Fabrication and Non-linear Modeling of Conducting Polymer-Based Actuators:

Toward Catheter and Tactile Display Applications

by

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Abstract

The low voltage operation and relatively high strain response of conducting polymer actuators have made their use in different applications of great interest. In this thesis, modeling and characterization of the chemoelectromechanical behaviour of the linear freestanding and bending trilayer conducting polymer-based actuators are presented. In the modeling approach, a combination of state space representation and a two-dimensional RC transmission line was employed to develop the time domain model. Electrical and ionic conductivities and also Young’s modulus versus oxidation state were measured and incorporated into the model. Significant changes in conductivity and Young’s modulus make using a non-linear model necessary for accurate modeling. Implementation of the non-linear functions for electrical and mechanical properties in the model is one of the major advantages of the modeling approach. Capability of the model to predict the linear strain and radius of curvature for bending trilayer actuators versus time and position with good agreement with experiments are shown in this thesis. Voltage drop along the length of the film, away from the attachment point and the variation in electrical conductivity with state of charge along this length necessitated the use of a 2D non-linear model to obtain effective predictions of response for the film dimension used.

Tubular actuators using conducting polymers as the active material for a catheter application are developed. Laser micromachining to pattern the actuators is demonstrated. A 0.95 mm diameter device is shown to achieve a 22 mm radius of curvature under activation of 2 V. A closed form beam bending model for trilayer actuators with tubular and rectangular cross sections is derived. These formulations predict the radius of curvature as a function of applied voltage and free strain considering different Young’s modulus for conducting polymer layers. This derivation is also useful for other multilayer actuators.
The force generated by trilayer actuators is an important parameter which is investigated in this work. Mathematical derivation and simulations are employed to determine this parameter. Some solutions and their effects on force generated by trilayer actuators are presented to show how the force can be enhanced for tactile interface application.
Preface

The author is the main researcher in all of the work done in the presented thesis. This work has been done in the Molecular Mechatronics Lab under the supervision of Prof. John D. W. Madden and Prof. Farrokh Sassani.

Material presented in chapter 2, has been published in IEEE/ASME transaction on mechatronics (“Non-linear two-Dimensional transmission line models for electrochemically driven conducting polymer actuators”, IEEE/ASME transaction on mechatronics) and also presented at SPIE conference on electroactive polymer actuators and devices, 2014 (“Non-linear time variant model intended for polypyrrole-based actuators”, SPIE, 2014, pp. 90561-90569). All of the modeling, characterizations and experimental validations have been performed by author with the supervision of Prof. John D. W. Madden. Vincent Woehling, Cedric Plesse and Frederic Vidal from University of Cergy-Pontoise reviewed the results and provided some samples. Ashwin Usgaocar and Yuta Dubashi helped to setup the experiments.

In Chapter 3 of this thesis, all of the derivations, modeling, characterizations and experiments have been conducted by author under supervision of Prof. John D. W. Madden and Prof. Farrokh Sassani. The tested actuators for experimental validations have been made at the University of Cergy-Pontoise for this purpose by the team of Adelyne Fannir, Giao Nguyen, Cedric Plesse and Frederic Vidal.

Actuators presented in Chapter 4, have been fabricated as partially collaboration between the author and the University of Cergy-Pontoise. All of the derivations, modeling and simulations have been done by author under the supervision of Prof. John D. W. Madden and Prof. Farrokh Sassani. The PEDOT/IPN rod used for this work was made at the University of Cergy-Pontoise by the team of Vincent Woehling, Cedric Plesse, Giao Nguyen and Frederic Vidal.
Some of the trilayer actuators used in chapter 5 of this thesis have been made at the University of Cergy-Pontoise. All of the modeling and simulations have been performed by author. Section 5.4.1 of this chapter was presented SPIE conference on electroactive polymer actuators and devices, 2015 (“Stacking trilayers to increase force generation”, SPIE, 2015, pp. 94301-94307).
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride</td>
</tr>
<tr>
<td>AIS</td>
<td>Acute Ischemic Stroke</td>
</tr>
<tr>
<td>CP</td>
<td>Conducting polymer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl-peroxide</td>
</tr>
<tr>
<td>DCPD</td>
<td>Dicyclo-hexylperoxidicarbonate</td>
</tr>
<tr>
<td>DEM</td>
<td>Diffusive elastic model</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>IPN</td>
<td>Interpenetrating polymer network</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>KVL</td>
<td>Kirchhoff Voltage Law</td>
</tr>
<tr>
<td>LITFSI</td>
<td>Lithium bis(trifluoromethanesulfonyl)imid</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile Butadiene Rubber (NBR)</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethyl-enedioxythiophene)</td>
</tr>
<tr>
<td>PEGM</td>
<td>Poly (ethylene glycol) methacrylate methyl ether</td>
</tr>
<tr>
<td>PEGDM</td>
<td>poly(ethylene glycol) dimethacrylate</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIBS</td>
<td>Poly(styrene-b-isobutylene-b-styrene)</td>
</tr>
<tr>
<td>SMA</td>
<td>Shape memory alloy</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid polymer electrolyte</td>
</tr>
<tr>
<td>SSR</td>
<td>State Space Representation</td>
</tr>
<tr>
<td>TBAPF$_6$</td>
<td>Tetrabutylammoniumhexafluorophosphate</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>tPA</td>
<td>Tissue plasminogen activator</td>
</tr>
</tbody>
</table>
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I am greatly indebted to my family, my wife and my parents for their immeasurable support, encouragement, patience and unconditional trust. They have always been my firmest support in my life.
Dedication

This thesis is proudly dedicated to

Dr. Majid Shahriari and Dr. Masoud Alimohammadi

این تز با افتخار تقدیم می‌گردد به سرداران رشید اسلام در عرصه علم و فن آوری

شهید دکتر مجید شهریاری و شهید دکتر مسعود علی محمدی
Chapter 1: Introduction and Overview

1.1 Objectives

Conducting polymers exhibit physical deformations in response to an applied voltage and reversibly expand and contract, similar to natural muscles. Low operating voltage, moderate strain, high force, controllability, ease of fabrication and low cost are attractive properties of conducting polymer actuators. Applications of conducting polymers in actuation of micro pumps [1], [2], miniature grippers [3], micromanipulators [4], active catheters [5], [6], active optical components [7], mechanical sensors [8], [9], gas sensors [10] biosensors [11], and energy storage devices such as batteries and supercapacitors [12], [13] have been investigated. Furthermore biocompatibility as a specific property of these materials makes them potentially suitable to employ in biomedical applications [14], [15].

In this thesis, two applications of conducting polymer in catheter application and tactile interfaces are presented. Modeling, synthesis and characterization of the polypyrrole linear actuators as conducting polymer-based actuators are described. Trilayer actuators for application in catheters and tactile interfaces are investigated and modeling, fabrication processes, finite element simulation and some experimental results are discussed.

Finally, the contribution of the thesis and achievements are presented in the conclusions.

1.2 Mechanism of Actuation

Conducting polymers are electronically and ionically conductive materials often containing positive charge carriers and charge balancing ions (known as dopants), and have a high and reversible capacity for ion storage. The mechanism of actuation of the conducting polymers is
based on insertion and removal of ions. When a positive/negative voltage is applied to conducting polymer electrodes, electrons leave/enter from/to the polymer electrode and ions are attracted/expelled to/from porous structure of polymer to balance the electrical charge and polymer is expanded/contracted. This inclusion and exclusion of ions can create expansion and contraction and make this polymer suitable to use in freestanding linear actuators or bilayer and trilayer bending actuators. Conducting polymer electrodes act electrically like capacitors and position is held steady with fixed voltage and negligible current. Figure 1.1 shows the mechanism of actuation of a trilayer structure which is made of two conducting polymer (CP) layers at top and bottom and a solid polymer electrolyte or ionically conductive separator in between. This flux results in one side of actuator expanding (anion insertion) while the other side is contracting (anion expulsion). In this case, the aqueous solution has salt (NaPF$_6$) with mobile negative ions (PF$_6^-$) within the conducting polymer.

Figure 1.1 Conducting Polymer trilayer actuator with two CP layers at the top and bottom and ionically conductive separator in between before (a) and after (b) actuation.
1.3 Biomedical Application

Minimally invasive diagnosis, therapy and catheterization are increasingly used by physicians and surgeons. Presently, 40% of surgeries are performed by minimally invasive procedure and it is growing rapidly [16]. Catheters are extensively employed in a wide range of medical procedures such as angiography, intravascular ultrasound, coiling of cerebral aneurysms, stent deployment and treatment of thromboembolic diseases. Navigation of the catheters is performed using guide wires that are manipulated from outside of the body using a combination of pushing, pulling and torque. Catheters then slide over the wires to reach the area of interest to the surgeon. Some disadvantages of this traditional technique including the limitations on its use in narrow and complex passages (such as in the brain), motivate us to propose a conducting polymer controllable micro active catheter. This is to be inserted into narrow cerebral blood vessels in the brain to enable navigation with precision and – at least in the final tortuous stages of navigation – without guide wires. Previous work has shown that some degree of bending can be achieved [15] by applying polypyrrole to commercial catheters and performing actuation in an electrolyte. In this work an aim is to achieve the degree of bending specified by the medical collaborator (Victor Yang, St. Michael’s Hospital), and eliminate the need to run currents through a surrounding electrolyte (such as blood). Follow on work is needed to optimize the design and demonstrate the active catheters in vivo.

1.3.1 Problem Statement for Biomedical Application

Acute Ischemic Stroke (AIS) is the most common type of stroke (about 88 percent of all strokes), is the third leading cause of mortality and is the leading cause of chronic, serious and long-term disability in the western world [17]. There are a number of reasons for AIS, but the narrowing of
the arteries in the neck or head because of a clot, is the most common cause. Reperfusion or opening the blocked arteries has to be done as a goal of treatment as quickly as possible. Tissue plasminogen activator (tPA) is the most commonly used drug to breakdown or dissolve blood clots [18].

Using tPA in treating AIS is only effective for patients if applied within 4-5 hours of stroke symptom onset [3]. Rate of restoration of the lumen of an occluded blood vessel (i.e. recanalization rate) remains at 60% for large-vessel arterial occlusions with tPA. After 4 hours of stroke the tPA is not effective and the experimental data showed just 8% of patient with severe stroke had significant improvement with tPA [19]. Due to some limitations of tPA such as short time to use and recanalization rate, other techniques such as mechanical thrombus removal are used in selected cases to improve recanalization rate and increase treatment options for patients [17]. An ultimate aim of this project is to demonstrate the feasibility of creating a controllable catheter for assisting catheter insertion for mechanical thrombus removal, or direct delivery of clot melting substance. Another motivation of the project is to enable treatment of cerebral aneurysms via improved insertion of coils. An aneurysm is a weakened area in the walls of blood vessels in the brain where the pressure of blood creates a balloon-like bulge and where rupture can take place. 3 to 5% of all new strokes are because of ruptured aneurysms and it is fatal for about 40% of cases. 66% of persons who survive suffer a permanent neurological deficit [20]. As a common alternative to surgery, neurosurgeons insert a platinum wire into the aneurysm and a clot is created inside the aneurysm, effectively eliminating it. In the current method of treatment neurosurgeons need to reach to the aneurysm neck with a catheter and then insert the platinum wire. Poor control via guidewires inside the tortuous passages in the brain makes it a difficult and time consuming
procedure and the risk of blood vessel wall damage is significant. The aim of this project is to improve catheter positioning in order to make the treatment of aneurysms faster and easier. Currently catheters are used to guide a therapeutic device to some part of the body such as coronary arteries, but navigation of the catheter is more difficult in cerebral arteries, and thus neurovascular catheter use is much more limited. The presence of only a very thin muscular media layer, lack of surrounding tissue support, absence of external elastic lamina, greater fragility and tortuous and tapered passages make cerebral arteries hard to navigate. To pass through narrow cerebral vessels with precision, minimize damage and reduce catheterization time, increase the controllability, efficiency and decrease the cost of this type of mechanical therapy, it is proposed to construct a novel controllable miniaturized micro catheter, which is active and maneuverable instead of using low controllable guidewire. Contributions of this work are mathematical derivation and modeling, simulation, design, optimization and fabrication of the tubular actuator to use in active catheter.

1.3.2 Specification of the Actuator

Catheterization and catheter-based procedures enable doctors to reach via blood vessels a specific part of the body which needs diagnosis and treatment. The conventional method of positioning a catheter is by first using a guide wire, with the catheter sliding over the guide wire to reach the treatment location once the guide wire is in place. Guide wires are controlled by pushing, pulling and twisting from the outside of the body. When the guide wire reaches to target site, the tubular catheter is inserted over the guide wire. The guide wire is then pulled out and leaves the catheter to provide a working channel for medical microdevices, which can be inserted into the catheter. Operations using guide wires and catheters need a high level of skill, especially in narrow and tortuous blood vessels with complex configurations [21]. There are some limitations in current
guide wire and catheter designs such as long procedural times, and risk of lumen or vessel wall damage because of inexact guidance [22].

The proposed device has two main parts. The first long part is passive and the second short part is the active section. The active part consists of a tip and neck as shown in Figure 1.2. The surgeon is to insert entire catheter into the body from the groin (Femoral Artery) and use the active part to guide the motion to reach to the target point in the brain. The neck is designed to have a large radius of curvature (around 20-30 mm) and the tip is to have small radius of curvature (10 mm ideally) to move inside the tortuous path in the brain. The active portion has one or two degrees of freedom.

![Diagram](image)

Figure 1.2 Total shape of the device. Passive and active part (top), Tip and Neck (middle), Actuation of the Tip (bottom).
Based on current devices and consulting with our collaborating neurosurgeon, specifications of the proposed active catheter for the tip have been devised, as presented in Table 1.1.

Table 1.1 Specifications for the proposed active catheter.

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>0.5-0.7 mm</td>
</tr>
<tr>
<td>Lumen Diameter</td>
<td>0.3-0.4 mm</td>
</tr>
<tr>
<td>Radius of Curvature</td>
<td>±10 mm</td>
</tr>
<tr>
<td>Current Leakage</td>
<td>&lt; 10μA [45]</td>
</tr>
<tr>
<td>Cycles</td>
<td>1000</td>
</tr>
<tr>
<td>Response Time</td>
<td>&lt;20 s</td>
</tr>
<tr>
<td>Material Compatibility</td>
<td>Biocompatible</td>
</tr>
</tbody>
</table>

This device is intended to be disposable making its lifetime relatively short. More details on these specifications and how they will be met are provided in this thesis.

1.3.3 Actuator Selection

To increase the efficiency and performance during minimally invasive medical procedures, advanced active catheter designs with more controllability are required. One option is to activate the tip of the catheter with some smart materials and control the catheter motion without using guide wire. Some smart materials have been previously used to make catheters active. Table 1.2 shows the advantages and disadvantages of the active materials employed to date.

In this thesis, it is proposed to use conducting polymer actuators to actively deform a catheter [5], [23]. Previous works show that by deposition a thin layer of polypyrrole on commercial catheter we can reach a 10 mm radius of curvature in 30 seconds with 4% strain [17]. A challenge with polypyrrole is the need for transfer of ions in order to actuate. The other problem is the radius of
curvature which is sometimes limited when using commercial catheters due to their high stiffness in bending. In this specific application, surgeons need a smaller radius of curvature as stated in Table 1.1. There are some proposed methods to solve these problems that are outlined in the next section.

<table>
<thead>
<tr>
<th>Actuator</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Polymer Metal Composite (IPMC) [28]–[32]</td>
<td>- Low voltage (&lt;10 V).  - Moderate strain (0.5-3.3%).</td>
<td>- Low coupling and efficiency.  - Consumes energy in holding a position.  - Requires encapsulation.  - Expensive.</td>
</tr>
<tr>
<td>Piezoelectric Material [33]</td>
<td>- Fast response (~kHz).  - Fine controllable positioning.  - Low current.  - Good coupling.</td>
<td>- Low strain (0.1%) so needs very large mechanical amplification.  - High voltage (100-1000 V).  - Rigid.</td>
</tr>
<tr>
<td>Conducting Polymer [4], [5], [23], [34]–[37]</td>
<td>- High stress (5-120 MPa).  - Moderate to large strain (2-6% typical).  - Low voltage (&lt;2 V).  - High work density (100 kJ/m³).  - Moderate stiffness (0.2-1 GPa).  - Low energy required for holding it in place (catch state).  - Inexpensive and facile fabrication</td>
<td>- Low electrochemical coupling.  - Slow (seconds).  - Needs encapsulation.</td>
</tr>
</tbody>
</table>

1.3.4 The Approach

In this section, it is proposed to use of a multilayer structure to satisfy the required specifications. Each layer of this structure does a specific job. As a catheter body, it is proposed to use ionically conductive material that can play the role of transferring the ions from one conducting polymer to the other, as necessary for actuation. The catheter body has the required mechanical properties
including low stiffness (enabling tight bending) and good toughness (preventing breakage). This tubular substrate is coated with a thin layer of conducting polymer to make it active, as depicted in Figure 1.3. An encapsulation layer keeps currents confined to the device and is intended to eliminate ion and solvent exchange with the blood.

This layered structure can create the bendable tip of a catheter as shown in Figure 1.4. The tip of the active catheter can actuate in one or two planes (as shown in Figure 1.4 gray silhouettes) when voltage is applied between patterned strips of polypyrrole (black), and through the ionically conductive catheter (orange in Figure 1.4).

![Figure 1.3 Cross Section of Encapsulated Catheter Design, a) four-electrode configuration b) two-electrode configuration.](image1)

![Figure 1.4 Active Catheter tip in a) two planes and b) one plane.](image2)
**Active Layer:** Conducting polymer actuator technology is one of several emerging ‘artificial muscle’ technologies [23]. Using conducting polymer in bending catheters was first proposed by Mazzoldi and de Rossi in 2000 [37].

Despite limitations in the lifetime of conducting polymer actuators, thousands of cycles are sufficient to satisfy the needs of disposable catheters. Recent work by Vidal *et al.* has shown that over 3.5 million cycles [38] can be obtained in PEDOT-based structure, which is more than enough for one-time use catheter. Conducting polymer-based actuators need only low voltages (< 3 V typically) to drive them, which eases acceptance of the technology [39], compared to higher voltage actuator technology. For the size of device I propose, the peak current reaches the milliamp range (< 60 mA) and must be isolated from brain tissue. The maximum allowed current is 50 μA [40] in the brain.

According to the geometry of the device and the required specifications, my simulation shows that to respond faster than 20 seconds, RC time should be less than 20 seconds and this value sets an upper bound on the total resistance of the conducting polymer layer. RC time is used to estimate rate since the conducting polymer itself is known to act as a capacitor, whose charging rate is limited by electronic and ionic resistances.

By increasing the conductivity or decreasing the resistance - especially electrical resistance -, RC time decreases. Because of the high aspect ratio of the device (Length/Thickness) the electrical conductivity has a strong effect on actuation time as the distance for electrons movement is much higher than the ions, even when scaled by effective diffusion coefficient.

**Body/Ionically Conductive layer:** To achieve to quick actuation, the ionically conductive catheter that is used as an electrolyte layer must have a high ionic conductivity. This property enables fast transfer of charge and decrease the actuation time. In order to support the conducting
polymer actuators and avoid buckling during insertion, the entire structure must be stiff enough to avoid buckling during insertion and bending induced by flow, have a high ionic conductivity and its Young’s modulus should be low to enable bending. There is a trade-off between stiffness, flexibility and conductivity. A suitable magnitude of toughness is also needed to ensure that the catheter body will not fail mechanically and be left behind in the arterial system. A promising choice is a swellable material, swelling with highly conductive liquid electrolyte (enabling high ionic conductivity and low bending stiffness), providing such a material can be found that is also tough and that the overall structure is stiff enough. Double network polymer also known as interpenetrating polymer networks (IPN) are one of the candidate materials for use in our application. In this type of material, it is possible to change or control the mechanical properties and also ionic conductivity by mixing and interpenetrating two or more different polymers to reach to our desired properties.

**Encapsulation Layer:** The device needs an encapsulation layer that is able to prevent ions and current passage without adverse effects on bending and flexibility. This must also be low in friction to facilitate device motion on its passage. There are some candidate materials for encapsulation. Parylene, polydimethylsiloxane (PDMS), Polyvinylidene fluoride (PVDF), Polytetrafluoroethylene (PTFE) and Poly(styrene-b-isobutylene-b-styrene) (SIBS) are biocompatible and good candidates to use as insulator [41]–[44]. Flexibility and mechanical stiffness, biocompatibility, thermal stability, dielectric properties, nonreactivity and chemical corrosion resistance are necessary requirements for insulator material that have to be investigated for these materials. This section has not been mentioned in this thesis and is one of the important future work that has to be considered.
1.3.5 Device Characteristics

The catheter is more than 1.5 meters in length including the passive and active parts. The passive part and all of the materials that are used in the active section should ideally be biocompatible (at a minimum on the exterior) and the active part is encapsulated to avoid the current leakage, exchange of ions and to ensure biocompatibility. The outer diameters of these two parts are different. The outer diameter of passive part is 1 mm and this value for active part is 0.5 to 0.7 mm.

After fabrication of the active part, it is connected to the long passive section and then the entire catheter is connected to a voltage supply. A battery provides the required power. A simple open loop position controller at the head of the passive part will control the active part by applying voltage to the conducting polymer electrodes and change the direction of motion by bending the multilayer actuators at the neck and the tip. During the insertion of the catheter into the body, the surgeons can use the X-Ray machine to see the situation of the catheter in the screen and continue the insertion to reach to the target point and use this visual feedback to control the device. The neck and the tip have to be detectible by the X-ray machine. The minimum required thickness of the gold to be detectible is around 100 nm [58]. Gold semi ring or sign at the end of the catheter should be added to make it detectible.

Design, mathematical derivation, simulation and fabrication process of the tubular actuator for use in active catheter are discussed in this thesis. Connecting the actuator to the commercial catheter, depositing gold ring and the electrical connections have not been covered in this these but have to be considered in future work.

The details of the design and fabrication are discussed in Chapter 4.
1.4 Tactile Interface Devices

The environment is experienced by the human five senses: sight, hearing, touch, taste and smell but the first two senses are more used in daily interaction and well understood by scientific observation. Recently, other senses are being sought to understand the detail of measurements. Touch sensing (taction) is one of the complex and interesting abilities of human skin, which is able to sense force, force position, softness, texture, shape, temperature, viscoelasticity and vibration [45]. The fingertip has greatest density of receptors and most of the tactile information is gathered through the interaction of fingertips with objects [16]. Although touch is experienced by the entire body and, some other regions of the skin are more sensitive, most of the touch-based (haptic) devices focus on the fingertip [46].

Making devices to interact with human skin, and especially the fingertip, to generate detectable displacement and force is of interest. In addition, devices with sensing ability are very useful for some applications especially in bioengineering and minimally invasive surgery and diagnosis [16]. Teletaction systems are made of three different elements including a touch sensor array, signal processing and conversion, and finally a tactile display. The information from the sensor array is transferred to the processing section and then tactile display actuates and changes the texture, stiffness, shape and other properties [16].

Conducting polymers have shown their ability to be employed as an actuator and sensor. Bilayer and trilayer actuators have been used to amplify the displacement of conducting polymer actuators since the inception of the field [47]–[49]. These structures have the advantage that they can be formed in a plane using a small number of microfabrication steps [50], [51], providing the potential for high scalability of manufacture, and allowing application as thin low voltage active layers on flat surfaces. For example, these may be of interest in tactile interfaces. However, a tactile display
must be able to provide enough force (minimum of 30 – 50 mN [52] for certain cases) to effectively stimulate the mechanoreceptors involved in the sense of touch. Previous work to create tactile feedback with conducting polymers has used long linear actuators [53] or proposed thick folded structures to drive the pins in Braille cells. These make use of the relatively high operating stresses (> 1 MPa) and stiffnesses (~ 300 - 800 MPa) of conducting polymer actuators [54], but require substantial device depth. In this thesis, trilayer actuators are considered for possible use in tactile interface devices. Mathematical derivations and finite element simulations have been performed to find the deflection of the trilayer actuator and also its generated force as a first step in an effort to determine the appropriate trilayer geometries for tactile feedback implementations.

The fabricated trilayers having a geometry similar to that shown in Figure 1.1, are made of interpenetrating polymer network (IPN) as a separator or solid polymer electrolyte and PEDOT as an active layer at the top and bottom of the separator. Effective parameters to achieve the higher generated force without scarifying the deflection have been obtained by modeling and simulation.

1.5 Mathematical Modeling

In this thesis, conducting polymer-based actuators ultimately intended for two different applications have been demonstrated. To enable effective prediction of the behaviour of this type of actuator we should model the charge transfer including the diffusion-like process associated with the incorporation and exclusion of ions. Numerous studies have been done to derive a mathematical models for this process and to model the actuation. The model followed in this thesis is an extension of work by Madden [55], who proposed an electrical circuit model or diffusive-elastic model to describe the charge accumulation in a film of polypyrrole (PPy). This model includes an RC transmission line circuit to model the diffusion resistance, solution resistance and the double layer capacitance at the interface of the polymer film and the solution in parallel with
the transmission line. The total admittance for this linear circuit model is solved in the frequency domain.

Shoa et al. have used this RC transmission line for their model to analyze ion diffusion through the thickness and added the electrical resistance along the length to model the electron transfer resistance, as presented a 2-D model[56]. Charge transfer starts from the electrical connection point and then spreads out to other parts of the polymer by charging the capacitances along the length and through the thickness. A constant value of resistance and capacitance is assumed for each element of the transmission line and the frequency dependent impedance of the 2-D circuit is derived. They also continued their study and found the total charge of the polymer structure as a function of position and time[57].

The polymer structure has been modeled with a simple resistor and capacitance in series and an extra resistor in parallel with the RC line acting as leakage, and the double layer capacitance has been ignored because of its very small time constant[58]. In addition, a different configuration has been proposed and the charge transfer resistance in parallel with double layer capacitance at the interface between PPy film and PVDF layer as a source of ions has been considered[59]. In this work, Nguyen et al. also have used the diffusive model to find the impedance associated with ion diffusion in the PPy film and put it in series with the double layer capacitance and charge transfer resistance. They have derived the total impedance of this model in the frequency domain. Warren and Madden have employed the finite difference method and simplified the RC transmission line to create a time domain model for the PPy layer. They also implemented a sigmoidal function for electrical conductivity as a function of oxidation state in their model, and used constant values for ionic conductivity and capacitance[60]. Khalili et al. used two dimensional transmission line
circuit model to find the total impedance of a trilayer sensor to relate applied voltage to current passing through the polymer structure [8].

