ACTUALIZING FAST CONDUCTING POLYMER ACTUATORS:
DESIGN OPTIMIZATION, FABRICATION, AND ENCAPSULATION

by

Saeedeh Ebrahimi Takalloo

B.Sc., The University of Tehran, 2007
M.Sc., The University of Tehran, 2009

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Electrical and Computer Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

March 2019

© Saeedeh Ebrahimi Takalloo, 2019
The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

**Actualizing fast conducting polymer actuators: Design optimization, fabrication, and encapsulation**

submitted by Saeedeh Ebrahimi Takalloo in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Electrical and Computer Engineering

**Examiner Committee:**

John D. W. Madden
Co-supervisor

Edmond Cretu
Co-supervisor

Dana Grecov
University Examiner

Mu Chiao
University Examiner

**Additional Supervisory Committee Members:**

Kenichi Takahata
Supervisory Committee Member

Shahriar Mirabbasi
Supervisory Committee Member
Abstract

Conducting polymer actuators offer large strain (> 1%) and high work density, operate at low voltages and can resonate at tens to hundreds of Hertz. Unfortunately, they dry out in air if a solvent-based electrolyte is used, and exchange ions in wet environments, both of which cause their performance to change over time. They also lack a scalable fabrication process through which devices with reproducible performance (especially with fast actuation) are achieved.

In this work, we show that a 100 µm poly(styrene-\textit{b}-isobutylene-\textit{b}-styrene) encapsulation helps these devices to retain 80% of their stored solvent more than 1000 times longer compared to when there is no encapsulation. The shelf life of the encapsulated device, which is around 4 days when there is no encapsulation, is expected to improve by 600 times with encapsulation.

We also developed a new, easily reproducible, and scalable fabrication process through which conducting polymer films as thin as 400 nm can be obtained. High electronic and ionic conductivities of $4 \times 10^4$ S/m and $4 \times 10^{-3}$ S/m, volumetric capacitance of $2.4 \times 10^7$ F/m$^3$, and strain difference of ~0.65 %, were obtained from thin sprayed films of poly(2,3-dihydro-thieno-1,4-dioxin)-poly(styrene-sulfonate) on porous polyvinylidene fluoride membranes with thicknesses of ~3.5 µm. Using this technique, we showed that 10 mm long, 2 mm wide and 0.125 mm thick trilayers with a steady state peak to peak displacement of ~4.5 mm, and cut off frequency of ~2 Hz, produce a ~0.5 mm displacement up to 50 Hz.

In this work, we also modified the already developed 2D transmission line model of trilayer conducting polymer actuators to take into account the effect of contact electrodes and the non-uniform charge-induced strain throughout the volume of the conducting polymer layers. Based
on this model, we created a web-based graphical user-interface tool, named ActuaTool, to facilitate the design and modeling of trilayer conducting polymer actuators.

This work is paving the way to employ fast conducting polymer actuators in real applications through developing a new fabrication process, their encapsulation and creating a design optimization tool.
Lay summary

Actualizing fast trilayer conducting polymer actuators first requires a reproducible and scalable fabrication process through which sub-micron thick films of conducting polymer with relatively large electronic and ionic conductivities can be obtained. Secondly, the devices need to be encapsulated not to limit our choices of ionic medium to nonvolatile ionic liquids, nor the operation environment of the device to air. Having the first two prepared, thirdly, a design tool based on the electro-chemo-mechanical model of these devices is needed to facilitate their design optimization through easily predicting their behavior and proposing dimensions through which the desired operation speed can be obtained.

The following dissertation involves the details of each of the aforementioned steps.
Preface

The research work presented in this dissertation is largely carried out in Molecular Mechatronics Laboratory in the Department of Electrical and Computer Engineering at the University of British Columbia, Point Grey campus, under the supervision of Dr. John Madden and Dr. Edmond Cretu.

Chapter 1 and Chapter 6, namely the Introduction and Conclusion, respectively, are framed and written by me, with feedback from Dr. John Madden.

In Chapters 2 and 3, Dr. Adelyne Fannir was involved in the fabrication of the trilayer actuators under the supervision of Dr. Frederic Vidal in Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), University of Cergy-Pontoise, Cergy, France. I, independently, carried out all other aspects of the research, including material characterizations, design of the experiments and performing the related measurements, data collection, and analysis, with the supervisory input from Dr. John Madden and Dr. Edmond Cretu, and comments from Drs. Cedric Plesse and Giao T. M. Nguyen (both from LPPI, University of Cergy-Pontoise, Cergy, France). I was also responsible for the manuscript composition for both chapters, which were further edited by Dr. John Madden. Drs. Cedric Plesse and Giao T. M. Nguyen were also involved in editing a version of Chapter 2, which is published at the Journal of Multifunctional Materials,

The primary results of Chapter 3 were presented at MRS meeting as a poster,

S. Ebrahimi Takalloo, K. Dixon, A. Fannir, C. Plesse, G. Nguyen, F. Vidal, J. Madden,
“Long-Life Operation of Flexible Ionic Devices Using a Spray-Coated Elastomeric
Encapsulation”, Poster presented at MRS fall meeting, Nov. 26- Dec. 1 2017, Boston,
Massachusetts.

At the time of this writing, a version of chapter 3 is also prepared to be submitted to a journal
venue,

S. Ebrahimi Takalloo, A. Fannir, G. T. M. Nguyen, C. Plesse, F. Vidal, J. D.W. Madden,
“Impermeable and compliant- SIBS as a promising encapsulant for ionically electroactive
devices”, to be submitted to a journal venue.

In Chapter 4, I was the primary contributor in the development of the electro-chemo-
mechanical model of the trilayer conducting polymer actuators with the supervisory input from
Dr. John Madden. I was also responsible for developing the idea of ActuaTool and its different
aspects and functionalities. Dr. Hasti Seifi was involved in the code implementation of a pre-
alpha version of ActuaTool (predicting force, deflection and cutoff frequency of the device)
using standard web technologies (JavaScript, HTML, and CSS), based on a simple electro-
chemo-mechanical model of trilayer conducting polymer actuators which was then presented in
SPIE conference,

S. Ebrahimi Takalloo, H. Seifi, and J. D.W Madden. "Design of ultra-thin high-frequency
trilayer conducting polymer micro-actuators for tactile feedback interfaces." In SPIE Smart
Structures and Materials+ Nondestructive Evaluation and Health Monitoring, pp. 1016312-
1016312. International Society for Optics and Photonics, 2017.

I further improved ActuaTool to be used as a design optimization tool based on the same
model and the Alpha version was presented in BAMN conference,


The Gamma version of ActuaTool was further developed by me based on the modified electro-chemo-mechanical model presented in section 4.2.

I was the main investigator in developing the idea of enabling trilayer conducting polymer actuators in tactile feedback interfaces, with the supervisory input from Dr. John Madden. The design presented in figure 4.10 along with several other embodiments were published as a US patent,


I was the main author responsible for manuscript composition for chapter 4, which was then edited by Dr. John Madden.

In Chapter 5, I was the main investigator who developed the fabrication process, conducted all the measurements, data collections and data analysis with the supervisory input from Dr. John Madden. An undergraduate student, Xu Fan, carried out the stress-strain measurements and data collection presented in section 5.3.2, and free vibration experiments and data collection presented in section 5.3.9, under my direction. I was the main responsible for manuscript composition for this chapter which was further edited by Dr. John Madden.

Spray-coating, metal deposition, Scanning Electron Microscope (SEM) and Energy-dispersive X-ray (EDX) spectrophotometer, and thickness characterizations of the samples were carried out
using the shared facilities at the 4DLabs in Simon Fraser University.

Optical microscopy characterization was carried out in Advanced Fibrous Materials Laboratory (AFML), University of British Columbia, under the supervision of Dr. Frank Ko.
# Table of contents

Abstract.................................................................................................................................................. iii

Lay summary........................................................................................................................................... v

Preface..................................................................................................................................................... vi

Table of contents ..................................................................................................................................... x

List of tables............................................................................................................................................ xvi

List of figures.......................................................................................................................................... xviii

List of abbreviations ............................................................................................................................ xxix

Acknowledgements ............................................................................................................................... xxxii

Dedication .............................................................................................................................................. xxxiv

Chapter 1: Introduction .......................................................................................................................... 1

1.1 Trilayer conducting polymer actuators: a brief history of their development ......................... 1

1.2 The scope of this thesis ..................................................................................................................... 4

1.3 Thesis overview ............................................................................................................................... 6

1.4 List of contributions ....................................................................................................................... 8

Chapter 2: Evaluating performance of wet unencapsulated PEDOT trilayer actuators operating in air and water ......................................................................................................................... 10

2.1 Introduction and Motivation ........................................................................................................... 10

2.2 Experiments .................................................................................................................................. 13

2.2.1 Materials .................................................................................................................................. 13

2.2.2 Trilayer Conducting Polymer actuators fabrication................................................................. 13
3.4.3.1 Electromechanical modeling of trilayer conducting polymer actuators ..........57
3.4.3.2 Effect of encapsulation on the extent to which the trilayer can bend ..........60
3.4.3.3 Effect of encapsulation on the cycling response of trilayers in flowing air......62
3.4.3.4 Effect of encapsulation on the cycling response of trilayers in DI water .........66
3.5 Conclusion ........................................................................................................68

Chapter 4: ActuaTool: a web-based graphical user-interface (GUI) to design and study trilayer conducting polymer actuator beams ..........................................................................70
4.1 Introduction and motivation ................................................................................70
4.2 Modeling conducting polymer trilayer actuators .................................................73
  4.2.1 Electro-chemo-mechanical modeling of trilayer conducting polymer actuators .....75
  4.2.2 Force, displacement and stiffness ..................................................................85
  4.2.3 Cutoff frequency ............................................................................................89
  4.2.4 Resonance frequency .....................................................................................91
  4.2.5 Average power consumption .........................................................................92
    4.2.1 Electrical efficiency .....................................................................................93
    4.2.2 Electromechanical coupling ..........................................................................94
    4.2.3 Mechanical efficiency ..................................................................................96
    4.2.4 Effect of encapsulation ...............................................................................97
4.3 ActuaTool ...........................................................................................................98
  4.3.1 “Frequency response” mode ........................................................................101
  4.3.2 Parameter response mode ..............................................................................104
  4.3.3 Design mode ..................................................................................................105
4.4 Design of trilayer conducting polymer actuators for a tactile feedback interface ......109
Conclusion ........................................................................................................... 120

Chapter 5: Fabrication and characterization of PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers
........................................................................................................................................ 124

5.1 Introduction and motivation ..................................................................................... 124

5.1.1 Rate limiting factors in trilayer conducting polymer actuators ......................... 124

5.1.1.1 Material properties .............................................................................................. 126

5.1.1.1.1 Ionic medium .................................................................................................. 126

5.1.1.1.2 Conducting polymer ....................................................................................... 127

5.1.1.1.3 Separator ....................................................................................................... 128

5.1.1.1.4 Contact electrode .......................................................................................... 129

5.1.1.2 Dimensions of the device .................................................................................... 130

5.1.1.2.1 Length of the beam ....................................................................................... 130

5.1.1.2.2 Thickness of the conducting polymer layer ..................................................... 130

5.1.1.2.3 Thickness of the separator layer .................................................................... 131

5.1.1.2.4 Contact area .................................................................................................. 131

5.1.2 Challenges in fabrication towards fast trilayer conducting polymer actuators ...... 131

5.2 Experiments .............................................................................................................. 134

5.2.1 Materials ............................................................................................................... 134

5.2.2 Trilayer Conducting Polymer actuators fabrication ............................................ 135

5.3 Results ....................................................................................................................... 135

5.3.1 PEDOT:PSS film characterization ....................................................................... 135

5.3.2 Young’s modulus ................................................................................................ 137

5.3.3 Electronic conductivity and contact resistance .................................................... 140
5.3.4 Ionic conductivity .............................................................................................................144
5.3.5 Cyclic voltammetry (CV) measurement .........................................................................149
5.3.6 PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer characterization ........................................152
  5.3.6.1 Effect of voltage on the displacement of trilayer actuators: .................................152
  5.3.6.2 Actuation ................................................................................................................154
5.3.7 Displacement frequency response versus PEDOT:PSS thickness ...........................155
5.3.8 Strain and Strain to charge ratio ..................................................................................158
5.3.9 Resonance frequency and damping ratio ....................................................................160
5.3.10 Displacement versus length of the trilayer ...............................................................163
5.3.11 Cutoff frequency .........................................................................................................164
5.3.1 Power consumption .......................................................................................................169
5.3.2 Cycle life ........................................................................................................................170
5.3.3 ActuaTool prediction vs measurement ..........................................................................171
5.4 Conclusion .........................................................................................................................172

Chapter 6: Conclusion .............................................................................................................175
6.1 Summary and Conclusions ............................................................................................175
6.2 Future work .......................................................................................................................180
  6.2.1 Further studies on PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers ................................180
    6.2.1.1 Force measurement ...............................................................................................180
    6.2.1.2 Patterning .............................................................................................................183
    6.2.1.3 Encapsulation .......................................................................................................184
    6.2.1.4 Investigating the performance of the device with other electrolytes ...............184
    6.2.1.5 Efficiency limitation and energy storage ...............................................................185

6.2.2  PEDOT:PSS/PVDF/PEDOT:PSS trilayer structure, used in other application......185

6.2.2.1  Supercapacitor..............................................................................................................185

6.2.2.2  Electrochromic displays...............................................................................................185

6.2.3  Feasibility study of different applications for trilayer conducting polymers using ActuaTool ........................................................................................................................................186

References.......................................................................................................................................188

Appendices..........................................................................................................................................200

Appendix A : PEDOT and PEO:NBR thickness estimation..............................................................200
Appendix B : Estimation of PC mass loss from the experiment’s raw data........................................202
Appendix C : 2D transmission line-related formulas derivations.......................................................209
  C.1  Impedance of trilayer CP actuator and local frequency-dependent voltage .....................209
  C.2  Displacement of a uniformly bent beam under rotation ...................................................212
List of tables

Table 3.1 Typical material properties of common polymeric barriers ................................................. 40
Table 3.2 Summary of the properties of the trilayers and the corresponding encapsulating layer’s performance .......................................................................................................................... 56
Table 4.1 Properties of a typical fast actuating PEDOT/PEO:NBR/PEDOT trilayer actuator which is theoretically studied in this chapter .................................................................................................................. 81
Table 4.2 Young’s modulus of different conducting polymer and separators commonly used in trilayer CP actuators .................................................................................................................. 115
Table 4.3 Properties of a PEDOT:PSS/PVDF/PEDOT:PSS trilayer actuator to be designed for a tactile feedback interface .................................................................................................................. 119
Table 4.4 A list of dimensions of a trilayer with $h_g=110 \, \mu m$ and described otherwise in table 4.3 which can potentially be used in the tactile feedback display shown in figure 4.13(a) along with the corresponding values of its outputs at 150 Hz with a 1 V input sinewave voltage. ........... 120
Table 4.5 $D_u(f)$, the displacement of the beam with specified $h_p$ and $L$ after the application of $F_u(f) = 10K_u \, du(f)$ to its tip (other parameters are the device are described in table 4.3)........ 122
Table 5.1 Electronic characteristics of sprayed PEDOT:PSS on PVDF membrane with gold as the electrode ................................................................................................................................................. 143
Table 5.2 Ionic resistance and ionic conductivity of EMITFSI, PVDF, and PEDOT:PSS at various number of layers, soaked with EMITFSI as the electrolyte ................................................................. 149
Table 5.3 Calculated strain to charge ratio, free strain, and external strain ($L \times W = (10.5 \pm 0.25) \, mm \times (2 \pm 0.25) \, mm$) .................................................................................................................. 160
Table 5.4 Electronic characteristics of sprayed PEDOT:PSS on PVDF membrane with gold as the electrode \((L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm})\) ................................................................. 162

Table 5.5 Predicted and measured Cutoff frequency of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers with \(L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm}\) .................................................................................. 165

Table 5.6 Calculated material properties of the fabricated PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, namely \(P_n\) \((n\) being the number of PEDOT:PSS spray scans). For the actuator’s characterization, the length and width of the device are \((10.5 \pm 0.25) \text{ mm} \text{ and } (2 \pm 0.25) \text{ mm}, respectively, unless otherwise is stated................................................................. 174

Table 6.1 Comparison of different fabrication processes for trilayer conducting polymer actuators ........................................................................................................................................ 181

Table B.1 Measured and estimated masses of the components of the set-up measurement for sample \(S_5\) \((t_s = 50 \mu\text{m})\) ......................................................................................................................... 204

Table B.2 measured and estimated masses of the components of the set-up measurement of sample \(S_8\) \((t_s = 100 \mu\text{m})\) ......................................................................................................................... 205

Table B.3 Measured and estimated masses of the components of the set-up measurement of sample \(S_{10}\) \((t_s = 100 \mu\text{m})\) ........................................................................................................................................ 207
List of figures

Figure 1-1 (a) Schematic of a trilayer conducting polymer actuator, and (b) its mechanism of actuation with anions being the mobile ions................................................................. 2

Figure 2-1 Fabrication process of (a) PEO:NBR interpenetrated polymer network (IPN) films and (b) PEDOT formation on the two sides of PEO:NBR IPN to make a PEDOT/ PEO:NBR/ PEDOT trilayer structure................................................................. 14

Figure 2-2 Optical micrographs of the cross sections of (a) PEO:NBR double network polymer and (b) PEDOT/ PEO:NBR/ PEDOT trilayer films before being swollen with the electrolyte, (c) PEO:NBR double network polymer and (d) PEDOT/ PEO:NBR/ PEDOT trilayer films fully swollen with a 1 M solution of Li\(^{+}\)TFSI\(^{-}\) in PC. (e) SEM micrograph of the cross-section (vertical orientation) and (f) EDX mapping (color-coded with turquoise) and EDX line scan (in yellow) of sulfur distribution in the cross-section of the PEDOT/ PEO:NBR/ PEDOT trilayer film before being swollen with the electrolyte. ....................................................................................... 18

Figure 2-3 (a) Normalized mass of a bare PEDOT/ PEO:NBR/ PEDOT trilayer (circles) and normalized retained mass of PC (triangles), over time. Normalizations are relative to initial values which are indicated next to the arrows pointing the corresponding axis. The samples were stored and measured in a room with controlled humidity and temperature at \( T = (23 \pm 2)\)ºC and RH = (50 ± 3)%, respectively. (b) Thickness of the trilayer versus the retained mass of PC in the PEDOT/ PEO:NBR/ PEDOT trilayer as it dries. The inset image is the optical micrograph of the cross-section of the trilayer when all the PC is evaporated from it. ....................................................................................... 20
Figure 2-4 (a-f) Optical images of peak to peak maximum deflection of a trilayer as the retained mass of PC in it decreases, and (g) normalized differential curvature versus retained percentage of PC mass. The absolute values of their initial amounts are indicated in each graph. ........................................ 22

Figure 2-5 Normalized (a) maximum current passing through the trilayer and time constant of the trilayer and (b) charge being transferred in each half cycle versus retained percentage of PC mass. The absolute values of their initial amounts are indicated in each graph. ............................... 25

Figure 2-6 Normalized displacement and current of bare PEDOT/PEO:NBR/PEDOT trilayers cycling in air and in water over time. The normalizations were relative to their initial values which are indicated in the corresponding legend. The applied voltage is a square wave with amplitude of 2V and frequency of 0.5 Hz. .................................................................................................................. 29

Figure 3-1 Comparison of the permeability modulus product, showing that SIBSTAR has the best combination of compliance and low permeability among encapsulating materials, as determined by the figure of merit, $\gamma_w$ of common polymeric barriers. ...................................................... 41

Figure 3-2 Molecular structure of styrene-b-isobutylene-b-styrene (SIBS) ................................. 42

Figure 3-3 Schematic of the spray coating process. ...................................................................... 43

Figure 3-4 Encapsulated actuators (a) hung over a rod using paper clamps and (b) placed into a capped container which is stored in a controlled humidity and temperature (CTH) room at $(23 \pm 2)^\circ$C and $(50 \pm 3)\%$. .................................................................................................................. 45

Figure 3-5 (a) Top view optical micrograph, (b) 3D surface mapping and (c) thickness versus distance along the length of a SIBSTAR film prepared by 50 spray coats on a glass substrate. Thickness is uniform over ~2.5 cm ($t_s = (100 \pm 5) \mu$m). (d) SIBSTAR film’s thickness at the center of glass slide substrate versus number of scans. Thickness linearly increases as the number of spraying coats increases. ................................................................................................................. 46
Figure 3-6 (a) Top view optical image of an as-prepared encapsulated PEDOT/PEO:NBR/PEDOT trilayer actuator. The red dashed line shows the encapsulation margin. (b) Cross section optical micrograph of an encapsulated PEDOT/PEO:NBR/PEDOT trilayer actuator after two months of encapsulation with 100 µm thick SIBSTAR.

