in force exerted when sample made a week before actuation is actuated under normal condition (blue) and is actuated after being dipped in liquid salt (green)

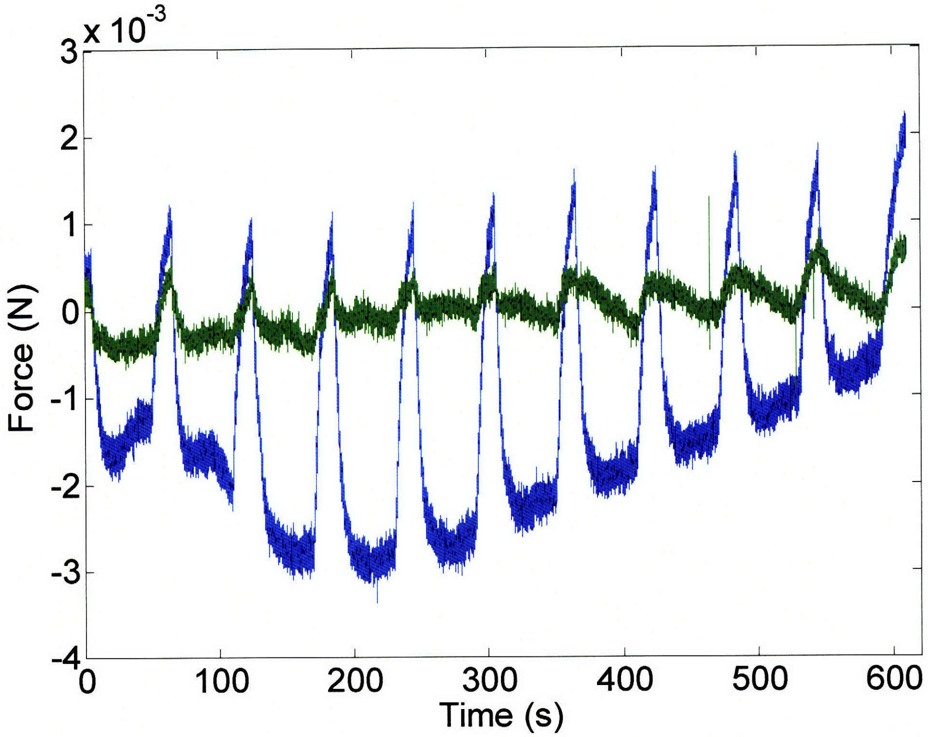


Figure 23: Forces of a sample not wetted by $BMIMBF_4$ (blue) and a sample soaked in the liquid salt are compared (green). Both samples are freshly made before the test.

When the week old sample is dipped in liquid salt, $BMIMBF_4$, force recovery increases significantly. Figure 22 demonstrates that the trilayer soaked in $BMIMBF_4$ is able to "exert" positive force by moving away from the sensor when a zero voltage is applied. The average force applied onto the sensor, though, does not change much. This increases the quality of the trilayer because the liquid salt is one of the main ingredients of the electrolytic gel. It gives the gel its ionic properties. However, a dramatic difference in results, illustrated in Figure 23, occurred when the freshly made trilayer is soaked in $BMIMBF_4$. Though recovering in the positive direction stayed the same, the force actuated decreased by half. The reasoning behind this must be further investigated. In both tests though, the liquid salt speeds up the degradation of the polypyrrole, causing the trilayer to wrinkle once it is dried, making the sample unusable.