By reviewing the previous studies, it is evident that all these models have capacitance, ionic resistance and electrical resistance as the main parameters. These parameters can reasonably explain the behaviour of the polymer structure during redox providing voltage ranges are not large or time scales are short compared to the diffusion time. The resistances and capacitances, however, are not constant during the oxidation and reduction of the polymer and they depend on the local charge [61]. This means that the electrical and ionic conductivity and capacitance of the PPy are functions of local charge or voltage. Changing oxidation or reduction state during the actuation causes a change in the local charge in the polymer, which leads to variation in conductivity and capacitance.

The dependence of electrical conductivity of PPy on the oxidation state has been observed and the experimental results show a sigmoidal behaviour for this dependency [61]. Based on this type of measurements, the electrical conductivity of PPy decreases with the applied voltage and drops dramatically in the negative voltage range [61],[62]. Capacitance of the polymer also changes with oxidation state, but the variation is within a small range, such that we can assume that the capacitance of the PPy film is approximately constant [39]. The ionic conductivity of PPy is another important parameter that plays a role in the actuation behaviour and that varies with oxidation state and the applied voltage[63].

To have an accurate prediction and modeling results consistent with the experiment developing a time variant model is the natural next step. This time domain model should be able to provide the linear or non-linear function for conductivity and capacitance vs. oxidation state or local charge. The issue that makes this modeling more complex than what has been done previously is
the fact that these parameters are functions of local charge and the properties of each lumped element changes with the charge that is passing through it.

The non-linearity of these functions limits the choice of modeling approaches of the polymer structure. One issue with the frequency domain modeling and simulation is that we cannot define and dynamically enter the specific functional relationships between oxidation state and conductivity or capacitance as this makes the system non-linear. Previously reported time domain models had issues as they do not provide the local charge for each spatial element and only yield the equivalent impedance or total charge vs. time [60]. These do not allow the consideration of the non-linearity of element inside the RC transmission line model.

In this thesis, a combination of transmission line modeling and a state space representation to find the charge for each lumped capacitance and resistance is proposed. The most important advantage of this approach is the ability to include a charge-dependent function for each element and update it by changing the oxidation state for all the elements through the thickness and along the length at each time step. Furthermore, by using this modeling approach we can obtain the relationship between the input voltage and output current or, for small signals, the equivalent impedance in the frequency domain.

In this thesis, an electrochemical model of conducting polymer layers that employ one and two dimensional transmission lines is presented. Conducting polymer films can be considered as a porous electrode in solution within an electrochemical cell. Electrical excitation of this electrode changes the equilibrium oxidation state of the polymer, leading to a transient movement of ions between the polymer chains. The insertion or removal causes charging of the polymer structure to balance the electric charge inside the polymer. Diffusion of ions can be modeled to derive the analytical model for simulating the behaviour of polypyrrole actuators. In modeling of porous
electrodes, specific behaviour has been modeled by electrical elements. The storage of ions between chains is modeled by capacitors ($C$), and the resistance to the movement of ions inside the chains and polymer network is modeled by ionic resistance ($R_i$). Also the resistance to the electronic transfer through the polymer structure is modeled by electrical resistance ($R_e$) and the accumulation of ions at the interface between the solution and the polymer is represented by a double layer capacitor ($C_{dl}$). Furthermore, the resistance to conduction of ions inside the solution between electrodes and electrical contact has been modeled by a resistor ($R_s$)[64]. In this modeling approach, the diffusion impedance ($Z_D$) consists of an RC transmission line of electrical and ionic resistances and the volumetric capacitance of the polymer. The double layer capacitor is in parallel with this impedance as shown in Figure 1.5.

In some studies [65], [66] a charge transfer resistance ($R_{CT}$) has been added in series with the diffusion impedance as depicted in Figure 1.5 (b). The diffusion impedance of the polymer structure, has been simulated using a Warburg impedance and transmission line have been employed in several investigations. In this thesis, a transmission line to represent the impedance to ion migration across the thickness of the polymer film and charging of the polymer structure, as well as resistors, $R_e$, to account for losses due to electronic propagation along the length is used. My proposed configuration for 1-D model is depicted in Figure 1.6. When the conducting polymer is deposited on a conductive substrate, the electrical resistance along the length can be ignored and the 1-D circuit model can be used. When the thickness of the polymer is very small in comparison with the length, the electrical resistance versus the ionic resistance is negligible and can be removed. The transmission line for the thin layer of conducting polymer on conductive substrate contains the volumetric capacitance and ionic resistance. In conducting polymers on a non-
conductive substrate, the electrical resistance along the length is significant and should be considered. Figure 1.7 shows the schematic of the 2-D configuration of the equivalent circuit.

![Equivalent circuit model for polypyrrole electrode.](image)

Figure 1.5 Equivalent circuit model for polypyrrole electrode. a) without charge transfer resistance b) with charge transfer resistance. $V$ represents the external voltage source.

The electrical conductivity of conducting polymer is several orders of magnitude larger than ionic conductivity (electrical conductivity is approximately $8 \times 10^3 \, S/m$ and ionic conductivity is approximately $2 \times 10^{-3} \, S/m$ for polypyrrole [67]). In this modeling, I assume that the ions are inserted through the thickness only and there is negligible ion transfer or movement along the length and this means that ionic resistance has not been taken into account along the length.

![1-D transmission line circuit model](image)

Figure 1.6 1-D transmission line circuit model for conducting polymer film on a conductive substrate through the thickness.

Modeling in previous studies has some limitations. Using a constant value for ionic and electrical conductivity and the inability to define these conductivities as functions of oxidation state is the
main limitation. To overcome this issue, lumped elements with individual specifications as a function of oxidation state are employed, adding the ability to update the specifications of the element during the application of potential to the polymer.

As stated earlier, the properties of conducting polymers are voltage or charge dependent and some previous studies have shown these dependencies [61]. In the transmission line model, lumped parameters for each element and we have to define the dependency of these parameters on the local voltage or charge are used. To develop a suitable model of charge distribution for the polymer structure, these parameters should be able to change with charge or the oxidation state.

Using the transmission line circuit model instead of a Warburg impedance- a continuum model-enables us to find the charge distribution as a function of position inside the polymer structure. Another advantage of this approach is that we can include the non-linearity of the parameters in each element, which is not possible when using Warburg impedance. In Warburg impedance modeling, it is assumed that the entire polymer film is a single element with real and imaginary parts without considering the distribution of charge and current inside this lumped element, and we do not have any information about the charge vs. position inside the porous structure. In transmission line modeling, we are able to track the charge and discharge trends inside the structure, assign local resistance and capacitance values based on local charging, and understand and interpret the mechanism of actuation more accurately and realistically.
1.5.1 Frequency Domain Response

To determine the total impedance for 1-D and 2-D models, we can use the transmission line RC circuit method. This method employs the Laplace transform and obtains the total impedance in Laplace or frequency domain. This impedance generally is not amenable to conversion into the time domain. Shoa et al. have presented the equivalent impedance for 1-D and 2-D models and have observed good agreement between the analytical results and the experimental observations. In comparison with my proposed approach, their analytical derivation does not include the charge transfer model. They believe the non-pure capacitive behaviour of the polypyrrole in low frequencies is due to the leakage and they have added an additional resistance (leakage of charge) in parallel with the entire 2-D transmission line to match the simulation with the experiment and justify the deviation in low frequencies [67]. The frequency model is not invertible to the time
domain. Modeling in time domain is important however to have a good prediction of behaviour of the actuator, so a time domain modeling approach has been developed. Proposed model has the ability to convert the time domain model to the frequency domain in the case of small signal or in general constant values for conductivities and capacitance of the elements in transmission line model. It is able to produce the transfer function for the total impedance of the circuit model.

1.5.2 Time Domain Response

The ability to predict the behaviour of the actuator vs. time and to find the optimal parameter values with greater accuracy before fabrication is desired from any modeling technique. A time domain model allows one to improve the design and obtain optimal parameter values such as the thickness of the conducting polymer layer, substrate dimensions and the required electrical and ionic properties. As well, with an accurate time domain model, it should be possible to predict the actuation time of the device and determine the influence of every model parameter on the actuator performance and to validate further refinements of the device design.

Depending on the application of the actuator, this prediction will differ in importance. In high precision biomedical applications such as minimally invasive procedures, surgeons have to be able to predict the responsiveness of the actuator to avoid unexpected issues during the treatment. Conducting polymer-based actuators due to their interesting characteristics such as low operation voltage, relatively high strain and ease of fabrication are attractive in minimally invasive surgery [61] and possible for use in driving tactile displays. To have a satisfactory prediction of actuation response we should first identify the effective parameters. In conducting polymer-based actuators the electrical and ionic conductivity, volumetric capacitance, mechanical properties and especially the Young’s modulus are very important to identify. Many investigations have been conducted on identification of these parameters for conducting polymers. In this thesis, a non-linear time variant
model for this kind of actuators is presented. This modeling can be extended to other porous electrodes, batteries and super capacitors. For example, in a parallel effort, a non-linear approach to modeling of lithium ion cells is being developed in which capacitance and resistance are function of state of charge [68], [69].

The presented model is a combination of transmission line modeling and uses a state space representation. All of the components and layers in Figure 1.7 must be modeled to have an accurate simulation result. Simulations can reveal the relationship between the applied voltage and the charge stored in the conducting polymer layers and the RC charging time. By changing some specifications of the device in the experiments, such as the ionic or electrical conductivity, the model can be readily updated. The model is dynamic and ionic and electrical conductivity change as a function of local charge. This means that when running simulations for each step, the local charge states are the output of preceding step, enabling updating of the conductivities as a function of position in the current step. In this simulation, we can change the number of elements through the thickness and along the length to arrive at a more accurate response.

Details of the mathematical modeling and experimental verification for conducting polymer linear actuators are presented in Chapter 2 and for trilayer actuators in Chapter 3.

1.6 Thesis Overview

In Chapter 2 of this thesis, the details of the modeling approach are presented. First, the frequency domain modeling based on the diffusive elastic model is discussed and then, the details of the proposed non-linear time domain modeling are explained and justified. Then, the ability of the model to predict the electrical behaviour of a freestanding film of conducting polymer is shown. To validate the capability of the model to predict the mechanical behaviour and actuation, the non-linear model has been employed to track the linear actuation of the freestanding film under constant
load and the modeling result and experimental data are in good agreement. The result of the non-linear model in the time domain and its ability to incorporate the non-linear function for electrical and ionic conductivities is presented in this chapter.

To incorporate the non-linear functions for conductivity, electrical and ionic conductivity versus applied oxidation state have been measured and then incorporated into the model. Details of the experiments and also implementation of the model are discussed.

In Chapter 3, the non-linear model is extended to trilayer conducting polymer-based actuator to predict the electrical and mechanical behaviors. Electrical conductivity and Young’s modulus of PEDOT/IPN/PEDOT trilayer as a function of oxidation state were measured and included in the model. A mathematical derivation for radius of curvature as a function of geometry and the mechanical properties of the active layers and of the separator was derived for the trilayer configuration. This derivation is a generalized version of previous derivations, which do not account for asymmetries and position dependencies of mechanical properties in trilayers [70].

Radius of curvature as a function of position and time is predicted by model. Non-uniform bending along the length of a trilayer before steady state due to the non-uniform charge distribution along the length of actuator during operation was observed in experiments and explained via simulations. The non-linear simulation results showed good consistency with experimental results.

In Chapter 4, a self-contained tubular actuator for eventual use in catheter applications is presented. The mathematical derivation for the deformation of trilayer actuators with circular cross sections is derived and validated with finite element simulations. The design and fabrication process of the tubular actuator is explained. In this actuator, an interpenetrating polymer network has been employed as a solid polymer electrolyte and poly (3,4-ethylenedioxythiophene) (PEDOT) is employed as the active layer at the surface of a rod-shaped interpenetrating polymer network
(IPN). Laser micromachining and micro drilling have been used to pattern the electrodes around the IPN rod and hollow the IPN.

Trilayer actuators for potential use in tactile interfaces are investigated in Chapter 5 of this thesis. A mathematical derivation for maximum deflection and also maximum generated force is derived and validated by finite element simulation. One of the issue with conducting polymer-based actuator is their small generated force. Some methods including stacking approaches, strengthening of the base and change the geometry have been investigated and simulated in finite element software to find a way to increase generated force by cantilever trilayer actuator. The effect of an encapsulation layer is investigated by simulations for two different materials. In other simulations, maximum deflection and stress generated on a fingertip due to a trilayer actuation in contact with the fingertip are presented to demonstrate the feasibility of using conducting polymer-based actuator in tactile display.

Chapter 6 presents conclusions and the contributions of this work.
Chapter 2: Non-linear Two Dimensional Time Domain Modeling for Electrochemically Driven Conducting Polymer Actuators

2.1 Introduction

Conducting polymers change oxidation state under electrochemical control, resulting in color change [71], electrical conductivity variation [72], ionic conductivity change [63], [73], and displacement/actuation [23], [48], [51], [74]–[80]. Applications of conducting polymers in actuation of micro pumps [1], [2], miniature grippers [3], micromanipulators [4], active catheters [5], [6], active optical components [7], mechanical sensors [8], [9], gas sensors [10] biosensors [11], and energy storage devices such as batteries and supercapacitors [12], [13] have been investigated. In some specific applications, a control system is required to follow the desired input, thus creating a need for a mathematical model. Many attempts have been made to understand the details of operation of conducting polymers [47], [65], [81], [82] and to model their electrochemical, electromechanical and sensing responses [57], [59], [83]–[86]. However very little work has incorporated the non-linear electrochemical response. In this work, we explicitly include these non-linearities and show that they are important to consider under certain conditions. The electro-chemo-mechanical behaviour of polypyrrole and other conducting polymers is a combination of migration, diffusion, redox behaviour/capacitance and resistivity should be understood in order to obtain accurate and dynamic models to enable good predictions. Applying voltage to the polypyrrole (PPy) electrode generates a current through the electrolyte due to electrophoretic forces. Ionic charge accumulates at the interface between solution and polymer by electrophoretic force. The interface double layer capacitance, $C_{dl}$, is charged. The concentration difference and potential difference across this interface drives ion transport into or out of the
polymer until equilibrium is reached (Figure 2.1). Many models have been proposed for this charging process including Refs. [86]–[91].

In this chapter the mass transport in the polymer by an RC transmission line, represented by $Z_D$ in Figure 2.1 is described [55]. At the bottom of Figure 2.1 a two dimensional transmission line is depicted, where resistance to ion transport through the polymer thickness is described by elements, $R_i$, and the electronic resistance along the length is divided into elements, $R_e$. The local capacitance $C$, provides the storage produced by ions coupled to electronic carriers on the polymer backbone (typically bipolarons in polypyrrole [72]). In the work presented the ionic and electronic resistances are functions of charge state (the degree of charging of the capacitor). The capacitor can in general be made a function of oxidation state so that it can even represent classical Nerstian (non-interacting particle) or quasi-Nerstian behaviours as might be found in batteries for example. In this case the capacitance is treated as independent of oxidation state to mimic the experimentally observed capacitance in low temperature grown hexafluorophosphate polypyrrole [92].

Advantages of the transmission line approach are that the small signal/linear region can readily be modeled in the frequency domain, and, for our purposes in this thesis, the local variation in properties can readily be treated by using lumped elements whose properties are oxidation state dependent. The use of transmission lines to model conducting polymer electrochemistry is not new [89]. Recently there has been interest in using transmission line models to describe polypyrrole actuators. Shoa et al. for example used an RC transmission line to analyze the ion diffusion through the thickness. They also added the electrical resistance along the length for modeling the electron transfer resistance and finally presented the 2-D model similar to the one shown in [56]. Shoa found the total charge of the polymer structure as a function of position and time [57].
Figure 2.1 Conducting polymer charging progress immersed in the electrolyte with equivalent circuit. $Z_D$ is the diffusion impedance that has been modeled with transmission line, $C^+$ and $A^-$ are cations and anions respectively. a) Applied potential drives ions to migrate and accumulation of ions at the interface of polymer/electrolyte to form the double layer capacitance ($C_{dl}$). b) Charge is storing inside the polymer structure with volumetric capacitance ($C_V$).

Nguyen et al. also employed two dimensional transmission line models to find the impedance associated with ion diffusion in polypyrrole film and added it in series with the double layer capacitance and charge transfer resistance [59]. Khalili et al. used two dimensional transmission
line circuit model to find the total impedance of a trilayer sensor to relate applied voltage to current passing through the polymer structure [8]. These models do not incorporate the non-linear dependence of conductivities on oxidation state, which is the main goal of the current work.

Non-linear properties have been studied in one dimensional transmission lines. Xu, Shapiro and Smela have shown the importance of variations in ion transport rates with oxidation state using finite element models, showing that migration rather than diffusion determines transport rates [87] – as is also thought to be the case in hexafluorophosphate doped polypyrrole [93]. Warren and Madden employed the finite difference method and simplified one dimensional RC transmission line to find the time domain model for the PPy layer. A sigmoidal function for electrical conductivity as a function of oxidation state was used, which showed that for large changes in conductivity with oxidation state Nernstian like cyclic voltammograms are expected from purely capacitive systems [60]. This model treats the transport through the thickness of the polymer with one RC time constant, which is a valid assumption providing the RC time constant for the system is determined by the electronic resistance. Here we explore the situation where both ionic and electronic resistances are relevant, and also include solution resistance effects.

Conducting polymer electronic conductivity varies with doping level [60], [61], [72]. There can be a substantial drop in conductivity as the neutral state is approached, which can in turn limit charging rate, particularly for long samples. Decreased ionic conductivity – that can also be observed as the neutral state is approached and ions are expelled [93] – also can significantly reduce charging rate. These oxidation state dependent effects can lead to several orders of magnitude reduction in conductivity [94], [95] which should be considered in the models. In order to account for the effect of oxidation state, Fang et al. proposed a redox level-dependent impedance model for conjugated polymers based on Nernst-Planck non-linear partial differential equation.
They extended diffusive-elastic-metal model and used perturbation techniques to linearize the equation in Laplace domain. Their model is able to incorporate polymer oxidation state, ion diffusion and migration to find the effect of oxidation state on the impedance spectrum [96]. This model is useful for predicting the small signal response (small changes in voltage).

In this thesis, a time-domain model is proposed that accounts for variations in conductivity with oxidation state. Furthermore, it allows for variation in oxidation state as a function of position within the electrodes. Elastic modulus and strain to charge ratio [59], [97]–[100] also change during operation and vary with applied voltage. These aspects are not treated in the work here. The model we are developing can be expanded to cover such effects once they are quantified.

A mathematical model in the time domain is employed that uses a state-space representation to solve a transmission line model. Each model step solves the response to small charging increments and in small time steps. In this way the evaluation of the system in response to large degrees of charging and changes in voltage can be estimated.

The most important advantage of the approach is its ability to implement oxidation state dependent conductivity, with the oxidation state being position dependent. The non-linear conductivity of PPy as a function of oxidation state was measured and incorporated into the non-linear time variant model. The oxidation state of each element is tracked and the property variation determined after each step for all the elements through the thickness and along the length.

In this work the semi-empirical physical view is that:

- The capacitance of the polymer structure is assumed to be constant and not changing with oxidation state. This assumption has been shown to be reasonable when using hexafluorophosphate doped polypyrrole [92], [39]. If the capacitance as a function of...
oxidation state changes significantly, then this assumption can be relaxed, and the capacitance can be made oxidation state dependent also.

- The properties are purely charge state dependent. The model does not account for any history and time dependent behaviour.

- After applying voltage, the charge state of the double layer at the interface of the polymer film and solution is changed which drives ion transport into or out of the polymer until equilibrium is reached.

- Ion transport within the polymer electrode is assumed to be described by an RC transmission line, which in the continuum limit is described by the diffusion equation. This transport may in fact be determined by a combination of local charge storage and finite ionic conductivity rather than concentration gradients [60], [93], [95].

- The electrical conductivity of the conducting polymer is a non-linear function of oxidation state.

- Ionic conductivity or diffusion coefficient is a non-linear function of redox level.

- The local strain is proportional to the charge density via an empirically estimated and constant strain to charge ratio.

- Elastic modulus is assumed to be real and constant.

- Charging and actuation of the conducting polymer are functions of local charge density, and thus vary as a function of position within the electrode.

The final step in the validation of the model is to show that the physical deformation of a polypyrrole actuator as a function of position is predicted by the non-linear transmission line simulation.
2.2 Frequency Domain Model

To determine the total impedance for 1-D and 2-D models, we can use the transmission line RC circuit method (Figure 2.2). This method employs the Laplace transform and obtains the total impedance in Laplace or frequency domain. This impedance is very complex to convert into the time domain. Shoa et al. have presented the equivalent impedance for 1-D and 2-D models and have observed good agreement between the analytical results and the experimental observations. In comparison with my proposed approach, their analytical derivation does not include the charge transfer model. They believe the non-pure capacitive behaviour of the polypyrrole in low frequencies is due to the leakage and they have added an additional resistance (leakage of charge) in parallel with the entire 2-D transmission line to match the simulation with the experiment and justify the deviation in low frequencies[67]. The frequency model is not invertible to time domain. We need the modeling in time domain to have a good prediction of behaviour of the actuator, so we have developed a time domain modeling approach. My proposed model has the ability to convert the time domain model to frequency domain when we assume constant values for conductivities and capacitance of the elements in transmission line model. It is able to produce the transfer function for the total impedance of the circuit model.

The storage of ions in the polymer structure is modeled by capacitors (C), while resistance to electronic transfer is modeled by spatially distributed resistors (R_e) and the resistance to the movement of ions inside the polymer network is modeled by ionic resistance (R_i). R_i and R_e are functions of the charge state, with this function estimated through measurements. The accumulation of ions at the interface between the polymer and solution is described by a double layer capacitor (C_d). The resistance to conduction of ions inside the solution between electrodes and electrical contact is modeled by a resistor (R_s) [64]. The total solution resistance is the given
by the parallel summation of the resistors, $R_s$, with a number $m$ resistors resulting in a resistance of $R_s/m$. This representation is valid only if the reference or counter electrode is much closer to the working electrode than the total length of the electrode.

![Diagram](image)

Figure 2.2 Transmission line Circuit Model for conducting polymer in ionic solution a) 1-D model for polymer film on conductive substrate b) 2-D model for freestanding film of polypyrrole of finite electronic conductivity.

### 2.2.1 Diffusive Elastic Model

Frequency domain modeling of conducting polymer actuators has been looked at extensively [55], [70]. Here the derivation of one such model - the diffusive elastic model - is reviewed. It is also shown that it can predict short and long time responses. However, it is not able to predict responses at intermediate times, as the model cannot readily be inverted to the time domain.
In DEM model, we assume that the electrons move along the length, ions only move in perpendicular direction through the thickness and the electrical resistance through the thickness in comparison with ionic resistance is negligible. In this model, we have just electrical resistance along the length and ionic resistance through the thickness to model the resistivity of the polymer to the movement against movement of electrons and ions. In the DEM modeling approach an RC transmission line has been used to model the diffusion of ions through the thickness and simple resistance to model the electrical resistivity of the polymer film along the length. The details of the derivation have been mentioned in Appendix A.

The total electronic resistance of the polymer with $h$ as a thickness, $w$ as a width and $\sigma_e$ as an electronic conductivity, against electron flow is purely resistive [101] and equal to:

$$Z_{e\text{total}} = \frac{L}{\sigma_e w h}. \quad (2-1)$$

The admittance of the polymer strip on ionic side is more complex. It includes the diffusion of ions into polymer structure, charging of double layer capacitor at the interface between polymer and solution and charge transfer through the electrolyte by ions. The expression of total admittance of the strip has been derived by Madden [55]:

$$Y_{l\text{total}}(s) = \frac{s}{R_s \sqrt{D} \frac{\sqrt{s}}{\delta} \tanh\left(\frac{h}{\sqrt{2} \sqrt{D}}\right) + \sqrt{s} \left(\frac{3}{\sqrt{2}} + \frac{3}{\sqrt{s}} + \frac{3}{\sqrt{s}} \tanh\left(\frac{h}{\sqrt{2} \sqrt{D}}\right)\right)}. \quad (2-2)$$

where $D$ is the diffusion coefficient of the polymer, $R_s$ is the solution resistance, $h$ is the polymer thickness, $\delta$ is the thickness of double layer capacitor and $s$ is the Laplace variable, give by the square root of -1 times the angular frequency.

Now we are able to find the voltage and current as a function of frequency and position. Here we obtained the voltage and current in the limits of high and low frequency for the strip of polymer.
At high frequency or very short time after applying the voltage to the one end of the polymer strip, the voltage as a function of position can be obtained. When the frequency goes to infinity
\[ Z_{e,\text{total}}(s \to \infty) = R_{e,\text{total}} \quad \text{and} \quad Y_{i,\text{total}}(s \to \infty) = \frac{1}{R_s}. \]

and for current and voltage we have:
\[
i_e(x) = I_0 \frac{\sinh(k(L-x))}{\sinh(kL)}, \quad (2-3)
\]
\[
V_e(x) = V_0 \frac{\cosh(k(L-x))}{\cosh(kL)}. \quad (2-4)
\]

At high frequency, the double layer capacitance and polymer capacitance have very low impedance, they are effectively shorted and the polymer has purely resistive behaviour. (2-3) and (2-4) show the current and voltage as a function of position. For \( x = 0 \):
\[
i_e(0, s \to \infty) = I_0, \quad (2-5)
\]
\[
V_e(0, s \to \infty) = V_0, \quad (2-6)
\]
and for \( x = L \):
\[
i_e(L, s \to \infty) = 0, \quad (2-7)
\]
\[
V_e(L, s \to \infty) = \frac{V_0}{\cosh(kL)}. \quad (2-8)
\]

By increasing the electrical resistance of the polymer, voltage at the other end will be smaller versus applied voltage.