Figure 3-7 (a) Normalized mass of propylene carbonate (PC) stored in trilayers with no encapsulation over time. Normalized mass of propylene carbonate stored in trilayers plus toluene trapped in the corresponding SIBSTAR encapsulation shields with thicknesses of (b) \( t_s = 50 \) µm, (c) \( t_s = 100 \) µm, (d) \( t_s = 190 \) µm over time. All the normalizations were done relative to the corresponding initial mass of propylene carbonate stored in each trilayer.

Figure 3-8 (a) Schematic of the mechanism of permeation through a non-porous polymeric barrier. (b) Predicted mass transfer through the polymeric film over time.

Figure 3-9 Comparison of the normalized mass decay of propylene carbonate stored in a trilayer with no encapsulation and trilayer with encapsulation thicknesses of \( t_s = 50 \) µm, 100 µm, and 190 µm over time. All the normalizations are relative to the initial mass of the PC.

Figure 3-10 Maximum bending of trilayers with (a) no encapsulation, (b) 50 µm (c) 100 µm and (d) 190 µm thick SIBSTAR encapsulating layers. The dimensions of the trilayers before encapsulation are \((L \times W \times h_t = 10 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm})\). Images are overlaid to show the full extent of deflection after voltages of +2 V and -2 V applied each for 10 s.

Figure 3-11 Normalized peak to peak (a) displacement and (b) current of a bare trilayer and (c) displacement and (d) current of an encapsulated trilayer with 100 µm thick SIBSTAR, cycling in air. The dimensions of both trilayers are \((L \times W \times h_t = 10 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm})\) and distance of the laser beam from the base of the trilayer is \((8 \pm 0.5) \text{ mm}\). \( D_0 \) and \( i_{00} \) are the initial values of the measured displacement and the peak current passing through the corresponding trilayer,
respectively. The graphs in grey show the peak to peak current variation through time while the black lines represent the smoothened ones.

Figure 3-12 Normalized peak to peak displacement (filled dots) and current (solid lines) for (a) a bare trilayer and (b) an encapsulated trilayer with 190 µm thick SIBSTAR, cycling in DI water. The dimensions of both trilayers are \((L \times W \times h_t = 20 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm})\) and distance of the laser beam from the base of the trilayer is \((9 \pm 1) \text{ mm})\). \(D_0\) and \(i_{00}\) are the initial values of the measured displacement and the peak current passing through the corresponding trilayer, respectively. The graphs in grey show the peak to peak current variation through time while the black lines represent the smoothened ones.

Figure 4-1 (a) Schematic of a trilayer conducting polymer actuator. \(L\) and \(W\) represent the length and width of the part of the trilayer which contributes in actuation and \(L_c\) and \(W_c\) represent the length and width of the part of the trilayer which is sandwiched between two contact electrodes. (b) mechanism of actuation of a trilayer CP actuator with anions being mobile.

Figure 4-2 (a) Equivalent transmission line circuit, modeling the electrochemical behavior of a trilayer conducting polymer along its length. The part which is darker is fixed between the two contact electrodes. The plane laterally passing the middle of the trilayer has a zero potential since the circuit is symmetric (b) equivalent RC transmission line circuit of the element, \(Z_i\), modeling the diffusion of ions through the thickness of the CP layers.

Figure 4-3 Strain along the length and through the thickness of the conducting polymer layer in a trilayer structure with parameters described in table 4.1. \(l = 0\) is at the fixed end and \(h = 0\) is at the interface of the conducting polymer and the separator layers.

Figure 4-4 (a) Schematic of an actuated trilayer conducting polymer actuator beam divided into \(m\) segments with uniform curvature in each segment. Segment \(S_j\) bends to angle \(\theta_j\) as a result of
the differential strain induced in its CP layers and rotates by \( \varphi_j \) due to the bending of the segments located prior to it. (b) Segment \( S_j \) with conducting polymer layers divided each into \( n \) sub-segments in which the induced electrochemical strain is uniform.

Figure 4-5  Frequency responses of the vertical tip displacement of a trilayer beam with parameters described in table 4.1, obtained through the uniform bending model without considering the effect of contact electrodes (black dotted line), varying curvature without considering the effect of contact electrodes (green dashed line) and varying curvature with considering the effect of contact electrodes (red straight line).

Figure 4-6  (a) Estimated shape of the trilayer beam actuator, with parameters described in table 4.1, at its extent at 0.1 Hz under different external forces. The blocking force, \( F_B \), is 9.9 \( \mu \)N. (b) Force versus displacement graph of the trilayer beam, as described in the inset image.

Figure 4-7  Frequency response of the blocking force of the trilayer with parameters described in table 4.1, obtained through the uniform bending model without considering the effect of contact electrodes (black dotted line), varying curvature without considering the effect of contact electrodes (green dashed line) and varying curvature with considering the effect of contact electrodes (red straight line).

Figure 4-8  Frequency response of the average power consumption of the trilayer with parameters described in table 4.1.

Figure 4-9  Electrical efficiency versus frequency of the trilayer with parameters described in table 4.1.

Figure 4-10  Electromechanical coupling versus frequency of the trilayer with parameters described in table 4.1.
Figure 4-11 Mechanical efficiency versus frequency of the trilayer with parameters described in table 4.1 .................................................................................................................................................................................. 97

Figure 4-12 Comparison of the shape of trilayers, with parameters described in table 4.1, at 0.1 Hz, freely bending to their extent (light color) and blocked (dark color), without encapsulation (green) and with encapsulation (orange). Note that the value and direction of the blocking force are different for the two trilayers .................................................................................................................................................................................. 99

Figure 4-13 Screenshot image of the input interface of ActuaTool in the “Frequency Response” mode .................................................................................................................................................................................................................................................. 102

Figure 4-14 Screenshot image of the graph visualization of ActuaTool in “Frequency Response” mode demonstrating frequency response graphs of (a) vertical displacement (“m” on the vertical axis values indicates 0.001), (b) lateral displacement, (c) blocking force, (d) average power consumption, and (e) shape of the freely bending beam and (f) force-displacement at 0.1 Hz . 103

Figure 4-15 Screenshot image of the input interface of ActuaTool in the “Parameter response” mode. Thickness of the encapsulating layer is selected as the varying parameter ........................................ 106

Figure 4-16 Screenshot images of graph visualization of ActuaTool in “Parameter Response” mode demonstrating graphs of (a) displacement-determined cut-off frequency, (b) vertical displacement, (c) lateral displacement, (d) blocking force, (e) average power consumption, (f) stiffness and (g) resonance frequency versus encapsulating layer’s thickness. Operating voltage and frequency are 1V and 0.1 Hz, respectively. .......................................................................................................................... 107

Figure 4-17 Screenshot image of the input interface of ActuaTool in the “Design” mode. Cutoff frequency is selected as the dominant output .................................................................................................................. 110

Figure 4-18 Screenshot images of the table visualization including dimensions of the trilayer actuators with parameters defined in figure 4.17, which result in devices with values of cutoff
frequency at (8.5 ± 0.5) Hz, along with their corresponding values of blocking force, vertical and lateral displacements, average power consumption, stiffness and resonance frequency at the defined voltage and frequency of 1 V and 0.1 Hz, respectively. The table is sorted so that the design which leads to a larger vertical tip displacement sits on top. ........................................ 111

Figure 4-19 Neural threshold for vibration detection. Adapted from [97] ................................. 112

Figure 4-20 (a) Top and (b) side views of the schematic of a possible design for a tactile feedback interface using trilayer CP actuators. (c) schematic of the interaction of a trilayer CP actuator with a fingertip. $F_u$ represent the threshold of the reaction force, which fingertip applies to the trilayer due to the threshold deformation it made into the fingertip. ................................. 113

Figure 4-21 Maximum vertical tip displacement versus young’s modulus of the conducting polymer layer for trilayers with separator’s Young’s modulus, $E_g$, of 1 MPa e.g., PEO:NBR copolymer (red circle dots) and 70 MPa, e.g., PVDF membrane without (black triangle dots) and with (green square dots) encapsulation with a 10 µm thick SIBSTAR. Other parameters of the device are as described in table 4.1 ........................................................................................................ 116

Figure 4-22 Comparison of the minimum detectable penetration in human skin (black diamonds) with the tip displacements of encapsulated trilayers described in table 4.3 with $h_g$=110 µm, $0.35 \mu m \leq h_p \leq 1 \mu m$, and $L = 1$ mm (half-filled square) and $L = 1.5$ mm (empty square) when $F_u(f) = 10K_u du(f)$ is applied to its tip (as demonstrated in the inset image). ......................... 121

Figure 5-1 (a) Thickness of PEDOT:PSS doped with DMSO on glass slide versus the corresponding number of coats, and (b) top view optical image of the fabricated trilayers. The underlying texts shows the corresponding number of PEDOT:PSS coats. ................................. 136

Figure 5-2 (a) Optical and (b) SEM micrographs of the cross-section (vertical orientation) and EDX line scan (in yellow) of sulfur distribution in the cross-section of the PEDOT:PSS/ PVDF/
PEDOT:PSS trilayer film before being soaked in the electrolyte. PEDOT:PSS is obtained through 10 spray scans. ........................ .......................................................... 138

Figure 5-3 Stiffness of PEDOT:PSS/PVDF/PEDOT:PSS trilayers versus number of PEDOT:PSS spray coats. The length and width of the tested samples are 2 cm and 1.43 cm, respectively, and the thickness of the PVDF membrane is 125 µm. .......................................................... 139

Figure 5-4 Schematic of the set up used for four-line electronic conductance measurement .... 141

Figure 5-5 (a) IV characteristics and (b) sheet resistances of PEDOT:PSS/PVDF/PEDOT:PSS trilayers at various number of PEDOT:PSS coats. IV characteristics demonstrate an ohmic resistance and sheet resistance decreases as the number of PEDOT:PSS coats increases. .... 142

Figure 5-6 Specific contact resistance of PVDF/ PEDOT:PSS/ gold versus number of PEDOT:PSS coats. The contact area is (80 ± 5) mm². .................................................................................. 145

Figure 5-7 (a) Schematic of the set up used for four-probe ionic conductivity measurement, (b) equivalent electric circuit model of the ionic conductivity measurement setup. $R_{ls}$, $R_{lp}$, and $R_{lg}$, are the ionic resistances of EMITFIS between the samples and the closest cannula end, PEDOT:PSS layer and PVDF membrane. .................................................................................. 146

Figure 5-8 (a) Ionic I-V characteristics and (b) ionic resistance of PEDOT:PSS/PVDF/PEDOT:PSS trilayers through its thickness versus number of PEDOT:PSS coats. $n = 0$ denotes pure PVDF membrane. IV characteristics demonstrate an ohmic resistance which increases as the number of PEDOT:PSS coats increases................................................................. 147

Figure 5-9 (a) CV measurement setup composed of two gold foils between which the trilayer is sandwiched, and (b) the corresponding simplified equivalent electrochemical circuit, modeling the CV measurement setup. .................................................................................. 150
Figure 5-10 CV curves of trilayers with PEDOT:PSS layers composed of (a) 2 (P2), (b) 6 (P6), and (c) 10 (P10) spray scans of PEDOT:PSS on each side of PVDF membrane. (d) The areal capacitance of trilayers versus number of PEDOT:PSS coats................................. 151

Figure 5-11 (a) Displacement and (b) impedance magnitude of a PEDOT:PSS/ PVDF/PEDOT:PSS trilayer actuator (P10) versus the amplitude of the applied sine wave voltage. The amplitude of the applied voltage was first increases (orange dots) and then decreases (green dots) to evaluate the electrochemical degradation of PEDOT:PSS................................................. 153

Figure 5-12 Top view optical images of the peak to peak actuation of a PEDOT:PSS/ PVDF/PEDOT:PSS trilayer actuator (P10), operating through the application of a sine wave voltage with amplitude of 1 V and frequencies of (a) 0.1 Hz, (b) 1 Hz, (c) 10 Hz, (d) 80 Hz, and (e) 100 Hz, respectively. The length, L, and width, W, of the device are (10.5 ± 0.25) mm and (2 ± 0.25) mm, respectively. The corresponding displacement of a point on the trilayer located at a length, L' (= (10 ± 0.25) mm) from its fixed end (indicated with red arrow in each graph) when the device is operated through the application of a sine wave voltage with amplitude of 1 V and frequencies of (f) 0.1 Hz, (g) 1 Hz, (h) 10 Hz, (i) 80 Hz, and (j) 100 Hz, respectively. The red lines in is a sinusoidal curve fitted to the measured data (gray)................................................................. 155

Figure 5-13 (a) Frequency response of the tip displacement and the Bode (b) magnitude and (c) phase plots of the impedance of P2, P6, and P10 trilayers 0.5 mm away from their tips. (W × L= (2 ± 0.25) mm × (10.5 ± 0.25) mm)......................................................................................................................... 157

Figure 5-14 Tip displacement of the Pn trilayer actuators versus number of PEDOT:PSS spray scans under the application of a sine wave voltage with an amplitude of 1 V and frequency of 0.1 Hz................................................................................................................................. 158

Figure 5-15 Free vibration of P10 trilayer beam (L × W = (10.5 ± 0.25) mm × (2 ± 0.25) mm) 161
Figure 5-16 Resonance frequency of the Pn trilayer actuators versus \( n \), being the number of PEDOT:PSS coats. The values were obtained through the free vibration (black triangular dots), actuation (red circular dots), and ActuaTool (green diamond dots).

Figure 5-17 Peak to peak displacement of the P10 actuator with width, \( W \), of \((2 \pm 0.25)\) mm and length, \( L \), of \((10.5 \pm 0.25)\) mm, \((7.5 \pm 0.25)\) mm, and \((4.5 \pm 0.25)\) mm. The laser is illuminating on the trilayers \(~0.5\) away from their tips.

Figure 5-18. Cutoff frequency of the trilayers calculated through the Bode phase plot of the impedance of the trilayers (cyan square dots) and their displacement frequency response (orange circle dots), and predicted by ActuaTool (diamond dark gray dots). \((L \times W = (10.5 \pm 0.25)\) mm \( \times \) \((2 \pm 0.25)\) mm\)

Figure 5-19 (a) Bode phase plot of the impedance of 1 cm \( \times \) 1 cm PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers (denoted as Pn, \( n \) being number of PEDOT:PSS spray scans) sandwiched between two gold foils. (b) Cutoff frequency obtained through the Bode phase plot of impedance versus number of PEDOT:PSS coats in the corresponding trilayer.

Figure 5-20 Resonance frequency of the Pn trilayer actuators versus \( n \), being the number of PEDOT:PSS coats \((L \times W = (10.5 \pm 0.25)\) mm \( \times \) \((2 \pm 0.25)\) mm\).

Figure 5-21 Displacement and admittance of P10 trilayer \(((L \times W = (10.5 \pm 0.25)\) mm \( \times \) \((2 \pm 0.25)\) mm\)) versus time normalized by the corresponding initial values as indicated in the legend. The input voltage is a sine wave with an amplitude and frequency of 1 V and 2 Hz, respectively. The distance at which the displacement was measured is \((10 \pm 0.25)\) mm away from the fixed end of the device.