4.3 Gold-Coated PVDF Trilayer Testing Results

A deposition of the Au-PVDF-polypyrrole trilayer yields a film with a thickness of 230 μm. A sample is run at the same electrochemical setting as the electrolytic gel trilayers, but the voltage was too high which destroyed the trilayer. Therefore, a new setting is used. For the sake of making comparisons, the only the amount of voltage and the maximum current settings are changed. Like before, the samples are run for either 10 or 15 cycles. Each cycle consists of 45 seconds of actuation at 1 V and 15 seconds of actuation at 0 V. The current setting is altered to 100mA to prevent overloading. Furthermore, the direction of actuation changed on the new trilayers. The working electrode is adjusted to be placed on the bottom gold clip instead of the counter and reference electrodes. Two samples are run three times each to see whether degeneration occurs with time. After the third run, the second sample is soaked in liquid salt $BMIMBF_4$ to observe the effects. Since there is a variation of reaction to the liquid salt for trilayers made using the electrolytic gel method, a new sample is also soaked in it to see how it behaves differently from a sample that had already been actuated. Because the correlation between force and current has not change between trilayers made by the old and new methods, the focus is once again on the forces applied. The active forces exerted by the Au-PVDF trilayer range from 5×10^{-3} N to 14×10^{-3} N under normal conditions. When soaked in liquid salt $BMIMBF_4$, they range from around 20×10^{-3} N and less than 4×10^{-3} N.

First, current and force data recorded of the Au-PVDF trilayers are compared to the data collected for the electrolytic gel trilayers. Data from the freshly made electrolytic gel trilayer are selected for this comparison because it exhibits the largest amount of force applied to the sensor by an electrolytic gel trilayer. Below, Figures 24 and 25 graph out the current and force comparisons respectively.

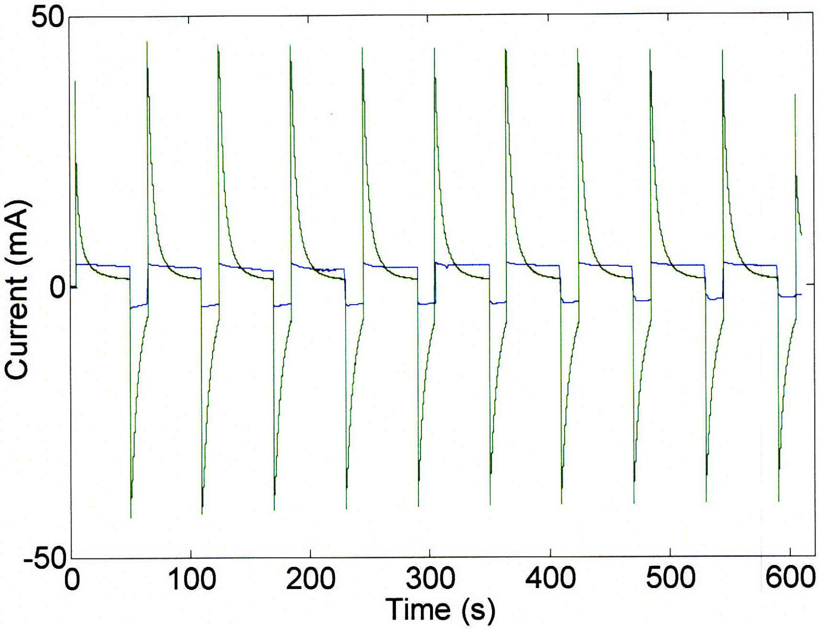


Figure 24: Comparison of currents going through an electrolytic trilayer (blue) and Au-PVDF trilayer (green).