At low frequency or long time \( (s \to 0) \), the admittance of the polymer in DEM model is purely capacitive and can be simplified as follows:
\[
Y_{i,\text{total}}(s) = sC \left( \frac{a}{2\delta} + 1 \right). \quad (2-9)
\]

For the current and voltage, we have:
\[ I_e(x, s \to 0) = 0, \quad (2-10) \]
\[ V_e(x, s \to 0) = V_0. \quad (2-11) \]

Equations (2-10) and (2-11) show that in long time after applying the voltage at one end, voltage at the other end reaches to applied voltage and there is no current passing through the polymer then the entire polymer has uniform voltage in long time and polymer strip becomes fully charged.

The above discussion and derivations provide the short and long time voltage distributions along the length of the polymer. The time domain modeling that is now discussed has the advantage of providing voltage and current distributions at all times.

### 2.3 Time Domain Modelling

When a voltage is applied to one end of the PPy film immersed in a solution with mobile ions, it starts to charge from the point of applied voltage at the solution/film interface. The charge then propagates to the whole polymer with time. This propagation of charge is depicted in Figure 2.3a at a certain time after the application of a voltage step at the top right hand corner. In this case, the right hand side of the film is in contact with the electrolyte, and the left hand side is not. There is a gradient in charge density through the thickness resulting from the finite ion transport rate, as is evident from the color bars. There is also some difference along the length due to electronic voltage drop from the finite electronic resistance.
Figure 2.3 Mechanism of actuation of PPy-based actuators a) Schematic of charge percentage vs. position in PPy film after application of voltage at top right hand corner. b) Expansion/contraction due to inclusion/exclusion of negative mobile ions.

Based on the mechanism of actuation of conducting polymer-based actuators, strain induced by polypyrrole is a function of charge density and position. By propagation of charge and insertion/expulsion of ions into the polymer structure, strain is induced and the polymer expands/contracts. Application of a positive voltage to a polymer, oxidizes the polymer backbone. Mobile anions penetrate the polymer structure to maintain charge neutrality, causing an expansion of the polymer structure. Application of a negative potential has the opposite effect of reducing the polymer backbone, absorbed anions are expelled from the polymer structure, and causing polymer contraction (Figure 2.3b). Since the charge along the length is not the same at all points, the strain is a function of position. We assume that each small element of the polymer has its own capacitance, and the charge of each element determines the free strain for that specific position.
An accurate model of the charging and actuation should be able to describe the dependency on time and position simultaneously. Previous transmission line models were able to find the voltage, current and charge as a function of frequency and position through the thickness [99] and in both thickness and length [57].

In the diffusive elastic model (DEM), an RC transmission line has been used to model the transport of ions through the thickness and a simple resistance to model the electrical resistivity of the polymer film along the length. Total impedance of the strip in 2D has been derived in the DEM model [57], [15]. By using the diffusive elastic model, it is possible to obtain voltage and current for the strip of polymer in the frequency domain. Converting the expression for voltage and current from the frequency domain to the time domain is not possible without substantial approximations. As the DEM model is solved in the frequency domain it cannot implement the non-linearity of parameters such as ionic and electronic conductivity.

In this work, the same transmission line circuit representation as the 2D-DEM model is solved in the time domain. One advantage of my time domain modeling approach is the ability to find current and voltage versus time without approximations and complex mathematics. Another big advantage is the capability to implement the non-linearity of conductivity, capacitance and Young’s modulus.

To predict the charging and actuation behaviour as a function of time, we need to develop the time domain model. We know that the conductivities are a function of local charge/oxidation state and as mentioned the charge in polymer is a function of position. These effects are captured in a previous model of two dimensional transport [57], but here we show how to extract local charge state in two dimensions. Furthermore, the accurate model should have the capability to find the
local charge as a function of position and time with ability to capture the nonlinearity of conductivity, which is the unique contribution of the present work.

We report the time domain modeling approach using a state space representation to implement a transmission line model (Figure 2.2). The charge of all branches of the transmission lines are defined as a state vector. Charge for all capacitors and current passing through the resistors is obtained as outputs. The important advantage of this approach is ability to define the electrical conductivity, ionic conductivity, capacitance and Young’s modulus of the polymer film as a function of oxidation state, as represented by local charge density. For example, the electronic conductivity of the polymer is a function of oxidation state and the modeling approach presented here can capture the non-linear behaviour. Distribution of the charge along the length and through the thickness and charge time constant of the film can be determined by this model. In this method, we can track the movement of ions through the thickness by tracking the charge stored in an array of capacitors. In addition, the movement of electronic charges can be tracked from the voltage drop along the length to reach to a fully charged state.

In the implementation presented here it is assumed that the volumetric capacitance is not a function of oxidation state [39], though such a dependence can readily be added. We used the circuits shown in Figure 2.2 to model the behaviour of the freestanding polymer film on conductive and nonconductive substrates in ionic solution, as is now described. Two models are investigated, one accounting for ion transfer through the thickness of the polymer (Figure 2.2a), and the second accounting also for electronic voltage drop along the length of the film (Figure 2.2b). These correspond to one dimensional (1D) and two dimensional (2D) transmission line models.
2.3.1 State Space Representation

In the State Space Representation (SSR) a vector of state or state variables \( x \) is created, which is the smallest possible vector that can show the state of the system at any given time. In this method, the physical system is described by four matrices \( (A, B, C, D) \) and these matrices define the relationship between the state variables and the input and output of the system. Equation (2-12) shows the general form of these matrices and the SSR:

\[
\dot{x} = Ax + Bu \\
y = Cx + Du,
\]

(2-12)

where \( x \) is the state variables or state vector, \( u \) is the input and \( y \) is the output of the system.

Here we use the Kirchhoff's Voltage Law (KVL) to write the differential equations of the circuit and then utilize the state space representation to derive the closed form configuration. State space representation can help us to solve the differential equations in the time domain and have all of the state variables at any given time. To introduce my method, we can start with a simple RC circuit as shown in Figure 2.4.

![Figure 2.4 A simple RC circuit](image)

First, we assign current to each individual line and then we write the Kirchoff Voltage Law (KVL) for each closed loop. By applying the KVL, we have four independent equations and this is a sufficient number of simultaneous equations as we have four state variables as well.
\[
\frac{1}{C_4}q_4 + R_4\dot{q}_1 = V \\
\frac{1}{C_1}(q_1 - q_2) + R_1(\dot{q}_1 - \dot{q}_2) - \frac{1}{C_2}(q_2 - q_3) = 0 \\
\frac{1}{C_2}(q_2 - q_3) + R_2(\dot{q}_1 - \dot{q}_3) - \frac{1}{C_3}(q_3 - q_4) = 0 \\
\frac{1}{C_3}(q_3 - q_4) + R_3(\dot{q}_1 - \dot{q}_4) - \frac{1}{C_4}q_4 = 0,
\]

Where \( q_i \) represents the integral of the current, \( i \).

These equations are cast in matrix form as in equation (2-17):

\[
\alpha[\dot{q}] + \beta[q] = [\gamma]V
\]

where:

\[
\alpha = \begin{bmatrix} R_4 & 0 & 0 & 0 \\
R_1 & -R_2 & 0 & 0 \\
R_2 & 0 & -R_3 & 0 \\
R_3 & 0 & 0 & -R_3 \end{bmatrix}, \quad \beta = \begin{bmatrix} 0 & 0 & 0 & \frac{1}{C_4} \\
\frac{1}{C_1} & -\frac{1}{C_1} & -\frac{1}{C_2} & \frac{1}{C_2} \frac{1}{C_3} & 0 \\
0 & \frac{1}{C_2} & -\frac{1}{C_2} & -\frac{1}{C_3} & \frac{1}{C_3} \frac{1}{C_4} \\
0 & 0 & \frac{1}{C_3} & -\frac{1}{C_3} & -\frac{1}{C_4} \end{bmatrix}
\]

\( [\gamma] = [1] \) and \( [\gamma] = [0] \)

My selected state variables that completely represent the model circuit at any given time are \([q_1 \ q_2 \ q_3 \ q_4]\) and we are able to find the charge for each capacitor and current in each resistor when we know the magnitude of this vector. In the next step, we convert the equation (2-17) into the standard form in state space representation (given by equation (2-12)).

\[
[\dot{q}] = A[q] + Bu \quad \text{where} \quad A = \alpha^{-1}\beta \quad \text{and} \quad B = \alpha^{-1}\gamma
\]

By defining the suitable output matrix \((C)\), we can have our desired output. For instance, the charge for \( c_1 \) is \( q_1 - q_2 \) and the current passed through \( R_2 \) is \( \dot{q}_1 - \dot{q}_3 \) and so on.

When we write KVL for a larger circuit, we can see the trend on how to acquire matrices \( \alpha, \beta \) and \( \gamma \) and convert their relationship to the standard form. We pursue this approach for the 2-D circuit with a large number of elements. In case of m branches along the length and n elements
along the thickness, Matrices $A$ and $B$ have $m \times n$ elements. Matlab has a command that enable to the definition of the input signal ($u$) and the solution of the state space system regarding to our defined output matrix ($C$). lsim code in Matlab is the specific code to solve a linear time invariant state space system.

2.3.2 Solution Mechanism

Using state space representation is very helpful to derive the closed form configuration and solve the differential equation in the time domain. The model can be made more precise by increasing the number of elements along the thickness ($n$ as shown in Figure 2.2) and number of lines along the length ($m$).

We use state space linear expression to solve for the evolution of the state of the system in small steps. First we found the non-linear function for electrical and ionic conductivity and then incorporate them into the model. In the model, first the charge or local voltage is obtained from the initial conditions and applied voltage, then the linear equations are solved to find the local charge or voltage for a small step of the time (a few milliseconds). Finally, these local charges and voltages are used to update the local conductivity (from the non-linear functions) and update the matrices $A$, $B$, $C$ and $D$. The equations are then solved again over a small step in time by using these new conditions as an initial values. For each small step in the time we have specific $A$, $B$, $C$ and $D$ which are updated based on the local charge or voltage and the non-linear functions.

It should then be considered as to whether the step size is small enough. In order to check that the step size is sufficiently small to make the values of the matrices accurate, we tested the simulation output over a range of step sizes. We then chose to use step size (10 ms) at which results are consistent with those obtained from even smaller step sizes.

The flowchart of solution mechanism for the proposed approach is shown in Figure 2.5.
2.4 Experiment and Results

An experimental procedure was derived in order to capture the effects of voltage dependent conductivities and resistive drop along the film. Properties of the films used including ionic and electrical conductivities as functions of oxidation state were also determined in order to compare model predictions with experimental results. We first outline the deposition procedure and conductivity characterization, followed by voltage drop measurement along the length of the polymer.

2.4.1 Polymerization Procedure

Polypyrrole was polymerized on a glassy carbon (GC) crucible as a conductive substrate by electrochemical deposition, using the method of Yamaura et al. [102]. In this method, deposition solution is composed of 0.06 M distilled pyrrole, 0.05 tetrabutylammonium hexafluorophosphate (TBA.PF$_6$) and 1 vol.% distilled water in propylene carbonate (PC) (TBA.PF$_6$, pyrrole and PC from Sigma-Aldrich). The solution is stirred by magnetic stirrer for 20 minutes and then is deoxygenated by nitrogen bubbling for 20 minutes. A polished GC crucible is used as a working electrode and clean copper foil serves as a counter electrode. Deposition is performed at -35 °C by
applying a 0.125 mA/cm² current for 8 hours to reach 12-14 μm thickness of polypyrrole. During the electrochemical polymerization, polymerized pyrrole or polypyrrole is deposited on glassy carbon crucible, with the deposition region set by masking with Kapton © tape, as seen in Figure 2.6. After deposition, the PPy film on the crucible was rinsed with pure propylene carbonate, immersed in propylene carbonate for few hours, and then was rinsed with water and air-dried on the crucible. The edges of the film were taped with Kapton © tape to prevent curling and peeling off spontaneously. After drying, cyclic voltammetry (CV) was performed on the film to ensure about the quality of the film and its capacitance behaviour. The film was then carefully peeled off the crucible to avoid tearing.

The morphology analysis has been done previously [95], [103] and these work have shown the effect of the morphology on the electronic conductivity. In my thesis all of the samples were made using same procedure as employed in previous work.

Figure 2.6 shows the PPy deposited film on the glassy carbon crucible. The thickness of the film after 8 hours was 14 μm.

![Polypyrrole deposited film on glassy carbon crucible](image)

*Figure 2.6 Polypyrrole deposited film on glassy carbon crucible.*
2.4.2 Electrical Conductivity Measurement

Experiments show that the conductivity of the polypyrrole is not constant during the actuation and it is a function of oxidation state [62], [95], [104]. This has been shown to lead to unusual current, voltage and cyclic voltammogram responses [60], [73]. The relationship between applied voltage and electrical conductivity was found by oxidizing and reducing the film and measuring the conductivity. In this experiment, after electrochemically depositing the polymer film on glassy carbon, cyclic voltammetry was performed to condition the sample and ease insertion/expulsion of ions into/from the polymer.

To ensure the oxidation and reduction of the film are achieved, we applied a positive and negative potential to the PPy film on glassy carbon (to achieve good electrical contact) in 0.2 M NaPF₆ in water versus an Ag/AgCl reference electrode (from BASi). In this experiment, at first zero volts were applied for 1 hour and then a film of PPy was peeled off from the glassy carbon crucible. The film conductivity was measured. To avoid the parasitic reactions between solution and glassy carbon in next step, the bare area of glassy carbon was taped after peeling off the PPy. In next step, 0.2 volts versus Ag/AgCl reference electrode were applied for 1 hour to the crucible and another piece of the film was peeled off to measure the conductivity. After each positive or negative voltage, zero volts were applied for 1 hour to ensure about the similarity of the initial condition for oxidation and reduction and remove the rest of ions inside the polymer from previous step. The test was repeated at several voltages from zero to 0.4 volts and zero to -0.4 volts versus Ag/AgCl in 0.2 M NaPF₆ aqueous solution. We had challenges at voltages larger than 0.4 V and smaller than -0.4 V and could not get the same value for repeated measurements in electrical conductivity measurement. This was likely due to parasitic reactions and resulting drift in oxidation state with
time. The film after oxidation and reduction at extreme potentials was very brittle and unstable in measurement.

The four-line-probe measurement was used to measure the electrical conductivity. Some researchers have used the four-point-probe measurement [2], [105], [106] but four-line-probe measurement was chosen because it measures the average conductivity through the width. In this test, a constant current was applied to two external lines and the voltage between two internal lines was measured. When the applied current, thickness of the polymer film and the distance between lines are known, we can obtain the conductivity.

Figure 2.7 depicts the four-line probe stuff to measure the electrical conductivity.

![Four-line probe for measuring electrical conductivity.](image)

Finally, we found the trend of changing the electrical conductivity of the PPy film versus applied voltage. This non-linear function is shown in Figure 2.8. The trend is similar to that seen in previous measurements [61], [95].
2.4.3 Ionic Conductivity Measurement.

As in electrical conductivity measurements, we oxidized and reduced the polymer film and then peeled it off to measure the ionic conductivity. For these measurements we used custom glassware and followed a previously established procedure \[107\]–\[110\]. In particular my method is described in detail by Yoo et al. \[109\] and Fekri \[111\], as is now described. The basic operation of this test is similar to four-line-probe test. In this test we have two reference electrodes and two counter electrodes. In this set up, we applied small current between the counter electrodes and put two reference electrodes before and after the PPy film as a membrane. Figure 2.9 shows the setup of the test. By sweeping the frequency and plotting the Nyquist and Bode plots, we can identify the frequency range where ionic conductivity dominates the impedance and thus determine ionic resistance of the membrane and solution. In the analysis we model the polymer film with an RC transmission line and solution resistance with a simple resistor before and after the membrane. When the frequency is very high, all of the capacitors in transmission line are shorted and total impedance is solution resistance. By decreasing the frequency and reaching to very low frequencies, capacitors in transmission line model are opened and current just passes through the resistors and total impedance is the sum of solution resistance and polymer film ionic resistance.

Figure 2.8 Electrical conductivity of PPy vs. applied voltage vs. Ag/AgCl in 0.2 M NaPF6 in water.
By subtracting these two values, we are able to find entire ionic resistance for the PPy membrane and then ionic conductivity. Figure 2.10 presents the electrical circuit model used to extract ionic conductivity from the measurements.

![Figure 2.9 Ionic conductivity measurement set up.](image)

**Figure 2.9** Ionic conductivity measurement set up.

![Figure 2.10 Electrical circuit model used in ionic conductivity measurements to model the polypyrrole film and solution.](image)

**Figure 2.10** Electrical circuit model used in ionic conductivity measurements to model the polypyrrole film and solution.

The captured function of ionic conductivity versus applied voltage is illustrated in Figure 2.11. The drop of conductivity in the reduced state is obvious in this plot. It is important to mention that the results are probably different with polypyrrole synthesis conditions, and also with solvent and ion content. A direct relationship between individual ion size and mobility is not made here.

Working at potential extremes, especially in aqueous solutions, is challenging due to parasitic reactions and relatively fast relaxation of the oxidation state. For instance the PPy film takes 1 hour to reach to an oxidation state of 0.8 V vs. Ag/AgCl but potential drops very fast at open circuit
once this potential is reached, and it is not possible to measure the conductivity at this potential.

The ionic conductivity trend shown in Figure 2.11 is used in the simulations that are presented below in order to help describe and predict charging rate as a function of position.

Fitted curves (shape functions) for electrical and ionic conductivities are free parameters that I used to fit the results with simulation.

![Figure 2.11 Ionic conductivity of PPy vs. applied voltage.](image)

**Figure 2.11 Ionic conductivity of PPy vs. applied voltage.**

### 2.4.4 Voltage Drop Measurement

The experimental setup used to measure the voltage drop along the length of long (6 cm) freestanding films of PPy is shown in Figure 2.12. Voltage was applied at the left end of the film between the Ag/AgCl reference electrode and the PPy film in 0.2 M of NaPF6 aqueous solution, and the voltage was measured at points along the length. To eliminate the contact resistance, we connected the working and first reference electrodes at separate points to the film and used the four-point setup. In this experiment, we used an Autolab PGSTAT 110 to measure the voltage and a Solartron-SI 1260 to apply the voltage. To measure the voltage drop, we used the open circuit potential mode of the Autolab and connected one reference input to the PPy film at the desired distance and the other one to the reference 1 connected to PPy film at left end from Solartron. Carbon fiber paper (from Fuelcellstore.com) was used for counter electrode in a four-electrode
setup for applying the voltage. This counter electrode was aligned parallel to the polypyrrole electrode along the entire length, spaced from it by approximately 1 cm. The reference electrodes sat such that the 5.6 mm diameter of the glass housing was within 0.5 mm of the PPy film. A solution resistance of 3-5 Ω was measured using EIS test. The voltage was measured at two different distances from the applied point to investigate the voltage drop along the length.

![Diagram of setup](image)

**Figure 2.12** Set up for measuring voltage drop along the PPy film with 6 cm length, 1 cm width and 14 μm thickness. The carbon electrode actually runs parallel to the PPy film along its entire length, but is shortened in this figure for clarity of view.

It was observed that the voltage drop between two different points with 3 cm and 6 cm distance from the applied point was significant (Figure 2.13). For instance, the drop is more than 150 mV at the peak by applying 400 mV and more than 90 mV 10 second after the peak. At some of the peaks, the amplitude of voltage drop is larger than 800 mV because the Solartron applies larger than 400 mV at the switching point between positive and negative voltage.
Figure 2.13 Voltage drop for different positions (points D and B) after applying voltage (0.4 V and -0.4 V vs. Ag/AgCl) at point A.

The electrical conductivity is an important limiting factor that should be improved to have fast actuation. Electrical conductivity is several order of magnitude larger than ionic conductivity for polypyrrole film [57].

For long actuators, increasing the volume of the actuator increases total capacitance and the RC time constant, thus increasing the charging time for the actuators. To increase the speed of actuation, the quality of the polypyrrole deposited film should be improved to obtain higher electrical conductivity. The deposition procedure and purity of pyrrole monomers are very important to improve the electrical conductivity and morphology of the film to have better ionic conductivity.
2.5 Simulations and Discussions

2.5.1 Electrical Simulation

Previous work in the frequency domain, including the DEM model, finds the voltage as a function of position and frequency. The disadvantage of this previous work is the inability to show the voltage versus time and to implement non-linear functions for conductivity. Unlike the DEM model, the proposed time domain model has the capability to obtain voltage and charge for each lumped element along the length or through the thickness at each given time. By using this model, voltage or charge as a function of time and position is available to analyze the behaviour of conducting polymer layer during actuation. In addition, as we mentioned in the time modeling section, by expanding the time domain modeling approach proposed here, it is straightforward to implement the non-linearity not only of conductivity, but also of capacitance and Young’s modulus. Using this capability, the conductivity of polypyrrole (and other properties where appropriate) is updated in the simulation based on a defined function of charge for each time iteration. To validate the proposed model, we compare the simulated behaviour of the film with experimental results. In the simulation, we implemented the non-linear functions for ionic and electrical conductivity derived from measurements shown in Figure 2.8 and Figure 2.11. No free parameters were used in this simulation. The result of the simulation (in this case of a step change in applied potential) shows reasonable consistency with experiment (Figure 2.14). In this case voltage is applied at one end of the film (a 0.4 V step vs. the reference electrode), and measured 6 cm from the point of application. As a result of IR drop along the film, there is a difference between the applied and measured voltages, which drops with time as the charging of the film tends towards completion, and current drops to zero. The measured and predicted voltages match within 20 mv and 5%. The simulation was similarly able to predict voltage drop 3 cm from the electrical contact
point. The measurements and the simulations clearly show the importance of IR drop in this charging case.

How much do the non-linearities in conductivities influence the results, and are these needed to give a good description of charging?

In the next simulation, we attempted to answer this question by investigating the sensitivity of the model to changes in electrical and ionic conductivity. First, we assigned a constant value for ionic conductivity \((12e^{-3} \text{ S/m})\) and changed the electrical conductivity from 5000 S/m to 40000 S/m, approximately the range of measured values.

![Figure 2.14 Measured voltage in experiment and non-linear model at 6 cm from the applied voltage point.](image)

The simulation result is shown in Figure 2.15. The behaviour of the CP layer is clearly very sensitive to the change of the electrical conductivity. Also as seen from the results using a constant value for both conductivities, especially at negative potentials, does not lead to a good match between experiment and simulation. Some potential dependent variation in conductivity is needed for the model to fit the experimental results.
Figure 2.15 Simulation with constant value for ionic conductivity \(12e^{-3} \text{ S/m}\) and a range of electrical conductivities at 6 cm away from applied voltage point.

Similarly, the effect of non-linearities in ionic conductivity was investigated by employing a constant value for electrical conductivity in the model (30000 S/m) and changing the ionic conductivity. The results show that the system response is not sensitive to the variation of the ionic conductivity (Figure 2.16), which is again similar in range to that found in ionic conductivity measurements. This result has several implications. The first is that the charging – for the particular geometry used – is more sensitive to electronic than to ionic conductivity. Second, in cases where ionic conductivity is not known, fitting cannot be used to readily estimate its value. Finally, the insensitivity to ionic conductivity suggests that it is not a critical rate limiting factor, but rather solution and electronic transport determine rate of charging, particularly at the end of the film away from the electrical contact.

Measuring the voltage drop along the polypyrrole film for short time actuation showed that we have to use the 2-D circuit model and consider the drop in voltage along the length. It means that the conductivity changes by oxidation state and the PPy film has different potentials along the length depending on position and 1-D model is not accurate for long actuators. Dependency of conductivity to oxidation state results that the ionic conductivity or ionic resistance through the
thickness is not the same and each resistance has different value due to its different oxidation state during charge and discharge. The film becomes charged from the surface that is in contact with solution toward the thickness. Previous work [67] has shown the necessity of using 2-D transmission lines in the frequency domain to model conducting polymers film charging and actuation. The results from time domain modelling confirm this requirement.

![Graph](image)

Figure 2.16 Simulation with constant value for electrical conductivity (30000 S/m) and different value of ionic conductivity at 6 cm away from applied voltage point.

2.5.2 Mechanical Simulation

As we discussed, the voltage and charge state along the length is a function of position during charging. Strain of the polymer is a function of charge and charge depends on local voltage. When the voltage varies along the length of the polymer film, the actuation also is not uniform. Once the
actuator has enough time to fully charge and there is no current or voltage drop along the length, the actuator is expected to exhibit uniform actuation.

In this section, the linear actuation of the freestanding film of PPy is investigated. The PPy film (3.5 cm length, 1.5 cm width, 14 μm thickness) was immersed in the solution (0.1 M NaPF₆ in water) and small magnets were attached to the free end of the film to apply constant 40 kPa stress during actuation. The magnets were electrically isolated from the PPy using Kapton tape. The stress holds the film straight during actuation and can pull the film back into its original position after the contraction that is observed upon applying negative potential.

A square wave potential (± 1 volt) was applied to the film and the expansion and contraction of the film was recorded by camera. The actuator was cycled for few hundred times in few hours to make sure about the stability of the actuator during time and the linear displacement was similar in all cycles. Large lifetime (more than 10⁵ cycles) for PPy in ionic liquid has been reported before [106].

Three markers were applied to the film to measure the displacement and allow calculation of strain at points 6 mm, 15 mm and at the end of the film (33 mm). The average strain was estimated for each film section between markers. Two carbon fiber paper sheets were used as counter electrodes were on the right and left sides of the PPy film to generate symmetric field. The counter electrodes were three times larger than the sample in width with the same sizes. The Ag/AgCl reference electrode was very close to the PPy film and to the applied voltage point inside the solution. Detail of the setup is shown in Figure 2.17.
Figure 2.17 Set up for measuring strain along the length of the PPy freestanding film as a function of position.

By applying positive voltage to the film, the negative mobile ions (PF$_6^-$) are inserted to the film and it expands. Negative voltage causes the expulsion of ions and the film shrinks and brings up the magnets. The strain as function of position during contraction of the film was measured.