Figure 5-22 Measured peak to peak displacement of P10 trilayer actuator \((L \times W = (7.5 \pm 0.25)\) mm \( \times \) \((2 \pm 0.25)\) mm\) \((7 \pm 0.25)\) mm away from the fixed end of the trilayer (pink diamond dots)
and the tip displacement of the beam with the same geometry predicted by ActuaTool (black line). The input voltage is a sine wave with amplitude of 1 V. .......................... 172

Figure 6-1 PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, (a) (P1) and (c) (P2) before the application of voltage and (b) (P1) and (d) (P2) after application of a 0.5 V square wave voltage, demonstrating the electrochromic behavior of thin films of PEDOT:PSS/ DMSO. ............... 186

Figure B.1 Mass of the setup + encapsulated sample, $S_5$ ($t_s = 50 \, \mu m$) (measured data).......... 204

Figure B.2 Mass of the setup + encapsulated sample, $S_8$ ($t_s = 100 \, \mu m$) (measured data)........... 207

Figure B.3 Mass of the setup + encapsulated sample, $S_{10}$ ($t_s = 190 \, \mu m$) (measured data). ....... 208

Figure C.1 Equivalent transmission line circuit which models the electrochemical behavior of a trilayer conducting polymer along its length. (b) equivalent RC transmission line circuit of the element, $Z_i$, modeling the diffusion of ions through the thickness of the CP layers................. 209

Figure C.2 Schematic of a beam (orange) bent to a uniform angle of $\theta$ (green) and rotated to an angle of $\varphi$ (blue). .................................................. 212
### List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>CF₄</td>
<td>Tetrafluoromethane</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>CP</td>
<td>Conducting polymer</td>
</tr>
<tr>
<td>CSS</td>
<td>Cascading Style Sheets</td>
</tr>
<tr>
<td>CTH</td>
<td>Controlled Temperature and Humidity</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl-peroxide</td>
</tr>
<tr>
<td>DCPD</td>
<td>Dicyclo-hexylperoxidicarbonate</td>
</tr>
<tr>
<td>DCPD</td>
<td>Dicyclohexylperoxidicarbonate</td>
</tr>
<tr>
<td>DMSP</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-ethylenedioxythiophene</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray</td>
</tr>
<tr>
<td>EMITFSI</td>
<td>1-Ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide</td>
</tr>
<tr>
<td>EW</td>
<td>Electrochemical window</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>Iron III chloride</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drugs Administrative</td>
</tr>
<tr>
<td>GUI</td>
<td>Graphical user-interface</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density Polyethylene</td>
</tr>
<tr>
<td>HTML</td>
<td>Hypertext Markup Language</td>
</tr>
<tr>
<td>IPMC</td>
<td>Ionic Polymer Metal Composite</td>
</tr>
<tr>
<td>IPN</td>
<td>Interpenetrating polymer network</td>
</tr>
</tbody>
</table>
ITO  Indium tin oxide
LC    Liquid Crystal
LDPE  Low-density polyethylene
LDPE  Low-density Polyethylene
LiClO₄ Lithium perchlorate
LiTFSI Lithium bis(trifluoromethanesulfonyl)imid
NaPF₆ Sodium hexafluorophosphate
NBR   Nitrile Butadiene Rubber (NBR).
O₂    Oxygen
OLED  Organic light emitting diodes
OTR   Oxygen transmission rate
PANI  Polyaniline
PB    Polybutadiene
PC    Propylene carbonate
PDMS  Polydimethylsiloxane
PEDOT Poly(3,4-ethyl- enedioxythiophene)
PEDOT:PSS Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEGDM Poly(ethylene glycol) dimethacrylate
PEGM  Poly (ethylene glycol) methacrylate methyl ether
PEGMA Poly-(ethylene glycol) monomethyl ether methacrylate
PEO   Poly(ethylene oxide)
PET   Polyethylene terephthalate
PI    Polyimide
PPy   Polypyrrole
PSS   Poly-(styrenesulfonic acid)
Pt    Platinum
PTFE  Polytetrafluoroethylene
PU    Polyurethane
PVC   Polyvinyl chloride
PVDC  polyvinylidene chloride
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDC</td>
<td>Polyvinylidene Chloride</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
</tr>
<tr>
<td>RFE</td>
<td>Rigid finite element</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SBC</td>
<td>Styrene block copolymers</td>
</tr>
<tr>
<td>SBS</td>
<td>Poly(styrene-b-butadiene-b-styrene)</td>
</tr>
<tr>
<td>sde</td>
<td>Spring-damping elements</td>
</tr>
<tr>
<td>SEBS</td>
<td>Poly(styrene-b-ethylene-butylene-b-styrene)</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>SIS</td>
<td>Poly(styrene-b-isoprene-b-styrene)</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid polymer electrolyte</td>
</tr>
<tr>
<td>TCE</td>
<td>1,1,2-trichloroethane</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water vapor transmission rate</td>
</tr>
</tbody>
</table>
Acknowledgements

On March 1st, 2014, Drs. John Madden, Edmond Cretu, and Shahriar Mirabbasi came to my office, telling me that they have decided to accept me as their new PhD student. After three years as already being a PhD student with another supervisor at UBC, that was the moment which switched my PhD towards one of the most prosperous times of my life. I deeply thank them for giving me another chance to finish my PhD at UBC.

I would like to express my most sincere gratitude to my supervisor, Dr. John Madden, for all the research mentorship I received during these years, and for his support and compassion during the most difficult times in my PhD studies. I thank him for teaching me how to enjoy science, not only in the lab, but also in my everyday life. I thank him for his trust on me, which hugely helped me to grow up both in my professional and my personal lives. I thank him for every moments of my PhD with him.

I am grateful to my co-supervisor, Dr. Edmond Cretu, for his thought-provoking questions and suggestions on my research. I thank my supervisory committee, Drs. Kenichi Takahata and Shahriar Mirabbasi for their constructive feedback in our meetings. I am also grateful to Drs. Alvo Aabloo, Dana Grecov, and Mu Chiao for agreeing to be on my examination committee and for their comments on this thesis.

I would like to give special thanks to my student collaborators, in particular, Dr. Kätlin Rohtlaid, Dr. Nguyen Ngoc Tan, and Xu Fan for the amazing teamwork we had together and for their care to my work as if it is theirs. Also, special thanks to Dr. Seyed Mohammad Mirvakili and Ehsan MousaviMehr for our discussions and their comments and suggestions on my work. Also, special thanks to our collaborators, Drs. Frederic Vidal, Cedric Plesse, Giao T. M. Nguyen
(LPPI, University of Cergy-Pontoise, Cergy, France), and Eric Cattan (IEMN, University of Lille, Lille, France), for all our productive remote discussions and their help during my stays in their labs. These collaborations enabled me to aim higher and achieve more than what would be possible by me. I would like to thank other past and present members of molecular mechatronics lab, Dr. Ali Mahmoudzadeh, Claire Prest, Dr. Meisam Farajollahi, Yuta Dobashi, Mirza Saquib Sarwar, Ali Rafie, Graham Allegretto, Soheil Kianzad, Dr. Adam Frasier, Justin Wyss, Bertille Dupont, Katlin Dixon, Dickson Richard Yao, and Leanna Hogarth. I also thank 4D labs staff at Simon Fraser University for always well maintaining the equipment. I also thank Dr. Frank Ko for letting me use the optical microscope in his lab.

I am very grateful for having many wonderful friends who made these years a memorable experience. In particular, I thank Dr. Hasti Seifi, Mahsa Khalili, and Maryam Beygi, not only for their friendship, but also for the countless number of times we discussed about my work and I have benefited from their advice and experience. I would like to thank Peyman Rouhandeh, Firouzeh Peyvandi, and Nasrin Sarbazpour for many joyful moments which we made together, filled with music, care and love.

I am also grateful of my Persian calligraphy teacher, Kamran Kouhestani, my manuscript illumination teacher, Rafat Mousavi, my Persian painting teacher, Farhad LalehDashti and my singing teacher, Jamal Salavati Kurdestani, who thought me the deep joy of classic arts, kept me connected to my other areas of interest, and helped me develop them.

Lastly, I have immense appreciation for my parents, Tahereh Amini and Dr. Alimorad Ebrahimi, who gave me birth, raised me with love, and thought me how to enjoy life. I thank my siblings, Reyhaneh Ebrahimi, Mazdak Ebrahimi, Dr. Azadeh Ebrahimi, and Maziar Ebrahimi for their emotional support and for being my best mentors and friends even though we are apart.

xxxiii
To Iran-Iraq war veterans with PTSD, who lived the life they’ve sacrificed.

cción به بیماران اعصاب و روان جنگ ایران و عراق؛
"آنان که در راه عدالت به خون خویش غلطیدند ",
و نرفتند.
Chapter 1: Introduction

1.1 Trilayer conducting polymer actuators: a brief history of their development

Electronically conducting conjugated polymers (simply called conducting polymers (CPs)), such as polyaniline (PANI) [1], polypyrrole (PPy) [2]–[6], and poly(3,4-ethylenedioxythiophene) (PEDOT) a[7]–[11], are smart organic materials with the ability to change their redox state and store ions when they are operated electrochemically. During this process, their conductivity, volume and optical absorption spectrum changes [12], which gives them the ability to be used as batteries [13], supercapacitors [14], mechanical actuators [1]–[11], [15]–[18], electrochromic displays [19], etc.

The idea of using conducting polymers to convert electrochemical energy to mechanical energy was first proposed by Ray Baughman in 1990 [20]. Due to their soft nature and large work density, these ionically and electronically conducting polymers were introduced as potential materials to realize “artificial muscles”: actuators which can mimic the behavior of mammalian muscles. The first study on the fabrication and characterization of a bending actuator using conducting polymers was done by Pei et al. in 1992 [21]. He electrochemically polymerized pyrrole monomers on a gold-coated low-density polyethylene (LDPE) sheet and actuated the bi-layer structure in a shallow cell, equipped with a silver/silver chloride (Ag/AgCl) reference electrode, a platinum foil as the counter electrode and a 0.1 M aqueous solution of lithium perchlorate (Li+ClO₄⁻) as the electrolyte. John Madden devoted his PhD thesis (graduated in 2000) to study the electrochemically induced volume change in PPy conducting polymers, including investigating the nature of the mentioned electrochemical coupling, fabrication and optimization of PPy in terms
of the generated strain, strain rate, power to mass ratio and force, as well as developing an electro-
chemo-mechanical model to relate the electrical input to the mechanical output [22]. While most
of the primary research on conducting polymer actuators was carried out on single-layer or bi-
layer structures, which require an electrolyte environment to be operational, the proof of concept
of air-operation of conducting polymer actuators was demonstrated by Kaneto et al. in 1995 [1].
He prepared solution-processed and cast films of polyaniline and soaked them into a 1 M aqueous
solution of hydrochloric acid followed by affixing them to the two sides of a double-sided
cellophane tape. For just a couple of seconds, the so-called “shell-type” actuator operated in air by
applying a 1.5 V voltage to the two conducting polymer electrodes.

The trilayer structure, schematically demonstrated in figure 1.1(a), later on attracted most
attention in the field of conducting polymer actuators due to its air operating capability by
substituting the double-sided cellophane tape in Kaneto’s structure with a porous membrane such
as a commercially available polyvinylidene fluoride (PVDF) membrane [2]–[6], or a solid
polymer electrolyte which can be an interpenetrated polymer network of an ion hosting polymer
such as polyethylene oxide (PEO) to provide ionic conductivity of the film and an elastic
polymer with large molecular chains such as polybutadiene (PB) or nitrile rubber (NBR)

![Figure 1.1](image_url)

**Figure 1.1** (a) Schematic of a trilayer conducting polymer actuator, and (b) its mechanism of actuation with
anions being the mobile ions.
to maintain its mechanical robustness [7]–[11], [23]. The ionic medium involved can be a solution of a salt in a solvent such as water or propylene carbonate (PC) or an ionic liquid such as 1-Ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (EMITFSI). As a potential difference is applied to the two CP electrodes, ions move from one electrode to the other one through the ionically conducting separator. This, as schematically shown in figure 1.1(b) for anions being mobile, causes the CP layer with the increase of ions to expand and the other one with the decrease of ions to contract, and the whole structure to bend.

In 2003, Dezhi Zhou et al. demonstrated actuation of electrochemically polymerized polypyrrole films on two sides of a platinum coated commercially available PVDF membrane for 3600 cycles at 1 Hz using a polymer-in-ionic liquid electrolytes [2]. Soon later in 2004, Vidal et al. proposed a novel fabrication procedure for conducting polymer actuators by chemical polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) into the two sides of a film of an interpenetrated polymer network of polybutadiene (PB) and polyethylene oxide (PEO) [7]. This synthetic method provides a gradual dispersion of the conducting polymer (here, PEDOT) through the thickness of the IPN polymer, making the structure electronically conductive at the two surfaces with conductivity decreasing through the thickness of the IPN membrane. This structure has two main advantages over PPy/ PVDF/ PPy structure; first is eliminating delamination thanks to its interpenetrated polymer structure and second is the ability to store electrolyte for a longer time [6], [11]. In addition to these, the low Young’s modulus of PEO:NBR copolymer separator layer (~1 MPa) generally helps the trilayer to bend more easily compared to a trilayer with a PVDF membrane (Young’s modulus of ~70 MPa [3]). The disadvantages are the smaller ionic conductivity of PEO:NBR copolymers compared to the porous PVDF membranes [24] and the volume change of the structure after it is soaked in the electrolyte or after the solvent is evaporated.
Using this structure and EMITFSI as the electrolyte, Vidal et al. claimed one month continues operation of conducting polymer actuators without delamination [7].

1.2 The scope of this thesis

Since the invention of trilayer conducting polymer actuators, there have been a lot of studies on tuning the electrochemical and mechanical properties of the polymers involved as well as developing fabrication methods to engineer their dimensions and to make them practical for different applications [4], [5], [9], [10], [18], [25]. Encapsulation of these devices has also been addressed by using polymeric barriers to protect them from exchanging molecules as they operate in air or in a liquid environment [6], [26]. In addition to these, the output characteristics of the device such as its displacement and force have been theoretically studied through using their electro-chemo-mechanical models [27]–[29] and ANSYS simulation [30]. The effect of material properties and their thicknesses as well as the dimensions of the trilayer CP actuators on the deformation, blocking force, and actuation speed of the device has also been investigated experimentally [3], [5], [10], [31].

Having a combination of properties such a compliance, biocompatibility, low mass density, low operating voltage (< 2 V), relatively large strain (> 1%), ease of fabrication and scalability [32], [33], trilayer conducting polymer actuators, so far, have been demonstrated to be used in applications such as catheters [15], robotic fish [34], micro-manipulators [35], etc. Each of these applications or other potential applications such as tactile feedback displays [31] have different requirements from the employed actuator in terms of its key output characteristics. These output characteristics include the extent of deformation, blocking force (the force needed to return the bent tip of the actuator to its pre-actuation location), average power consumption (which is always needed to be minimized) and speed. These depend on many factors including the
dimensions of the device, thickness, Young’s modulus, electronic and ionic conductivities of each of the layers, the volumetric capacitance of the conducting polymer layer, the shape and the magnitude of the applied voltage, etc. Being influenced by many parameters, the effect of one parameter on one output may vary depending on the values of other parameters. Also, there is sometimes a tradeoff between the outputs as one parameter is changed [31]. These make optimizing the design of these devices for different applications challenging, especially for those which require fast actuation since more parameters are involved.

The other challenge that these actuators are facing is to have a scalable fabrication process through which reproducible conducting polymer trilayers with fast actuation can be obtained. This mainly requires the ability to finely tune the thicknesses of each of the layers, especially that of the conducting polymer down to several micrometers or below. All the fabrication methods which are so far developed, include an in situ chemical, electrochemical, or thermal polymerization process, through which it is difficult to finely tune the thickness of the resulting films. Maziz et al. demonstrated resonance actuation just below 1 kHz in sub-millimeter long and micrometer thick PEDOT/ PEO:NBR/ PEDOT trilayers thanks to the micro-scale fabrication and patterning methods [10]. Despite this method opens the possibility for these devices to be used in MEMS applications, the fabrication method does not provide a repeatable and reproducible recipe and the engineer cannot reliably used them in real MEMS applications.

In addition to these, regardless of the actuation speed, bringing these ionic devices closer to real applications and eventually commercializing them, requires them to be encapsulated. So far, there are only two reports which are thoroughly dedicated to this topic [6], [26], none of which could demonstrate significant improvements on the operation lifetime of the device after encapsulation.
1.3 Thesis overview

Within the scope of this thesis, the goal is to actualize fast trilayer conducting polymer actuators. Accordingly, we took three steps towards achieving this goal:

1. Encapsulating trilayer conducting polymer actuators,
2. Creating a design optimization tool, and
3. Developing a robust, reproducible, and scalable fabrication process through which fine tuning (sub-micron) thickness of each of the layers can reliably be obtained.

In chapter 2, we studied the change in the performance of a 360 µm thick PEDOT/PEO:NBR/PEDOT trilayer actuator operating with a 1 M solution of Li+TFSI− in PC as the solvent evaporates to investigate the sensitivity of these devices to losing their electrolyte and further use in the selection of the encapsulating layer. Following the results in chapter 2, the effectiveness of using spray coated films of poly(styrene-block-isobutylene-block-styrene) (SIBSTAR) in protecting the PEDOT/PEO:NBR/PEDOT trilayer actuators from losing their electrolyte solvent (here, PC) were studied in chapter 3. The effect of encapsulation on the performance of the devices in terms of their operation lifetime in air and water as well as their extent of actuation were also studied.

Frequency domain electro-chemo-mechanical modeling of trilayer conducting polymer actuators below its resonance frequency is presented and discussed in chapter 4. This model is based on the already developed 2D transmission line model for these devices [27], [28] and includes extensions to take into account the effects of contacts as well as the non-uniform distribution of ions throughout the volume of the CP layers which leads to a non-uniform curvature of the beam along its length at operation frequencies above the cut-off frequency of the device (or before the device reaches its extent of displacement when operated at low
frequencies). The presented model includes extra calculations to find the local charge induced to the CP layers and hence the local curvature of the beam which can also further be used to predict the frequency-dependent shape of the device as it actuates. We then presented an interactive web-based tool, so-called “ActuaTool”, based on the frequency domain model of trilayer conducting polymers. ActuaTool uses standard web technologies (HTML, CSS, and JavaScript) and can run on all web browsers, which makes it accessible for everyone. This tool enhances the practicality of the model and facilitates the design of the trilayer conducting polymer actuators for various applications through its three modes of operation: “Frequency response”, “Parameter response” and “Design”. Using ActuaTool in “Frequency response” mode, users can enter the dimensions of the device as well as its material properties such as ionic and electronic conductivities and Young’s modulus of each layer, volumetric capacitance and the strain to charge ratio of the active CP layer. The tool then visualizes the frequency responses of the tip displacement, blocking force and average power consumption of the designed device, in addition to its shape at a given frequency when a given force is applied to its tip. The resulting graphs visualizations in “Parameter response” mode show how the cutoff frequency, tip displacement, blocking force, average power consumption, stiffness, and resonance frequency of the device change as a function of a change in one of the parameters at a given frequency. In the “Design” mode of operation, the user enters the material properties mentioned above as well as a range of her/ his desired output at a selected frequency including cutoff frequency, tip displacement, blocking force, average power consumption, stiffness, and resonance frequency. ActuaTool then calculates the values of length and the thicknesses of the CP and separator layers which lead to the user’s desired output at the selected frequency. The values of bandwidth, tip displacement, blocking force, average power consumption, stiffness, and resonance frequency of each
configuration is also calculated, and all are visualized in a table. Using ActuaTool, we then optimized the design of these actuators for a tactile feedback display application.

In chapter 5, a novel method of fabrication of trilayer conducting polymers based on commercially available products, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the conducting polymer layer and PVDF as the separator layer, is presented and discussed. The conducting polymer layers were fabricated using spray-coating technique which can provide uniform films of PEDOT:PSS as thin as 400 nm. A thorough study on the characterization of the sprayed films of PEDOT:PSS on PVDF membrane as well as the resulting trilayer actuators, was carried out and the details of the fabrication method, measurements, and the corresponding results are presented in chapter 5.

A summary and conclusions of this research along with the future work associated with it is presented in Chapter 5.

The details of the objectives and related literature review of each chapter are provided accordingly.