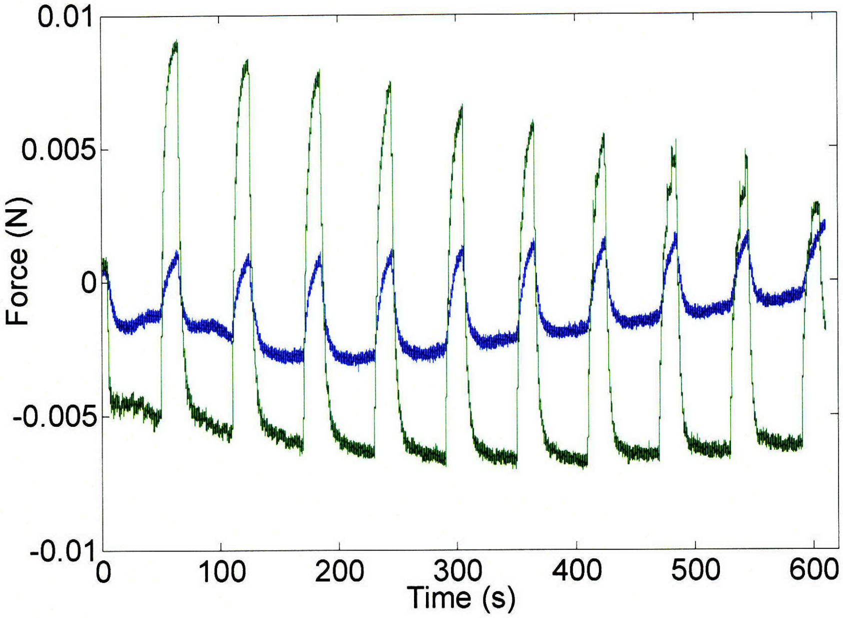


Figure 25: Force comparison between trilayers fabricated with the electrolytic gel method (blue) and the gold coated PVDF method (green).

The current measured for the gold coated PVDF membrane trilayer is about eight times higher than the current running through the trilayer made by the old method. The force comparison in Figure 24 reveals that under normal conditions, the Au-PVDF trilayer can exert three times as much force as the electrolytic sample on the first run. It is important to point out, though, that the force exerted by the gold sputtered trilayer is diminishing faster than the gel trilayer. Even so, after three runs, the force applied by the same gold coated membrane trilayers is consistently at around 6×10^{-3} N. This number is still at least twice as much as the electrolytic gel trilayers on the third run.

Because soaked and non-soaked data exhibit very different results for electrolytic gel trilayers, it will be interesting to observe what happens to the gold coated membrane trilayers when dipped in $BMIMBF_4$. Figure 26 shows the comparison for the first 600 seconds of actuation between soaked and non-soaked Au-PVDF trilayers. Another 600 second run is done for the trilayer dipped in liquid salt which is compared to the second run force data from the sample under normal condition, which demonstrates the unexpected results displayed in Figure 27.

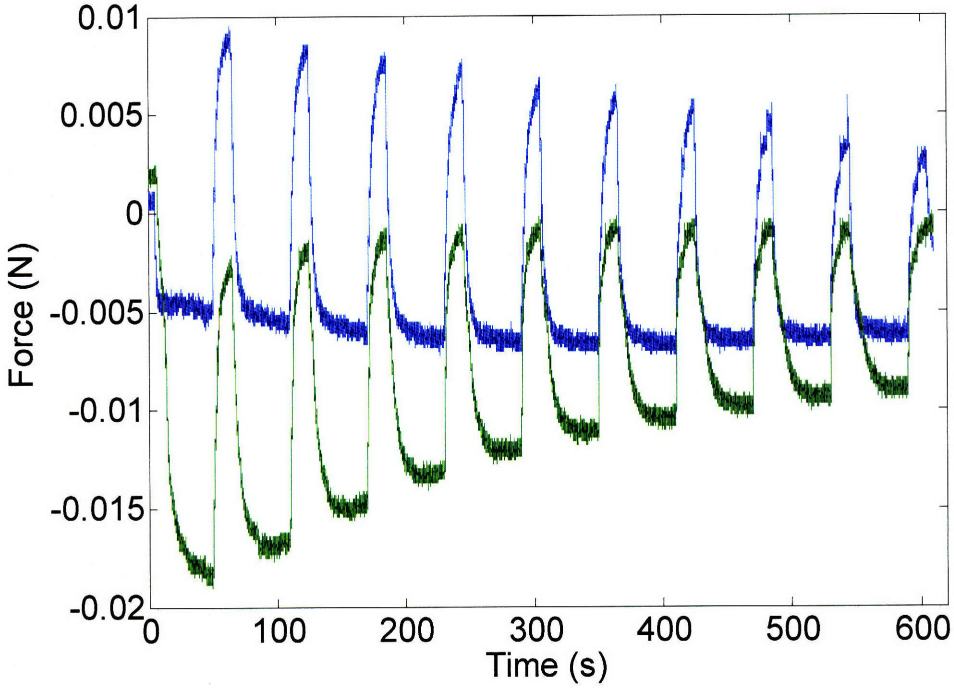


Figure 26: Force data of the first testing run of an Au-PVDF sample performing under normal condition (blue) and a sample dipped in liquid salt $BMIMBF_4$.