Proposed non-linear model was employed to estimate the strain of the film as a function of position along the length. When we know the local charge as a function of position in my model, we are able predict the strain along the length of the PPy film during its actuation. There is a simple relationship which relates the charge per volume ($\rho$) to the active strain ($\varepsilon$) by strain to charge ratio ($\alpha$) [55]. This formula ($\varepsilon = \alpha \rho$) was incorporated into the model to predict the strain of the film versus position along the length with assumption that strain to charge ratio is constant during actuation. This parameter is found empirically [61] and incorporated into the model to enable accurate prediction. A value of $2.7 \times 10^{-11}$ m$^3$/C was used, consistent with the range expected for hexafluorophosphate-doped polypyrrole operated in an aqueous environment [61]. The lumped parameter model was used to estimate the accumulated charge in each segment of the film.
following the application of the square wave potential to the film. As before, the non-linear functions for conductivities were included. Figure 2.18 shows the resulting non-linear model prediction for current, which is in good agreement with experiment over most of the experiment. The match is very good except immediately following the positive step in voltage. The model predicts a spike in current while the experiment shows a step followed by a gradual rise. The cause of this difference in response over the short period following the step may be the drop in conductivity and hence high resistance of the polypyrrole immediately above the solution to air interface, which takes larger to switch back to high conduction as it is not in contact with the electrolyte. This offset results in a 7 % underestimate of charge. Otherwise the match is excellent.

![Figure 2.18 Current response to the applied square wave potential (±1 volt) in experiment and non-linear model.](image)

Using the formulation above, the strain for each section was predicted by model. The same procedure was performed for the experiment and the strain for each section was calculated from the recorded actuation. Experimental and modeling results are presented in Figure 2.19. Experiments done for lower voltages are consistent with obtaining result with relatively smaller strain and the model can predict this smaller actuation as well.
This experiment shows that the different positions along the length of the PPy film experience different charges and different strains and also different strain rates. Depending on the conductivity of the film, it takes time to reach uniform strain along the whole length of the sample. This response shows necessity of using non-linear 2D model to predict the actuation of the PPy-based linear actuators with ability to incorporate non-linear functions for conductivities. It also helps confirm the electrochemical results described in the previous section.

In comparison with previous studies, proposed model has certain advantages. The most important advantage is the ability to implement functions of oxidation state for electrical conductivity, ionic conductivity, as well as properties not varied in this study including capacitance, Young’s modulus and strain to charge ratio in a 2-D model. Most of the existing models are initially developed in the Laplace domain and then converted into the time domain by some approximations or order reduction. Direct time domain derivation is another benefit of the model presented in this work. Prediction of voltage, charge and also linear actuation as a function of time and position along the length of actuator is another useful property of the model. The derivation approach of the model

Figure 2.19 Strain for different sections of the PPy freestanding film under 40 kPa tensile stress.

This experiment shows that the different positions along the length of the PPy film experience different charges and different strains and also different strain rates. Depending on the conductivity of the film, it takes time to reach uniform strain along the whole length of the sample. This response shows necessity of using non-linear 2D model to predict the actuation of the PPy-based linear actuators with ability to incorporate non-linear functions for conductivities. It also helps confirm the electrochemical results described in the previous section.

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using a state space representation makes it easy to convert the model to frequency domain and analyze the result in frequency domain if desired.

The model is able to predict charging and actuation at various points along the length of the polypyrrole. Adding width will simply scale up the amplitude of the current and charge. Adding thickness will slow the charging. This aspect has previously been studied and fit for linear models [55]. Experiments using samples of various lengths and widths confirmed this expectation.

The state space model is extremely versatile, and can represent other circuit models. In changing circuit models, the state equations are changed, and thus a re-derivation is required.

In the approach presented a potential disadvantage is the effort required to change the circuit configuration, as it takes some effort to update the matrices $A$, $B$, $C$ and $D$ to the new configuration. The matrices $\alpha$ and $\beta$ are dependent on the circuit configuration. The current code has been written for the transmission line as shown in Figure 2.2. If we want to use the model for a different configuration, we need to change the code to derive the new matrices $\alpha$ and $\beta$ which are related to new circuit. For instance, in the written code it has been set that the last capacitance of each line through the thickness is a double layer capacitance but if the new circuit model does not have double layer, we have to change this line of code to update those matrices. We have sought to overcome this disadvantage by starting with a general formulation.

2.6 Conclusions

In this work, a two dimensional non-linear time domain transmission line model is employed to predict the electrical and mechanical behaviour of conducting polymer-based electrodes and actuators. Both ionic and electronic conductivities are known to be functions of oxidation state. These non-linear functions of oxidation state for electrical and ionic conductivity of polypyrrole were measured and implemented in the model. This model is able to capture the behaviour of the
polymer film in the time domain and estimate local charge or voltage as a function of position and time. We validated the model with experiments and showed the consistency of the results with experimental data. For long strips of polypyrrole, we measured the voltage drop along the length and were able to describe the response effectively. Significant drop in voltage along the length due to electronic resistance makes the 2-D model necessary to properly simulate the electrical response, while significant change in resistance with oxidation makes the non-linear model a necessity to achieve good accuracy. On the mechanical side, the model has the capability to predict the strain at specific positions through time. Local charge or voltage has been used in the model to update the conductivities and also strain as a function of position and time to predict linear expansion and contraction. Reasonable consistency (within 5 %) was observed between results from the model and the experiment.
Chapter 3: Fabrication, Characterization and Dynamic Charge Dependent Modeling of Conducting Polymer Trilayer Bending

3.1 Introduction

Conducting polymer (CP) actuators with trilayer configurations consist of two active layers at the top and bottom with a separator layer between them. The structure bends when a voltage is applied between the active layers, and ions are transferred from one to the other, including counteracting volume change. The separator, which is electrically inert but ionically conductive, acts as an ion transfer medium and enables the actuator to work in air [3], [112], [113]. This type of actuator, which has self-contained electrolyte, has attracted attention for application in soft robotics [114], grippers [3], micropumps [1] and, with a tubular cross-section, as actively deformable catheters [37], [57], [115].

Electrophoretic force generated by voltage application causes current and ionic charge accumulation at the double layer interface between the polymer and the separator. The concentration gradient and potential across the interface drives ions to penetrate into the polymer structure, or leave it, until equilibrium is reached. The insertion or removal of ions leads to an expansion or contraction in polymer dimensions [116].

During operation, one layer is oxidized and one layer is reduced and this oxidation process influences electrical properties. Decreasing electrical conductivity can increase the time constant and will be a limiting factor for fast actuation. This drop in conductivity due to oxidation state variation and also the drop in voltage along the length of the actuator should be considered in modeling and design. In the current chapter, these effects are incorporated into a trilayer model.
In order to obtain a dynamic and accurate model, the electro-chemo-mechanical behaviour of conducting polymer, which is a combination of diffusion, migration, resistivity and capacitance should be understood. The model presented here enables a good prediction of actuation and also helps identify important rate and deformation limiting factors.

By applying a potential difference between two conducting polymer electrodes, the resulting oxidation and reduction induce positive and negative charge in the layers, which leads to positive and negative strain. When one layer is reduced by introducing electrons, negative mobile ions are expelled from the polymer layer and negative strain is generated. In another layer at the same time, positive strain as a result of positive charge is induced. This expansion is due to the insertion of mobile negative ions from the separator to the polymer layer after leaving electrons (Figure 3.1). The curvature caused by expansion in one layer and contraction in another layer in steady state has been derived [101].

To model this charging process, many models have been proposed [86]–[91], [117]. An RC transmission line model has been proposed to describe the charge and discharge process in conducting polymers and find the impedance associated with ion transport [55]. This model has been applied to predict the degree of bending achieved in conducting polymer driven catheters [57]. The model works well but does not account for changes in oxidation state, and so is limited in the oxidation state and time range over which it is effective. In particular, with longer times held at extreme potentials, changes in electronic conductivity may significantly slow actuation.
Figure 3.1 Trilayer actuator with two CP layers at the top and bottom and ionically conductive separator in between before (a) and after (b) actuation.

To model each CP layer in trilayer actuators, a 2-D transmission line has been employed by Nguyen et al. in series with the double layer capacitance. They proposed a symmetric configuration for trilayers with a resistor between CP layers to model the separator resistance [86]. To relate the current passing through the CP layers to the applied voltage, total impedance of the trilayer was obtained using the 2-D transmission line model [8]. A diffusion element in series with a double layer capacitance represents each CP layer and a single resistor connects the two transmission lines. These models do not include the non-linear behaviour of conductivity and also elastic modulus as a function of oxidation state which is main goal of the current chapter.

In Chapter 2, the transport of ions and electrons in the conducting polymer layers is represented by 2-D RC transmission line models and showed that the voltage drop along the length of the CP layer can be significant. Use of a 2-D charge state dependent model was necessary to describe the
response. It was also shown that the electrical and ionic conductivities of polypyrrole change with applied voltage, which is consistent with previous findings [60], [61], [72]. In Chapter 2, the non-linear relationship between conductivity and applied voltage was measured, incorporated into the model, and a non-linear time domain modeling approach was demonstrated [118]. This non-linear model is for a stand-alone linear actuators. In the present chapter, this model is extended to a bending actuator. When voltage drop is significant along the length of the CP layers, voltage varies with position and time. Strain is proportional to local charge and charge is determined by local voltage. When the voltage varies along the length, the strain and also bending moment are not uniform which causes non-uniform bending along the length. If the actuator has enough time to fully charge and reaches equilibrium, the entire length of each CP layer will have the same potential with uniform deformation. It is this process that we seek to describe here.

Elastic modulus and strain to charge ratio also are not constant [59], [97]–[100] during operation and vary with applied voltage and should be considered in the accurate model.

Modeling of this phenomenon is more complex if we want to simultaneously incorporate the non-linearity and predict the behaviour of each electrode. To predict the behaviour of the actuator with good accuracy, the oxidation state dependent functions for elastic modulus, strain to charge ratio, conductivities and capacitance should be obtained and incorporated into the model.

This chapter models conducting polymer-based trilayer actuators, including the effects of oxidation state dependent electrical conductivity and Young’s modulus. These dependencies are measured and incorporated into the model. Key to this approach is the use of an asymmetric beam model, wherein CP moduli and conductivities differ between adjacent segments and through the thickness, and the neutral axis can no longer be assumed to be in center of the beam.
Trilayer actuators in this chapter are made of two poly 3,4-ethylenedioxythiophene (PEDOT) conducting polymer layers and an interpenetrating polymer network (IPN) as the separator between them. More specifically PEDOT is penetrated into the IPN layer from the top and bottom surfaces to create a trilayer structure. Time domain non-linear electrochemomechanical model of the trilayer configuration is presented and predicted responses are compared with observed behaviour.

3.2 Mechanical Model

Charge transfer determines the induced strain in the conducting polymer layer which causes the trilayer to bend. Since the charge transfer changes with time, the radius of curvature varies during operation until a steady state or fully charged state is achieved. In this section, a mathematical derivation is presented to enable predictions of the radius of curvature of the conducting polymer-based trilayer actuators as a function of time.

In trilayer actuators, there are two active layers of conducting polymer (CP) at the top and bottom, and a passive separator layer or solid polymer electrolyte (SPE) between them. By applying voltage to the conducting polymer layers, for instance, the top layer tends to expand and bottom layer tends to contract. The separator resists against the expansion and contraction and tensile and compressive forces are generated between the CP and SPE layers. Figure 3.2 shows the free body diagrams of the actuator parts under load.

If the Young’s moduli of the CP layers are different due to a difference in oxidation state, the forces between each CP layer and the separator will be unequal.

The effect of this inequality is that the location of neutral axis is not exactly at the center of the cross section.
Figure 3.2 Free body diagram of the trilayer. Top CP layer has positive induced strain and bottom CP layer has negative induced strain. Since the bending conditions may be asymmetric due to differences in F and E, we have taken the neutral axis at a general off-centre location.

The strain for the SPE layer is:

\[
\varepsilon_1(t) = -\frac{F_3 - F_2}{A_1 E_1} + \frac{z}{R_1(t)}, \quad -z_2 \leq z \leq z_1, \tag{3-1}
\]

where \(z_1\) and \(z_2\) are distances from neutral axis (\(z = 0\)) to the top and bottom surfaces of the SPE layer respectively and \(R_1\) is the radius of curvature. Strains in the CP layers at the top, \(\varepsilon_2\), and bottom, \(\varepsilon_3\), are:

\[
\varepsilon_2(t) = \alpha \rho(t) - \frac{F_2(t)}{A_2 E_2(t)} + \frac{z - (z_1 + h_2/2)}{R_2(t)}, \quad z_1 \leq z < z_1 + h_2, \tag{3-2}
\]

\[
\varepsilon_3(t) = -\alpha \rho(t) + \frac{F_3(t)}{A_3 E_3(t)} + \frac{z + (z_2 + h_3/2)}{R_3(t)}, \quad -z_2 - h_3 < z \leq -z_2, \tag{3-3}
\]

\(R, E\) and \(A\) are the radius of curvature, Young’s modulus and cross section area and index 1,2 and 3 refer to separator layer and CP top and bottom layers respectively. \(\alpha \rho(t)\) is the induced strain or free strain in conducting polymer which is generated by charge transferred by ion
insertion/expulsion into/from the polymer structure. \( \rho(t) \) is charge transferred per volume which is a function of time and is related to volumetric capacitance, \( C_v \), and voltage, \( V \), \( (\rho(t) = C_v V) \). \( \alpha \) is strain to charge ratio which along with \( C_v \) is assumed to be constant in this chapter during operation. Since the voltage is a function of time and not the same for different positions along the length of the trilayer due to voltage drop, charge also is a function of time. When the trilayer is fully charged and voltage in the entire length of the CP layer is the same and equal to the applied voltage, then it is possible to express \( \rho = C_v V_{\text{applied}} \). Otherwise, the charge transferred is not uniform along the length which causes non-uniform strain distribution.

In the surface between SPE layer and CP layers, strain is equal. It leads to:

\[
\varepsilon_2(t) = \varepsilon_1(t), \text{ at } z = z_1, \tag{3-4}
\]

\[
\rightarrow \alpha \rho(t) - \frac{F_2(t)}{A_2 E_2(t)} - \frac{h_2/2}{R_2(t)} = -\frac{F_3-F_2}{A_1 E_1} + \frac{z_1}{R_1(t)}, \quad A_2 = b h_2, \tag{3-5}
\]

and

\[
\varepsilon_3(t) = \varepsilon_1(t), \text{ at } z = -z_2, \tag{3-6}
\]

\[
\rightarrow -\alpha \rho(t) + \frac{F_3(t)}{A_3 E_3(t)} + \frac{h_3/2}{R_3(t)} = -\frac{F_3-F_2}{A_1 E_1} - \frac{z_2}{R_1(t)}, \quad A_3 = b h_3. \tag{3-7}
\]

Since the thickness of the trilayer is much smaller than the radius of curvature \( (h_1, h_2, h_3 << R) \) it is assumed that the entire thickness has one common radius of curvature. Using equation (3-5) and (3-7) and use \( z_2 = 2h_1 - z_1 \) and also assuming \( R_1 = R_2 = R_3 = R \) gives:

\[
F_3 = \frac{2A_2 E_2 + A_1 E_1}{2A_3 E_3 + A_1 E_1} \left( \frac{A_3 E_3}{A_2 E_2} \right) F_2 + \frac{2(z_1-h_1) + (h_2-h_3)}{R(t)} \frac{A_1 E_1 A_3 E_3}{2A_3 E_3 + A_1 E_1}. \tag{3-8}
\]

From the free body diagram for each layer:

\[
M_1 = (F_2(t) + F_3(t))(h_1), M_2 = F_2(t)\left(\frac{h_2}{2}\right), M_3 = F_3(t)\left(\frac{h_3}{2}\right). \tag{3-9}
\]

Summing left sides and right sides of equation above leads to:
\[ M_1 + M_2 + M_3 = (F_2(t) + F_3(t)) \left( h_1 + \frac{h_2}{2} \right). \]  

(3-10)

We also have:

\[ \frac{1}{R_1} = \frac{M_1}{E_1 I_1}, \quad \frac{1}{R_2} = \frac{M_2}{E_2 I_2}, \quad \frac{1}{R_3} = \frac{M_3}{E_3 I_3}. \]  

(3-11)

Substituting equation (3-11) in equation (3-10) with \( R_1 = R_2 = R_3 = R \) gives:

\[ \frac{E_1 I_1}{R(t)} + \frac{E_2 I_2}{R(t)} + \frac{E_3 I_3}{R(t)} = (F_2(t) + F_3(t)) \left( h_1 + \frac{h_2}{2} \right). \]  

(3-12)

Using equation (3-8) and (3-12) we determine:

\[ F_2(t) = \frac{(2A_2 A_3 E_2(t) E_3(t) + A_1 A_2 E_3 E_2(t))}{(4A_2 A_3 E_2(t) E_3(t) + A_1 A_2 E_3 E_2(t) + A_3 E_3(t))} \left( \frac{2(E_1 I_1 + E_2(t) I_2 + E_3(t) I_3)}{R(t)(2h_1 + h_2)} \right) - \frac{2(z_1 - h_1) + \frac{(h_2 - h_3)}{2}}{R(t)} A_1 E_1 A_3 E_3 \]  

(3-13)

and

\[ F_3(t) = \frac{(2A_2 A_3 E_2(t) E_3(t) + A_1 A_2 E_3 E_2(t))}{(4A_2 A_3 E_2(t) E_3(t) + A_1 A_2 E_3 E_2(t) + A_3 E_3(t))} \left( \frac{2(E_1 I_1 + E_2(t) I_2 + E_3(t) I_3)}{R(t)(2h_1 + h_2)} \right) \frac{2A_2 E_2 + A_1 E_1}{2A_3 E_3 + A_1 E_1} A_3 E_3 + \frac{2(z_1 - h_1) + \frac{(h_2 - h_3)}{2}}{R(t)} A_1 E_1 A_3 E_3 \]  

(3-14)

where \( I_2 = \frac{bh_2^3}{12}, \ I_3 = \frac{bh_3^3}{12} \) and \( I_1 = \frac{2bh_1^3}{3} \) are second moments of area.

In the case of perfectly symmetric trilayer \( (E_2 = E_3, h_2 = h_3 \text{ and } F_2 = F_3) \) which means \( z_1 = h_1 \) and the neutral axis is in the middle of SPE layer, the force between CP layer and separator is obtained from equation (3-15) in the simplified form:

\[ F_{\text{symmetric}}(t) = \frac{(E_1 I_1 + 2E_2(t) I_2)}{R(t)(2h_1 + h_2)}. \]  

(3-15)
Refer to mechanics of material and using bending of beam made of several materials helps to find the $z_1$ which is location of neutral axis. In this method, one of the materials is used as a reference and depends on the fraction of Young’s modulus of materials versus this references, width of the layer is determined. Now, we have trilayer with uniform material but with different widths. Summation of cross section area multiplied by distance between centroid of the layer and neutral axis for all layers must be zero. This equation gives second order equation and the solution is location of neutral axis. In our trilayer, $\frac{E_3}{E_1}$, $\frac{E_2}{E_1}$, $h_1$, $h_2$, $h_3$ are used to find $z_1$.

In a trilayer beam, this equation is:

$$z_1^2 + \eta_1 z_1 + \eta_2 = 0,$$

where $\eta_1 = -2h_1 - \frac{E_3}{E_1} h_3 + \frac{E_2}{E_1} h_2$ and $\eta_2 = \frac{E_3}{2E_1} h_3 h_2 + \frac{2E_3}{E_1} h_3 h_1$. 

Solving equation (3-16) determines the location of neutral axis ($z_1$). At each instant of time, $h_2$ and $h_3$ have new values which should be updated. These values are determined by charge or strain which change with voltage and time. It means that the location of neutral axis, varies during operation and voltage application. In this chapter, we assume that the strain to charge ratio along the length and thickness are similar and for instance updated $h_2$ is $h_2' = h_2(1 + \varepsilon_2(t))$.

Substituting $F_2$ and $F_3$ in equation (3-5) with ignoring very small expressions the radius of curvature is determined in terms of the design and material parameters as follows:

$$R(t) = \frac{1}{\alpha \rho(t)} \left\{ \frac{(2x_1 + h_2)^2}{2} + \lambda_1 \left( \frac{\frac{1}{2}(E_1 h_1^2 + E_2(t)h_2^2 + E_3(t)h_3^2)\lambda_2 + (-h_1 E_1 - 2h_2 E_2)(2h_1 + h_2)\lambda_3}{(2h_1 + h_2)h_1 h_2 E_1 E_2} \right) \right\},$$

where $\lambda_1 = \frac{(2h_2 h_3 E_2(t)E_3(t) + h_1 h_2 E_1 E_2(t))}{(4h_2 h_3 E_2(t)E_3(t) + h_1 E_3(h_2 E_2(t) + h_3 E_3(t)))}$, $\lambda_2 = \frac{h_1 E_1(h_2 E_2 + h_3 E_3 + h_1 E_1)}{(2h_3 E_3 + h_1 E_1)}$ and

$$\lambda_3 = \frac{h_1 E_1(h_2 E_2 + h_3 E_3 + h_1 E_1)}{(2h_3 E_3 + h_1 E_1)}.$$
\[ \lambda_3 = \frac{(2(z_1-h_1)+\frac{(h_2-h_3)}{2})h_1E_1h_3E_3}{2h_3E_1+h_1E_1}. \]

If Young’s moduli of active layers change during actuation due to a change of oxidation state, radius of curvature also changes with this variable.

When the charge transferred \( (\rho(t)) \), \( E_2(t) \) and \( E_3(t) \) are known versus time, the radius of curvature can be obtained as a function of time using equation (3-17).

In steady state \( (\rho(t) = C_vV_{applied}) \), radius of curvature versus applied voltage is calculated by:

\[
R_{SS} = \frac{1}{\alpha C_v} \left( \frac{(2z_1+h_2)}{2} + \lambda_1 \left( \frac{\frac{2}{3}E_1h_1^3+E_2(t)h_2^3+E_3(t)h_3^3}{(2h_1+2h_2)h_1h_2E_1E_2} \right) \right) \frac{1}{V_{applied}}. \tag{3-18}
\]

With the assumption that the Young’s moduli of CP layers does not change during operation versus time and also oxidation state, and the neutral axis is exactly passing through middle of SPE layer, the formulation for radius of curvature in steady state can be simplified as:

\[
R_{SS,\text{Symmetric}} = \frac{2h_2 \left( \frac{h_1}{h_2} \left( \frac{E_1}{E_2} - 1 \right) + \frac{h_1}{h_2} + 1 \right)^3}{3 \left( 1 + 2 \frac{h_1}{h_2} \right) \alpha C_v} \frac{1}{V_{applied}}. \tag{3-19}
\]

The formulation above, shows the relationship between geometry and mechanical properties of the layers and the radius of curvature. To achieve smaller radius of curvature, the Young’s modulus of the solid polymer electrolyte versus Young’s modulus of conducting polymer as an active layer should be small. This suggests using compliant materials as the separator. In the trilayer presented in this chapter, the density of the PEDOT at the penetrated layer can increase the Young’s modulus of the active layer which causes smaller radius of curvature. IPN which is compliant material \( (E_1 = 1 \text{ MPa}) \) is used and the density of PEDOT increased to 25 wt% to improve the Young’s modulus.
\( E_2 = 220 \text{ MPa} \). If the \( \frac{E_1}{E_2} \) is very small which achieved in our case, the equation (3-19) can be presented in simplified form:

\[
R_{SS, \text{symmetric, simplified}} = \frac{\frac{h_1}{h_2} \left( \frac{3(h_1)}{h_2} + \frac{3(h_1)}{h_2} + 1 \right)}{3 \left( 1 + \frac{2h_1}{h_2} \right)} \frac{1}{\alpha c_0 V_{\text{applied}}}. \tag{3-20}
\]

Maximum actual strain at the top surface of the trilayer in steady state is:

\[
\varepsilon_{\text{actual-max}} = \frac{h_1 + h_2}{R_{\text{steady state}}}. \tag{3-21}
\]

In the case of symmetric trilayer, substituting \( R_{SS, \text{symmetric}} \) from equation (3-19) into equation (3-20), the relationship between induced strain and actual strain in steady state is given by:

\[
\varepsilon_{\text{actual-max}} = \frac{3 \left( 1 + \frac{h_1}{h_2} \right) \left( 1 + \frac{2h_1}{h_2} \right)}{2 \left( \frac{h_1}{h_2} \right)^3 \left( \frac{E_1}{E_2} \right)^2 + 1} \varepsilon_{\text{induced}}. \tag{3-22}
\]

### 3.3 Electrochemical Model

When a potential difference is applied between two CP layers, one layer starts to charge from the point of applied voltage. After application of positive voltage, which causes oxidation of the polymer backbone, mobile anions penetrate the polymer structure to balance the charge. At the same time, negative potential on the other layer causes opposite effect and reduces the polymer backbone and absorbed anions are expelled to maintain the charge neutrality. This redox process then propagates to the entire polymer layers with time. In the case of a trilayer, one side of each CP layer is in contact with the separator as an ion conductor. Finite ion transport rate results in a gradient in charge density through the thickness of each layer. Electronic voltage drop also exists due to finite electronic resistance along the length of each CP layer. Our aim is to understand and simulate this process.
The diffusive elastic model (DEM) uses an RC transmission line to represent the ion transportation through the thickness [55]. This model can be extended by adding resistors to represent the electrical resistance of the polymer layers along their lengths. Total impedance of the polymer layer in 2D has been derived [15], [57]. This model is able to obtain voltage and current responses of a freestanding conducting polymer film in the frequency domain, but converting these to the time domain without substantial approximations is not possible, and does not allow non-linear properties to be introduced.

In this chapter, a two-dimensional RC transmission line circuit previously solved in the time domain for a freestanding conducting polymer actuators [118] is applied to trilayer actuators. Ability to find the current and voltage as a function of time and position, and to incorporate non-linearities in electronic conductivity and Young’s modulus are advantages of this approach.

It is known that the electrical and ionic conductivities of conducting polymers and also Young’s Modulus are a function of local charge or oxidation state [60], [99]. In trilayer actuators, when one layer is oxidized and one layer is reduced, the conductivities and Young’s moduli of layers vary due to differences in oxidation state. This oxidation state results in a significant drop in conductivity in electro-chemically reduced layers while the conductivity of oxidized layers is high so the distribution of charge in both CP layers is affected.

To predict the electrical and mechanical behaviour of a trilayer actuator, it is important to develop a time domain model with the ability to capture the non-linearity. This time domain non-linear model should be able to estimate the local charge and strain of each CP layer accurately and at the same time to predict the actuation of the trilayer. Such a model can enable us to predict the curvature of the trilayer actuator versus time and position. An equivalent circuit model for trilayer
actuators made of two conducting polymer layers and ionically conductive separator in between is depicted in Figure 3.3a.