1.4 List of contributions

1. Demonstrating a successful encapsulation method for trilayer conducting polymer actuators through encapsulation of a 360 µm thick PEDOT/PEO:NBR/PEDOT trilayer actuators with a 1 M solution of Li⁺TFSI in PC as the electrolyte, through using uniformly spray-coated poly (styrene-block-isobutylene-block-styrene) (SIBSTAR). Results anticipate that by using a 100 µm thick SIBSTAR encapsulation, these devices retain 80% of their stored PC for more than 1000 times longer compared to when there is no encapsulation.

2. Modification of the frequency domain 2D transmission line model of trilayer conducting polymer actuators to take into account the non-uniform distribution of ions throughout the
volume of the conducting polymer layer at frequencies below the cutoff frequency of the device as well as the effects of contact resistance and contact area. A new method of geometrical calculations was proposed to estimate the frequency-dependent shape of the trilayer actuators under an applied load to its tip as well as an accurate method of estimating the blocking force.

3. Creating ActuaTool, a web-based graphical user interface tool based on the modified 2D transmission line to visualize the frequency-dependent output characteristics of the device and optimize the design of actuators for different applications.

4. Developing a low cost, reliable, reproducible, and scalable method of fabrication of trilayer conducting polymer actuators based on commercially available products: PEDOT:PSS/DMSO as the conducting polymer layer and PVDF membrane as the separator, and a well-characterized method of film deposition, spray-coating. This method provides the possibility of tuning the thickness of PEDOT:PSS down to 400 nm, which has not been demonstrated before for trilayer conducting polymer actuators.
Chapter 2: Evaluating performance of wet unencapsulated PEDOT trilayer actuators operating in air and water

2.1 Introduction and Motivation

Being electrochemically active, trilayer conducting polymers require an ionic medium such as an electrolyte or an ionic liquid to operate. Electrolyte is a solution of a salt in a polar solvent with a high dielectric constant and low viscosity, such as water, propylene carbonate (PC) or organic ethers [36]. The separator layer acts both as an electronic insulator between the two conducting polymer layers and a reservoir for the ion-containing medium. If the ionic medium is an electrolyte, when the device operates in air, the solvent evaporates over time, which affects the ionic conductivity of the conducting polymer and separator layers. It may also change the dimensions of the device. This means the performance of the device varies over time and eventually degrades as no more solvent is left within the trilayer structure.

Recently, the use of ionic liquids as substitutes for electrolytes has been vastly increased [37]. These salts are in liquid form at room temperature and hence they make it feasible for trilayer CP actuators to operate in air for a long time. Despite their non-volatile nature and their large electrochemical potential window [38], they may not generate as much strain in the conducting polymer layers and their ionic conductivity is generally not as high [39], [40]; So, ionic liquids cannot completely substitute solvent-based electrolytes and the use of electrolytes in these structures is still favorable. Also, in some applications where the device is required to work in a liquid environment other than its ionic medium, such as in water or blood, ionic liquids cannot be
of much help, since similar to electrolytes, if the device is not well protected against the environment, the ionic liquid will leave the device over time and will be substituted by the environment molecules. Hence, it is important to add an encapsulation layer to protect the electrolyte’s solvent from evaporation or the ionic medium from being lost when the device operates in a liquid environment.

The expectation of the trilayer actuator from its encapsulation material depends on its sensitivity to losing its electrolyte’s solvent (when operating in air) or the whole electrolyte (when operating in a liquid environment other than its own electrolyte). In this chapter, we present a detailed study of the performance of bare trilayer conducting polymers over time when they work in air or in a liquid environment. Some previous work has reported the effect of drying of trilayer actuators on their performance [41]. For a trilayer actuator comprised of a 110 µm thick commercially available polyvinylidene fluoride (PVDF) membrane (pore size of 0.45 um) as the separator layer and 8 µm thick electropolymerized polypyrrole (PPy) conducting polymer with 0.1 M solution of Li⁺TFSI⁻ in propylene carbonate (PC) as the electrolyte, after 2.7 h actuating in air (10⁴ cycles at 1 Hz), 30% of the initial displacement of the device is retained. When the device operates in water, it takes only ~5 min (~300 cycles at 1 Hz) to lose the same amount of displacement. The change in the dimensions of these trilayers over time is negligible because the electrolyte is stored in the pores inside the PVDF membrane, so probably the behavior of the drying device is dominated by the effect of change in the ionic conductivity.

This behavior is different if a different separator layer and conducting polymer with different thicknesses are used to comprise the trilayer structure. Solid polymer electrolyte (SPE) comprised of interpenetrated polymer network of nitrile butadiene rubber (NBR) with an ionically conducting polymer such as polyethylene oxide (PEO), is an alternative material to the
PVDF membrane as the separator in trilayer CP actuators [42]. In contrast to PVDF membranes, PEO:NBR double network polymer films are not porous and swell as they uptake electrolyte. Their benefits over commercially available PVDF membranes are that their mechanical properties and ionic conductivity can be tuned through the type and the ratio of the polymers involved in the network. Their low Young’s modulus (~1 MPa) helps the trilayer to bend more easily compared to a trilayer with a PVDF membrane (Young’s modulus of ~70 MPa [3]) and the same conducting polymer. Moreover, when poly(3,4-ethylenedioxythiophene) (PEDOT) is chemically polymerized within the two sides of the PEO:NBR double network polymer, a conductive interpenetrated polymer network is formed, making a continuous structure with a larger density of PEDOT on the two sides [43], [44]. The density of PEDOT decreases towards the thickness of the SPE layer and eventually vanishes and leaves an electrically insulating layer in the middle of the film. Having a continuous structure, as opposed to PPy/ PVDF/ Ppy trilayer actuators, delamination would not occur between the layers.

In this chapter, we characterize fabricated PEDOT/ PEO:NBR/ PEDOT trilayers in terms of their material properties. We then present a detailed study of the intermittent and cycling performance of these trilayer actuators as they operate in air and their solvent evaporates from the device, as well as their cycling performance as they operate in water and lose their electrolyte. The responses of the actuators over time in these conditions provide device designers with data on the longevity of the actuators without encapsulation. It also provides a ground for the subsequent studies on their encapsulation. Note that the drying performance is a function of the composition and structure of the materials involved, the geometry of the device and the environment. The point at which the user needs encapsulation for her/ his trilayer actuators is thus not unique, and also depends on the application.
2.2 Experiments

2.2.1 Materials

1,1,2-trichloroethane (TCE, Aldrich), nitrile butadiene rubber (NBR, from Lanxess), poly(ethylene glycol) methacrylate methyl ether (PEGM, $M_w = 475$ g/mol, Aldrich), poly(ethylene glycol) dimethacrylate (PEGDM, $M_w = 875$ g/mol, Aldrich), dicumyl-peroxide (DCP, Aldrich), dicyclohexylperoxidicarbonate (DCPD, from Groupe Arnaud), iron III chloride (FeCl$_3$, from Acros), and Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, $M_w = 287.09$ g/mol, Aldrich), were used without further purification. 3,4-ethylenedioxythiophene (EDOT, from Heraeus) was distilled before use.

2.2.2 Trilayer Conducting Polymer actuators fabrication

Trilayer conducting polymers, as demonstrated in figure 2.1, were synthesized through an in situ process following the work done by Festin et al. [43]. In this process an NBR network is polymerized within the PEO network, forming a double network of interpenetrated polymers (IPN), which when swelled with an electrolyte, serves as the solid polymer electrolyte (SPE). This layer also electrically separates the two active conducting polymer layers. Here the PEO network, being polar, largely hosts the ionically conductive electrolyte of the SPE layer and the NBR network, having large molecular chains, maintains the mechanical robustness of the film [45].

As shown in figure 2.1(a), first, a 20% w/w solution of NBR was made by adding the NBR and TCE into a flask and letting the mixture stir for 24 hours. The precursors of PEO network (PEGM/PEGDM at 75/25 w/w) were then added to the solution in order to obtain 60% w/w of PEO in compare to total IPN polymer. The mixture was stirred for 15 min and then 3% of DCP by weight of NBR and 2% of DCPD by weight of PEO were added to the solution and stirred for
Figure 2.1 Fabrication process of (a) PEO:NBR interpenetrated polymer network (IPN) films and (b) PEDOT formation on the two sides of PEO:NBR IPN to make a PEDOT/PEO:NBR/PEDOT trilayer structure.
15 min. DCP and DCPD were used as the vulcanization agent and the methacrylate radical initiator for NBR and PEO, respectively. The mixture was then poured into a mold made of two glass plates clamped together with a 250 µm spacing in between, which was created by a frame made of Teflon. The mold containing the solution was then placed into an oven at a controlled temperature of 50°C for 3 h, post-cured for 1 h at 80 °C and cooled down to room temperature for 30 min. It was then returned into the oven at 160°C for 30 min for the vulcanization of the NBR network. The resulting yellow elastomeric double network polymer film was then removed from the glass mold after it was cooled down to the room temperature. The un-polymerized substances and solvent were then removed by soaking and swelling the film in methanol overnight followed by rinsing it thoroughly again with methanol before drying under vacuum.

To apply the two PEDOT electrodes, as shown in figure 2.1(b), the interpenetrated polymer network of PEO and NBR was swollen with EDOT until its mass increases by ~150% of its initial value. Then, the film was placed under a fume hood for two minutes to let EDOT be dispersed evenly throughout the film. The swelled double-network polymer film was immersed into a 1.5 M aqueous solution of FeCl\textsubscript{3} at a controlled temperature of 21˚C for 20 hours. FeCl\textsubscript{3}, acting as an oxidizing agent, started polymerizing EDOT into the double network polymer of PEO and NBR from the two surfaces to form the two PEDOT-dominated active layers and leaving an electronically insulating region between them. The resulting film was then washed in Methanol to remove the excess of FeCl\textsubscript{3} and unpolymerized EDOT in the film (until the color is disappeared). It was then left under the fume hood for 2 hours to let the Methanol evaporate. The trilayer membrane was then immersed into a 1 M solution of Li\textsuperscript{+}TFSI\textsuperscript{-} in propylene carbonate (PC) for a month to ensure it was fully swollen.

2.2.3 Material characterization
Mass and thickness of the trilayers were measured using an analytical balance (Mettler Toledo, accuracy of 0.1 mg) and a digital micrometer (Mitutoyo 293-676 Quickmike IP54, precision of 2.5 µm), respectively. The thickness measurements were then calibrated through an optical micrograph of the cross section of the samples using a Nikon Eclipse LV100 polarized light microscope. Cross-section images and elemental analysis of the trilayers were done using an FEI/Aspex Explorer scanning electron microscope (SEM) which is equipped with an Energy-dispersive X-ray (EDX) spectrophotometer. The energy of electron-beam was set to 25 kV for all the three measurements. The samples were cut using a razor blade prior to the SEM and EDX analysis. Young’s moduli of the PEO:NBR double network and the PEDOT/PEO:NBR/PEDOT films were obtained through stress-strain measurements using a Bose ElectroForce®-3100 system in tension mode (a strain of 1% at 0.1 Hz).

2.2.4 Actuation test

A square wave voltage with an amplitude of ±2 V was applied to the two conductive sides of the trilayer using a Solartron 1287A Potentiostat/Galvanostat, Hampshire, UK. The trilayers were held so they actuate horizontally, and their top view actuation was captured using a Nikon D5100 DSLR Camera. Displacement was measured using a laser displacement sensor (Keyence LK-G32, repeatability of 50 nm) by illuminating the laser on a point on the trilayer and measuring the excess of distance the laser travels to reach the trilayer surface as it actuates.

2.3 Results

2.3.1 PEDOT/PEO:NBR/PEDOT trilayer characterization

Figures 2.2(a-d) show the optical micrographs of the cross-sections of the PEO:NBR double network film and PEDOT/PEO:NBR/PEDOT trilayer films before and after being swollen with a 1 M solution of Li’TFSI’ in PC. Comparing figures 2.2(a) and (b) shows PEO:NBR film
shrinks by ~25% (thickness changes from 245 µm to 180 µm) as the PEDOT polymer penetrates it to form the trilayer. When both films fully uptake the electrolyte, the thickness of PEO:NBR film changes by 160% (from 245 µm to 390 µm) while that of the PEDOT/PEO:NBR/PEDOT trilayer film changes by 200% (from 180 µm to 360 µm).

Figure 2.2(e) and (f) show a scanning electron microscopy image and an energy dispersion (EDX) map of sulfur content, respectively, through the cross-section of the trilayer before being swollen with the electrolyte (both films in a vertical orientation). The yellow line in figure 2.2(f) is the cross section EDX line scan. Since only PEDOT contains sulfur atoms, the location and relative concentration of PEDOT is indicated by the location and the relative concentration of sulfur atoms (color-coded in turquoise in figure 2.2(f)). EDX analysis of the cross-section of PEDOT/PEO:NBR/PEDOT film shows that the density of PEDOT is maximum at the two outer surfaces and it reduces towards the centre of the device. As seen, there is no distinct boundary between the three layers in this structure and the polymers are interpenetrated into each other with a larger density of PEDOT at the two outer sides. Here for simplicity, although the structure does not have three sharply separated layers, we call the device as “trilayer”, the PEDOT-dominated regions in the trilayer as just “PEDOT electrodes” and the electronically insulating region made of a double network of PEO and NBR as “separator”.

From the EDX mapping of sulfur atoms, the thickness of PEDOT layer before soaking the trilayer in the electrolyte (the region in figure 2.2(f) where we see > 50% of the maximum sulfur concentration) is (24 ± 0.5) µm. According to the calculations provided in Appendix A, the thicknesses of the PEDOT electrodes and the separator layer when the device is fully swollen with a 1 M solution of Li+TFSI in PC are estimated to be (31.5 ± 0.6) µm (∼1.3-fold increase compared to when it is dry) and (297 ± 1.2) µm, respectively. Young’s modulus of the separator
Figure 2.2 Optical micrographs of the cross sections of (a) PEO:NBR double network polymer and (b) PEDOT/PEO:NBR/ PEDOT trilayer films before being swollen with the electrolyte, (c) PEO:NBR double network polymer and (d) PEDOT/PEO:NBR/ PEDOT trilayer films fully swollen with a 1 M solution of Li'\text{TFSI}' in PC. (e) SEM micrograph of the cross-section (vertical orientation) and (f) EDX mapping (color-coded with turquoise) and EDX line scan (in yellow) of sulfur distribution in the cross-section of the PEDOT/PEO:NBR/ PEDOT trilayer film before being swollen with the electrolyte.

Layer and the PEDOT electrode were calculated through stress-strain measurements on pure PEO:NBR film and PEDOT/PEO:NBR/ PEDOT trilayers, when they are fully swollen with the electrolyte and are equal to 1.2 MPa and (180 ± 6) MPa, respectively. The uncertainty comes in
part from the uncertainty in the thickness of the PEDOT layer. These values agree with the corresponding values obtained previously [43].

2.3.2 Effect of evaporation of solvent on bare trilayer films

As depicted in figures 2.2(b, d), the trilayer swells by almost two times as it fully stores the electrolyte (1 M solution of Li+TFSI− in PC). Propylene carbonate has a vapor pressure of 23 mTorr at 25°C [46], which is almost 1000 times smaller than that of water (23.8 Torr at 25°C) [47]. This means its evaporation rate is almost 1000 times slower than the evaporation rate of water in similar conditions. Propylene carbonate, however, evaporates over time if there is no encapsulation.

Figure 2.3(a) shows the normalized mass of trilayer (circles) relative to its initial value and the retained mass percentage of PC (triangles) over time when there is no encapsulation. The results were obtained by averaging the results of three trilayers with the same thicknesses (~360 µm) and roughly the same areas (~150 mm²). The trilayers were stored and measured in a Controlled Temperature and Humidity (CTH) room with the set temperature and relative humidity of (23 ± 2)°C and (50 ± 3)%, respectively. Comparing the initial and final masses of the trilayers shows the initial mass of propylene carbonate which is stored in the trilayer is ~45% of the initial mass of the trilayer. This amount of PC leaves the device within 8 days with an initial fast decay, which decreases over time (~40% of the initial amount of PC evaporates within a day). The corresponding change in the volume of the trilayer is ~46% of its initial volume, which is close to the volume of the evaporated PC. This suggests that the structure of the trilayer is non-porous and its volume changes at a 1:1 solvent volume to film volume change ratio as it uptakes electrolyte.

Figure 2.3(b) displays the thickness of the trilayer versus the retained percentage of PC mass
Figure 2.3 (a) Normalized mass of a bare PEDOT/PEO:NBR/PEDOT trilayer (circles) and normalized retained mass of PC (triangles), over time. Normalizations are relative to initial values which are indicated next to the arrows pointing the corresponding axis. The samples were stored and measured in a room with controlled humidity and temperature at $T = (23 \pm 2)^\circ\text{C}$ and $RH = (50 \pm 3)\%$, respectively. (b) Thickness of the trilayer versus the retained mass of PC in the PEDOT/PEO:NBR/PEDOT trilayer as it dries. The inset image is the optical micrograph of the cross-section of the trilayer when all the PC is evaporated from it.

in it. Considering any mass change in the trilayer over time is due to PC loss, the initial mass of PC was obtained from the difference between the initial and final masses of the trilayer (~45% of the initial mass of the device). It shows trilayer thickness decreases linearly as PC evaporates...
from the device ($R^2 = 0.995$) with the rate of $\sim 1.78 \mu m/\%$. The cross-section optical micrograph of the trilayer when the device lost all the PC stored into it is also shown in figure 2.3(b). The corresponding thickness of the trilayer is $\sim 186 \mu m$. The difference between this value and the thickness of the trilayer before being swollen with the electrolyte ($\sim 180 \mu m$ from figure 2.2(b)) is partially because LiTFSI is a hygroscopic salt and the remaining LiTFSI in the trilayer either keeps a small amount of PC with it or absorbs humidity from the surrounding. This value, however, is basically small due to the large solubility of LiTFSI in polar solvents ($> 20 M$ at 25°C in water [48]). In this work, the presented retained percentage of PC mass does not include the amount of solvent (either PC or water) which LiTFSI salt holds due to its hygroscopic nature.

The linear relationship between the thickness of the trilayer and its mass also supports the non-porous structure of the trilayer. In contrast, for a porous structure such as PVDF membrane, the electrolyte fills the pores inside the film so little or no volume change would occur as the electrolyte’s solvent evaporates. The non-porous structure of the trilayers used in the current study helps them to store the electrolyte for a longer time. However, it also causes the dimensions of the device to shrink as it dries. This dimensional change affects the deflection of the trilayer.

### 2.3.3 Intermittent response of drying trilayer actuator

A square wave voltage with an amplitude of $\pm 2 V$ and a varying period was applied to the two sides of the PEDOT layers through copper contacts for 25 cycles. In each measurement, the time constant was set to make sure that over a half cycle, the equilibrium is obtained, and the device reaches its maximum displacement. An electric fan was used between measurements to facilitate the evaporation of PC from the device. The optical images of the maximum peak to peak bending of the trilayer with decreasing PC content are depicted in figures 2.4(a-f). The retained
percentage of PC mass in the device, \( m_{pc} \), its time constant, \( \tau \), and the equivalent time during which the same amount of PC is retained from the device if it is stored in a CTH room at \((23 \pm 2)\)°C and \((50 \pm 3)\%\) RH, \( t_{eq} \), are also indicated in the corresponding figure. Rough values of the normalized peak to peak curvature difference of the trilayer versus the retained mass of PC (until ~50\% of PC is retained) are shown in figure 2.4(g). The values were obtained by fitting a circle.