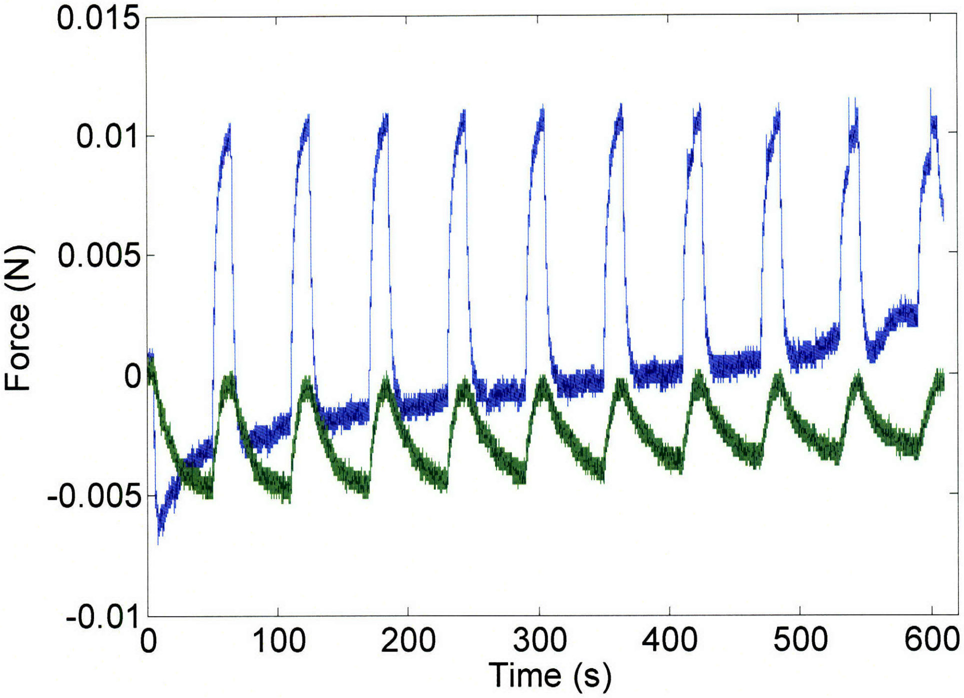


Figure 27: A plot which compares the forces of second testing runs done on both Au-PVDF trilayers not soaked in liquid salt (blue) and trilayer that is soaked (green).

Figure 26 shows a huge spike to 2×10^{-2} N for the trilayer soaked in the liquid salt in the first cycle of the first test run compared to the 1×10^{-2} N by the non-soaked sample. This large force output does not last long though, by the end of this run, the force of the trilayer soaked in $BMIMBF_4$ is lower than the non-soaked sample because of a large diminishing rate of exertion. When a second run is done using the same samples, the degradation of the trilayer by $BMIMBF_4$ causes it to only be able to apply only less than 4×10^{-3} N as oppose to the 1×10^{-2} N for the non-wetted trilayer.

The deposition of the polypyrrole onto the gold-coated PVDF membrane was not completely successful. The electrical contact on one side of the working electrode, namely the gold coating-stainless steel-metal clip complex, came loose in the MicroChamber, preventing polypyrrole from depositing onto the gold coating. Therefore, only one side deposited. Another 10 hour deposition is made on the side that did not deposit using the same technique which yields a decent trilayer.

Because of their high flexibility and conductivity, the Au-PVDF trilayers tend to bend in different ways if the initial position of actuation is different each time. For example, during one test, a trilayer made with the new method started off already curling along its long edges at its initial position. When voltages are applied, it curled farther inward into almost a tube-like configuration instead of pushing the sensor with its short edge.

5. Conclusions and Future Work

The new trilayer making method produces better trilayer actuators than the old electrolytic gel method. The trilayers made are more conductive and yields higher forces. Not only that, observation of the Au-PVDF trilayers shows a wider range of motion. Since it is not fabricated by pressing each part together like the older method, there is no need to worry about the pieces separating during actuation. Its double sided deposition technique saves time and allows the trilayers produced to be more consistent. Instead of spending more than 24 hours alone on the preparation of polypyrrole, flattening out the films, and then waiting for at least an hour and 50 minutes for curing the electrode, everything can be done in around 12 hours. Since no peeling of the polypyrrole off the crucible is needed, the Au-PVDF trilayers can be patted dry gently with a Kim wipe and used almost immediately after the deposition. Though further material degradation studies need to be done, the new trilayers are more likely to last longer in storage because electrolytic gel crosslinking is no longer the limiting factor. This improves the value of this particular trilayer as an actuator greatly.