Figure 3.3 a) Equivalent circuit for trilayer actuator made of two conducting polymer layers and an ionically conductive separator in between. $Z_D$ is the diffusion impedance that is modeled with transmission line. Applied voltage drives ions to migrate from one conducting polymer layer to another by passing through the ionically conductive separator with resistance, $R_s$. The applied potential difference causes an accumulation of ions at the interface of separator/polymer to charge the double layer capacitances ($C_{dl}$), which then drives the charging of the diffusion element. b) 2-D Transmission line circuit model for conducting polymer-based trilayer actuators. Electronic resistivity of the polymer layer along the length and ionic resistivity through the thickness are modeled by resistors $R_e$ and $R_i$. Charge stored in the polymer structure is modeled with capacitors, $C_{ij}$. c) Small section of the transmission line to show how equations are derived.

Figure 3.3b shows the transmission line for each CP layer and a set of resistances, $RS$, in parallel to model the separator ionic resistivity between two layers. Resistance to electronic transfer along the length of CP layers is modeled by distributed resistors, $R_e$. In addition, resistance to movement of ions through the thickness of the polymer structure is modeled as ionic resistance, $R_i$, which both can be functions of oxidation state. Capacitors, $C_{ij}$ represents the ion storage capacity in the polymer network.
Double layer capacitors are employed to model the accumulation of ions at the interfaces between the separator and conducting polymer layers. Ionic resistance inside the separator and between CP layers is modeled by the parallel summation of resistors, $R_s$. This representation is valid when the thickness of the separator is very small in comparison with length of the CP layers.

The entire circuit model shown in Figure 3.3b with all elements is used to develop the mathematical derivation. In this representation, a state vector is defined by the charge of all branches of the transmission line and local charge and current for each discrete region along the length and thickness are obtained as outputs.

Capability to define electrical and ionic resistance and also Young’s modulus as a function of local charge or oxidation state is an important advantage of this approach. This model is able to capture the non-linearity of electrical and mechanical properties of conducting polymer layers and incorporate them into the model. The charging time constant and distribution of charge in all branches are obtained in the method. Movement of ions through the thickness of the whole trilayer (from one CP layer to another passing through the separator) can be tracked in this model as a function of time and position by tracking the stored charge in capacitors. In addition, voltage drop or local electronic charge distribution along the length for each CP layer is also obtained.

To derive the governing differential equation, Kirchhoff's Voltage Law (KVL) is written for all loops. By defining $q$ and $\dot{q}$ as charge injected at a given position and current passing through the branches respectively, it is possible to write a first order differential equation for the circuit.

The number of elements along the length and through the thickness determines the number of independent equations. In the case of $2n$ elements for the thickness and $m$ elements for the length of the polymer layer, there are $(2n - 1) \times m$ independent equations, which are needed to find the
same number of unknown q’s that there are in equations. For instance, for the two selected loops in Figure 3.3c, KVL gives:

\[
\frac{1}{c_{11}} (q_{11} - q_{12} - q_{21}) + R_{i11} (\dot{q}_{11} - \dot{q}_{12} - \dot{q}_{21}) - \frac{1}{c_{12}} (q_{12} - q_{13}) = 0.
\]

\[
\frac{1}{c_{12}} (q_{12} - q_{13}) + R_{i12} (\dot{q}_{11} - \dot{q}_{13} - \dot{q}_{21}) - \frac{1}{c_{13}} (q_{13} - q_{14}) = 0.
\]

By writing KVL for all loops, it is possible to put all equations in matrix form for whole circuit.

\[
[\alpha][\dot{q}] + [\beta][q] = [\gamma]V
\]

(3-24)

\(\dot{q}, q\) are vectors and their lengths are determined by the number of circuit elements circuit along the length and through the thickness.

For example, for the selected loops, equations in matrix form, which include two \(\dot{q}, q\) vectors and also \(\alpha, \beta\) matrices are:

\[
\begin{bmatrix}
R_{i11} & -R_{i11} & 0 & 0 & -R_{i11} \\
R_{i12} & 0 & -R_{i12} & 0 & -R_{i12}
\end{bmatrix}
\begin{bmatrix}
\dot{q}_{11} \\
\dot{q}_{12} \\
\dot{q}_{13} \\
\dot{q}_{14} \\
\dot{q}_{21}
\end{bmatrix}
+ 
\begin{bmatrix}
\frac{1}{c_{11}} & -\frac{1}{c_{11}} & -\frac{1}{c_{12}} & \frac{1}{c_{12}} & 0 \\
0 & \frac{1}{c_{12}} & -\frac{1}{c_{12}} & -\frac{1}{c_{13}} & \frac{1}{c_{13}} \\
0 & 0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
q_{11} \\
q_{12} \\
q_{13} \\
q_{14} \\
q_{21}
\end{bmatrix}
= 0
\]

(3-25)

After forming the equation in matrix form, we are able to convert them to the state space standard form and find matrices \(A, B, C\) and \(D\).

\[
[\dot{q}] = A[q] + Bu \text{ where } A = -\alpha^{-1}\beta \text{ and } B = \alpha^{-1}\gamma
\]

(3-26)

\[
y = C[q] + Du
\]

(3-27)

In state space standard form, \(A, B, C\) and \(D\) are state matrix, input matrix, output matrix and feedforward matrix respectively. \(y\) is the desired output vector, which can be obtained by defining...
the appropriate matrices $C$ and $D$. We can find the charge for each capacitor and current passing through the branches. For instance, the charge in capacitor $C_{11}$ is $q_{11} - q_{12} - q_{21}$ which leads matrices $C$ and $D$ to be in $y = C[q] + Du$ equation:

$$
[C] = \begin{bmatrix} 1 & -1 & 0 & 0 & -1 \end{bmatrix}, D = 0
$$

(3-28)

Increasing the number of elements along the length and through the thickness can improve the accuracy of the model. The code written in MATLAB has the capability to increase the number of elements and also change the time step size. Four elements across the entire thickness of each CP layer and two elements along the length for each millimeter were used in the simulations.

In order to solve the model, electrical conductivity and also Young’s modulus of PEDOT conducting polymer for the mechanical portion of the model as functions of charge state are measured and then incorporated into the model. These measurements are presented below. Applied voltage and initial conditions determine the local charge and voltage for first time step of time by solving the set of linear equations (equation (3-25)) for charge and current. Accuracy as a function of time step size is checked by running the simulation for a range of step sizes and selecting a value which gives results that are consistent with those obtained from even smaller steps. Then the solution of this step is used as initial condition for next step and also used for updating the local conductivity and Young’s modulus values. These new values update the matrices $A, B, C$ and $D$ and the linear equation is solved again to find the new local charge and voltage. For each small step of time new $A, B, C$ and $D$ matrices based on functions for conductivity and Young’s modulus which are updated by local charge and voltage are calculated. The method has been implemented in MATLAB. The local and total charge are obtained from the model and then local and total strain is predicted by multiplying the strain to charge ratio by the local charge density. Bending beam
theory for bending actuators is used to calculate the radius of curvature and deformation of the actuator (Equation (3-7)).

### 3.4 Fabrication

To make trilayer actuators, the procedure described in reference [119] was used. First, an interpenetrating polymer network (IPN) made of poly (ethylene oxide) (PEO) and nitrile butadiene rubber (NBR) is synthesized. This double network polymer is used as a solid polymer electrolyte or separator layer. In the next step, poly 3,4-ethylenedioxythiophene (PEDOT) conducting polymer is polymerized inside the IPN to form a PEDOT penetrated layers localized to the surface of the IPN (Figure 3.4). 35 $\mu$m thickness for PEDOT penetrated layer was observed with a PEDOT content of 25 wt% versus the whole Trilayer. This procedure avoids delamination of the PEDOT layer from solid polymer electrolyte which has been a challenge in previous trilayer structures [120].

The PEDOT penetrated layer works as an active layer at the top and bottom of the PEO/NBR IPN film to create the trilayer actuator. The fabricated trilayer (22 mm×2 mm×240 $\mu$m) is immersed in 1 M LiTFSI in propylene carbonate (PC) to swell for a few days and then the trilayer is ready to work in air as a bending actuator. In case of 1 M LiTFSI in PC, the Li$^+$ ions are surrounded by PC molecules which – a polar aprotic solvent - creating a significant solvation sphere around Li$^+$. As a result, TFSI$^-$ is more mobile ion and determine the actuation direction [121]. It was approved in the experiment as well because oxidized electrode expands and reduced electrode contracts due to the movement of TFSI$^-$ ions.
Figure 3.4 a) Cross section of the trilayer actuator before and after PEDOT polymerization. PEDOT is polymerized inside the IPN network and the density of polymerization increases toward the surface of IPN. b) Energy dispersive X-ray spectroscopy of the trilayer cross section which shows penetration of the PEDOT into the IPN. 35 \( \mu m \) for PEDOT penetrated layer was observed.

3.5 Characterization

In order to capture the properties of the PEDOT conducting polymer used in the trilayer actuators, properties of the PEDOT penetrated layer including electrical and ionic conductivities, Young’s modulus, volumetric capacitance and strain to charge ratio were measured to incorporate into the model.

Strain to charge ratio, volumetric capacitance and ionic conductivity of the trilayer were measured using methods described in Chapter 2. It is assumed that these values are constant during operation or the changes are very small and don’t have significant effect on the behaviour of the trilayer [39], [118], [122].

The total transferred charge and measured strain were used to calculated the strain to charge ratio for PEDOT/IPN/PEDOT trilayer which was \( 1.7 \times 10^{-10} \, m^3/C \).
Cyclic voltammetry was performed to find the volumetric capacitance \( C_v = 1 \times 10^8 \text{ F/m}^3 \). Ionic conductivity of PEDOT penetrated layer \( \sigma_{i_{PEDOT}} = 25 \times 10^{-3} \text{ S/m} \) and IPN \( \sigma_{i_{IPN}} = 0.3 \text{ S/m} \) were measured using method described in chapter 2.

Electrical conductivity and Young’s modulus as a function of applied voltage were measured and incorporated into the model to enable more accurate prediction.

### 3.5.1 Electrical Conductivity Measurement

It has been shown that for conducting polymers including polypyrrole, electrical conductivity is a function of oxidation state [62], [95], [104]. Electrical conductivity was measured in this chapter to explore the behavior of the PEDOT conducting polymer as grown and used in the trilayer actuators. To measure the electrical conductivity of the PEDOT penetrated layer, positive and negative voltages were applied to the trilayer versus reference electrode (Ag/Ag\(^+\)) and then the electrical conductivity for each applied voltage was measured. Carbon fiber paper (from Fuelcellstore.com) was used as a counter electrode. The trilayer was immersed in 1 M LiTFSI in PC between two carbon fiber counter electrodes with a 1 cm distance between the trilayer and the carbon fiber on each side. The reference electrode was held very close to the top clamped portion of the trilayer. In this case, both the PEDOT penetrated layers were connected and act as the working electrode. Both are oxidized and reduced and the measurement was conducted for both layers. A four-line-probe (Figure 3.5a) measurement was used to determine the average conductivity along the length and through the thickness of the sample.

Figure 3.5b shows the electrical conductivity of the PEDOT penetrated layer as a function of applied voltage. As expected the conductivity drops markedly (by factor of 24) as the polymer approaches its undoped state. A fit line as also shown which is used in the non-linear model.
Figure 3.5 a) Four-line setup for measuring electrical conductivity b) Electrical conductivity of the PEDOT penetrated layer as a function of applied voltage versus Ag/Ag+ reference electrodes. c) Setup of the measurement, the clamped is moved down by given value and the force is measured by the transducer. d) Young’s modulus of PEDOT penetrated layer as a function of applied voltage.

3.5.2 Young’s Modulus Measurement

The elastic modulus of some conducting polymers change during operation as a function of oxidation state [98].

In this section, the Young’s moduli of PEDOT/IPN/PEDOT trilayer actuators were measured to find the variation of this property versus applied voltage. This function is incorporated into the model. To measure the Young’s modulus of the PEDOT penetrated layer versus applied potential, different positive and negative voltages (0 and ±1 Volts) were applied to the sample to oxidize and reduce PEDOT layers. After applying voltage, open circuit potential was measured to ensure that the trilayer has reached to desired potential. Then sample was taken out from the solution and
Young’s modulus of each sample was measured. Thickness of PEDOT and IPN layer after swelling was measured using EDX (Figure 3.4b). As is shown in Figure 3.5c, the right side of the sample was clamped which can move up and down. The left side rested on the arm of the force transducer to measure the force (Aurora Scientific Inc.). The system was calibrated before use to ensure the accuracy of the results. Then the clamped side of the sample was moved down by 2 mm and the force generated by the trilayer was measured by the force transducer. Measured force, \( F \), corresponding to given displacement, \( \delta \), and beam dimensions (length, \( L \), and moment, \( I \)), enables us to calculate the effective bending Young’s modulus of trilayer using:

\[
\delta = \frac{FL^3}{3EI}, \quad \rightarrow E = \frac{FL^3}{3\delta I},
\]

(3-29)

The Young’s modulus of IPN pure film (1 MPa) [51] and of the total trilayer device, \( E_{\text{trilayer}} \), are known. Using formulation below gives the Young’s modulus of PEDOT penetrated layer.

\[
E_{\text{trilayer}} = \frac{E_{\text{IPN}} I_{\text{IPN}} + 2E_{\text{PEDOT}} I_{\text{PEDOT}}}{I_{\text{IPN}} + 2I_{\text{PEDOT}}}
\]

(3-30)

For pure IPN, it has been reported that in the case of small strains (< 10%), the Young’s modulus of PEO/NBR IPN is quite constant [51]. Figure 3.5d shows the dependency of Young’s modulus on applied voltage, which is seen to drop by 16% over the range of oxidation state probed. The linear fit of modulus as a function of potential shown in the figure was incorporated into the model to enable estimation.

### 3.6 Results and Discussion

Electrical conductivity is a parameter with significant effect on the response of the actuators and should be considered in modeling approaches. In this chapter, the non-linear function of electrical conductivity versus applied potential is incorporated into the electrochemical model with the aim of achieving more accurate predictions, followed by the incorporation of the electrochemical
response into the mechanical model. In the mechanical model, the oxidation state dependence of modulus is incorporated.

Simulations assuming constant conductivity and that include the non-linear conductivity are compared with experimental results to show the ability of the proposed non-linear model to track the current response to 20 s long step changes of applied potential between ± 1 V. (red dash line) shows the current predicted by the non-linear model, which is in good agreement with experimental results (black line). The models with constant values for electrical conductivity (maximum and minimum) also are shown to compare the linear and non-linear predictions.

As seen from the results, using constant values for electrical conductivity does not show a good match between simulation and experiment. The change in conductivity with oxidation state of more than an order of magnitude shown in Figure 3.5c, combined with an observation that curvature is not uniform along the length of the trilayer during charge and discharge (as will be seen below), suggest that electronic resistance is an important rate limiting factor and that the mismatch is likely the result of a failure to incorporate variation in electronic conductivity. Incorporation of the variation in conductivity leads to an excellent match between the observed and the predicted responses.

As we discussed, the voltage along the length is a function of position during charging. Strain of the polymer is a function of charge and charge depends on local voltage. When the voltage varies along the length of the polymer film, the actuation also is not uniform. Once the actuator has enough time to fully charge and there is no current or voltage drop along the length, the actuator exhibits uniform actuation.
Figure 3.6 Measured current for an applied square wave potential (±1 volt). Experimental results are in black. Simulations using the non-linear model (red dash line) and the model with constant values for electrical conductivity (blue and green dash).

In this chapter, we investigate the behaviour of the conducting polymer-based trilayer actuator to verify the ability of the proposed model to track the mechanical behaviour of the trilayer bending actuator. Actuation of the trilayers was recorded by camera to find the radius of curvature as a function of time and position. A ±1 Volt square wave voltage was applied for 100 seconds. Image processing in MATLAB was employed to find the radius of curvature by fitting circles to the actuator. After 100 seconds, the entire actuator is fully charged and exhibits uniform curvature (Figure 3.7). This corresponds to a strain of about 2 % on the outer surface of the trilayer. During charging however it was observed that the radius of curvature is not uniform. After 3 seconds, for example, we fit four circles to the actuator at different positions (Figure 3.8) with curvature varying from 16 to 33 mm. Due to the uncertainty in finding the radius of curvature by matching circles to the actuator in 1 and 2 seconds after actuation, we compared the results of experiment and simulation at 3 seconds after voltage application. This variation in curvature can be explained by
a difference in local charge density resulting from the voltage drop along the length of the trilayer, as will now be demonstrated.

![Image](image.png)

**Figure 3.7 Finding radius of curvature by using image processing to fit circles to the actuator a) recorded picture b) after image processing.**

Dividing the actuator into small sections along the length, it is possible to estimate the volumetric charge for each section as a function of time by applying the electrochemical model. We can then predict the radius of curvature for each section as a function of time from the mechanical model because we know the time dependent volumetric charge. When the formulation for radius of curvature is incorporated into the model and the volumetric charge and Young’s modulus are updated for each time increment or step size, the radius of curvature is also updated. Free strain is equal to strain to charge ratio multiply by volumetric charge \( (\varepsilon = \alpha \rho) \).

The results of the model and experiment for actuation 3 and 20 seconds after a step in potential is applied to a trilayer that was originally nearly straight are presented in Figure 3.9. The 22 mm long, 2 mm wide actuator was divided into four equal sections along the length and the radius of curvature for each section was recorded and modeled. The proposed model shows its ability to predict the actuation behaviour.
Figure 3.8 Radius of curvature using image processing to fit circles to 4 different sections of actuator. The black arc is the observed bending as found by video analysis.

In the next experiment, the radius of curvature of the trilayer was captured during the actuation every 10 seconds after applying a step in potential. Figure 3.10 shows that the non-linear model is able to predict radius of curvature (within 4%) over the course of the experiment. For the PEDOT-based trilayer actuator, a linear model with conductivity set at the maximum measured value shows underestimation of curvature. This is likely because it assumes that entire trilayer is at the maximum conductivity. As expected the linear model is only accurate once the charging is nearly complete, and there is minimal voltage drop along the length. It is expected that the discrepancy between constant conductivity models and experimental results will be worse for actuators with a large difference between maximum and minimum conductivity such as polypyrrole-based actuators.
Figure 3.9 Radius of curvature of trilayer actuator in experiment and modeling after 3 and 20 seconds at different positions.

Several experiments have been done for actuators with different lengths and widths and the ability of the model to predict the electrical and mechanical behaviour was observed. Figure 3.10 shows the results for trilayer with 22 mm length and 2 mm width.

In the actuation of conducting polymer-based actuators there are some rate limiting factors expressed here as time constants - which affect speed of actuation. These include the diffusion time constant, polymer electronic resistance charging time constant and double layer capacitance charging time.

The diffusion time constant for a conducting polymer layer which has interaction with an electrolyte from one side, is a function of thickness, $h_2$ and diffusion coefficient, $D$ ($\tau_D = \frac{h_2^2}{D}$) [123]. In the case of migration limited transport, the effective diffusion coefficient can be determined from the ionic conductivity, $\sigma_i$ and the volumetric capacitance, $C_v$ ($D = \frac{\sigma_i}{C_v}$). For the polymer electronic resistance charging time constant, we can use $R_{CP}C$ where $R_{CP}$ is the electrical...
resistance of the conducting polymer layer and $C$ is the total capacitance of this layer. Double layer also has $R_s C_{dl}$ time constant, where $R_s$ is solution resistance and $C_{dl}$ is double layer capacitance at the interface of the conducting polymer and the electrolyte. For a trilayer actuator with 22 mm length, 2 mm width and 35$\mu$m thickness, the time constants or charge limiting factors are shown in Table 3.1. Due to the drop in electrical conductivity in the reduced conducting polymer layer, the polymer charge time constant is limiting factor which limits actuation speed.

Table 3.1 Three different time constants for trilayer with 22 mm length, $l$, 2 mm width, $w$, and 35$\mu$m thickness, $h_2$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion time constant (s)</td>
<td>$\tau_D = \frac{h_2^2}{D} = \frac{h_2^2}{\frac{D}{C_v}} = \frac{(35\times10^{-6})^2}{25\times10^{-3}1\times10^8} = 5s$</td>
</tr>
<tr>
<td>Polymer charge time constant (s)</td>
<td>$\tau_{CP} = R_{CP} \times C_v \times volume = 4s$ for maximum electrical conductivity and 80s for minimum electrical conductivity for one electrode.</td>
</tr>
<tr>
<td>Double layer capacitance charge time constant (s)</td>
<td>$\tau_{dl} = R_s C_{dl} = 3 \times 8.8 \times 10^{-6} = 26 \mu s.$</td>
</tr>
<tr>
<td></td>
<td>where $C_{dl} = 0.2 \times (w \times l)$, we used $0.2 \frac{F}{m^2}$ for double layer capacitance [123].</td>
</tr>
</tbody>
</table>

The non-linear model matches well when compared with experimental results. In comparison with previous studies, our proposed model has some advantages. The most important advantage is the ability to implement functions of oxidation state and of electrical conductivity, Young’s modulus, as well as properties not varied in this study including capacitance, ionic conductivity
and strain to charge ratio in a 2-D model. Direct time domain derivation is another benefit of the model presented in this work as several other models are initially developed in the Laplace domain and then converted into the time domain by some approximations or order reduction. Prediction of voltage, charge and also radius of curvature as a function of time and position along the length of actuator is another useful property of the model. The derivation approach of the model using a state space representation makes it easy to convert the model to the frequency domain and analyze the results in frequency domain if desired for the small signal case.

![Graph showing radius of curvature vs. time for first 5 mm and average over the total length (22 mm) of the actuator. Error bars indicate the uncertainty in the estimation of the experimental radius of curvature. After 30 seconds, the modeling results show less than 2% error vs. experiment and the error bars are not shown.]

One potential disadvantage of this approach presented is the effort required to update the matrices $A$, $B$, $C$ and $D$ if the circuit configuration changes. These matrices are obtained from matrices $\alpha$ and $\beta$ and they change with circuit configuration and geometry. The code has been derived for general type of transmission line for trilayers as shown in Figure 3.3b. To use the model for a different configuration requires an update to the code to derive the new matrices $\alpha$ and $\beta$. It is also possible to write a code for very general cases and then simplify as appropriate. For instance,
electrical resistance through the thickness or leakage resistance in parallel with capacitors can be added and these elements open or short circuited when appropriate to represent simple cases.

3.7 Conclusions

In this chapter, a time domain two-dimensional non-linear model based on transmission lines and a state space representation is demonstrated. Electrical conductivity and Young’s modulus of PEDOT/IPN/PEDOT trilayer versus applied voltage were measured and implemented in the model. This model is able to predict the behaviour of the trilayer in the time domain and find the voltage and charge as a function of time and position. Non-uniform radius of curvature along the length of trilayer actuator indicates voltage drop along the length forcing the use of a two-dimensional transmission line and consider the electrical resistance along the length or voltage drop. On the mechanical side, the model has the capability to predict the radius of curvature at specific positions through time. Local charge or voltage is used to update the electrical conductivity and Young’s modulus and also strain which is related to local charge to predict the radius of curvature. The model was validated with experiments and the reasonable consistency (Within 4%) was observed between non-linear model and experimental results.
Chapter 4: Self-Contained Tubular Bending Actuator Driven by Conducting Polymers

4.1 Introduction

Tubular actuator configurations are used for positioning and are being considered for biomedical applications, especially in scanners and catheters. Tubes that can actively bend on command are attractive for use in diagnosis and treatment in human internal organs, such as the heart and brain. The ultimate objective of the ongoing work presented here is to create actively bendable catheters for use in the treatment of aneurysms and stroke.

Previous work on piezoelectric tubes for scanning probe microscopy (SPM) [124] and to drive scanning mechanisms for imaging in vivo [33] showed good accuracy and speed. However, low strain limits the use of piezoelectric actuators, particularly for certain biomedical applications, which need large curvature and deflection.

Shape memory alloy (SMA) actuators have been employed to create active bending in tubes including catheters [24]–[27], [125]. A key advantage is that they can generate large strain and force (up to 2 N at 20% elongation [27]) with large bending angle. Such large strain however requires coiling which can be a challenge to miniaturize. Overall complexity of fabrication, control challenges, operating temperature and leakage of electrical current make SMAs problematic for using in the small diameter catheters employed in the brain.

Low voltage driven conducting polymers and ionomeric polymer metal composites (IPMCs) are attractive materials that have been employed in biomedical applications and tubular devices [28], [30], [32], [126]. Their mechanism of actuation is based on insertion and removal of ions, associated solvent flux and perhaps also polymer rearrangement, which results in swelling or
contraction, respectively. Conducting polymers are both electronically conductive and ionically conductive. Usually in conducting polymers only one ion (e.g. the anion) is mobile within the conducting polymer. When a positive voltage is applied to a conducting polymer electrode, electrons leave the polymer electrode and anions are attracted to and inserted into the polymer to balance the electrical charge. As a result of this anion insertion the polymer is expanded. To complete the circuit a second electrode is used which acts in the opposite direction, expelling ions when it is negatively biased. This inclusion and exclusion of ions can create expansion and contraction on the opposite sides of a structure such as a catheter, producing bending. The catheter configuration is shown in Figure 4.1, with the black conducting polymer electrodes that face each other across the tube acting in opposition to each other to produce deflection. In our design, the tube itself is ionically conductive, providing an internal path for ions to shuttle between opposing electrodes.

Low operating voltages, relatively high strains, controllability, ease of fabrication are advantages of conducting polymer and IPMC artificial muscles. Furthermore, biocompatibility as a specific property of some of these materials makes them suitable to be employed in biomedical applications [14], [15].

Conducting polymers have been applied on existing commercial catheters by chemical and electrochemical deposition. These catheters operate in an electrolyte bath, as demonstrated by Shoa et al. [22], [115], or in blood [4], [34] as shown earlier by Jager. In this approach, relatively low exhibited strain is observed from the polypyrrole due to reliance on ions present in the blood rather than more optimal choices [15]. In an approach by Yokota et al. a silicone rubber tube was employed as the catheter body and coated with copper. Polypyrrole was then deposited on the
copper and patterned. Their device was immersed in electrolyte and reached a 12 cm radius of curvature. Large radius of curvature and also the requirement to work in electrolyte once again are the challenges to use as an active catheter in the brain. In the neurovascular applications, higher strain is needed than is available using blood plasma [15], thus requiring the use of an internal electrolyte. This work demonstrates the use of such an internally contained electrolyte.