Figure 2.4 (a-f) Optical images of peak to peak maximum deflection of a trilayer as the retained mass of PC in it decreases, and (g) normalized differential curvature versus retained percentage of PC mass. The absolute values of their initial amounts are indicated in each graph.
to each of the actuators. The normalization was done relative to the initial value of curvature difference, $\kappa_0$, which is equal to 1.5 cm$^{-1}$. Figures 2.4(a-f) show the full deflection of trilayer increases as the solvent evaporates until the remaining mass of PC is ~14% of its initial mass ($t_{eq} = 4$ days). When this amount reduces further, so only 2.4% of PC is retained in the device ($t_{eq} = 6$ days), a very small degree of bending is observed.

The surprising increase in bending seen in the trilayers when they are partially dry can be explained by investigating the mechanism of actuation of trilayer conducting polymers. As a square wave voltage with an amplitude of $v$, and period of $T$, is applied across the two sides of the device, ions migrate from one PEDOT electrode to the other through the ionically conducting separator layer over the half period of the applied voltage. So, the density of ions increases in one electrode and decreases in the other which causes strains with the same values and opposite directions to be generated in the two PEDOT layers. This strain, $\epsilon$, linearly depends on the density of charge in the PEDOT film through the equation, $\epsilon = \alpha Q (WLh_p)^{-1}$, where $Q$ is the transferred charge, $\alpha$ is the strain to charge ratio and its value can be obtained empirically and $W$, $L$, and $h_p$ are the width, length and thickness of the conducting polymer layer, respectively. The value of $Q$ is estimated through integrating the current, $i$, passing through the trilayer over the half period of the applied voltage, $T/2$. So, in each half cycle, the strain generated in the PEDOT electrode through the insertion of ions into it can roughly be obtained through equation 2.1;

$$\epsilon = \alpha \int_0^{T/2} \frac{i \, dt}{h_pWL}.$$  \hspace{1cm} (2.1)

The moment when the polarity of the applied voltage switches, the PEDOT layer acts as a short circuit [27]. Hence, the current passing through the trilayer has its maximum value. The current
then decreases approximately exponentially over time (similar to an RC circuit), as ions transfer from one PEDOT electrode to the other to balance the charge. The total charge which is transferred in each half cycle for an exponentially decaying current, given the half period of the applied voltage is well larger than the time constant of the device, is equal to \(i_0 \tau\) (\(i_0\) being the peak current and \(\tau\) being the time constant of the device).

Figure 2.5(a) shows the normalized values of the peak current passing through the device, as well as the corresponding time constant, versus the retained mass of PC. The normalizations were relative to their initial values which are indicated in the corresponding figure. Both the time constant and the peak current depend on the ionic conductivity of the electrolyte (the former inversely and the latter directly) [49], [50]. As the PC evaporates, the concentration and the viscosity of the electrolyte increase, which reduces the ions’ mobility and hence, the ionic conductivity of the electrolyte decreases. This explains the observed decrease in the maximum current and increase in the corresponding time constant in figure 2.5(a). In the current measurement, the half period of the applied voltage is set to be larger than the time constant of the device. So, in each half cycle, the maximum possible number of ions is transferred from one side to the other and the corresponding charge is roughly equal to \(i_0 \tau\) (current passing through the device decreases roughly exponentially over time). The normalized value of the maximum charge which is transferred in a half cycle versus the retained mass of PC in the device are estimated from the two graphs shown in figure 2.5(a) and are depicted in figure 2.5(b). It shows the transferred charge is almost unchanged (stays within 4% of the initial value) until the retained mass of PC is ~14% of the initial value. This is somewhat expected since the ions are given enough time to move from one PEDOT electrode to the other. However, when PC further evaporates so only ~2.4% of its initial value is retained, the amount of charge
Figure 2.5 Normalized (a) maximum current passing through the trilayer and time constant of the trilayer and (b) charge being transferred in each half cycle versus retained percentage of PC mass. The absolute values of their initial amounts are indicated in each graph.

transferred decreases drastically. This is probably due to the very high concentration of the electrolyte which prevents the ions from moving in the device. The constant charge transferred in each half cycle suggests that, according to equation 2.1, the strain generated in the PEDOT layer is mainly affected by the dimensional changes. The length of the actuator (length from the clamped end to its tip) is kept constant at 2 cm but both the thickness and width of the PEDOT electrode decrease as the trilayer dries over time (thickness decreases from 360 µm to 186 µm and width
decreases from 2.2 mm to 2 mm). This causes the strain induced in the trilayer to increase until ~14% of PC is retained in the device. As the trilayer further dries so only 2.4% of PC is retained, the strain decreases due to the drop in the amount of transferred charge (figure 2.5(b)).

The curvature of a three-layer structure, with zero internal strain in the middle layer and uniform internal strains of $+\varepsilon$ and $-\varepsilon$ in the two outer layers, is obtained through equation 2.2 [51],

$$\kappa = \frac{\epsilon}{h_p} \frac{12(m + 1)}{(nm^3 + 6m^2 + 12m + 8)}$$

where $m = h_g/h_p$, ($h_g$ and $h_p$ being the thicknesses of the separator and conducting polymer layers, respectively) varies from ~10.5 (fully swollen) to ~5.5 (fully dry). $n = E_g/E_p$, ($E_g$ and $E_p$ being the Young’s moduli of the separator and conducting polymer layers, respectively) is equal to 0.01 when the trilayer is fully swollen with the electrolyte. Previous study shows that swelling does not have much effect on the young’s moduli of separator and PEDOT layers [43]; So, the change in their ratio, $n$, stays in the same range and compared to $m$, has a negligible effect. Given that $m > 1$ and since $n \ll 1$, equation 2.2 can be roughly simplified to equation 2.3 for the trilayers which are studied in this chapter,

$$\kappa = \frac{2\epsilon}{h_g}$$

According to equation 2.3, both the increasing charge-induced strain in the PEDOT layers and the decreasing thickness of the separator layer cause the curvature of the trilayer to increase as PC leaves the device until ~14 % PC is remained (figures 2.4(a-e)). After then, the strain drastically decreases and consequently causes the curvature to decrease (figure 2.4(f)).

As demonstrated in figures 2.4(g) and 2.5(a), for the geometry of PEDOT actuators studied here, after losing 20% of the mass of the propylene carbonate, the time constant of the device
increases by 10% and its curvature roughly increases by 20%, thanks to the decrease of the device’ thickness as it dries. If we assume 10% decrease in the response time of the device is acceptable (considering the fact that this time the device sweeps a larger displacement), we can conclude the consequences of losing 20% of PC are acceptable for intermittent operations; Hence, the performance is reasonably stable over half a day under the controlled temperature and humidity of (23 ± 2)ºC and (50 ± 3)%, respectively. In intermittent operation, large deflections can be obtained even after losing 86% of the PC content (taking place within ~4 days in the conditions mentioned above). For disposable applications such as a skin patch with an occasional operation, depending on the speed requirements, such a time scale of operation without the need for encapsulation might be reasonable. However, if a stable performance for a longer time is required, the device needs to be encapsulated.

Note that while the overall trend of performance variation is valid for PEDOT/PEO:NBR/PEDOT trilayer actuators regardless of their dimensions, the extent of this performance variation depends on the thicknesses of each of the layers. For PVDF-based actuators, since the volume change is negligible as the solvent evaporates, no significant change in the extent of displacement is expected. The speed of the device, however, decreases due to the decrease of the ionic conductivity of the electrolyte. (larger electrolyte viscosity as the solvent evaporates).

2.3.4 Cycling response of drying trilayer actuators

A continuous square wave voltage with amplitude and period of ±2 V and 2 s, respectively, was applied to the samples through gold contacts. For the trilayer actuator operating in water, since the laser could not keep focused on the immersed trilayer, the actuating device was alternatively immersed in water and briefly removed from it for the measurement. The position of the laser on the device was kept unchanged during the displacement measurement.
Assuming the trilayer beam has a uniform curvature along its length, the value of curvature, \( \kappa \), can be obtained by measuring the lateral displacement, \( D \), of a point at distance \( l \) from the fixed end of the trilayer, through the equation, \( \kappa = 2D/(D^2 + l^2) \) [52]. If the value of \( l \) is sufficiently larger than the displacement (in our case, \( l = 8 \text{ mm} \) and \( D \leq 1.3 \text{ mm} \)), the curvature equation can be simplified to,

\[
\kappa \approx \frac{2D}{l^2}.
\]  

(2.4)

So, the normalized value of curvature is roughly equal to the normalized value of displacement.

Figure 2.6 shows the normalized displacements of bare trilayers operating in air and in water, along with the peak current passing through each device over time. The number of cycles is shown on the top \( x \)-axis. The normalization was done relative to the initial values which are indicated in the corresponding legend in the graph. The plot shows that for both samples, the peak to peak displacement decreases over time and largely follows the maximum current passing through each device. In both samples, an initial sharp decrease in displacement is observed (~100 \%h\(^{-1}\) for ~30 min actuating in open air and ~200 \%h\(^{-1}\) for ~15 min actuating in water). After that, displacement decreases with a relatively slow rate (~4 \%h\(^{-1}\) after 2 h actuation in air and ~14 \%h\(^{-1}\) after ~14 \%h\(^{-1}\) after 30 min actuation in water). The trilayer actuating in water loses 80\% of its displacement after almost an hour (~1800 cycles at 0.5 Hz), which takes ~5.5 h (~10\(^4\) cycles at 0.5 Hz) for the trilayer actuating in air. The displacement decay is faster in water because the device loses both solvent and ions over time.

In the measurements carried out in this section, the conducting polymer layers do not have enough time to get fully charged or discharged in each half cycle and the transferred charge per
cycle follows the peak current passing through the device. The curvature and hence displacement of the device over time depend on charge transfer, as well as any change in the device’s volume with solvent loss or exchange (equations 2.1 and 2.2). The fact that the displacement follows the peak current passing through the device suggests that the effect of decaying charge transfer rate dominates the effect of shrinkage of the device.

![Normalized displacement and current of bare PEDOT/PEO:NBR/PEDOT trilayers cycling in air and in water over time. The normalizations were relative to their initial values which are indicated in the corresponding legend. The applied voltage is a square wave with amplitude of 2V and frequency of 0.5 Hz.](image)

Comparing the mass of the trilayer before and after the experiment shows ~25% of the stored PC is remained in the device after cycling for 5.5 h in open air. According to figure 2.2(a), this amount of PC loss takes ~3 days if the trilayer is stored in a CTH room at T = (23 ± 2)°C and (50 ± 3)% RH. A possible explanation for the faster evaporation of the PC when the device is actuating compared to when it is stored is that the temperature increases in the trilayer because of the power consumption of the device (∝ 𝜈𝑖₀). The generated thermal energy is large and causes the temperature of the device to increase, which then facilitates the evaporation of propylene.
carbonate. This, along with other factors such as air-flow around the device when it actuates are possible reasons why the rate of evaporation of PC when the device is actuating is faster than when it is stored in the CTH room.

Trilayers actuating at cycling period of 2 s lose their displacement as soon as the device starts to lose its solvent in air or its electrolyte in water. The rate of change in displacement depends on the ratio of the half period of the actuation to the time needed the device reaches its extent, \( \tau_f \). The smaller the value of this ratio is, the faster the displacement decreases as the device dries. If the half period is set to a value beyond \( \tau_f \), the system initially operates close to its equilibrium in each half cycle and the displacement may even increase over time (as shown in section 2.3.3). This means we can tune the rate of change in displacement of the device through the selection of the dimensions of the device (which defines its time constant [51]), or the period of the applied voltage. This, however, might be limited due to the application requirements and the consequences of changing the dimensions of the device on the output force and displacement [51].

2.3.5 Conclusion

In this chapter we evaluated the performance of a 360 \( \mu \)m thick PEDOT/ PEO:NBR/ PEDOT trilayer actuator with a 1 M solution of Li\(^{+}\)TFSI\(^-\) in PC as the electrolyte. Drying ultimately leads to a slowing response due to the reduction of the ionic conductivity of the electrolyte; For the devices studied in this chapter, if the device is to operate intermittently, the slow actuation is accompanied by an increasing displacement because of the shrinkage of the device. If the device is cycling, a reduction in deflection is observed as a result of the decrease in the generated strain due to a drop in charge transfer rate, as the solvent evaporates. For the trilayer actuators studied in this work, in both cases, the device is still operational as long as \(~14\%\) of the solvent is retained. This might be acceptable, e.g., in disposable applications. However, for applications where a long
operation time with a stable performance is expected or where the device is required to operate in a liquid other than its electrolyte, the use of encapsulation is inevitable.
Chapter 3: Impermeable and compliant: SIBS as a promising encapsulant for ionically electroactive devices

3.1 Introduction and Motivation

As demonstrated and discussed in chapter 2, if a solvent-based electrolyte is used in trilayer conducting polymer actuators, the solvent evaporates over time as the device is operated in air which causes its performance to vary. Moreover, in some applications where the device is required to work in a liquid environment other than its electrolyte, such as in water or blood, if the device is not well protected against its environment, ions and solvent will leave the device over time and will be substituted by the environment molecules. So, encapsulation is desirable to prevent the solvent from escaping the device and to have the device operate reliably. The encapsulating layer can also serve as a protection against the escape of hazardous electrolytes for applications where direct user interactions are involved, such as biomedical devices [15], [35] and tactile interfaces [31]

If a solvent-based electrolyte is employed in conducting polymer trilayers, the rate at which the solvent is lost and hence the performance changes, depends on the thickness of the conducting polymer layer and how the separator layer stores the electrolyte. For a trilayer with a 110 μm thick PVDF membrane (pore size of 0.45 μm) as the separator layer, and 8 μm thick polypyrrole (PPy) conducting polymer layers and a 0.1 M solution of Lithium bis(trifluoromethanesulfonyl)imide (Li^+TFSI^-) in propylene carbonate (PC) as the electrolyte, 80% of the initial displacement is lost after 3.6 h of actuation in air (1.3 × 10^4 cycles at 1 Hz), or
6 min of actuation in water (~360 cycles at 1 Hz) [6]. We showed in chapter 2 that a trilayer with a (297 ± 1.2) µm thick separator comprised of an interpenetrated network of polyethylene oxide (PEO) and nitrile butadiene rubber (NBR), on which (31.5 ± 0.6) µm thick poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer layers are applied and a 1 M solution of Li+TFSI- in PC is used as the electrolyte, 80% of the initial displacement is lost after ~5.5 h (10^4 cycles at 0.5 Hz) continuous actuation in air, which takes ~1 h (1.8 × 10^3 cycles at 0.5 Hz) if the device actuates in water. PEDOT/PEO:NBR/PEDOT trilayers, are non-porous and swell as they store the electrolyte inside and shrink when the electrolyte is withdrawn. We also showed in chapter 2 that the maximum extent of bending of the tested trilayer, if operated intermittently in air, increases thanks to its thickness shrinkage, until only ~14% of PC is retained in the device. This takes ~4 days if the device is stored in a Controlled Temperature and Humidity (CTH) room at (23 ± 2)˚C and (50 ± 3)% RH. After then, the displacement drastically decreases and the device is no longer operational. The observed increase in the displacement, however, is at the expense of an increase in the time constant of the trilayer actuator from 2 s (when it freshly starts to operate) to 13 s (when only 14% of PC is retained). After 20% of the stored PC is lost, the maximum extent of bending of the actuator increases by 20% and its time constant increases by only 10%. This takes half a day if the device is stored in the CTH room and might be acceptable for disposable applications such as a skin patch. However, for applications where a long operation time with a stable performance is expected or where the device is required to operate in a liquid other than its electrolyte, the use of encapsulation is unavoidable.

An encapsulating material for ionic bending actuators should

1) be a good barrier that limits the exchange of molecules with the environment,
2) be flexible enough not to prevent the bending,
3) be able to be deposited under conditions compatible with the materials that the device is made of, and

4) be stable over the lifetime of the device in its operation and storage environments.

Among all electronic devices, organic light emitting diodes (OLEDs) demand the highest impermeability from their encapsulating material (water vapor transmission rate, WVTR, of \( \sim 10^{-6} \text{ g.m}^{-2}.\text{day}^{-1} \) at (37.5 to 40)˚C and oxygen transmission rate, OTR, of \( (10^{-5} \text{ to } 10^{-3}) \text{ cm}^3.\text{m}^{-2}.\text{day}^{-1} \) at standard temperature and pressure conditions (0˚C and 1 bar)) [53]. For such devices, multilayer structures comprised of alternating organic/ inorganic layers are used, which are fabricated through solution processing and atomic layer deposition (ALD) methods, respectively. Although these types of encapsulation provide excellent protection against humidity and oxygen and can be flexible [54], they are not compatible with the wet electrochemical devices due to the low vacuum pressure required for ALD deposition (0.02 mTorr) and the stiff structure they have due to the inorganic layers. More importantly, ionic devices are not as sensitive to losing their solvent or absorbance of humidity from the surrounding as the OLEDs or other organic electronic devices are [53]; Hence, for conducting polymer actuators, the search for the encapsulating material among the polymeric barriers is more reasonable considering the low-cost fabrication process they can offer, their possible lower Young’s modulus and generally better tolerance towards mechanical deformation.

Ionic Polymer-Metal Composite (IPMCs) are another type of ionic electroactive polymer actuators and sensors, which share a similar structure with conducting polymer trilayers. They typically use a solvent-based electrolyte which requires them to be encapsulated to maintain their performance. S. Kim et al. [55] showed an improvement in the operation lifetime of IMPC actuators with water as the electrolyte’s solvent of 22 times (from 6.5 min to 2.5 h) by
encapsulating them with 1.5 µm thick Parylene C. Hong Lei et al. [56] showed that by increasing the thickness of Parylene C to 25 µm, the operation lifetime of IPMC sensors can be further improved. However, Parylene C has a large Young’s modulus (~3 GPa [57]) which significantly limits the flexibility of the device and reduces the extent to which the device can bend. In addition to this, its low-pressure deposition requirement (< 100 mTorr [55]) is generally not compatible with the wet ionic devices, especially if the ionic element expands as it uptakes electrolyte (which is the case for most solid polymer electrolytes (SPEs)).