Even with its advantages, many steps in the procedure as well as parts of the deposition device need to be investigated further or improved. The most needed area of improvement for the deposition device is establishing good electrical contact between the potentiostat and the electrodes in order to avoid unsuccessful depositions. The stainless steel pieces should be permanently attached to the inside of the frame instead of just being held down by the clips that go on top of the frame. Machining a slot in the bath that holds the copper mesh better may also help. Although the frame holds the gold sputtered membrane tightly throughout the entire electrochemical process, parts of the edges still curl in certain directions, making it hard to flatten out the trilayers. More depositions should be done using this device including trying out different time lengths of deposition. Trilayer thickness should be reduced. This may be achieved by shortening the deposition time. However, since PVDF is as thick as the electrolytic gel trilayers, it can be hard to make the new trilayers thinner unless another membrane can be used as a substitute. The sputtering method also tends to burn PVDF, perhaps a lower current setting and better placement in the sputter can help. It will also be interesting to conduct experiments where different metals such as silver and platinum are used as the working electrode to be coated onto the PVDF membrane. On a similar note, using different solutions for the deposition may also increase the quality of the actuators. Besides force and current, there are other properties of the Au-PVDF trilayer which had not been explored in this paper such as temperature effects and strain rate.

Also, further studies on the effects of $BMIMBF_4$ should be done since it could turn out to be a promising method to revive older electrolytic gel trilayers as well as improve Au-PVDF trilayer force exertion. It will also be interesting to understand the electrochemical reasoning behind why soaking week old electrolytic gel trilayer can result in such different reaction from one that is freshly made, and why the force data from those two are so different than the data from the Au-PVDF trilayer. Going beyond the new fabrication method and the trilayer's material properties, actual applications of this actuator should be attempted. One of the applications for trilayers Chen mentioned in her thesis is the construction of autonomous underwater vehicles. It will be interesting to observe whether this trilayer will be able to actuate underwater without encapsulation.

References

[1] Hara, S., T. Zama, W. Takashima, and K. Kaneto. "Free-Standing Gel-Like Polypyrrole Actuators Doped with Bis(Perfluoroalkylsulfonyl)Imide Exhibiting Extremely Large Strain." Smart Material and Structures (2005).

[2] Bar-Cohen, Y., ed. Electroactive Polymer (EAP) Actuators as Artificial Muscles. Bellingham, Washington: SPIE P, 2001.

[3] Vandesteeg, N. A. *Synthesis and Characterization of Conducting Polymer Actuators.* PhD Thesis. Massachusetts Institute of Technology, 2006.

[4] Chen, A. *Large Displacement Fast Conducting Polymer Actuators.* Masters of Science Thesis. Massachusetts Institute of Technology, 2006.

[5] Spinks, G. M., D. Zhou, L. Liu, and G. G. Wallace. "The Amounts Per Cycle of Polypyrrole Electrochemical Actuators." Smart Materials and Structures (2003).

[6] Hara, S., T. Zama, W. Takashima, and K. Kaneto. "Tris(Trifluoromethylsulfonyl)Methide-Doped Polypyrrole as a Conducting Polymer Actuator with Large Electrochemical Strain." Synthetic Materials 156 (2006).

[7] "Actuator Selection Tool." Department of Electrical and Computer Engineering, University of British Columbia. 22 Feb. 2008 <http://www.actuatorweb.org/index.php?page=browser&f1=All&f2=Polypyrrole>.

[8] Reece, D. A. *Development of Conducting Polymers for Separations.* PhD Thesis. University of Wollongong, 2003.