Two approaches have included electrolyte within the catheter. A silicone tube was used as a catheter body which was coated by thin layer of gold and then by polypyrrole. The entire device was then coated with an electrolyte gel in order to have the ability to work in air. Radius of curvature of less than 20 mm was achieved [127] in a 0.8 mm diameter tube, which is approaching the 10 mm required for neurovascular applications, and showing the promise of this approach. Delamination of the polypyrrole layer [128], decreasing electrical conductivity of the gold layer with cycling and also the gold layer’s adverse effect on bending due to its stiffness are some issues in this multilayer structure. In the first conducting polymer driven catheter reported, developed by Mazzoldi and De Rossi, a solid polymer electrolyte tube is employed as the catheter body. Conducting polymers fibers or films sit around the polymer electrolyte [35]–[37], creating a bending tube with a 0.8 mm outer diameter. Large radius of curvature due to high Young’s modulus of the solid polymer electrolyte and the use of a stiff copper wire as a counter electrode are some of the disadvantages of this approach.

Vidal and his colleagues demonstrated a long life trilayer actuator that operates in air [129]. This actuator approach is based on using interpenetrating polymer network (IPN) as a solid polymer electrolyte and poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer as an active layer. The IPN is a double network polymer, which is made of polyethyleneoxide network which
promotes ionically conductive and interpenetrated with a rubbery polymer network to provide good mechanical stability [113]. The IPN swells in aqueous, non-aqueous or ionic liquid electrolytes and works both as a substrate and as a source of ions. In the fabrication process, PEDOT penetrates into the IPN structures on the top and bottom surfaces and creates a conductive layer at these surfaces. There are some important advantages in this approach. No delamination is observed and there is no need for a metal layer for deposition as electrodeposition is not used. The process is scalable [51], produces moderate strains and the PEDOT shows good electrical conductivity [119].

The goal of the present work is to demonstrate a unibody tubular bending actuator capable of one degree of freedom actuation. In this design, the tube is composed of IPN. The actuating elements are made of a PEDOT layer itself penetrated into the IPN. This conductive layer can eliminate the need for metals. The relative compliance of the IPN tube (1 MPa, compared to 65 - 300 MPa of a commercial catheter tube [15]) also makes it easy to bend. This double network polymer tube swells with electrolyte, making it a good ionic conductor. Using this ionically conductive substrate enables the actuator to be self-contained, without the need for ion external to the device. Penetration of the PEDOT into the IPN eliminates delamination [38]. Patterning the PEDOT penetrated layer to create two separate electrodes on the surface of the tube produces a cylindrical trilayer-like structure that bends in much the same was as a trilayer actuator. The low Young’s modulus of IPN allows actuator to achieve a small radius of curvature as required for catheterization in neurovascular operation in the brain. Here our aim is to show that the unibody approach works. Fabrication steps and procedures needed to create a tubular IPN trilayer actuator is shown. Following this work, there remains the demonstration of an encapsulated version, which
is necessary to keep the blood out of the IPN and vice-versa. The device also must be mechanically and electrically connected to the tip of a much longer catheter. The tip of the device also needs to have a smaller outer diameter than is currently employed (0.7 mm instead of 0.9 mm), which will allow it to fit in the vessels of interest, and enable the desired bending radius to be achieved.

In this work, a further contribution is the derivation of cylindrical beam bending equations, and implementation of finite element simulations that are used to predict the radius of curvature. These derivations and modeling efforts can in general be used to help the designer of tubular actuators understand, optimize and predict actuator performance as a function of device properties (layer thicknesses, active strain, applied voltage and moduli of the layers).

### 4.2 Device Design

The proposed configuration of the device that we are working towards is depicted Figure 4.1. The layered cylindrical structure can create the bendable tip of a catheter as shown in Figure 4.1a. As this figure shows, the actuator can bend in one plane (gray silhouettes) when voltage is applied between patterned strips of conducting polymer (black), and through the ionically conductive actuator body (orange). The cross-section of the actuator is seen in Figure 4.1b. In this thesis, results from an un-encapsulated device are presented.

The tube of solid polymer electrolyte is an ionically conductive substrate that is used to transport ions between the conducting polymer active electrodes. This tube must have a high ionic conductivity to enable fast ion transfer and actuation, but also be sufficiently compliant to enable bending. It was chosen to employ an IPN matrix to achieve the combination of low stiffness and high ionic conductivity.
PEDOT is selected as the active layer. It is a conducting polymer with good electrical conductivity, and also offers moderate to large strains (~3 - 5% depending on the electrolyte [130]). This polymer has exhibited chemical, electrochemical and thermal stability and has attracted particular attentions in recent years [119].

![Diagram of actuator configuration](image)

**Figure 4.1 Proposed Configuration** a) Actuation of the actuator in one plane, b) Cross section of encapsulated actuator design.

The desired radius of curvature, $R$, is 10 mm [15], as needed for neurovascular applications such as the treatment of aneurysms and stroke. Typical neurovascular catheters have an external diameter of 0.5 to 0.7 mm. Given that the catheter body is highly compliant and the actuating layer is thin, it is possible to estimate the required actuator strain for a 0.5 mm diameter catheter to be:

$$\varepsilon = \frac{y}{R} = \frac{0.25\text{ mm}}{10\text{ mm}} = 2.5\% .$$

Here $\varepsilon$ is the strain at the surface of the catheter, and $y$ is the distance between the neutral axis and the actuator’s outer layer. Typically, the catheter is also required to bend in the opposing direction, so the total free strain will be twice this value, or at least 5%. Additional strain is needed to overcome substrate and encapsulation layer stiffnesses. In our proof of principle described in this thesis, a catheter with a 0.95 mm external diameter is used due to ease of handling during the
synthesis and fabrication phases. For this diameter, the expected radius of curvature will be larger for the same strain, a 22 mm radius of curvature will be achieved with a 2.5% active strain.

The chapter begins by deriving the relationship between actual observed strain and free induced strain. This relationship is used to find a configuration in which the actual observed strain in the PEDOT-penetrated layer [113] is 4.5% (bending in both directions). In the mechanical modeling section of this chapter, also the influence of modulus and geometry in general on curvature are explored.

4.3 Mechanical Modeling and Simulation

To predict the behaviour of the actuator and guide its design, an analytical model is derived. A finite element model is also employed as it helps to describe some of the non-linearity in the system in order to have more accurate predictions. The behaviour of the actuator is simulated in ANSYS finite element and compared with the analytical model and experimental results.

4.3.1 Analytical Derivation

The tubular actuator is modeled as a multilayer structure, where there are two conducting polymer layers that are electromechanically driven. The solid polymer electrolyte that is used as an ionically conductive separator is a tube that acts as a substrate into the surface of which the active layers are applied. The conducting polymer active layer interpenetrates with the outer region of the tube. This layer is patterned to form 2 electrodes (for planer bending) or 4 electrodes (for bi-planer bending). By applying voltage between conducting polymer electrodes, the mobile anions are transported from the reduced electrode and inserted into oxidized electrode. The insertion of anions causes expansion of the oxidized electrode and ion expulsion from the reduced electrodes produces contraction, with the combined effect leading the actuator to bend. By changing the polarity of the applied voltage, the actuator is able to bend in opposite direction. In order to model this process
we need the mechanical properties and geometries of each layer, as well as the relationship between the free strain of the active layers and the density of inserted anions [61], [64], [131]. To first order, there is a simple relationship between charge and induced strain in conducting polymers. The strain to charge ratio ($\alpha$) relates volumetric charge ($\rho$) in the conducting polymer (which is proportional to ion concentration) and to the active free strain ($\epsilon$):

$$\epsilon = \alpha \rho .$$  \hfill (4-1)

The value of the strain to charge is obtained empirically [5]. The relationship between voltage and charge in conducting polymers is often found to be well described as a capacitor, with capacitance increasing with the volume of the polymer, increased volume enables storage of more ions [39], [119]. The volumetric charge also is related to the applied change in voltage ($\Delta V$) by volumetric capacitance ($C_v$):

$$\rho = C_v \Delta V. \hfill (4-2)$$

implying that,

$$\epsilon = \alpha C_v \Delta V. \hfill (4-3)$$

In other words, the strain is proportional to voltage change.

Strain due to the applied voltage induces normal stress to the conducting polymer. Positive normal stress due to positive strain resulting from ion insertion is generated in the conducting polymer layer. Negative normal stress due to negative strain in another conducting polymer layer creates bending moment, which induces a bending moment on the multilayer actuator Figure 4.2. The normal stress is related to the strain by Young’s modulus ($\sigma = E \epsilon$). By integrating the product of the stress and distance from the neutral axis over the thickness and width of the conducting polymer active layer, the total bending moment generated by applying voltage is computed.
Schematic of the cross section of the actuator showing the variables used in the mathematical derivation are shown in in Figure 4.3.

Figure 4.2 Anti-symmetric positive and negative normal stresses induce a bending moment that causes the actuator to bend

Figure 4.3 Cross section of the actuator a) Dimension used in calculating the deflection, b) Variables used in describing the Element’s parameters in conducting polymer layer.

The moment induced by the normal stress in the unbent structure, $M_{induced}$, in the anti-symmetric case and where $h \ll r_o$ as in our experimental conditions, is found from the integral:

$$M_{induced} = 2 \int_{\theta_1}^{\theta_1+\theta} \sigma_{CP} y dA_{CP} \quad \text{with} \quad dA_{CP} = r_o h d\theta \quad \text{and} \quad y = (r_o + \frac{h}{2}) \sin\theta,$$

where $y$ is the distance from neutral axis. Combining these relationships gives:

$$M_{induced} = 2 \int_{\theta_1}^{\theta_1+\theta} \sigma_{CP} y r_o h d\theta = 2 \int_{\theta_1}^{\theta_1+\theta} \sigma_{CP} (r_o h)(r_o + \frac{h}{2}) \sin\theta d\theta.$$  (4-5)

The stress in the unbent structure is given by:
\[ \sigma_{CP} = E_{CP}\varepsilon = E_{CP}\alpha \rho = E_{CP}\alpha C_v \Delta V. \]  \hfill (4-6)

Integrating the resulting equation and given that \( \theta_1 = 90 - \varnothing/2 \), then:

\[ M_{induced} = 2E_{CP}\alpha C_v \Delta V (r_o + h) \int_{\theta_1}^{\theta_1 + \varnothing} \sin \theta d\theta, \]  \hfill (4-7)

\[ \rightarrow M_{induced} = 2E_{CP}\alpha C_v \Delta V (r_o + \frac{h}{2}) (\cos(\theta_1) - \cos(\theta_1 + \varnothing)). \]

This generated moment is balanced by the bending moment generated by the elastic stresses induced in the solid polymer structure and the conducting polymer layer. Integrating the elastic stress over the thickness of the solid polymer, \( \sigma_{SP} \), and the stress over two conducting polymer layers, \( \sigma_{CP} \), provides the elastic moment:

\[ M_{Elastic} = 2 \int_{0}^{\pi} \sigma_{SP} y_{SP} dA_{SP} + 2 \int_{\theta_1}^{\theta_1 + \varnothing} \sigma_{CP} y_{CP} dA_{CP}, \]  \hfill (4-8)

\[ dA_{SP} = rd\theta dr. \]

Where the charges in two conducting polymer layers must be in the opposite sense to each other and it is known from the geometry that \( \varepsilon = \frac{y}{R} \) where \( R \) is the radius of curvature.

\[ \rightarrow M_{Elastic} = 2 \int_{0}^{\pi} \int_{r_i}^{r_o} E_{SP} y_{SP} y_{SP} rd \theta d\varnothing + 2 \int_{\theta_1}^{\theta_1 + \varnothing} E_{CP} y_{CP} y_{CP} r_0 dh d\varnothing. \]  \hfill (4-9)

\( y \) is distance from neutral axis and for solid polymer with circular cross section and conducting polymer layer are:

\[ y_{SP} = rsin\theta \]  \hfill (4-10)

\[ y_{CP} = (r_o + \frac{h}{2}) sin\theta. \]

If substitute these equations into the formulation for elastic moment, we will find the total elastic moment. If we assume that the conducting polymer layers cover nearly the entire circumference of the tube (i.e. \( \theta_1 = 0 \) and \( \varnothing = \pi \)) then the total induced moment and elastic moments approach:

\[ M_{induced} = 4E_{CP}\alpha C_v \Delta V \left( r_o + \frac{h}{2} \right). \]  \hfill (4-11)
\[
M_{Elastic} = \frac{\pi}{R} \left[ E_{CP} (r_o + h)^2 (r_o h) + \frac{E_{SP}}{4} (r_o^4 - r_i^4) \right].
\] (4-12)

As stated earlier, the elastic moment balances the induced moment and they are equal:
\[
4 E_{CP} \alpha C_v \Delta V (r_o h) \left( r_o + \frac{h}{2} \right) = \frac{\pi}{R} \left[ E_{CP} (r_o + h)^2 (r_o h) + \frac{E_{SP}}{4} (r_o^4 - r_i^4) \right].
\] (4-13)

Solving for radius of curvature the expression is:
\[
R = \frac{\pi \left[ E_{CP} (r_o + h)^2 (r_o h) + \frac{E_{SP}}{4} (r_o^4 - r_i^4) \right]}{2 E_{CP} \alpha C_v (r_o h)(2r_o + h)} \frac{1}{\Delta V}.
\] (4-14)

Dividing the numerator and denominator by \( E_{CP} \), the radius of curvature is:
\[
R = \frac{\pi \left[ 4(r_o + h)^2 (r_o h) + E (r_o^4 - r_i^4) \right]}{8 \alpha C_v (r_o h)(2r_o + h)} \frac{1}{\Delta V} \text{ where: } \bar{E} = \frac{E_{SP}}{E_{CP}}.
\] (4-15)

Maximum actual strain in the case of bending at the surface is \( \varepsilon_{actual} = \frac{r_o + h}{R} \) and free strain of conducting polymer layer is \( \varepsilon_{free} = \alpha C_v \Delta V \). Dividing both side of equation (4-15) by \( (r_o + h) \), we can write a relationship between the maximum actual strain and free strain in trilayer actuator with cylindrical cross section as:
\[
\varepsilon_{actual \_max} = \varepsilon_{free} \frac{8(r_o h)(2r_o + h)(r_o h)}{\pi \left[ 4(r_o + h)^2 (r_o h) + E (r_o^4 - r_i^4) \right]}.
\] (4-16)

In the case which \( h \ll r_o \), the radius of curvature can be estimated from equation (4-17):
\[
R_{Thin \_Active \_Layer} \cong \frac{\pi \left[ 4r_o^2 h + E (r_o^4 - r_i^4) \right]}{16 \alpha C_v h r_o^2} \frac{1}{\Delta V}.
\] (4-17)

and
\[
\varepsilon_{actual \_max} \cong \varepsilon_{free} \frac{16h}{\pi \left[ 4h + E r_o (1 - \frac{r_i^4}{r_o^4}) \right]}.
\] (4-18)

This formula gives a good estimate of the actual maximum strain for typical catheter geometry, as will be shown later. It is clear that by increasing the ratio of the Young’s modulus of the solid polymer electrolyte over the Young’s modulus of the conducting polymer (\( \bar{E} \)), the actual strain decreases.
In the case of thin active layer and thick wall tubes, equation (4-15) can be simplified to become:

$$R_{Thin\ Active\ Thick\ Tube} \approx \frac{\pi r_o}{4\varepsilon_{free}} + \frac{\pi r_o^2 \bar{E}}{16\varepsilon_{free}},$$

(4-19)

where if $r_t < \frac{r_o}{2}$ the error is less than 10% and if $r_t < \frac{r_o}{3}$ the accuracy is within 1%. In this equation the first term on the right hand side represents the bending that occurs if the inner passive tube has negligible stiffness. In this case bending is increased by increasing free strain. The second term represents the case where bending is limited by the stiffness of the inner passive tube, and the bending moment produced must be increased to reduce radius of curvature. This can be achieved by increasing the thickness of the active layer, increasing free strain, and by reducing the passive layer elastic modulus relative to the active layer elastic modulus. In both limiting cases, reducing the radius, $r_o$, improves bending. Understanding the influences of dimensions and material properties is important in guiding tubular actuator design for any application. In this work equation (19) is used to understand and justify the design selected. Figure 4.4 shows the dependency of the radius of curvature to the outer radius of the actuator, thickness of conducting polymer layer and $\bar{E}$ when other parameters in Table 4.1 are constant.
Figure 4.4 Radius of curvature of the actuator with ID=0.3 mm versus (a) \( r_o \), (b) \( \frac{E_p}{E_{cp}} \) when OD=0.95 mm, (c) \( h \), (d) \( h \) and \( r_o \) for exact formulation.

4.3.2 Finite Element Simulation

In finite element simulation, ANSYS is used to model the actuator. Charge transfer and strain due to this expansion have been modeled with thermal expansion in the conducting polymer layer that is analogous to the applied voltage [132]–[135]. In this chapter, this approach of simulating voltage driven expansion with thermal expansion is used. A temperature difference is applied between layers to induce positive strain in the expanded layer and negative strain in contracted layer.

For thermal strain due to applied temperature, the formula is:
\[ \varepsilon = C_T \Delta T, \]  
\hspace{1cm} (4-20)

where, \( C_T \) is thermal expansion coefficient.

To model the induced strain by temperature in analogy with charge transfer, we can compare the strain by thermal expansion and charge transfer. Comparing equation (4-3) and (4-20) gives us:

\[ C_T = \alpha C_v \text{ and } \Delta T = \Delta V. \]  
\hspace{1cm} (4-21)

For instance, with \( (\alpha = 0.9 \times 10^{-10} \text{ m}^3/C) \) as the strain to charge ratio, and \( (C_v = 1.2 \times 10^8 F/m^3) \) as the volumetric capacitance of conducting polymer, then \( C_T = 0.0108 T^{-1} \). If a \( 1^\circ \) C temperature change is applied, the conducting polymer exhibits 1.08% strain. In the finite element software, we are able to define the material and enter the values for their properties. The effective thermal expansion coefficient is computed and set as a material property.

Meshing the sample in finite elements is very important and care should be taken to have uniform and enough number of meshes for accuracy and also to converge the result. A range of mesh densities were tried until the results clearly converged. The large deflection option was selected in ANSYS to obtain more accurate results.

To compare the result of mathematical modeling and finite element simulation, an actuator geometry was modeled in ANSYS (Figure 4.5). The model geometry is the same as that shown in Figure 4.3a, with the angle \( \emptyset = 170^\circ \). Two actuators with two different lengths and outer diameters were modeled and the results for radius of curvature is compared with the analytical model described above and the experimental results. Table 4.1 shows the properties and dimension of the modeled actuators.
Table 4.1 Properties of modeled actuators.

<table>
<thead>
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<th>Property</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Outer diameter (mm)</td>
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<td>1.2</td>
</tr>
<tr>
<td>Inner diameter (mm)</td>
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<td>0.3</td>
</tr>
<tr>
<td>Thickness of PEDOT-penetrated layer (μm)</td>
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<td>35</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>Effective Young’s modulus of PEDOT-penetrated layer (MPa)</td>
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</tr>
<tr>
<td>Effective Young’s modulus of IPN (MPa)</td>
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<td>1</td>
</tr>
</tbody>
</table>

Figure 4.5 Finite element model of the actuator by applying temperature difference between top and bottom layers by using ANSYS Workbench. The outer diameter is 0.95 mm, and other dimensions are given in Table 4.1. The section shown is in the actuated state, with colors indicating deflection of the actuator.

Uniform and accurate meshing is very important in finite element model to obtain reasonable results. In the simulation, the steady state simulation is used and the result shows the final equilibrium state. However, it is possible to do transient simulation to model the diffusion of ions.
into the conducting polymer structure with diffusion of heat into the layers. All degree of freedoms at one end of the actuator was constrained to model the clamp in real state.

### 4.3.3 Design Improvement

To help find a configuration that achieves the smallest radius of curvature, some simulations were performed in finite element software. The questions probed were: (1) Is there an advantage to covering most of the tube in active material (e.g. PEDOT) or is it best to use a relatively large gap between the covered regions?, and (2) Should the active layer be placed closer or further from the neutral axis to improve deflection? In these simulations, the configuration of the conducting polymer electrodes around the tube was changed to justify distribution of PEDOT around the circumference.

These simulations show that by increasing the angular spread of the conducting polymer layer around the tubular substrate (Ø in Figure 4.3), deflection increases and a smaller radius of curvature is achievable. This is not unexpected since a wider angular spread leads to actuation close to the neutral axis, which in turn has the potential to produce a smaller radius of curvature.

The preceding result suggest that perhaps it is beneficial to put all of the actuator in strips close to the neutral axis, leaving ‘bald’ region on the top and bottom, as shown in Figure 4.6.

In other words, the PEDOT penetrated layer is kept close to neutral axis by using four electrodes instead of two electrodes around the tube and making an asymmetric arrangement. Symmetric and asymmetric configurations are shown in Figure 4.6. In these configurations, positive potential is applied to the two upper electrodes and negative potential to the two lower electrodes or vice versa. The conducting polymer with high Young’s modulus is not present on the top and bottom, which are far from neutral axis, to reduce the bending stiffness of the structure.
Figure 4.6 Four-electrode configuration a) symmetric, b) asymmetric used to explore means of increasing bending and reducing the radius of curvature. In this geometry, the top pair of the electrodes are held at one voltage and bottom pair at another, inducing bending up or down the page.

Simulations show that in fact this configuration not only does not improve deflection but decreases it. The bending stiffness of the tube decreases in the asymmetric configuration but the bending moment from active layers also decreases due to shortening of the moment arm. The decrease in bending moment has larger effect than the decrease in actuator stiffness for the geometry tested, and so the deflection drops.

It should be considered that this behaviour depends on the Young’s modulus of the active polymer layer relative to that of the substrate and the thickness of the active layer. In cases where the stiffness of the active layer is much higher than that of the substrate, the asymmetric configuration can help to generate more deflection. This case can be realized by making the substrate modulus much lower than the active layer modulus (low $\bar{E}$), and increasing thickness of the active layer. In the case described here there is a desire to limit the thickness of the active layer to avoid slowing the device response time, and so given the $\bar{E}$ for the materials employed, the asymmetric configuration does not reduce bending radius. The best configuration for one-
dimensional bending is using more PEDOT around the tube. Simulation results for different cases are presented in Table 4.2.

With symmetric arrangement and for the geometry used, the actuator is able to generate two-dimensional symmetric bending but the deflection drops by 25%. This is a tradeoff between more degrees of freedom and more bending curvature. Given the analysis described, the symmetric two-electrode design shown in Figure 4.1 is implemented.

Table 4.2 Radius of curvature and maximum deflection for actuator with different angular distribution of active layers around the circumference. The result are for substrate $2r_o = 0.95$ mm outer diameter (OD), $2r_i = 0.3$ mm inner diameter (ID), 20 $\mu$m thickness and $E = 0.03$.

<table>
<thead>
<tr>
<th>Arrangement of Electrodes</th>
<th>Maximum deflection (mm)</th>
<th>Radius of curvature (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two electrodes with 170 degrees for each electrode</td>
<td>3.72</td>
<td>21.5</td>
</tr>
<tr>
<td>Two electrodes with 135 degrees for each electrode</td>
<td>3.48</td>
<td>23</td>
</tr>
<tr>
<td>Two electrodes with 90 degrees for each electrode</td>
<td>2.95</td>
<td>27.3</td>
</tr>
<tr>
<td>Four electrodes with 45 degrees for each electrode (Symmetric)</td>
<td>2.81</td>
<td>28.7</td>
</tr>
<tr>
<td>Four electrodes with 45 degrees for each electrode (Asymmetric) with 10° angular separation</td>
<td>2.58</td>
<td>31.32</td>
</tr>
</tbody>
</table>

4.4 Fabrication Method

In this section, the method to fabricate the actuator is presented, which includes making IPN/PEDOT rod, patterning to create separate electrodes and hollowing the rod to have tubular actuator.

4.4.1 Materials

Nitrile butadiene rubber (NBR) (kindly provided by Lanxess), dicumyl-peroxide (DCP) (Aldrich), Poly(ethylene glycol) methacrylate methyl ether (PEGM, Mw = 475 g mol$^{-1}$, Aldrich), poly(ethylene glycol) dimethacrylate (PEGDM, Mw = 875 g mol$^{-1}$, Aldrich), dicyclohexylperoxidicarbonate (DCPD) (from Groupe Arnaud), anhydrous iron III chloride (from Acros),
lithium bis(trifluoromethane)-sulfonimide salt (LiTFSI) (From Solvionic), propylene carbonate (Aldrich) were used without further purification and 3,4-ethylenedioxythiophene (EDOT) (from H C Starck) was distilled under reduced pressure prior to use.

4.4.2 IPN/PEDOT Rod and Tube

Interpenetrating polymer network (IPN) is synthesized by following the method described in [113]. This double network polymer is based on nitrile butadiene rubber (NBR) and poly (ethylene oxide) (PEO). In this case, 40% NBR and 60% PEO were used. For NBR, 1 g of solid NBR is dissolved with 4 g of 1,1,2-trichloroethane during 24 h stirring at room temperature. Then 0.375 g poly(ethylene glycol) dimethacrylate (PEGDM) and 1.25 g poly (ethylene glycol) methacrylate methyl ether (PEGM) are added to the mixture and stirring is continued for 15 min. 20 mg (2 wt % of NBR) dicumyl-peroxide (DCP) as an initiator for NBR and 45 mg (3 wt % of PEGDM+PEGM) dicyclo-hexylperoxidicarbonate (DCPD) as an initiator for PEGM and PEGDM are also added to the mixture and are stirred for another 15 min. In next step, the oxygen of the mixture is removed by pumping the mixture under vacuum pump.

To fabricate the IPN hollow tube, two methods were tried. In first method, the rod of the IPN was made and then coated by PEDOT and it followed by hollowing the rod. In the second technique, IPN tube was made and then coated by PEDOT.

To make the IPN rod, the final mixture is pumped into capillary tubes to mold the rods and then put in an oven for polymerization. Capillary tubes are kept in the oven for 3 h at 50 °C, 1 h at 80 °C to post-cure and at 160 °C for 30 min. Then IPN rods are pulled out by putting the capillary tubes in liquid Nitrogen for few seconds and taking them out. The process is repeated several times until they are removed from the glass molds. Different thermal expansion between glass and IPN
helps to separate the rods from the glassy mold. The rods are dried under vacuum at 70°C for 2 days.