Jaakson et al. [26] tried different polymers to encapsulate PPy/ PVDF/ PPy trilayer conducting polymer actuators containing a 1 M solution of Li+TFSI- in PC as the electrolyte. They showed that amongst the polymers they compared, hot-rolled commercially available parafilm sheets and spray-coated polyvinylidene chloride (PVDC), have the least moisture penetration and the corresponding encapsulated trilayer actuators experience the least performance loss over time compared to their initial performance. However, the details of their methodology and their results were not fully presented, making it hard to generalize their conclusions. Moreover, the effect of the encapsulating layer on the extent of bending was not investigated. Naficy et al. [6] used poly (styrene-block-isobutylene-block-styrene) (SIBS) elastomer to encapsulate PPy/ PVDF/ PPy trilayer conducting polymer actuators containing a 0.1 M solution of Li+TFSI- in propylene carbonate as the electrolyte. Using a 100 µm thick manually spray-coated SIBS film, the time to lose 20% and 70% of the initial displacement of the device, cycling in air at 1 Hz, improved 2-fold (from 1.4 h to 2.7 h) and 20-fold (from 2.7 h to 55.5 h), respectively, at the expense of losing 30% of the initial displacement of the actuator due to the added stiffness by the encapsulating layer. This performance encouraged us to more fully explore this encapsulation approach, including a detailed study of the influence of thickness
and uniformity of the encapsulating layer on the electrolyte’s solvent mass loss and the cycle life of the trilayers actuating in air and water.

SIBS is the third generation of styrene block copolymers, (SBCs) with completely saturated backbone and mid-block side chains, both of which restrict the segmental mobility of the polymer chains and make it highly stable towards heat aging and weakly permeable to many gases [58]. Being a bio-stable and Food and Drugs Administrative (FDA) approved polymer with minimal tissue reaction, it has been shown to be a promising material to be used in various medical applications [59]. The laboratory-grade SIBS coatings are successfully being used as the carrier for a drug-eluting coronary stent (TAXUS® stent, Boston Scientific Corporation’s (Natick, MA) [60], [61]). Micro shunts made of SIBS has also been recently developed for glaucoma treatment by InnFocus LLC [62]. Other applications such as synthetic heart valves to possibly replace tissue valves are also being investigated [63].

In chapter 2, we characterized fabricated PEDOT/ PEO: NBR/ PEDOT trilayer actuators in terms of their material properties and then studied the effect of solvent evaporation on their performance [11]. Before reporting on the performance of SIBS as an encapsulating material for these actuators, we first review and analyzed several polymeric materials which are commonly used to protect foods, pharmaceuticals, implantable medical devices, electronic devices, etc. in terms of their Young’s moduli, $E_e$, water vapor transmission rate for unit thickness, WVTR$_n$, and strain at yield for plastic materials, or fracture strain for elastomers. The smaller the WVTR$_n$, of the material is, the smaller thickness of it is enough to provide a certain standard of encapsulation. The thinner the encapsulating layer and the lower its Young’s modulus are, the less stiff the actuator beam becomes after encapsulation and the less deformation it loses. Based on this fact, we introduce a figure of merit for polymeric materials as $\gamma_w$, being the product of
Young’s modulus, $E_e$, and the normalized water vapor transmission rate, WVTR, of the encapsulating film. The metric needs to be small, so the film provides a proper encapsulation with low impact on the flexural rigidity and hence the extent of deformation of the device. According to the introduced figure of merit, SIBSTAR, which is the trade name for the commercial grade of SIBS, can potentially work best for encapsulating trilayer conducting polymer actuators as it exhibits the smallest value of $\gamma_w$ amongst the standard polymer encapsulants that are compared. Using gravimetric techniques, in this chapter, we quantitatively investigated the ability of the spray-coated SIBSTAR films in protecting propylene carbonate from escaping a 360 µm thick PEDOT/PEO: NBR/PEDOT trilayer actuators and describe the results using a polymeric barrier permeation model. The effect of encapsulation on the performance of the trilayer actuators in terms of their retained percentage of displacement over time when continuously cycling in air and in water, as well as the extent to which they can bend after encapsulation are also studied.

3.2 Selection of encapsulating polymer for bending beam actuators

Encapsulation of ionic bending actuators such as trilayer conducting polymers is more challenging compared to batteries and other types of ionic devices since the application of the encapsulating layer can significantly influence the flexural stiffness and hence the extent to which the device can bend. The flexural stiffness of a beam is obtained through the familiar equation, $K_F = 3(EL)b/L^3$, where $L$ is the length of the beam and $EI$ is its flexural rigidity and is obtained through equations 3.1.a for an encapsulated beam (including three layers),

$$
(EL)_b = \frac{W}{12} \left( E_e(h_T^3 - h_t^3) + E_t h_t^3 \right) + \frac{t_s}{6} E_e h_T^3,
$$

(3.1.a)

where $E_e$ and $E_t$ represent the Young’s moduli of the encapsulating layer and the beam,
respectively. \( W \) is the width of the beam, \( h_T = 2t_s + h_t \), is the total thickness of the encapsulated beam and \( t_s \) and \( h_t \) are the thicknesses of the encapsulating layer and the beam, respectively.

According to equation 3.1.a, the smaller the Young’s modulus and the thickness of the encapsulating layer are, the less impact they have on the flexural rigidity and hence the flexural stiffness of the beam: \( WE_t h_t^3 / 4L^3 \), before encapsulation. In the case where \( h_t >> t_s \), the fractional stiffness added by the encapsulating layer is:

\[
\frac{\Delta K_E}{K_T} \approx \frac{W}{4L^3} \left( 6E_e h_t^2 t_s \right) = \frac{6E_e t_s}{E_T h_t}. \tag{3.1.b}
\]

So, clearly, the product of the encapsulating layer’s modulus and its thickness needs to be minimized. The same relationship applies to linearly deformed films.

The mass transfer rate across a polymeric film, \( a \), is inversely related to its thickness, \( t_s \), through equation 3.2 [64],

\[
a = \frac{VTR_n A}{t_s}, \tag{3.2}
\]

where \( A \) is the area over which the permeant transfers across and \( VTR_n \) is the permeant-vapor transmission rate of the polymer for its unit thickness and depends on various properties of the polymer material such as its saturation level, the degree of crosslinking, crystallinity, glass transition temperature and molecular weight, as well as the nature of the penetrant [64]. Equation 3.2 suggests a thicker film of polymer can compensate for a large vapor transmission rate, but this conflicts with the requirement for the flexural stiffness. Combining the requirements for minimum change on the flexural stiffness as the encapsulation film is applied with minimum transmission rate through it, we introduce a figure of merit for polymeric materials, \( \gamma = VTR_n E_e \), which is ideally small, so the film provides a proper encapsulation with low impact on
the flexural stiffness of the structure. In addition to that, the polymer needs to have a high enough fracture strain (for elastomers) or strain at yield (for plastic materials) to ensure a tolerance to bending. The required magnitude depends on the extent of bending of the trilayer actuator.

Table 3.1 shows a list of polymeric materials and their typical values for water vapor transmission rate for their unit thickness, WVTR\text{a}, Young’s modulus, $E_e$, and the strain at yield for plastic materials or the fracture strain for elastomers, as well as their calculated $\gamma_w$, which is the corresponding value of $\gamma$ for water vapor. The list is sorted based on the value of the Young’s modulus, showing the material with the smallest Young’s modulus on top. The selected materials are common polymers which are used to protect foods, pharmaceuticals, implantable medical devices, electronic devices, etc. Plastics selected for the table offer the minimum elastic deformation range needed for the trilayers. Figure 3.1 compares $\gamma_w$ of different polymeric barriers. The materials are sorted based on their WVTR\text{a} (lowest at the left). It shows SIBSTAR 103T (a commercial grade of SIBS [65]) with the water vapor transmission rate and Young’s modulus of 0.241 g.mm.m$^{-2}$.day$^{-1}$ [65] and 11.2 MPa, respectively, has the smallest value of $\gamma_w$, and can potentially work best for encapsulating trilayer conducting polymer actuators. Note that many materials are less permeable than SIBSTAR, so that if encapsulation alone is the key concern, it is not the best choice. Of those materials that are highly stretchable, (indicated by a * in table 3.1 and figure 3.1), SIBSTAR appears to be the best choice by more than an order of magnitude. What makes it a better barrier compared to other elastomers, such as polyurethanes and SEBS? Transport of a permeant into a polymeric barrier depends on various factors; The most important ones are the nature of the polymers (free volume within the polymer and the
<table>
<thead>
<tr>
<th>Material's name</th>
<th>Abbreviation or trade name</th>
<th>Young’s Modulus (MPa)</th>
<th>Strain at yield or fracture strain (%)</th>
<th>WVTR&lt;sub&gt;N&lt;/sub&gt; (g.mm.m&lt;sup&gt;2&lt;/sup&gt;.day&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>γ&lt;sub&gt;w&lt;/sub&gt; (MPa.g.mm.m&lt;sup&gt;2&lt;/sup&gt;.day&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(styrene-b-isobutylene-b-styrene)</td>
<td>SIBSTAR 103T*</td>
<td>11.2</td>
<td>700</td>
<td>0.24</td>
<td>2.7</td>
<td>[65], this work</td>
</tr>
<tr>
<td>poly(styrene-b-ethylene-butylene-b-styrene)</td>
<td>SEBS, Kraton G2701*</td>
<td>20</td>
<td>800</td>
<td>47</td>
<td>940</td>
<td>[57], [66]</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PU*</td>
<td>55</td>
<td>700</td>
<td>2.185</td>
<td>120</td>
<td>[57], [67]</td>
</tr>
<tr>
<td>Low-density Polyethylene</td>
<td>LDPE</td>
<td>250</td>
<td>19</td>
<td>0.5</td>
<td>125</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Polyvinylidene Chloride</td>
<td>PVDC, Saran 560</td>
<td>470</td>
<td>5</td>
<td>0.02</td>
<td>9.4</td>
<td>[57]</td>
</tr>
<tr>
<td>High-density Polyethylene</td>
<td>HDPE</td>
<td>1250</td>
<td>15</td>
<td>0.12</td>
<td>150</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>PET</td>
<td>2300</td>
<td>3.5</td>
<td>0.39</td>
<td>900</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Polyimide</td>
<td>PI, Upilex R</td>
<td>2500</td>
<td>4</td>
<td>0.56</td>
<td>1400</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Poly(p-xylene)-type C</td>
<td>Parylene C</td>
<td>2800</td>
<td>2</td>
<td>0.08</td>
<td>225</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>PVC</td>
<td>3000</td>
<td>3.5</td>
<td>1.18</td>
<td>3540</td>
<td>[57], [68]</td>
</tr>
<tr>
<td>Liquid Crystal</td>
<td>LC, Vectra A950</td>
<td>10000</td>
<td>2</td>
<td>0.05</td>
<td>500</td>
<td>[57]</td>
</tr>
<tr>
<td>Polyepoxides</td>
<td>Epoxy</td>
<td>80000</td>
<td>1.3</td>
<td>0.8</td>
<td>64000</td>
<td>[57], [68]</td>
</tr>
</tbody>
</table>

Those tagged with * are elastomers at room temperature.
Segmental mobility of the polymer chains), size and shape of the penetrant and temperature [64]. Segmental mobility of a polymer depends on its extent of saturation, degree of cross-linking, degree of crystallinity as well as the glass transition temperature of the polymer barrier [64]. SIBS is the third generation of styrene block co-polymers, (SBCs), a very well-known type of thermoplastic elastomer, with the molecular structure depicted in figure 3.2. It is composed of hard polystyrene end blocks and soft elastomer mid blocks. Compared to its previous generations, Poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-isoprene-b-styrene) (SIS), and poly(styrene-b-ethylene-butylene-b-styrene) (SEBS), SIBS has a completely saturated backbone and mid-block side chains, both of which restrict the segmental mobility of the polymer chains, making SIBS highly stable towards heat aging and weakly permeable to gases such as O₂, CO₂ and moisture [65]. SIBSTAR, which is the commercial grade of SIBS, comes in different grades based on the ratio of styrene to isobutylene and hence its molecular weight. For non-porous polymers, as the molecular weight increases, the number of chain ends decreases.
which provides less discontinuity and hence less permeability in the polymer [64]. Grade 103 T of SIBSTAR (30% Styrene content) is used in the current study due to its highest molecular weight ($M_w = 100,000$ g/mol [65]), compared to other similar grades. Although chemical cross-linking improves the barrier properties of the film, SIBSTAR film is not cross-linked in the current study to maintain its low Young’s modulus.

![Molecular structure of styrene-b-isobutylene-b-styrene (SIBS)](image)

**Figure 3.2 Molecular structure of styrene-b-isobutylene-b-styrene (SIBS)**

### 3.3 Experiments

#### 3.3.1 Encapsulation process

Spray-coating was carried out using a Sono-Tek ExactaCoat automatic spray-coating system. A 2% w/w solution of commercial grade poly(styrene-b-isobutylene-b-styrene) (SIBSTAR 103 T, $M_w = 100,000$ g/mol, Kaneka Americas Holding, Inc.) in toluene ($C_6H_5CH_3$, 99.8%, Sigma Aldrich) was prepared and loaded into a spray-coating syringe (Hamilton 1025 TLL, 25 ml). As schematically depicted in figure 3.3, the spraying follows a spiral path with spacing between paths of $d = 2$ mm to deposit SIBSTAR solution on the sample. Toluene starts evaporating from the solution as soon as it sits on the substrate and leaves a thin film of SIBSTAR. The nozzle to substrate distance, nozzle speed, shaping air pressure and flow rate were set to 9 cm, 20 mm/s, 0.8 kPa and 0.3 ml/min, respectively. The solution was spray-coated for 10 coats (equivalent of
~19 µm thick SIBSTAR film) following with a 5-minute dwell time to let much of the remaining toluene in the film evaporate. This process was repeated until the required thickness was reached. Encapsulation of trilayers was carried out by depositing the first SIBSTAR layer with the required thickness on a glass slide. Then a trilayer was freshly removed from the electrolyte, gently dried using a cleanroom wipe, placed on the as-prepared SIBSTAR film and then coated with the second layer of SIBSTAR with the same thickness as the first one. In order to coat the sides of the samples, they were tilted by 45° to expose the targeted side to the solution spray. The spraying path was aligned to the targeted side and coated it through a single linear path with the SIBSTAR solution for an equivalent number of coats as their flat surfaces. The weights of all the samples were measured using an analytical balance (Thorlab, AGCN200, the accuracy of 0.1 mg) prior to the encapsulation.

3.3.2 Material characterization

Thickness uniformity and 3D surface mapping of the SIBSTAR films were characterized using a Bruker Dektak XT profilometer (stylus diameter: 2 µm, force: 0.1 mN) and calibrated through the optical micrograph of the cross section of the sample using a Nikon Eclipse LV100 polarized light microscope. Stiffness measurements were carried out on SIBSTAR films using a
Bose ElectroForce®-3100 system in tension mode (a strain of 1% at 0.1 Hz).

3.3.3 Actuation test

The effect of encapsulation on the performance of the trilayer actuator was evaluated through measuring and comparing the maximum extent of curvature of the trilayer before and after encapsulation as well as its displacement change versus time as it cycles in open air and in water. Using a Solartron 1287A Potentiostat/ Galvanostat (Hampshire, UK.), a square wave voltage with an amplitude of ±2 V was applied to the samples through gold electrodes which were tightly holding the samples at one end. The sides of the samples were covered with a thick solution of SIBSTAR after being spray-coated. For the encapsulated samples, ~3 mm of the encapsulation was removed at one end to subsequently connect the electrodes to it. The trilayers were held so they actuate laterally, and their actuation was captured using a Nikon D5100 DSLR Camera. Displacement was measured using a laser displacement sensor (Keyence LK-G32, repeatability of 50 nm) by illuminating the laser on a point on the trilayer at distance $l$ from the fixed end of the trilayer and measuring the excess of distance the laser travels to reach the trilayer surface as it actuates. Displacement, $D$, is defined as the maximum change in deflection measured by the laser within the half cycle of actuation, $T/2$. Trilayer actuators cycling in air were subjected to an air flow provided by an electric fan during the measurement to increase the rate of solvent evaporation. Since the laser could not keep focused on the trilayers cycling in water, the devices were alternatively immersed in water and briefly removed from it for the measurement. The position of the laser on the device was kept unchanged during the displacement measurement.

3.3.4 Permeability measurement

Bare and encapsulated trilayers were hung over a rod using a paper clamp as demonstrated in
Figure 3.4(a). The whole setup was then placed into a container with a lid to prevent dust from settling on the samples, as shown in figure 3.4(b). The whole setup was then stored in a Controlled Temperature and Humidity (CTH) room with the set temperature and relative humidity, RH, of $(23 \pm 2)\degree C$ and $(50 \pm 3)\%$, respectively. The masses of the paper clamps along with the samples attached to them were measured and recorded over time using an analytical balance (Mettler Toledo AE100, the accuracy of 0.1 mg).

![Figure 3.4 Encapsulated actuators (a) hung over a rod using paper clamps and (b) placed into a capped container which is stored in a controlled humidity and temperature (CTH) room at $(23 \pm 2)\degree C$ and $(50 \pm 3)\%$.](image)

### 3.4 Results

#### 3.4.1 Characterization of spray-coated SIBSTAR film

Figure 3.5(a) shows the top view optical micrograph of a SIBSTAR film made of 50 spray coats (100 µm thick) deposited on a glass slide. It shows the film consists of randomly distributed droplets deposited one on top of the other which is typical for spray-coated films [69]. This is the result of the fast drying SIBSTAR solution droplets before they redissolve the layer underneath, forming coffee rings with a radius of $20 \mu m < r < 70 \mu m$. The 3D mapping of the surface of the same SIBSTAR film is shown in figure 3.5(b), demonstrating a root mean square (RMS) roughness and peak to valley (P–V) values of 1.4 µm and 12 µm respectively. Neither
Figure 3.5 (a) Top view optical micrograph, (b) 3D surface mapping and (c) thickness versus distance along the length of a SIBSTAR film prepared by 50 spray coats on a glass substrate. Thickness is uniform over ~2.5 cm ($t = (100 \pm 5) \mu m$). (d) SIBSTAR film’s thickness at the center of glass slide substrate versus number of scans. Thickness linearly increases as the number of spraying coats increases.
porosity nor pinholes were observed in the samples through their surface optical microscopy and 3D mapping. Figure 3.5(c) shows the profilometry of SIBSTAR film made of 50 spray coats along the length of the glass slide substrate which is patterned using a razor blade. It depicts a length of ~2.5 cm within which the SIBSTAR film thickness is uniform and is equal to (100 ± 5) µm. A larger area of uniformly thick film can be obtained by increasing the spraying area. Figure 3.5(d) shows the thickness of SIBSTAR film deposited at the center of its substrate versus number of spray coats, demonstrating a linear relationship between the two and deposition rate of 1.92 µm per coat. Young’s modulus of spray-coated SIBSTAR film was calculated and is equal to (11.3 ± 0.5) MPa. This value is 4 to 10 times larger than the values reported for cast films at the strain of 100 % [70]. While the difference can partially be due to the difference in the fabrication process, it has been shown that Young’s modulus of SIBSTAR vary with the magnitude of the applied strain and is larger at smaller values [70]. The obtained value in this work is in accordance with the value reported by Naficy et al. [6].