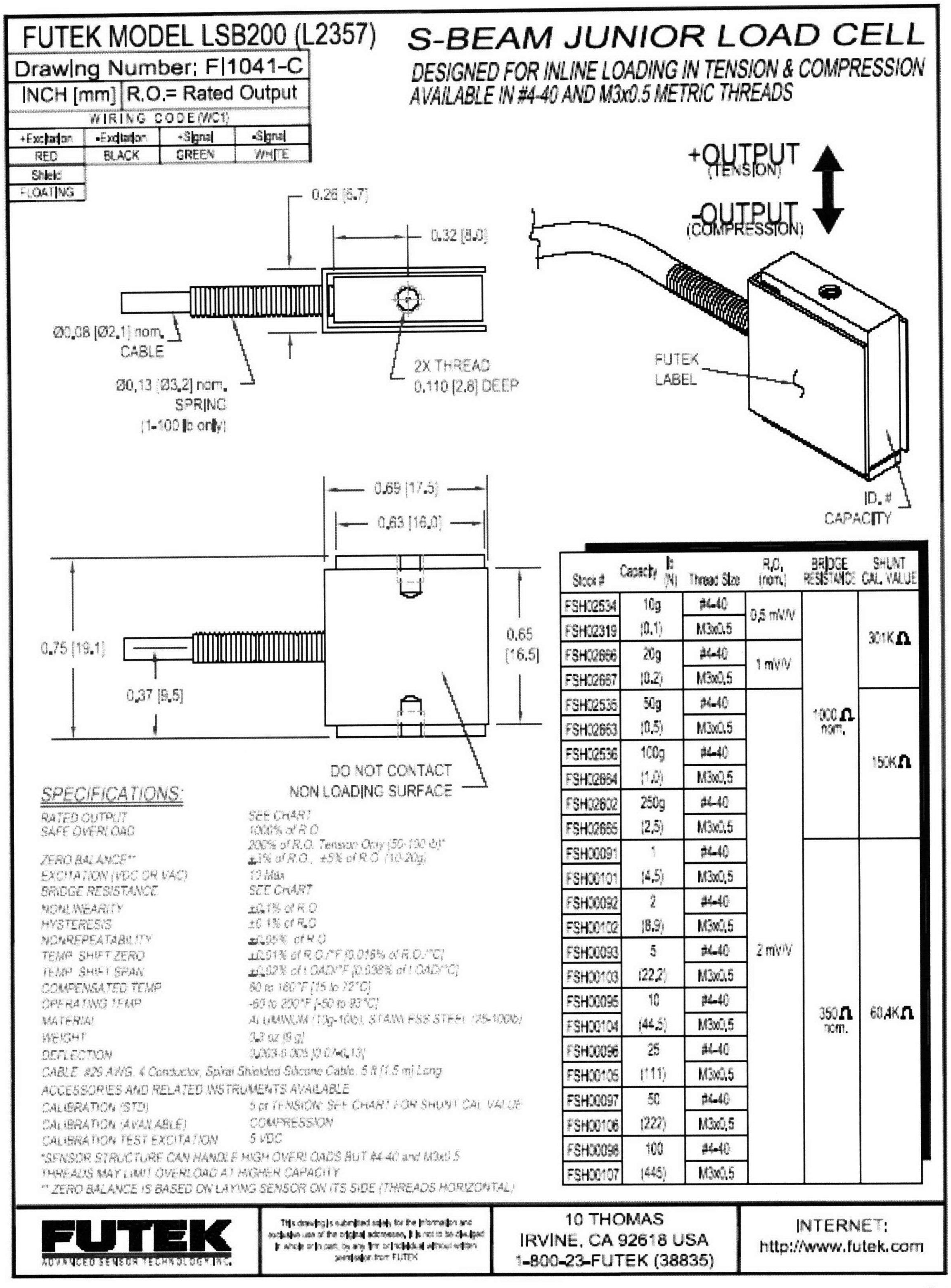
[9] Del Zio, M. R. *Cconducting Polymer Actuators: Temperature Effects.* Masters of Science Thesis. Massachusetts Institute of Technology, 2006.

[10] Madden, J. D. W. *Conducting Polymer Actuators.* PhD Thesis. Massachusetts Institute of Technology, 2000.