To make the IPN tube, the glassy rod with 300 μm outer diameter was used for dip coating. The glassy rod was dipped in the final mixture several times to achieve desired thickness (100-200 μm) around the rod and then curing the IPN was done as mentioned in previous method. To create the uniform deposition around the glassy rod, which is tricky, the viscosity of the final mixture is very important. For making tube in dip coating technique we decreased the viscosity and used 9 g of 1,1,2-trichloroethane instead of 4 g.

Then the IPN samples are immersed in EDOT monomers for around 20 minutes and in 1.5 M FeCl₃ aqueous solution for 20 hours at room temperature. The samples are removed and washed with methanol several times to ensure about removal of the excess solution and left to dry [113].

Finally, the dip-coated sample was immersed in the 1 M LiTFSI solution to swell and then the glassy rod was pulled out to have the IPN tube coated by PEDOT. The IPN rod and tube are shown in Figure 4.7a, b. As is seen in Figure 4.7a, c, the tube of the IPN is not perfectly uniform and decided to continue with first method.
Figure 4.7 IPN rod and tube before and after PEDOT deposition a) IPN tube, b)IPN rod, c) IPN tube coated by PEDOT, d) IPN rod coated by PEDOT

4.4.3 Patterning Two Strips

Laser micromachining is an interesting technique to produce 3D features with complex structure and using a wide range of materials. This method has been employed to fabricate actuators in active catheter including to pattern: shape memory alloy actuators [136]; copper layers on which to deposit polypyrrole actuators [137]; and polypyrrole itself on the surface of a catheter [115].

In this work, laser micromachining is used to pattern the PEDOT penetrated layer on the IPN structure to make two separate electrodes around the cylindrical substrate. First, clamping fixture to hold the sample as straight as possible (Figure 4.8a) was designed. To hold the sample in a straight line, it is clamped into a slot in part A, and a small tensile force is applied to using part B,
to which it is also attached. The design cross-section is shown right side of the fixture (Figure 4.8b). The schematic detail of the fixture is shown in Figure 4.9.

Figure 4.8 Fixture to hold the polypyrrole coated catheter body sample for laser micromachining showing a) the three dimension view of the sample and fixture and b) the side view of the fixture.

Figure 4.9 Detail of the Fixture.

After putting the fixture and sample into the laser cutter, we set up the laser parameters to remove the desired strips. Power and feed rate are two important parameters to determine the depth, thickness and quality of the removed layer. After a number of trials, we found that 5% power with 0.1 mm/s feed rate are suitable to remove the 20 μm PEDOT penetrated layer. During each pass,
the laser beam can remove a strip about 20 μm width. To ensure the separation of the PEDOT electrodes, three parallel machining cuts with 10 μm shift were performed to remove 40 μm wide strip. The laser equipment has an auto-focus system to focus on the surface of the sample but it is possible to change or adjust manually as well.

In the second round of trial, another setup was determined. I changed the focus point and increased the power to remove the wider strip with one cut. In this setup, the focus point was brought up 5 cm from the surface of the sample and laser machining was performed with 100% power. Both setup are shown in Figure 4.10.

![Figure 4.10 Setups for laser machining, a) using 5% power with focus point on the surface of sample, b) using 100% power and focus point at 5 cm at the top of the sample. Both with 0.1 mm/s rate of machining.](image)

SEM images of the removed strip along the length of the actuator for two different setup are shown in Figure 4.11.
Second method showed better performance and created more uniform removed strip. This method used for laser machining step. SEM image of the removed strip along the length of the IPN/PEDOT rod is depicted in Figure 4.12.

Figure 4.11 SEM images of samples with two different laser machining methods, a, b) setting focus point at the surface of the sample, c, d) setting focus point at the top of the surface with 5 cm distance.

Figure 4.12 SEM images of the polypyrrole covered cylinder showing the laser machined slit that runs axially using a close-up of the tip (left) and showing the full length of the cylinder with the slit on the top surface (right).
After soaking the sample in solution to absorb ions, the IPN rod swells and the width of the removed strips reaches \( \sim 70 \, \mu m \). Figure 4.13 shows a removed strip after expansion due to immersion in solution. The outer diameter of the sample expands to 0.95 mm.

![Figure 4.13 Removed strip (central line running diagonally) after expansion due to soaking in solution. The diameter of the black cylinder is 0.95 mm.](image)

### 4.4.4 Hollow Tube

Now that the IPN rod has been coated with PEDOT and this coating has been separated into two electrodes, the next step is to hollow out the tube to create a catheter. A tube can be molded but this has proven difficult to do uniformly.

Instead, laser micro machining is used to create hole in the center of the cross-section of the rod. Making the hole completely by the laser machining along the entire length (10 mm) is possible but takes a long time (a few hours). Hole with the desired diameter was made by laser machining to depth of few millimeters, which acts as a pilot hole for a metal drill to create a uniform and straight hole along the length of the sample.

During these processes the sample is held between two jaws and is fixed in place using a screw. The position of the rod between jaws is checked under a microscope to ensure that it is straight and fixed in its position. Setting of the drill exactly at the center of the hole is done under a microscope because the diameter of the drill is 300 \( \mu m \) and it is difficult to center by eye. In order
to drill the very soft material a low feed rate is used, combined with a high spindle speed (3000 RPM) to avoid damaging the sample. Figure 4.14 shows the SEM image of the hollow actuator. The resulting tube is now ready to test.

Figure 4.14 SEM image of cross section of the sample after drilling close to the tip (left) and showing most of the tube length (right)

4.5 Results and Discussion

In mathematical model and simulation, it is required to know some parameters such as volumetric capacitance, strain to charge ratio and Young’s modulus of IPN and PEDOT penetrate layer. Volumetric capacitance and strain to charge ratio were experimentally measured and the Young’s modulus was found in literature [113].

The patterned actuator, was immersed in 1 M lithium bis(trifluoromethane)-sulfonimide salt (LiTFSI) (TFSI⁻ is mobile anion) in propylene carbonate (PC) for 48 h. This electrolyte was chosen due to the large strain obtained [119]. The swelling was followed by application of steps in voltage switching +1 V and -1 V out of electrolyte solution. The current in response to this sequence of step is shown in Figure 4.15. Charge transferred per step is obtained by integrating current versus time. Total charge per half cycle is used to obtain volumetric capacitance which
was found to be $1.2 \times 10^8 \text{ } F/m^3$ for the PEDOT penetrated layer. The charge/discharge behaviour of the PEDOT layer is observable in Figure 4.15.

![Figure 4.15 Current vs. time by applying ± 1 volts to the sample with 1.2 mm OD and 20 mm length](image)

The steps in voltage lead to bending of the catheter, as depicted in Figure 4.16. The deflection is symmetric about the zero bending position. In order to achieve symmetry of actuation, it is critical to ensure that the laser machining cuts are symmetric about the axis. The resulting tip deflection is 6.5 mm. The radius of curvature is computed from the deflection using the equation:

$$R = \frac{\delta^2 + l^2}{2\delta}.$$ \hspace{1cm} (4-22)

The computed radius of curvature is 30.7 mm.

$R$, $\delta$ and $l$ are radius of curvature, deflection and projection of the curved actuator on the uncurved line respectively as shown in Figure 4.16.
Figure 4.16 Actuator before and after bending resulting from the application of ±2 volts to the actuator with 1.2 OD, 0.3 mm ID and 20 mm length. The actuator showed 6.5 mm deflection in open air.

MATLAB image processing was also used to find the radius of curvature by fitting a circle to the curved actuator. For the actuator with a 1.2 mm OD, the image processing shows a 31.0±0.5 mm radius of curvature (Figure 4.17), which is very close to result of equation (4-22) and finite element.

Figure 4.17 Image processing to find the radius of curvature for actuator with 1.2 mm OD

The models suggest that application of the larger voltage will lead to larger deflection and smaller radius of curvature. For the tubular actuators with 0.95 mm and 1.2 mm outer diameters (OD) and
0.3 mm inner diameters (ID), the radii of curvature were recorded as a function of voltage and compared with the mathematical prediction (equation (4-14)) and the result of finite element simulations, as depicted in Figure 4.18. The analytical and numerical models are in a good agreement with experimental data at ±1 V and ±2 V. Beyond this range, the actuation is saturated and increasing voltage does not have any further effect on bending but can increase the speed of actuation [113]. Degradation may happen by applying high voltage (> 2 Volts) at low frequencies. Saturation is not predicted at present included in the mathematical model or the numerical simulation, which otherwise give good predictions of the response.

Figure 4.18 Radius of curvature versus applied voltage a) 13 mm actuator with 0.95 mm OD and 0.3 mm ID b) 20 mm actuator with 1.2 mm OD and 0.3 mm ID

Lifetime is an important parameter that should be investigated. Delamination often limits cycling in conducting polymer bending structures [120]. It has been reported that the PEDOT/IPN/PEDOT trilayer actuator can be cycled for 3.5×10⁶ times without degradation [38]. This long cycle life attributed to the interpenetration of the IPN and the PEDOT. In order to test cycle life, steps of ±2 volts were applied with a period of 10 s producing deflections of the 20 mm long, 1.2 mm diameter PEDOT/IPN/PEDOT tubular actuator tip, which were recorded by camera. The tip
deflection increased over 40 cycles from 5 mm to reach a steady deflection of 6.5 mm. No loss of deflection was observed over the 100 cycles recorded.

Maintaining tubular actuator position is important for some applications including catheter application. Some work has been done to control the desired position of conducting polymer-based actuators with a closed-loop control system [59]. The tubular actuator has capability to keep the maximum deflection with a deviation of less than 0.2 mm (3 %) during 30 s of constant voltage input, representing an open loop control. At constant voltage in steady state the actuator holds its while drawing very little current (Figure 4.15). Current for 2 volts is 1.1 mA and for 1 volt is less than 0.8 mA, with the associated power consumptions of 2.2 and 0.8 mW for 2 and 1 volts respectively. This amount of power is less than 10% of peak power upon application of the step.

Ability to hold the position without expending energy (catch state) is desired in some applications. This ability is not necessary for the catheter application but certainly helps to decrease the power consumption and increase lifetime. Experiments in which 2 V steps are applied for 30 s show the actuator (20 mm length, 1.2 mm outer diameter) can hold 80 percent of its maximum deflection for 20 seconds under open circuit conditions. A longer catch state may be obtainable if the initial voltage is held longer to ensure complete charging.

4.6 Conclusions

A conducting polymer-driven small controllable tubular actuator with an outer diameter of less than 1 mm was developed. An interpenetrating polymer network (IPN) was used as an ionically conductive separator and as the actuator body. This soft material enabled the actuator to reach a 22 mm radius of curvature by applying 2 volts. In addition, laser micromachining was demonstrated to pattern the PEDOT penetrated IPN to make separate electrodes around the actuator. The laser machining also was used to make a pilot hole in the cross section for hollowing
the rod in order to form a tube. A mathematical formula was derived to predict the radius of curvature for trilayer tubular actuators. The effect of geometry and mechanical properties of conductive polymer and separator layers on radius of curvature was determined. Finite element simulations and experiments were employed to validate the model. The actuator showed reasonable position control (less than 3 % change in position at maximum deflection). In future, the actuator needs to be encapsulated to avoid the current leakage and mixing of electrolytes if it is to be used in a wet environment. In addition, improvement in fabrication techniques will help to scale down the outer diameter to reach to smaller radius of curvature, which is the aim of this work.
Chapter 5: Conducting Polymer Trilayers for Tactile Interfaces: Force/Displacement Tradeoff Simulations and the Effect of Encapsulation

5.1 Introduction

Tactile interfaces are devices which enable manual interaction with skin by using the touch sensing ability, and mostly are operated by interaction with a user’s hand or fingertip. These devices provide an ability to provide touch input and in general to produce shape, texture, roughness, vibration and/or temperature changes [16], [138]. Generally, tactile interfaces have two main functions, one is measuring tactile parameters i.e. force, force and contact position and the second is the display force, shape and texture change [139].

Different technologies have been developed for tactile display. Recently dielectric elastomer actuators [140], RC servomotors shape display, shape memory alloy actuators [141], [142], piezoelectric actuators [143], pneumatic actuators [144] have been demonstrated for tactile display.

Conducting polymer actuators, due to their attractive properties are of interest for use in tactile displays. Low operating voltage, ease of fabrication, relatively large strain, low cost and miniaturization are some of interesting properties. In this chapter, it is tried to use conducting polymer trilayer actuators to design a tactile display. Trilayer actuators consist of two layers of two actively contracting layers – in this case conducting polymers - between which an electronically insulating but ionically conductive separator sits. These actuators are attractive for use in tactile displays due to their thin, planar nature. However, it is not clear if they can produce the combination of force and displacement required for this application. This question is a focus of the investigation here.
Different configurations for conducting polymer actuators have been demonstrated, e.g., trilayer bending actuators with rectangular [112], [145] and tubular cross-section [37], [57], [115], bilayer bending actuators [146]–[149] and also linear extenders [78], [80], [105]. Trilayers due to the ability of working in air and no need for an external electrode, have attracted more attention in comparison with other configurations.

Radius of curvature and generated force by trilayers are two important parameters in the performance of this kind of actuators [3], [59], [70], [76], [131], [150]. Derived mathematical models show dependency of the radius of curvature and generated force on properties including the geometry of the trilayer, Young’s modulus of the conducting polymer layer and separator and thickness of the layers. Mechanical boundary conditions are very important in mechanical derivation, which have not have been considered properly in previous work.

In this chapter, a mathematical formulation for generated force for trilayer cantilever beams is derived including the influence of the clamped boundary condition. Due to complexity of the formulation for trilayer actuators in the cantilever plate configuration (wide trilayer actuator), finite element simulations are employed to predict the deflections and generated forces. Some methods such as stacking trilayers and change in the geometry and configuration to enhance the generated force are investigated by ANSYS finite element simulation. All simulations have modeled the steady state behaviour of the actuators.

Bilayer and trilayer actuators have been used to amplify the displacement of conducting polymer actuators since the inception of the field [47]–[49]. These structures have a further advantage that they can be formed in a plane using a small number of microfabrication steps [51], [151], providing the potential for high scalability of manufacture, and suggesting application as thin low voltage active layers on flat surfaces. These may be of interest in tactile interfaces. However, a tactile
display must be able to provide enough force (a minimum of 30 – 50 mN [52] for certain cases) to effectively stimulate the mechanoreceptors involved in the sense of touch. Previous work to create tactile feedback with conducting polymers has used long linear actuators [53] or proposed thick folded structures to drive the pins in Braille cells. These make use of the relatively high operating stresses (> 1 MPa) and stiffnesses (~ 300 - 800 MPa) of conducting polymer actuators [54], but require substantial device depth. In this chapter, we study through simulation a means of taking advantage of the planar structure of bending actuators, while increasing force output.

It has been shown previously that force can be increased by stacking trilayers in parallel [101]. In the previous work, no mechanical contact was made along the length of the stacked trilayers. What happens when the trilayers are compactly stacked? Can the forces be added without substantially decreasing deflection, which in turn may be useful in creating planer tactile displays?

This work explores the effect of several interface conditions on the deflection of two or more stacked trilayers, in terms of force generated and the maximum beam deflection. ANSYS finite element software is used to predict responses. Before describing the model and the results, factors influencing the force of actuation of trilayer conducting polymers are introduced. In the following sections, change of geometry and configuration also are investigated to find their effect on generated force and displacement. In addition, simulations have been done to find the effect of trilayers on the human finger, to check the ability of actuator to generate enough stress and displacement on fingertip to be detectable.

5.2 Mathematical Derivation

Theoretical analysis of force generated at the tip of a trilayer conducting polymer due to its bending can be performed based on conventional beam bending mechanics. In this model, as shown in
Figure 5.1, the trilayer of length, $L$, and width, $b$, is considered as a beam with an ionically but not electronically conducting separator of thickness of $2h_1$ sandwiched in between two active conducting polymers of thickness of $h_2$. The rest position, in which the conducting polymer is not actuated, is shown. It is then assumed that the layers are activated, with one side attempting to contract by strain, $\varepsilon_{CP}$, and the opposite side attempting to expand by the same amount. In this case, we have a cantilever, which is under induced moment generated by conducting polymer layers. Maximum deflection takes place at the free end of the beam. The force needed to prevent deflection of the beam is computed by balancing forces and moments.

As discussed in chapter 4, the induced moment by conducting polymer due to expansion of one layer and contraction of the other layer is:

$$M_{induced} = \int_{h_1}^{h_1+h_2} \sigma_{CP} y dA + \int_{-h_1}^{-h_1-h_2} \sigma_{CP} y dA, \quad \sigma_{CP} = E_{CP} \varepsilon_{CP}, \quad dA = b dy,$$

where $y$ is distance from neutral axis.

If we consider at this point that the oxidized and reduced CP layers have different Young’s moduli during operation, then the induced moment is obtained as:

$$M_{induced} = \int_{h_1}^{h_1+h_2} E_2 \varepsilon_b dy + \int_{-h_1}^{-h_1-h_2} E_2 \varepsilon_b dy,$$
where $E_2$ and $E_3$ are Young’s modulus of top and bottom CP layers respectively. Solving the integrals and using relationship between voltage, $\Delta V$, volumetric capacitance, $C_v$ and strain, $\varepsilon$, in steady state ($\varepsilon = \alpha C_v \Delta V$) gives:

$$M_{induced} = \frac{1}{2} (E_2 + E_3) b (h_2^2 + 2h_1 h_2) \alpha C_v \Delta V.$$  

(5-3)

![Figure 5.2 Trilayer actuator under induced moment and blocking force](image)

In the trilayer with cantilever configuration (Figure 5.2), there is a beam under distributed moment.

From mechanics of material, the bending moment equation for the cantilever beam is written as follows:

$$EI \nu'' = M_{induced} - F(L - x),$$  

(5-4)

where $\nu$ is vertical deflection at position $x$ measured from the clamped end.

Using two consecutive integrations with the boundary conditions ($\nu'(0) = \nu(0) = 0$) gives formulation for $\nu$:

$$\nu = \frac{1}{EI} \left\{ M_{induced} \frac{x^2}{2} - F \left( L \frac{x^2}{2} - \frac{x^3}{6} \right) \right\}.$$  

(5-5)

Vertical deflection must be zero at the free end which means $\nu(L) = 0$ and leads;

$$M_{induced} \frac{L^2}{2} - F \left( L \frac{L^2}{2} - \frac{L^3}{6} \right) = 0 \rightarrow F = \frac{3}{2L} M_{induced}.$$  

(5-6)

Using equation (5-3) for induced moment yields:
\[ F = \frac{3b}{4L} (E_2 + E_3)(h_2^2 + 2h_1h_2)\alpha C_v \Delta V. \]  

(5-7)

If we assume that the Young’s modulus of the CP layer for reduced and oxidized layers is similar, we can simplify the equation (5-7) to:

\[ F = \frac{3b}{2L} (E_{CP})(h_2^2 + 2h_1h_2)\alpha C_v \Delta V. \]  

(5-8)

The modulus of the separator is irrelevant because in this model bending is prevented by the applied force at the tip. The equation is not completely accurate for the case of a beam in free space held by a force at the tip since this force produces a moment that increases with distance away from the applied load. For example, if the deflection shown in Figure 5.3(a) is brought to zero by a force at the tip, as simulated in Figure 5.3(b), there is a slightly buckled structure with curvatures near the root and tip being in the opposite directions. Equation 1 thus provides guidance in relating force to geometry, free strain and stiffness, but is only exact when the trilayer is operating from a flat configuration. The equation suggests that to increase the force the ratio of width to length \((b/L)\) of the device can be increased. Although this can effectively improve the force, the extent to which this can be achieved may be limited by the allowed dimensions for a given application and by tip deflection requirements of the device. Also, force and deflection can be limited for wide, short beams, by curvature in the width direction. This unwanted curvature can be reduced by adding width-wise stiffeners.

In addition to aspect ratio, raising elastic modulus of the conducting polymer layer also can increase the generated force. This possibility is limited by the available choices of conducting polymer materials or other actuator. Increasing the force can also be achieved by employing a polymer with larger free strain. Here the effect of stacking trilayer actuators to increase the force by superposition is explored through simulation.
5.3 Simulation Approach

Trilayer actuator behaviour was simulated using ANSYS® Multiphysics by extending an analogy between thermally induced strain and voltage induced strain. The same analogy has been used previously to obtain bending angle and bending moment of trilayer actuators [133]. Based on the observed behavior of conducting polymer actuators, to a first order approximation, the free strain generated by a conducting polymer (\(\varepsilon\)) is proportional to the volumetric density of charge transferred (\(\rho = C_{\text{V}} V\)) through the equation (\(\varepsilon = \alpha \rho = \alpha C_{\text{V}} V\)) [84],[74],[90].

A similar model is used to describe thermal expansion. Thermally induced strain in a beam over a sufficiently small temperature range is proportional to the change of the beam temperature, \(\Delta T\), through the equation (5-9),

\[
\varepsilon = \beta \Delta T,
\]  
(5-9)

Figure 5.3 Conducting polymer trilayer under ± 2% strain (a) deflected by an amount \(\delta\) and (b) blocked by a force \(F\).
where $\beta$ is the thermal expansion coefficient of the material. Comparing thermally induced strain and voltage induced strain, in our ANSYS simulation, we can take advantage of equation (5-9) by simulating the voltage, $V$, and $\alpha C_V$ by the applied temperature difference, $\Delta T$, and the thermal expansion coefficient $\beta$ respectively. In this case the expansion is further simplified by assuming that each layer contracts by a fixed amount. Simulation of a single conducting polymer trilayer is performed by thermally inducing $\pm 2\%$ free strains to the two conducting polymer layers – which would typically correspond to the material being capable of $4\%$ total effective free strain. The device is fixed at one end while the other end is freely moving. The full trilayer deformation is computed, as demonstrated in Figure 5.3a. Tip deflection, $d$ - the distance, which the tip of the trilayer travels from its initial position to its fully bent position - is estimated under no external load. Also blocking force, $F$, (needed to maintain zero deflection) is estimated. The simulated trilayer deformation is shown in Figure 5.3b.

A buckling-like deflection is observed as a reversal in curvature between the top and bottom halves of the device as the blocking force is applied to the tip, as seen in Figure 5.3(b). As discussed, this buckling-like behavior is expected since the force used to bring the deflection seen in Figure 5.3(a) to the zero position in Figure 5.3(b) will create the largest moment near the base, thus reversing curvature.

5.4 Experimental Results

To check the mathematical derivation and finite element simulation, the force generated by single trilayer and its deflection were measured. In this measurement, the right side of the trilayer was clamped and the left side rested on the arm of the force transducer to measure the force (Aurora Scientific Inc.) (Figure 3.5c). Voltage ($\pm 1$ Volt) was applied to the trilayer and the induced force
by trilayer was measured. In another experiment, same voltage was applied and the deflection of
the free end of the trilayer was recorded by camera and then estimated.

For a trilayer with a length of 10 mm, a width of 3 mm and a thickness of 240 μm (h₁ = 85 μm, h₂ = 35 μm), the finite element simulation and mathematical derivation are compared with measured response. Due to the uncertainty in thickness of the PEDOT layer (h₂), the simulation for h₂ = 40 μm and h₂ = 30 μm also were done and it was realized that the results were in 5% deviation compare to h₂ = 35 μm. All of the parameters in the simulation and in the mathematical derivation are the same. The results are summarized in Table 5.1. The results are in good agreement with the mathematical derivation and simulations. The difference between experimental results and the finite element simulations probably are due to uncertainty in some parameters including thickness and Young’s modulus of PEDOT layer which together are on the order of 10%.

Table 5.1 Force and deflection of single trilayer obtained by simulation, mathematical derivation and experiment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Finite element Simulation</th>
<th>Mathematical derivation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Deflection (mm)</td>
<td>2.44</td>
<td>2.36</td>
<td>2.41</td>
</tr>
<tr>
<td>Maximum Force (mN)</td>
<td>3.5</td>
<td>3.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>

5.5 Force Enhancement

In this section, some different methods have been investigated to enhance the force generated by trilayer. Stacking trilayers and also strengthening the base of the trilayer are some of these methods.
5.5.1 Stacking Trilayer

Two parallel trilayers are stacked in order to enhance the generated force due to bending using three techniques. Figure 5.4 shows two stacked trilayers of equal lengths. A spacer layer is employed to electrically separate the trilayers and in some cases provide bonding. The thickness of the spacer is 250 \( \mu m \) and the modulus of elasticity is 1 MPa. The force of bending is very small for this low modulus. \( \pm 1\% \) strains are induced to the pairs of conducting polymer actuators. The tip deflection and blocking force are estimated.

![Cross section of stacked trilayers with a very soft spacer between them](image)

In the first configuration, referred to as “individual trilayers”, the three layers of trilayer/soft material/trilayer are arranged so that they can slide without friction and move apart. In the second configuration, called “bonded trilayers”, the three layers are arranged so that one layer is bonded to the neighboring layer and cannot slide over it. In the third configuration, named “sliding trilayers” the three layers are arranged so that one layer can freely slide over the neighboring layer but cannot move away from it. In this case, the gap in between the layers is always zero.

Figure 5.5 shows the trilayers of the three configurations deflected under the applied voltage (0.25 volts). The deflection of the device is approximately equal to the deflection of the single trilayer for the independent and Sliding cases. However, it is drastically decreased for the bonded trilayers. In all cases, there is some bending, with a slight curvature reversal near the root. The forces are similar for all the three types of stacked layers and are slightly less than twice the value
estimated for one trilayer. The values of force and tip deflection of the devices are summarized in Table 5.2.

Figure 5.5 Deflection of the Bonding, sliding and individual trilayer configurations by applying 0.25 Volts (Scales are not the same).