Water and PC absorbances of SIBSTAR spray-coated films were measured by immersing 190 µm thick SIBSTAR films with areas of 1 cm × 2 cm (equivalent mass of (34.6 ± 0.3) mg) in each of the liquids. No measurable mass change (< 0.1% or < 38 µg/cm²) was observed for the SIBSTAR film immersed in DI water after two weeks, while the mass of the one immersed in PC increased by 0.5 mg (~1.4% or 190 µg/cm²). After seven months, the film immersed in DI water absorbed 0.4 mg water (equivalent mass increase by ~1.15% or 152 µg/cm²) and the one in PC absorbed a further 0.6 mg of PC (equivalent total mass increase by 3.2% or 418 µg/cm²).

3.4.2 Characterization of permeant mass transfer in SIBSTAR sprayed films

As discussed in section 2, SIBSTAR is a good candidate as an encapsulating material for
ionic bending actuators. In this section, we will demonstrate how well sprayed films of SIBSTAR at different thicknesses can protect the propylene carbonate stored in trilayers from being evaporated.

Figure 3.6(a) shows a top view optical image of a 4 mm × 12 mm trilayer encapsulated with ~100 µm thick SIBSTAR films. The encapsulation’s margin is indicated with red dashed lines. The encapsulation extension is provided in all the samples to ease their holding and handling. The cross-section optical micrograph of a trilayer (thickness of ~360 µm when it was freshly removed from the electrolyte [11]) encapsulated with ~100 µm thick SIBSTAR is demonstrated in figure 3.6(b) (for this sample the sides were covered with a thick solution of SIBSTAR using a fine brush). The measurement was performed two months after the encapsulation was carried out. It shows after two months, no significant change in the thickness of the trilayer occurs if the device is encapsulated with a ~100 µm thick SIBSTAR film. We showed in chapter 2 that a similar trilayer with no encapsulation loses ~40% of its initial mass of PC within just a day. This mass loss shrinks the thickness of the device from 360 µm to ~290 µm and significantly affects

![Figure 3.6 (a) Top view optical image of an as-prepared encapsulated PEDOT/PEO:NBR/PEDOT trilayer actuator. The red dashed line shows the encapsulation margin. (b) Cross section optical micrograph of an encapsulated PEDOT/PEO:NBR/PEDOT trilayer actuator after two months of encapsulation with 100 µm thick SIBSTAR.](image-url)
the intermittent and cycling performance of the trilayer. Figure 3.7(a) demonstrates the retained normalized mass of propylene carbonate over time in three bare trilayers named as \( S_i \), where \( i = 1, 2, 3 \). The normalizations were done relative to the initial mass of propylene carbonate stored in each of the trilayers (45% of the initial mass of the trilayer [11]). During the measurement, the samples were all stored in a controlled humidity and temperature (CTH) room at \((23 \pm 2)\)°C and \((50 \pm 3)\)% RH. Results in figure 3.7(b) show that the samples have similar trend of mass loss over time and after one day, \((39 \pm 4)\)% of the initial mass of PC leaves the corresponding device. The mass decay rate then decreases in all the samples and the rest of the stored PC is withdrawn from the device after further 7 days. Note that LiTFSI is hygroscopic; So, it either holds some amount of PC within the device or absorbs humidity from its surrounding. We showed in chapter 2 that this amount is negligible compared to the initial mass of the PC. This can be due to the high solubility of LiTFSI in polar solvents (> 20 M at 25°C in water [71]).

Figures 3.7(b-d) show the retained total mass of propylene carbonate and toluene in encapsulated trilayers over nearly 300 days. These are named as \( S_i \) with 50 µm \((i = 4, 5, 6)\), 100 µm \((i = 7, 8, 9)\) and 190 µm \((i = 10, 11, 12)\) thick spray-coated SIBSTAR encapsulations. Similar to the bare trilayers, the measurements were done in a CTH room at \((23 \pm 2)\)°C and \((50 \pm 3)\)% RH. All the normalizations were done relative to the initial mass of the propylene carbonate stored in the corresponding trilayer (45% of the initial mass of the trilayer [11]) to demonstrate the percentage of propylene carbonate retained over time after the toluene in SIBSTAR shield is thoroughly evaporated. That is why the demonstrated masses in figures 3.7(b,d) are initially more than 1. The details on how to obtain these graphs from the raw measured data are provided in Appendix B. The average amounts of toluene trapped in the
encapsulating layers with the area of (350-400) mm² and thicknesses of 50 µm, 100 µm and 190
µm thick, are estimated to be ~1.6 mg, ~3.2 mg, and ~8 mg, which leave the device roughly
within 8 days, one month and two months, respectively. The sharp decay of the mass shown in
figures 3.7(b,d) corresponds to the loss of the trapped toluene in the encapsulating layer. After
the toluene is released, the mass decreases almost linearly over the period of the measurement for
all the samples except for \( S_6 \).

Figure 3.7 (a) Normalized mass of propylene carbonate (PC) stored in trilayers with no encapsulation over
time. Normalized mass of propylene carbonate stored in trilayers plus toluene trapped in the corresponding
SIBSTAR encapsulation shields with thicknesses of (b) \( t_s = 50 \) µm, (c) \( t_s = 100 \) µm, (d) \( t_s = 190 \) µm over time.
All the normalizations were done relative to the corresponding initial mass of propylene carbonate stored in
each trilayer.
Results for samples with 50 µm thick encapsulation (figure 3.7(b)) show that after ~300 days, samples $S_4$ and $S_5$ still maintain ~35% of the initial PC stored into them. The rate of mass loss in $S_6$ however, is almost twice as much as those of $S_4$ and $S_5$, and after 300 days, ~15% of the mass of PC is retained. In addition to that, the rate of mass loss in $S_6$ is initially higher and decreases over time (40% mass loss after ~70 days and additional 40% mass loss after further 210 days), similar to the PC mass loss trend observed in bare trilayers (figure 3.7(a)). Results for samples encapsulated with 100 µm SIBSTAR (figure 3.7(c)) show that after ~300 days, $S_7$ and $S_9$ lose only 10% and 15% of the PC stored in them. $S_8$ which was encapsulated with the same thickness of SIBSTAR and was stored in the same condition as the other two loses ~65% of the initial PC stored in it after ~300 days. For all the three samples, the PC mass loss is linear over the time of measurement. Figure 3.7(d) demonstrates the results for the trilayers encapsulated with 190 µm thick SIBSTAR. They show that the mass loss of PC is linear in all three samples and after ~300 days, 17%, 41% and 53% of the initial mass of PC are retained in $S_{10}$, $S_{11}$, and $S_{12}$, respectively.

3.4.2.1 Modeling the transport of permeant molecules in polymeric barriers and discussions:

As mentioned before, the storage condition and the main fabrication process for all the samples were the same and the obtained values of mass were normalized relative to the initial mass of the propylene carbonate in the corresponding encapsulated trilayer. Hence, we were expecting to obtain the same results for the samples in each set. In order to interpret the results shown in figure 3.7(b-d) and understand the unexpected difference in the mass loss of the encapsulated samples in each set, we took advantage of the model used to describe the process of transport of permeant molecules from their source towards a second ambient through a non-
porous polymeric barrier. This process is explained through the solution-diffusion theory and as schematically shown in figure 3.8(a), includes three fundamental processes: (1) solution of permeant molecules at the source/barrier interface, (2) diffusion of the dissolved permeant molecules across the membrane, and (3) desorption of the permeant molecules at the barrier/ambient interface. While the permeant molecules which are released in the third process are in the gas phase, they can be either in gas or liquid phases in the first and second processes [64], [72]. In both cases, the process of diffusion of the permeant molecules across the barrier follows Fick’s laws of diffusivity, since the driving force in both cases is the transmembrane permeant concentration difference, $\Delta C$. Solving the Fick’s equations for such system, the mass of permeant, $G$, which transmits through the thickness of the barrier, $t_s$, over area, $A$, and time, $t$, is described through equation 3.3 [73],

$$G = \frac{AP\Delta C}{t_s} \left( t - \frac{t_s^2}{6D} - \frac{2t_s^2}{D\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e\left(\frac{-Dn^2\pi^2 t}{t_s^2}\right)\right).$$

(3.3)

Here $P$ and $D$ are the permeability and diffusion coefficients of the permeant molecules into the barrier. Equation 3.3 is plotted in figure 3.8(b) against time, assuming $\Delta C$ is constant over time. The graph demonstrates an initial build-up period over which the system is in non-steady state and permeant molecules are penetrating through the membrane but mostly have not yet reached the other side of the barrier (so there is effectively no mass loss over a time of $t_s^2 / 6D$). After this, the gas linearly passes the barrier over time with a rate of mass loss (corresponding to the slope) of $a = AP\Delta C / t_s$.

For the case of vapors, it is common to report the “vapor transmission rate”, normalized by
the thickness of the barrier, \( \text{VTR}_n \), which is defined as the steady vapor flow rate, \( a \), passing through a barrier with area, \( A \), and thickness, \( t_x \), under specific conditions of temperature and humidity. Hence, \( \text{VTR}_n = a t_x / A = P \Delta C \) [74]. This metric, which has previously been introduced in equation 3.2, is an indication of how well a polymeric barrier resists against diffusion of a permeable vapor through it. Here, taking advantage of \( \text{VTR}_n \) definition, we adopted the normalized PC transmission rate, denoted as \( \text{TR}_{PC,n} \) and defined in equation 3.4, as an index to describe how well the samples are encapsulated:

\[
\text{TR}_{PC,n} = \frac{a_{PC} t_s}{A_s}
\]  

(3.4)

where \( a_{PC} \) is the PC mass loss rate, and for each sample (with a total area of \( A \) and encapsulating layer’s thickness of \( t_s \)) is obtained from the slope of the corresponding graph in the linear region shown in figures 3.7(b-d) (\( R^2 > 0.99 \)) and the initial mass of propylene carbonate stored in the corresponding sample. The smaller the value of \( \text{TR}_{PC,n} \) is, the better the encapsulation is performing.

**Figure 3.8** (a) Schematic of the mechanism of permeation through a non-porous polymeric barrier. (b) Predicted mass transfer through the polymeric film over time.
The values of area (surface area, side area and total area), initial mass of PC stored in the trilayer, PC loss rate, and normalized PC transmission rate along with the time to lose 20% of the stored PC and the time to lose 86% of the stored PC (operation lifetime) of the trilayers are summarized in table 3.2. It shows despite the repeatability of the spray coating of SIBSTAR films and their uniformity, TR\(_{PC,n}\) varies from 3.1 \(\mu\text{g.m.m}^{-2}.\text{day}^{-1}\) for a 100 \(\mu\text{m}\) thick encapsulating layer to 29.6 \(\mu\text{g.m.m}^{-2}.\text{day}^{-1}\) (~10 times larger) for a 190 \(\mu\text{m}\) thick one. It was shown in figures 3.5(b,c) that SIBSTAR spray-coated film is uniform and its roughness and peak to valley values, being equal to \(~1.3\ \mu\text{m}\) and 12 \(\mu\text{m}\), respectively, are well below the thickness of the encapsulating layers (> 50 \(\mu\text{m}\)). The wide range of TR\(_{PC,n}\) values, provided in table 3.2, makes us suspect that the thickness of the encapsulating layer is not the same in all the six directions. As mentioned before, spray-coating is not conformal and the sides of the trilayers, being relatively perpendicular to the direction of the spray, cannot be well coated along with their surfaces. To compensate that, we tilted the samples and spray coated the sides separately. However, we could not evaluate the thickness of the encapsulation in those areas. The area of the sides represents 8.2% to 10.7% of the total area of the trilayer, which is not negligible and if the thickness of the encapsulating layer at those areas is smaller than its intended thickness (that of the two surfaces), the sides can have a significant impact on letting the propylene carbonate escape from the trilayer faster. Hence, the variation in the values of TR\(_{PC,n}\) obtained for samples with different thicknesses of SIBSTAR encapsulation, can possibly be explained by that. In addition to this, the failure in spray-coating of the sides of the samples can also lead to a gap in it. In this case, the mass loss is no longer linear, and follows the corresponding trend in a bare trilayer (with a slower rate due to the smaller exposed area). This was observed in figure 3.7(b).
for $S_6$. Other samples demonstrate a linear mass decay rate over the time the measurement was carried out. Samples $S_3$, with no encapsulation, and $S_5$, $S_8$ and $S_{10}$ with $t_e = 50 \, \mu\text{m}$, $100 \, \mu\text{m}$, and $190 \, \mu\text{m}$ thick SIBSTAR encapsulations show the least PC mass loss compared to other samples with the same encapsulating layer’s thickness. The results of their mass loss over time are compared in figure 3.9. We showed in chapter 2 that for a bare trilayer actuating intermittently in air, the time constant of the device increases by 10% after losing 20% of its initial PC mass. This is accompanied by a 20% increase in its maximum curvature. According to figure 3.9, this mass loss takes less than half a day for a bare trilayer which is stored in a CTH room at $(23 \pm 2) ^\circ\text{C}$ and $(50 \pm 3)\% \text{ RH}$. If a $50 \, \mu\text{m}$ thick encapsulation is applied to the device, this time delays to more than 65 days (~120 times improvement), in the same measurement condition. This further improves if the encapsulation gets thicker to $100 \, \mu\text{m}$, as more than 500 days (nearly a year and a half, equivalent of more than 1000 times improvement) is estimated to be needed to lose 20% of the stored PC in the device. According to equation 3.4, this improvement was expected to further

![Figure 3.9 Comparison of the normalized mass decay of propylene carbonate stored in a trilayer with no encapsulation and trilayer with encapsulation thicknesses of $t_e = 50 \, \mu\text{m}$, $100 \, \mu\text{m}$, and $190 \, \mu\text{m}$ over time. All the normalizations are relative to the initial mass of the PC.](image-url)
Table 3.2 Summary of the properties of the trilayers and the corresponding encapsulating layer’s performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>Encapsulating layer’s thickness (µm)</th>
<th>Trilayer’s surface area (mm²)</th>
<th>Trilayer’s side area (mm²)</th>
<th>Trilayer’s total area (mm²)</th>
<th>Initial PC mass (mg)</th>
<th>PC mass decay rate ( (a_{PC}) ) (µg/ day)</th>
<th>Normalized PC transmission rate ( (TR_{PC,n}) ) (µg.m.m^{-2}.day^{-1})</th>
<th>Time to lose 20% of stored PC (days)</th>
<th>Operation lifetime (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>144.4</td>
<td>12.5</td>
<td>156.9</td>
<td>13.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>S₂</td>
<td>0</td>
<td>150.3</td>
<td>163.3</td>
<td>14.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>S₃</td>
<td>161.8</td>
<td>13.8</td>
<td>175.6</td>
<td>15.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>S₄</td>
<td>94.5</td>
<td>10.2</td>
<td>104.7</td>
<td>8.8</td>
<td>19</td>
<td>9.1</td>
<td>65</td>
<td>390*</td>
<td></td>
</tr>
<tr>
<td>S₅</td>
<td>50</td>
<td>96</td>
<td>106.2</td>
<td>8.9</td>
<td>20.3</td>
<td>9.6</td>
<td>65</td>
<td>370*</td>
<td></td>
</tr>
<tr>
<td>S₆</td>
<td>96</td>
<td>10.4</td>
<td>106.4</td>
<td>9</td>
<td>50.5</td>
<td>23.9</td>
<td>35</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>S₇</td>
<td>96</td>
<td>11.5</td>
<td>107.5</td>
<td>8.8</td>
<td>16.2</td>
<td>15.6</td>
<td>110</td>
<td>460*</td>
<td></td>
</tr>
<tr>
<td>S₈</td>
<td>100</td>
<td>120</td>
<td>132.2</td>
<td>11</td>
<td>4</td>
<td>3.1</td>
<td>550*</td>
<td>2350*</td>
<td></td>
</tr>
<tr>
<td>S₉</td>
<td>100</td>
<td>11.7</td>
<td>111.7</td>
<td>8.9</td>
<td>4.6</td>
<td>4.4</td>
<td>390*</td>
<td>1650*</td>
<td></td>
</tr>
<tr>
<td>S₁₀</td>
<td>126</td>
<td>13.3</td>
<td>139.3</td>
<td>10.5</td>
<td>6.4</td>
<td>9.9</td>
<td>330*</td>
<td>1400*</td>
<td></td>
</tr>
<tr>
<td>S₁₁</td>
<td>190</td>
<td>13</td>
<td>125</td>
<td>10.45</td>
<td>19.1</td>
<td>29.6</td>
<td>80</td>
<td>460*</td>
<td></td>
</tr>
<tr>
<td>S₁₂</td>
<td>165</td>
<td>14.8</td>
<td>179.8</td>
<td>14.25</td>
<td>17.4</td>
<td>20.3</td>
<td>180</td>
<td>700*</td>
<td></td>
</tr>
</tbody>
</table>

Values with a * were estimated assuming the mass loss stays linear
increase by increasing the thickness of the encapsulating layer to 190 µm. However, the results show that 20% of PC mass loss takes place after nearly 330 days (~11 months). This, as explained before, is probably due to the thinner encapsulation on the sides which let PC escape more easily from the sample.

According to the results obtained for these trilayers in chapter 2, the device is still operational after losing 86% of the initial mass of PC stored in it. While for a bare trilayer this operation lifetime is only 4 days, for trilayers encapsulated with 50 µm, 100 µm and 190 µm thick spray-coated SIBSTAR films this time delays to 390 days (over a year or ~100 times improvement), ~2400 days (6.5 years or 600 times improvement) and ~1400 days (nearly 4 years or 450 times improvement), respectively. This significant improvement in the operation lifetime of the device has not been reported previously.

3.4.3 Effect of encapsulation on the performance of the trilayer actuator

In this section, the effect of encapsulation on the performance of the trilayer actuators in terms of the extent to which they can bend after encapsulation as well as their retained percentage of displacement over time when continuously cycling in air and in water, are studied. Before reporting the results, in order to interpret them, we present the electromechanical model used to describe the mechanism of actuation of bare and encapsulated trilayer conducting polymers.

3.4.3.1 Electromechanical modeling of trilayer conducting polymer actuators

Conducting polymers are electroactive materials which react to electrochemical stimuli. When ions are inserted in/withdrawn from these electronically and ionically conducting polymers, a positive/negative strain is generated which causes them to expand/contract. To the first order approximation, the strain generated in a conducting polymer film with width, length, and
thickness of $W$, $L$, and $h_p$, respectively, is equal to,

$$\epsilon = \frac{\alpha Q}{WLh_p}, \quad (3.5)$$

where $\alpha$ is the strain to charge ratio and can be obtained empirically and $Q$ is the charge induced to/repelled from the conducting polymer film. In trilayer form, where two layers of conducting polymer sandwich an ionically conducting but electronically insulating separator layer, when a square wave voltage with an amplitude of $v$ and period of $T$ is applied across the device, as the voltage switches, ions move from one conducting polymer layer towards the other to balance the charge. This causes one layer with the increase of ions to expand and the one with the decrease of ions to contract and the whole structure to bend. The current passing through the device roughly has an exponential shape, $i \approx i_0 e^{-t/\tau}$, where $\tau$ is the time constant of the device and $i_0$ is the peak current passing through it [27].