[11] Alici, G., P. Metz, and G. M. Spinks. "A Methodoloy Towards Geometry Optimazation of High Performance Polypyrrole (PPy) Actuators." Smart Materials and Structures (2006).

[12] "Dynamic Mechanical Analysis (DMA)." Materials Research Lab, University of California, Santa Barbara. <http://www.mrl.ucsb.edu/mrl/centralfacilities/polymer/DMA.html>.

Appendix A



FUTEK MODEL LSB200 (L2357)

Drawing Number: FI1041-C

INCH [mm] R.O.= Rated Output

S-BEAM JUNIOR LOAD CELL

DESIGNED FOR INLINE LOADING IN TENSION & COMPRESSION
AVAILABLE IN #4-40 AND M3x0.5 METRIC THREADS

WIRING CODE (WC1)

+Excitation	-Excitation	+Signal	-Signal
RED	BLACK	GREEN	WHITE

Shield
FLOATING

SPECIFICATIONS:

RATED OUTPUT	SEE CHART
SAFE OVERLOAD	1000% of R.O. 200% of R.O. Tension Only (50-100 lb)*
ZERO BALANCE**	±1% of R.O., ±5% of R.O. (10-20g)
EXCITATION (VDC OR VAC)	10 Max
BRIDGE RESISTANCE	SEE CHART
NONLINEARITY	±0.1% of R.O.
HYSTERESIS	±0.1% of R.O.
NONREPEATABILITY	±0.05% of R.O.
TEMP. SHIFT ZERO	±0.01% of R.O./°F [0.018% of R.O./°C]
TEMP. SHIFT SPAN	±0.02% of LOAD/°F [0.036% of LOAD/°C]
COMPENSATED TEMP	60 to 160°F [15 to 72°C]
OPERATING TEMP	-60 to 200°F [-50 to 93°C]
MATERIAL	ALUMINUM (10g-10lb), STAINLESS STEEL (25-100lb)
WEIGHT	0.3 oz [9 g]
DEFLECTION	0.003-0.005 [0.07-0.13]

CABLE: #29 AWG, 4 Conductor, Spiral Shielded Silicone Cable, 5 ft [1.5 m] Long

ACCESSORIES AND RELATED INSTRUMENTS AVAILABLE

CALIBRATION (STD)	5 pt TENSION; SEE CHART FOR SHUNT CAL VALUE
CALIBRATION (AVAILABLE)	COMPRESSION
CALIBRATION TEST EXCITATION	5 VDC

*SENSOR STRUCTURE CAN HANDLE HIGH OVERLOADS BUT #4-40 and M3x0.5 THREADS MAY LIMIT OVERLOAD AT HIGHER CAPACITY

** ZERO BALANCE IS BASED ON LAYING SENSOR ON ITS SIDE (THREADS HORIZONTAL)

Stock #	Capacity lb (N)	Thread Size	R.O. (nom.)	BRIDGE RESISTANCE	SHUNT CAL. VALUE
FSH02534	10g	#4-40	0.5 mV/V	1000 Ω nom.	301K Ω
FSH02319	(0.1)	M3x0.5			
FSH02666	20g	#4-40	1 mV/V		
FSH02667	(0.2)	M3x0.5			
FSH02535	50g	#4-40	2 mV/V		150K Ω
FSH02663	(0.5)	M3x0.5			
FSH02536	100g	#4-40			
FSH02664	(1.0)	M3x0.5			
FSH02602	250g	#4-40			
FSH02665	(2.5)	M3x0.5			
FSH00091	1	#4-40		350 Ω nom.	60.4K Ω
FSH00101	(4.5)	M3x0.5			
FSH00092	2	#4-40			
FSH00102	(8.9)	M3x0.5			
FSH00093	5	#4-40			
FSH00103	(22.2)	M3x0.5			
FSH00095	10	#4-40			
FSH00104	(44.5)	M3x0.5			
FSH00096	25	#4-40			
FSH00105	(111)	M3x0.5			
FSH00097	50	#4-40			
FSH00106	(222)	M3x0.5			
FSH00098	100	#4-40			
FSH00107	(445)	M3x0.5			

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