Table 5.2 Finite element simulation result for applying 1 volt to the actuator with $12.5\text{ mm} \times 12.5\text{ mm}$ with and length and $240 \mu\text{m}$ thickness.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>One trilayer</th>
<th>Two Bonded trilayers</th>
<th>Two sliding trilayers</th>
<th>Two Individual trilayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Deflection (mm) at the top corner</td>
<td>5.02</td>
<td>1.276</td>
<td>5.226</td>
<td>5.239</td>
</tr>
<tr>
<td>Maximum Deflection (mm) at the top center</td>
<td>4.67</td>
<td>1.045</td>
<td>4.775</td>
<td>4.160</td>
</tr>
<tr>
<td>Maximum generated force at the tip (mN)</td>
<td>11.2</td>
<td>19</td>
<td>21</td>
<td>17.5</td>
</tr>
</tbody>
</table>

The deflection decrease for the case of bonded trilayers can be explained by two effects. First, the total structure is now thicker, so it takes more free strain to create the same deflection. Second, consider the two stacked trilayers instead as an inner trilayer acting to deflect to the right and an outer trilayer working to bend to the left. These two work against each other. The result is a net
doubling of the force due to the much greater thickness, as can be estimated from superposition of forces from the ‘outer’ and ‘inner’ trilayers using equation (5-8), a but a reduction in deflection. We should mention to this point that the force is applied to the top of the trilayer along the entire width. This force can keep the center of the trilayer at the zero deflection position but the corners, are not at a zero deflection point. The behaviour of the trilayers after applying force is depicted in Figure 5.6. The final modeling performed showed that stacking multiple trilayers – 5 and 10 – all of the same length, produced a corresponding increase in force without a reduction in displacement seen for the unbonded cases. For the bonded case, although force increased, further stacking led to displacement being negligible. Stacking of multiple trilayers that are unbonded offers a possible method of maintaining a planar structure while obtaining both high forces and displacements. This will require low friction and uniform construction.

![Figure 5.6 Finite element simulation results for three stacked trilayer configurations after applying blocking force (Scales are not the same).](image)

5.5.2 Effect of the Geometry on Generated Force

The mathematical derivation shows the force increases by increasing the width of the sample. To verify the mathematical derivation, finite element simulations for trilayers with different
dimensions were performed. All of the actuators have a 35 $\mu m$ thickness for PEDOT and 170 $\mu m$ of IPN. $\pm$1 volt has been applied to the actuators.

As it was expected from theory, Table 5.3 shows the dependency of the deflection of the cantilever structure to square of the length and force to $b/L$.

Simulations show that increasing the width of the actuator, enhances the generated force but also increase the deflection difference between the corner of the actuator and the center due to bending in the width direction. Interestingly, with the same width, this difference for longer actuators is very small.

<table>
<thead>
<tr>
<th>Actuator size $(b \times L)$</th>
<th>Force (mN)</th>
<th>Deflection of the corners with force (mm)</th>
<th>Free deflection at the centers (mm)</th>
<th>Free deflection at the corners (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mm $\times$ 5 mm</td>
<td>10.5</td>
<td>0.555</td>
<td>2.1</td>
<td>2.43</td>
</tr>
<tr>
<td>5 mm $\times$ 10 mm</td>
<td>5.2</td>
<td>0.576</td>
<td>7.15</td>
<td>7.19</td>
</tr>
<tr>
<td>10 mm $\times$ 5 mm</td>
<td>22</td>
<td>1.277</td>
<td>2.31</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Regarding to equation (5-8), thicknesses of the conducting polymer layers and of the separator also influence the generated force. Figure 5.7 Shows the generated force as function of thickness of layers.

It is not desirable to increase the thickness of conducting polymer too much because this layer determines the actuation speed and a thicker layer takes longer time to be fully charged, which leads to longer response time. Diffusion time constant depends on the thickness of the conducting polymer ($\tau = \frac{h^2}{D}$, where $D$ is the diffusion coefficient [84]). Increasing thickness of the separator or solid polymer electrolyte also influences the speed due to increase the IR drop along the thickness of this layer. When we apply constant voltage between two conducting polymer
electrodes, current passes through the separator layer and the thickness of this layer affects the drop of voltage, which decreases the performance.

Depending on the application and the desired specifications, there is a tradeoff between generated force, deflection and actuation speed. If friction can be made low, then stacking of sliding layers allows a large deflection combined with force increasing with the number of layers.

![Figure 5.7 Force vs. thicknesses of solid polymer electrolyte (h₁) and conducting polymer (h₂).](image)

**5.5.3 Strengthening the Base of Trilayer**

As mentioned in the previous section, increasing thickness of the SPE and CP layers has an adverse effect on actuation speed but increases the generated force. In order to avoid the drop in speed of actuation by increasing the thickness, one option to enhance the generated force is increasing the thickness of the layers at the base of actuator, including the separator layer, instead of over the entire length. Alici and colleagues tried this approach, using a thick separator near the root, thinning the cantilever progressively in steps towards the tip, showing an improvement if force while maintaining a reasonable displacement [152]. In this case, the tip of the actuator has a small thickness to allow the fast actuation and high curvature while the base is strengthened to increase the generated force when the tip is blocked by obstructions such as a human finger. Two approaches are followed in this section. First, the thickness of the SPE layer increases to strengthen
the base and in the second approach, the thickness of the CP layers increases. The results of the simulations are presented in Table 5.4 where the \( h_1' \) and \( h_2' \) are the thickness of the SPE and CP layers at the base, respectively.

Simulations show that strengthening the base will help to improve the generated force and depending on the application and specifications of the design, it is possible to play with thickness of the SPE and CP layer to increases the generated force while not dramatically reducing deflection. It should be mentioned that the deflection decreases by increasing the thickness and it is a tradeoff between deflection and generated force.

<table>
<thead>
<tr>
<th></th>
<th>Single trilayer with ( h_1 = 85, h_2 = 35 )</th>
<th>Single trilayer with ( h_1 = 85, h_2 = 35 )</th>
<th>Single trilayer with ( h_1 = 85, h_2 = 35 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( h_1' = 85, h_2' = 35 )</td>
<td>( h_1' = 585, h_2' = 35 )</td>
<td>( h_1' = 85, h_2' = 55 )</td>
</tr>
<tr>
<td>Maximum deflection at the free end (( \mu m ))</td>
<td>2444</td>
<td>918</td>
<td>2354</td>
</tr>
<tr>
<td>Maximum generated force (mN)</td>
<td>3.5</td>
<td>11</td>
<td>5</td>
</tr>
</tbody>
</table>

5.6 Encapsulation Effect

Since the conducting polymer actuator works with ions and needs electrolyte or in general a source of ions, their surfaces are wet or at least vulnerable to ion loss and typically need encapsulation. Basically, there are two important reasons for encapsulation regarding to the application. The firs
is avoiding loosing ions and solvent, which causes decreasing performance of the actuator. The ions and/or solvent also can contaminate the environment or media that the actuator is working in such as blood vessels or in interaction with human skin. The second reason is avoiding current leakage. Based on mechanism of actuation and their electrical conductivity, to avoid the current leakage which may be dangerous for some application such as catheter application in the brain, this type of actuator should be encapsulated.

Some materials are shown to be good candidates for use as encapsulants. Poly(styrene-b-isobutylene-b-styrene) (SIBS) [43] and parylene [44] have been used to encapsulate the ionic actuators (polypyrrole and IPMC).

To find the effect of encapsulation layer on actuation of trilayer actuators, finite element simulations were performed.

SIBS is a very soft material with low Young’s modulus (12 MPa) [43] while the parylene has a higher Young’s modulus (400 MPa) [44].

Parameters used in the finite element simulation are summarized in Table 5.5.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PEDOT</th>
<th>IPN</th>
<th>SIBS</th>
<th>parylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (MPa)</td>
<td>220</td>
<td>1</td>
<td>12</td>
<td>400</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>35</td>
<td>170</td>
<td>10, 20, 50, 200</td>
<td>10, 20, 50, 200</td>
</tr>
<tr>
<td>Applied free strain (%)</td>
<td>±0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Results of simulation are presented in Table 5.6. The maximum deflection of the trilayer without encapsulation is 9074 μm.

The trend of the drop in deflection versus thickness of encapsulation layer is shown in Figure 5.8. Increasing parylene thickness significantly decreases the deflection. SIBS shows less effect
on deflection, which is not surprising given its much lower modulus. Work by Nafici et al. [44] suggests a 25 μm layer of SIBS for encapsulation, though it is not clear how long this can be effective. Experiments are currently underway to fully test the effectiveness of this encapsulant.

Table 5.6 simulated deflection of trilayers with SIBS and parylene encapsulation layer.

<table>
<thead>
<tr>
<th>Thickness of the SIBS Encapsulated layer (μm)</th>
<th>Deflection (μm)</th>
<th>Thickness of the parylene Encapsulated layer (μm)</th>
<th>Deflection (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8934</td>
<td>10</td>
<td>5417</td>
</tr>
<tr>
<td>20</td>
<td>8777</td>
<td>20</td>
<td>3625</td>
</tr>
<tr>
<td>50</td>
<td>8190</td>
<td>50</td>
<td>1533</td>
</tr>
<tr>
<td>200</td>
<td>4233</td>
<td>200</td>
<td>143</td>
</tr>
</tbody>
</table>

Figure 5.8 Deflection of the encapsulated trilayer with two different encapsulation layers, SIBS and parylene.

5.7 Simulation of generated Stress on a Finger

Generating stress on the human figure is one of the criteria for using actuators in tactile interface devices. If the actuator at least reaches the lower limit of the detectable stress on the human figure, it could possibly be used in haptic devices. Otherwise, a way should be found to increase the generated force and stress by the actuator. To check the ability of the conducting polymer trilayer actuators to generated enough stress on human figure, some simulations have been done to estimate this stress. The human finger and trilayer actuators were modeled in ANSYS and the generated
stress on the fingertip in contact with at the tip of the actuator was measured. The finger was modeled as being composed a soft material, with a modulus of 2.5 MPa [153].

The sensitivity of the finger or the minimum detectable displacement and force changes with frequency [154]. For instance, in 100 Hz, the required displacement is less than 80 nm but for 1 Hz it is around 20 \( \mu m \). Also the minimum detectable force for 100 Hz is 1 mN and for 1 Hz is 10 mN. Different areas of the human body have different thresholds for displacement and force, which should be considered in tactile interface design [46].

Small amounts of detectable displacement allow decreasing the length of the actuator to increase generated force. Therefore, the length of the actuator is decreased to 2 mm with 1 mm width. The stress and deformation on the human fingertip for \( \pm 0.5 \) V, \( \pm 1 \) V and \( \pm 2 \) V inputs was simulated in ANSYS. The results are summarized in Table 5.7. A schematic of the deformation on the fingertip is illustrated in Figure 5.9.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( \pm 0.5 ) Volts</th>
<th>( \pm 1 ) Volts</th>
<th>( \pm 2 ) Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection of free actuator (( \mu m ))</td>
<td>105</td>
<td>210</td>
<td>420</td>
</tr>
<tr>
<td>Deflection on fingertip (( \mu m ))</td>
<td>25</td>
<td>34</td>
<td>80</td>
</tr>
<tr>
<td>Maximum induced stress on fingertip (kPa)</td>
<td>2.7</td>
<td>5.3</td>
<td>11</td>
</tr>
<tr>
<td>Maximum stress at the base of the actuator (MPa)</td>
<td>3.2</td>
<td>6.5</td>
<td>13</td>
</tr>
</tbody>
</table>

If we assume that, the maximum stress is applied on the finger with area equal to 2 mm × 1 mm, the peak stress of 11 kPa can generate a 22 mN force, which is not low for using in tactile display. Minimum detectable displacement and force on fingertip in low frequency (< 2 Hz) is 20 \( \mu m \) and 6 mN [154], [155] and the displacement and force induced by trilayers are larger than these thresholds. By increasing the input frequency, the minimum detectable displacement and force decreases.
Figure 5.9 Total deformation induced by a trilayer on a fingertip by applying ±2 Volts to CP layers.

5.8 Conclusions

Generated force by conducting polymer-based trilayer actuators is small and needs to be enhanced. Bonding trilayers, increasing width or thickness and also strengthening the base of the actuator are some useful methods to improve generated force, as is stacking of trilayers. The type of bonding between stacks of trilayers is very important and in some cases can dramatically drop the deflection of the device. Some parameters such as width of the actuator can improve the generated force but have the adverse effect of creating bending in undesired directions. There is tradeoff between effective parameters to achieve required deflection and generated force.

Encapsulation is another requirement of ionically driven devices and has a larger effect on performance. Stiffness of this layer affects the deflection and simulations show that SIBS can satisfy this requirement.
Chapter 6: Summary, Conclusions and Future Work

In this work, modeling, characterization, simulation, design and experimental verification of conducting polymer-based actuators for two different applications were discussed. Non-linear time domain modeling of a freestanding polypyrrole film linear actuator was developed. This modeling which is a combination of state space representation and a 2-D RC transmission line was able to predict the electrical and mechanical behaviours of the conducting polymer linear actuators as a function of time and position. Characterization of the polypyrrole can be summarized as:

1- Electrical conductivity of the polypyrrole film as a function of oxidation state was measured and the measurement showed a significant drop in electrical conductivity in the reduced state. Maximum electrical conductivity in oxidized state was 42000 S/m while the lower conductivity in reduced state was less than 500 S/m.

2- Ionic conductivity of the polypyrrole film changes with oxidation state and measurement showed a 55% drop in ionic conductivity in the reduced state versus the maximum value at oxidized state.

3- Voltage drop along the length of the polypyrrole film is significant and has to be considered in the modeling approaches to have more accurate model. This drop causes nonuniform strain along the length of the actuator.

After characterizing the polypyrrole film, the non-linear functions for ionic and electrical conductivities were incorporated into the model. The non-linear model predicted the current response to the applied voltage and also mechanical strain and movement as a function of time and position during oxidation and reduction.

Much of the work that has been reported in the literature, has modeled the CP layer in the frequency domain. Some showed a reasonable consistency with experiment by using constant values for
electrical and mechanical properties. A disadvantage of this approach that conversion to time domain has not been achieved without approximation, and the frequency domain models cannot include non-linear effects. However, in frequency domain and for small to moderate range of applied potential, they are able to predict the behaviour of actuators, which is useful for some applications. The model for polypyrrole linear actuation presented and validated in this thesis removes the linearity constraints and does not require approximations.

The model was extended to apply to a trilayer, and compared with the response of a PEDOT/IPN/PEDOT trilayer actuators. For the first time the asymmetry of the trilayer (one side reduced, one side oxidized), and the spatial variation of properties are incorporated into a simulation. The model is able to predict the electrical behaviour and also radius of curvature of the actuators. In the case of trilayer actuators, characterization was done to find electrical conductivity and Young’s modulus changes versus oxidation state, which were incorporated into the model. Experimental results showed:

1- Young’s modulus of the PEDOT/IPN/PEDOT trilayer varies with oxidation state. A 16% drop was observed in Young’s modulus by oxidizing the PEDOT layers.

2- Electrical conductivity of the PEDOT conducting polymer layer changes with oxidation state and increases from 350 S/m to 12000 S/m over a +1 Volt range in oxidation state.

The functions for Young’s modulus and electrical conductivity of the PEDOT layers were implemented into the non-linear model to predict the radius of curvature as a function of time and position. The model was in good agreement with experimental results and showed less than 4% error in predictions. The first derivation of the trilayer beam bending model for the case of an asymmetric, spatially non-uniform trilayer is presented and combined with the first non-linear spatially non-uniform electrochemical model of trilayer charging in order to predict bending
through time. An improvement in predictive power by using the non-linear approach is demonstrated.

PEDOT/IPN/PEDOT trilayers show interesting properties such as good cycle life time, relatively easy fabrication, miniaturization and no delamination. This approach was then extended for the first time to a device with circular cross-section, appropriate for example for a neurovascular catheter application. An IPN rod was made and then was coated with PEDOT to make a PEDOT penetrated layer around the rod. Laser micromachining was used to remove two strips around the rod to make two separate PEDOT electrodes. Laser micromachining and drilling was employed to hollow the rod and fabricate the tubular actuator. This actuator did not need the external electrolyte and worked in air without delamination and degradation for several hundred cycles.

In the proposed design, the IPN compliant material was used as a body and also ion reservoir to enable actuator to reach smaller radius of curvature. This effort led to the creation and demonstration of the first conducting polymer driven cylindrical actuator with internal ion transport.

The mathematical derivation to estimate the radius of curvature as a function of actuator free strain was conducted and the effects of different parameters on radius of curvature were investigated.

22 mm and 32 mm radius of curvatures with the tubular actuators with 0.95 mm and 1.2 mm outer diameters was achieved by applying 2 volts.

The ultimate desired value for radius of curvature is 10 mm and the mathematical derivation showed it is possible by using actuator with a smaller outer diameter (0.5 mm). Future work will be required to make a tube of diameter, which combined with hollowing it out should enable this specification to be satisfied.
Encapsulation of the inside and outside of the actuator is another challenges that should be solved. Some encapsulation materials have been proposed in this thesis and they need more efforts and experiments to find the best way to deposit and also find the best thickness to avoid adverse effect on performance.

Finally, the PEDOT/IPN/PEDOT trilayer actuators were investigated for possible use in a tactile display application. A key challenge with these bending structures is achieving the combination of displacement and force needed. Mathematical derivations and finite element simulations showed that the generated force by individual trilayers is small unless the trilayer is very short in length, in which case displacement is scarified. Change of geometry, stacking of trilayers and also strengthening the base of the trilayers are some methods to increase the generated force, which were investigated in this thesis through simulation. It was shown that stiffening the trilayer base by for example stacking layers in this region, while leaving the end of the trilayer thin and free to bend, can increase force while reducing the sacrifice in displacement. This is because the application of force to the tip of the trilayer has the greatest effect near the root of the cantilever, which when stiffened, leads to less bending. Meanwhile the contribution of each portion of a uniform trilayer to curvature is equal, so stiffening the end simply reduces the effective length. Alternatively, stacking trilayers that can slider with respect to each other will maintain deflection while linearly increasing force. Reducing friction between layers will be important in the effective implementation of this approach.

Finally, the encapsulation layer affects performance of the actuator and the material for this layer should be compliant to avoid decreasing deflection.

Overall this work has contributed to the full understanding a prediction of conducting polymer actuator driven structures by relating measured variations in electronic conductivity, ionic
conductivity and modulus to the observed electrochemical and actuation responses. This approach has been applied to bending trilayers, for the first incorporating asymmetry in the electrical and mechanical properties. New methods of increasing force generated by trilayer actuators have also been proposed. Finally, a new, self-contained tubular actuator geometry has been demonstrated, and the path towards its use in an active catheter set out.

It is hoped that these innovations and models will lead to commercial applications of conducting polymer actuators, including their use in catheters and tactile displays. The modeling approaches developed here should also be applicable to other electrochemically driven devices and actuators.
Bibliography


[35] A. D. Santa and D. De Rossi, “Intravascular microcatheter steered by conducting polymer


M. S. Ren, C. E. Fok, J. D. W. Madden, and W. G. Dunford, “Measurement and Equivalent


[85] A. Della Santa, A. Mazzoldi, C. Tonic, and D. De Rossi, “Conducting polymer


Appendix A Diffusive Elastic Model: Current and Voltage versus Frequency and Position

Figure A.1 shows this circuit model in two dimensions (2D model).

Figure 6.1 2D model for PPy film by using RC transmission line.

To derive the voltage as function of frequency and position, we can break down the long strip of the polymer with $m$ number of transmission lines and add the electrical resistance to model the electrical resistivity of polymer against movement of electrons between these transmission lines (Figure 2.1). Total impedance of the strip in 2D has been derived in DEM model [55] and here we derive the voltage and current. According to Figure A.1 we can write the following:
\[ i_e(x) - i_e(x + dx) = i_i(x). \]  
\( \text{(A-1)} \)

\[ V_e(x) - V_e(x + dx) = i_e Z_e. \]  
\( \text{(A-2)} \)

\[ i_i(x) = Y_i V_e(x) \text{ where } Y_i = 1/Z_i. \]  
\( \text{(A-3)} \)

By using the concept of finite element, the impedance of each small element is a fraction of total impedance then:

\[ Z_e(s) = \frac{Z_{e\text{ total}}(s)dx}{L}. \]  
\( \text{(A-4)} \)

\[ Y_i(s) = \frac{Y_{i\text{ total}}(s)dx}{L}. \]  
\( \text{(A-5)} \)

where \( Z_{e\text{ total}} \) is the total electronic impedance and \( Y_{i\text{ total}} \) is the total ionic impedance through the electrolyte to the counter electrode. \( L \) is the length of the strip and \( x \) is position of the element along the length.

By substituting (A-5) into (A-3) and using the result for (A-1), we can describe the current by a differential equation, and substituting (A-4) into (A-2) enable us to write the same differential equation for voltage:

\[ \frac{\partial i_e}{\partial x} = - \frac{Y_{i\text{ total}}(s)}{L} V_e(x, s). \]  
\( \text{(A-6)} \)

\[ \frac{\partial V_e}{\partial x} = - \frac{Z_{e\text{ total}}(s)}{L} i_e(x, s). \]  
\( \text{(A-7)} \)

The combination of these two equations, gives two second order differential equations with same variables in both sides:

\[ \frac{\partial^2 i_e(x, s)}{\partial x^2} = \left( \frac{Z_{e\text{ total}}(s)Y_{i\text{ total}}(s)}{L^2} \right) i_e(x, s). \]  
\( \text{(A-8)} \)

\[ \frac{\partial^2 V_e(x, s)}{\partial x^2} = \left( \frac{Z_{e\text{ total}}(s)Y_{i\text{ total}}(s)}{L^2} \right) V_e(x, s). \]  
\( \text{(A-9)} \)
The solution for this type of differential equation has an exponential form with two unknown parameters that can be obtained by applying the boundary conditions. The general solution is:

\[ u(x, s) = A(s)e^{k(s)x} + B(s)e^{-k(s)x}, \quad (A-10) \]

where \( k(s) = \sqrt{\frac{Z_e^{\text{total}}(s)Y_i^{\text{total}}(s)}{L^2}}, \)

and the boundary conditions are:

\[ i_e(0, s) = I_0(s). \quad (A-11) \]
\[ i_e(L, s) = 0. \quad (A-12) \]
\[ V_e(0, s) = V_0(s). \quad (A-13) \]
\[ V_e(0, s) = \frac{i(0, s)}{Z_e(s)} = \frac{1}{Z_e^{\text{total}}(s)} \frac{\partial i_e(0, s)}{\partial x}. \quad (A-14) \]

The boundary conditions for the strips were applied to find \( A(s), B(s) \) and total solutions for current and voltage are:

\[ i_e(x, s) = I_0 \frac{\sinh(k(s)(L-x))}{\sinh(k(s)L)}, \quad (A-15) \]

and

\[ V_e(x, s) = V_0 \frac{\cosh(k(s)(L-x))}{\cosh(k(s)L)}. \quad (A-16) \]

To fully determine the current and voltage in (A-15), (A-16) and, their relation to \( k(s) \), we have to find the total electrical impedance and ionic admittance first, because \( k(s) \) is a function of these two parameters and the length of the strip.

The total electronic resistance of the polymer with \( h \) as a thickness, \( w \) as a width and \( \sigma_e \) as a electronic conductivity, against electron flow is purely resistive [101] and equal to:

\[ Z_e^{\text{total}} = \frac{L}{\sigma_e w h}. \quad (A-17) \]
The admittance of the polymer strip on ionic side is more complex. It includes the diffusion of ions into polymer structure, charging of double layer capacitor at the interface between polymer and solution and charge transfer through the electrolyte by ions. The expression of total admittance of the strip has been derived by Madden [55]:

\[ Y_{i_{\text{total}}}^{s}(s) = \frac{s}{R_{s}} \frac{\sqrt{D}}{\sqrt{\delta}} \frac{h}{\sqrt{\Delta}} \text{tanh}(\frac{h}{2\sqrt{D}}) + \sqrt{s} \]

where \( D \) is the diffusion coefficient of the polymer, \( R_{s} \) is the solution resistance, \( h \) is the polymer thickness, \( \delta \) is the thickness of double layer capacitor and \( s \) is the Laplace variable, give by the square root of -1 times the angular frequency.

Now we are able to find the voltage and current as a function of frequency and position. Here we obtained the voltage and current in the limits of high and low frequency for the strip of polymer.

At high frequency or very short time after applying the voltage to the one end of the polymer strip, the voltage as a function of position can be obtained. When the frequency goes to infinity

\[ Z_{e_{\text{total}}}^{s}(s \rightarrow \infty) = R_{e_{\text{total}}}^{s} \text{ and } Y_{i_{\text{total}}}^{s}(s \rightarrow \infty) = \frac{1}{R_{s}} \text{ then:} \]

\[ k = \sqrt{\frac{1}{L^{2}} \frac{R_{s}^{\text{total}}}{R_{s}}} \]

and for current and voltage we have:

\[ i_{e}(x) = I_{0} \frac{\sinh(k(L-x))}{\sinh(kL)} \]

\[ V_{e}(x) = V_{0} \frac{\cosh(k(L-x))}{\cosh(kL)} \]

At high frequency, the double layer capacitance and polymer capacitance have very low impedance, they are effectively shorted and the polymer has purely resistive behaviour. (A-20) and (A-21) show the current and voltage as a function of position. For \( x = 0 \):
\[ i_e(0, s \to \infty) = I_0. \]  \hspace{1cm} (A-22)

\[ V_e(0, s \to \infty) = V_0, \]  \hspace{1cm} (A-23)

and for \( x = L \):

\[ i_e(L, s \to \infty) = 0. \]  \hspace{1cm} (A-24)

\[ V_e(L, s \to \infty) = \frac{V_0}{cosh(kL)}. \]  \hspace{1cm} (A-25)

According to (A-19), by increasing the electrical resistance of the polymer, \( k \) increases and then referring to (A-25), voltage at the other end will be smaller versus applied voltage.

At low frequency or long time, the admittance of the polymer in DEM model is purely capacitive and can be simplified as follows:

\[ Y_{t_{\text{total}}}(s) = sC \left( \frac{a}{2 \delta} + 1 \right), \]  \hspace{1cm} (A-26)

and \( k \to 0 \) when \( s \to 0 \). For the current and voltage we have:

\[ I_e(x, s \to 0) = 0. \]  \hspace{1cm} (A-27)

\[ V_e(x, s \to 0) = V_0. \]  \hspace{1cm} (A-28)

(A-27) and (A-28) show that in long time after applying the voltage at one end, voltage at the other end reaches to applied voltage and there is no current passing through the polymer then the entire polymer has uniform voltage in long time and polymer strip becomes fully charged.