The generated strain in the conducting polymer layers causes the device to bend to a curvature, $\kappa$, which is obtained through the familiar equation [75],

$$\kappa = \frac{M}{EI} \quad (3.6)$$

$M$ is the induced bending moment to the beam and is obtained by integrating stress over its cross section. Knowing the fact that the separator and encapsulating layers generate zero stress, the beam bends as a result of the charge-induced differential strain, $2\epsilon$, in the conducting polymer layers, and the bending moment is: $M = W\epsilon E_p (h_p^2 + h_p h_g)$. By substituting $\epsilon$ with equation 3.5, we have,
\[ M = \frac{\alpha Q E_p (h_p + h_g)}{L}. \]  

(3.7)

\( EI \) in equation 3.6, is the flexural rigidity of the beam and for bare and encapsulated trilayers, is obtained through equations 3.8.a and 3.8.b, respectively.

\[(EI)_b = \frac{W}{12} \left( E_p \left( h_t^3 - h_g^3 \right) + E_g h_g^3 \right), \]  

(3.8.a)

\[(EI)_e = (EI)_b + \frac{W}{12} \left( E_e \left( h_T^3 - h_t^3 \right) \right) + \frac{W'}{12} E_e h_T^3, \]  

(3.8.b)

where \( E_i \) represents the Young’s modulus and the subscript \( i = g, p \) and \( e \), represent separator, conducting polymer and encapsulating layers, respectively. \( W \) is the width of the device, \( h_t = 2h_p + h_g \), is the total thickness of the bare trilayer and \( h_p \) and \( h_g \) are thicknesses of the conducting polymer and separator layers, respectively. \( h_T = h_t + 2t_s \), is the total thickness of the encapsulated trilayer where \( t_s \) is the encapsulating layer’s thickness. \( W' \) is the total width of the encapsulation on the sides of the sample along its length, which is equal to \( 2t_s \) in the best case (sides of the sample being covered with SIBSTAR as thick as those on the top and bottom), but can be thicker or thinner depending on how the sides were covered. Hence, the curvature of a bare and an encapsulated trilayer are approximately obtained through equations 3.9.a and 3.9.b, respectively.

\[ \kappa_b \approx \frac{12\alpha Q E_p (h_p + h_g)}{LW \left( E_p \left( h_t^3 - h_g^3 \right) + E_g h_g^3 \right)}, \]  

(3.9.a)

\[ \kappa_e \approx \frac{12\alpha Q E_p (h_p + h_g)}{LW \left( E_e \left( h_T^3 - h_t^3 \right) + E_p \left( h_t^3 - h_g^3 \right) + E_g h_g^3 \right) + LW' E_e h_T^3}. \]  

(3.9.b)

Laser displacement sensor measures the lateral displacement of a point at distance \( l \) from the
fixed end of the trilayer as it actuates. Displacement, $D$, is defined as the distance the beam travels within the half cycle of the actuation. If the value of $l$ is sufficiently larger than $D$, (in our case $l/D > 5$), then,

$$D = \frac{\kappa l^2}{2},$$

(3.10)

where $\kappa$ is the curvature of the beam and is obtained through equations 3.9.a and 3.9.b for bare ($\kappa_b$) and encapsulated ($\kappa_e$) trilayers.

### 3.4.3.2 Effect of encapsulation on the extent to which the trilayer can bend

To investigate the effect of the encapsulating layer on the extent of bending of the trilayers, a square wave voltage with an amplitude of ±2 V and period of 20 s (half period being ~5 times larger than the time constant of the device) is applied to devices before and after encapsulation and their curvatures were compared. The devices were measured after we ensured the trapped toluene is removed from the encapsulating layer. Figure 3.10 shows top-view optical images of the peak to peak maximum bending of a trilayer with (a) no encapsulation, and trilayers with SIBSTAR encapsulations with thicknesses of (b) 50 µm, (c) 100 µm and (d) 190 µm, respectively. The curvatures of the beams were calculated through fitting circles to the images of the actuated trilayers. It shows that when a 50 µm thick SIBSTAR encapsulation is applied to the trilayer, its curvature decreases from $(0.72 \pm 0.02)$ cm$^{-1}$ to $(0.40 \pm 0.02)$ cm$^{-1}$ (~55% of the curvature before encapsulation). As the thickness of encapsulating layer further increases to 100 µm and 190 µm, the curvature of the trilayer further decreases to $(0.32 \pm 0.02)$ cm$^{-1}$ and $(0.21 \pm 0.02)$ cm$^{-1}$, which corresponds to ~44% and ~30% of the curvature of the trilayer before encapsulation, respectively.
As demonstrated in chapter 2, the thicknesses of the conducting polymer and separator layers, when they are fully swollen with the electrolyte, are equal to (31.5 ± 0.6) µm and (297 ± 1.2) µm, and the corresponding Young’s moduli are (180 ± 6) MPa and 1.2 MPa, respectively. Substituting these values in equation 3.8.a, the flexural rigidity of the bare trilayer (W = 2.3 mm) of the beam, is equal to (0.68 ± 0.02) × 10⁻⁶ m²Pa, ~99% of which is due to the conducting polymer layer; Hence, according to equation 3.9.a, the value Young’s modulus of both the conducting polymer and the separator layers do not have much effect on the curvature of the device. When the trilayer is encapsulated with SIBSTAR film (Young’s Modulus = (11.2 ± 0.5) MPa), according to equation 3.8.b (considering 1 mm encapsulation

![Images showing maximum bending of trilayers with different encapsulation thicknesses.](image)

**Figure 3.10** Maximum bending of trilayers with (a) no encapsulation, (b) 50 µm (c) 100 µm and (d) 190 µm thick SIBSTAR encapsulating layers. The dimensions of the trilayers before encapsulation are \(L \times W \times h_t = 10 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm}\). Images are overlaid to show the full extent of deflection after voltages of +2 V and -2 V applied each for 10 s.
extension on each side, hence, \( t_{\text{s}} = 2 \text{ mm} \), the flexural rigidity increases to \((0.96 \pm 0.02) \times 10^{-6} \text{ m}^2\text{Pa} \) \((t_s = 50 \mu\text{m})\), \((1.27 \pm 0.03) \times 10^{-6} \text{ m}^2\text{Pa} \) \((t_s = 100 \mu\text{m})\), and \((2.17 \pm 0.05) \times 10^{-6} \text{ m}^2\text{Pa} \) \((t_s = 190 \mu\text{m})\). Here the 50 \(\mu\text{m}, 100 \mu\text{m}\) and 190 \(\mu\text{m}\) thick encapsulating layers’ contributions to the flexural rigidity are ~30%, ~46%, and ~70%, respectively. The uncertainty in the calculated values comes from the uncertainty in the measured values of the Young’s moduli of the conducting polymer as well as the SIBSTAR encapsulating layers. If the strain generated in the conducting polymer layers stays unchanged after encapsulation (i.e. the charge being transferred in each half cycle stays unchanged assuming the dimensions of the trilayers do not change because of the encapsulation as shown in figure 3.6(b), according to calculated values of flexural rigidity, it is expected that the curvature of the trilayers decrease to 70%, 54%, and 30% of its value before encapsulation after adding 50 \(\mu\text{m}, 100 \mu\text{m}\) and 190 \(\mu\text{m}\) thick SIBSTAR encapsulating layers, respectively. The observed difference between the measured values of curvature and the predicted ones can partially be due to the errors in the measurement of the thickness and width of the encapsulation extension on the two sides of the device.

### 3.4.3.3 Effect of encapsulation on the cycling response of trilayers in flowing air

To investigate the effect of encapsulation on the lifecycle of a trilayer conducting polymer actuator operating in air, a square wave voltage with an amplitude of \(\pm 2 \text{ V}\) and a period of 2 s (frequency of 0.5 Hz), was applied to bare and encapsulated trilayers \((t_s = 100 \mu\text{m})\) and their displacements were measured over time, using a laser displacement sensor. An electric fan was used to facilitate the evaporation of the solvent from the device. Figure 3.11 shows the normalized peak to peak displacement \((= 2D)\) and the current passing through the trilayers with no encapsulation and with 100 \(\mu\text{m}\) thick SIBSTAR encapsulation, cycling in flowing air. The top
x-axis shows the number of cycles. The normalizations were done relative to the initial values, which are indicated in the corresponding graph. In all figures, the graphs in grey show the actual values of the normalized peak to peak quantity (current or displacement) and the black lines (dashed line for displacement and solid line for current) demonstrate the corresponding smoothened values.

As shown in figures 3.11(a), the displacements of the bare trilayer operating in flowing air decrease as soon as the actuation starts. The initial rate of displacement decay is 55 %/h which decreases over time and after 3 h (5.4 \times 10^3 cycles at 0.5 Hz), when only \sim 20% of the initial displacement is retained, drops down to \sim 9 %/h. As demonstrated in figure 3.11(b), the trend of displacement decay in this device is similar to the trend of drop in the current passing through it.

As demonstrated in chapter 2, PEDOT/PEO:NBR/PEDOT trilayers swell as they uptake electrolyte and shrink when they lose it. For a trilayer operating in air, the total thickness decreases with the rate of \sim 1.8 \mu m per mass percent loss of propylene carbonate. As the thickness of the beam decreases, both its flexural rigidity and bending moment decrease.

However, the flexural rigidity decreases more as the thickness decreases, since its dependence on the thickness of the beam is cubic while that of the bending moment is linear. Hence, the decrease of thickness in trilayer conducting polymers due to the evaporation of the PC over time has an overall positive impact on the deformation of the device. In each half cycle, if the trilayer is given enough time, so the conducting polymer layers get fully charged or discharged and the device reaches equilibrium, the curvature of the beam increases due to the thickness decrease as it gets dry over time. In the present experiments, the half cycle of the applied voltage is less than the time constant of the device \( T/2 = 1 \text{ s} \) and \( \tau > 2 \text{ s} \); So, the conducting polymer layers do not
Figure 3.11 Normalized peak to peak (a) displacement and (b) current of a bare trilayer and (c) displacement and (d) current of an encapsulated trilayer with 100 µm thick SIBSTAR, cycling in air. The dimensions of both trilayers are \(L \times W \times h_t = 10 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm}\) and distance of the laser beam from the base of the trilayer is \((8 \pm 0.5) \text{ mm}\). \(D_0\) and \(i_{\infty}\) are the initial values of the measured displacement and the peak current passing through the corresponding trilayer, respectively. The graphs in grey show the peak to peak current variation through time while the black lines represent the smoothened ones.
have enough time to get fully charged or discharged. In this case, the charge being transferred in each half cycle, being equal to the integration of current passing through the device over $T/2$, 

$$\sim \int_0^{T/2} i_0 e^{-t/\tau},$$

to the first order approximation is equal to $i_0 T/2$; Hence, the strain and subsequently the bending moment and displacement of the trilayer beam linearly depend on the peak current passing through it. The peak current itself directly depends on the ionic conductivity of the electrolyte [27]. As the trilayer actuator cycles in air, the stored PC in it evaporates and causes the viscosity of the electrolyte to increase and hence its ionic conductivity to decrease. This explains the observed decrease of the peak current passing through the bare trilayers operating in flowing air as shown in figures 3.11(b). In this case, the trilayer’s displacement also decreases, following the current passing through it. This suggests that the effect of the current loss in the trilayers is dominant compared to the effect of thickness decreases.

For the trilayer encapsulated with a 100 µm thick film of SIBSTAR, the decay rate of displacement is initially ~13 %/h and after ~3 h actuation in flowing air ($5.4 \times 10^3$ cycles at 0.5 Hz), when still 85% of the displacement is retained, drops down to less than 2 %/h. The normalized peak current passing through the encapsulated trilayers is demonstrated in figure 3.11(d) which shows it decreases with a relatively constant decay rate of ~2 %/h and after 3 h actuation in flowing air ($5.4 \times 10^3$ cycles at 0.5 Hz), still ~94% of the peak current passing through the trilayer, is retained. Comparing the current and displacement graphs of the encapsulated trilayer actuating in flowing air shows that the rate at which displacement decays is initially larger than that of the current. The larger initial decay rate of displacement in the encapsulated trilayer may be due to the change in the mechanical properties of the SIBSTAR layer due to the actuation. Clearly, encapsulation helps the trilayers to lose their displacement.
slower (by more than 20 times if the encapsulating layer’s Young’s modulus stays unchanged with time) compared to when they have no encapsulation.

3.4.3.4 Effect of encapsulation on the cycling response of trilayers in DI water

To investigate the effect of encapsulation on the lifecycle of trilayer conducting polymer actuators operating in DI water, a square wave voltage with amplitude of ±2 V and period of 2 s (frequency of 0.5 Hz), was applied to bare and encapsulated trilayers ($t_s = 190 \, \mu$m) and their displacements were measured over time, using a laser displacement sensor. Figures 3.12(a,b), respectively, show the normalized peak to peak displacement ($= 2D$) and current of two trilayers with no encapsulation and with 190 µm thick SIBSTAR encapsulation, cycling in DI water. The normalizations were done relative to their initial values, which are indicated in the corresponding graph. In both figures, the graphs in grey show the actual values of the normalized peak to peak current and the solid black lines demonstrate the corresponding smoothened values. As mentioned before, the samples were briefly removed from water for displacement measurement since the laser could not focus on the immersed trilayers. The displacement values were obtained by averaging the values of peak to peak displacement of the device over 20 cycles and normalizing them relative to the initial average values of displacement. The error bars come from the displacement variation over this period.

As shown in figure 3.12(a) for a bare trilayer, both the peak to peak displacement and the current passing through the device decrease over time with an initial large decay rate, which gradually decreases, and after ~100 min, only 15% to 20% of the current and displacement are retained.

The decaying current for bare trilayers cycling in DI water is because the electrolyte will be
substituted by water over time and the number of free ions in the trilayer decreases [76]. This causes the ionic conductivity of the electrolyte and hence the peak current passing through the device to decrease with time. As expected, the drops in displacement and current are closely correlated. The normalized peak to peak displacement and current of the trilayer encapsulated with 190 µm thick SIBSTAR film are shown in figure 3.12(b). It shows the peak current passing through the device decreases by 25% as it is immersed in DI water. It also shows current slightly increases when the device is continually cycled in water. The change in the peak current can be

![Graph showing normalized peak to peak displacement and current for (a) a bare trilayer and (b) an encapsulated trilayer with 190 µm thick SIBSTAR, cycling in DI water.](image)

**Figure 3.12** Normalized peak to peak displacement (filled dots) and current (solid lines) for (a) a bare trilayer and (b) an encapsulated trilayer with 190 µm thick SIBSTAR, cycling in DI water. The dimensions of both trilayers are \((L \times W \times h_t = 20 \text{ mm} \times 2 \text{ mm} \times 0.36 \text{ mm})\) and distance of the laser beam from the base of the trilayer is \((9 \pm 1) \text{ mm}\). \(D_0\) and \(i_{00}\) are the initial values of the measured displacement and the peak current passing through the corresponding trilayer, respectively. The graphs in grey show the peak to peak current variation through time while the black lines represent the smoothened ones.
power consumed in it. It has been shown previously that the ionic conductivity of a 1 M solution of Li\(^+\)TFSI\(^-\) in PC is highly temperature dependent – it drops by more than a factor of 2 if the temperature decreases from 30\(^\circ\)C to 20\(^\circ\)C [9]. When the sample is immersed in DI water, the heat transfer is more effective than in air, so its temperature decreases faster and hence the ionic conductivity of its electrolyte and the current passing through it decrease. When the trilayer cycles in DI water for a fairly long time, the temperature of the trilayer increases locally. This causes the ionic conductivity and, as observed in figure 3.12(b), the peak current passing through the device to slightly increase. For this sample, displacement measurement started as soon as the actuator was removed from DI water and it was shown that the displacement follows current and reaches a plateau in each occasion the device was removed from DI water. Displacement data points shown in figure 3.12(b) were obtained by averaging the peak to peak displacement over 20 cycles after it is stabilized, and the error bars demonstrate the displacement variation over that 20 cycles. It shows displacement variation does not have a specific trend and during ~2.5 h actuation in DI water (4.5 \times 10^3 cycles at 0.5 Hz), stays within (90 \pm 5)\% of its initial value. The large uncertainty is because the trilayer was alternatively immersed and removed from water, so the measurement condition was not well stable. A trilayer with no encapsulation can only retain this amount of displacement for only ~2 min.

### 3.5 Conclusion

Uniformly thick SIBSTAR films with Young’s moduli of ~11 MPa were obtained through a spray-coating technique. We showed in this chapter that by using spray-coated SIBSTAR films as encapsulating layers, the storage lifetime of PEDOT/PEO:NBR/PEDOT trilayer actuators significantly increases through protecting the device from getting drying in air over time. 20\% of
propylene carbonate in a bare trilayer evaporates after less than half a day if it is stored in a CTH room at (23 ± 2) °C and (50 ± 3)% RH. This time can be extended to over 2 months (~240 times improvement) and 18 months (>1000 improvement) if 50 µm and 100 µm thick spray-coated SIBSTAR are applied to the device, respectively. This is at the expense of losing the extent of bending of the trilayer due to the added layers which cause the flexural rigidity of the trilayer beam to increase.

The strong capability of spray-coated SIBSTAR films towards protecting conducting polymer actuators from losing their solvent or even the whole electrolyte as they are stored/operate in air or in DI water, respectively, along with their low Young’s modulus (~11 MPa) and ease of fabrication, makes them a promising candidate material to protect other ionic devices such as IPMCs [55], [56], bucky gel actuators [77], flexible batteries [78] supercapacitors [79], and ionic-electrode capacitive sensors [80]. Moreover, laboratory grade SIBS, being a bio-stable and FDA approved polymer with minimal tissue reaction, has already been used in commercialized implantable devices. Hence, applying SIBS coatings on ionic devices can also expand their applications towards in vivo and implantable devices.
Chapter 4: ActuaTool: a web-based graphical user-interface (GUI) to design and study trilayer conducting polymer actuator beams

4.1 Introduction and motivation

Breakthroughs have been made in conducting polymer actuators since their emergence in the 1990s. Important among these are novel and reproducible materials and reliable fabrication methods to enhance the robustness of the trilayer structure [7]. Researchers could show advances in tuning material properties such as the ionic and electronic conductivities and Young’s modulus of each of the layers [9], [23], increasing the endurance of the device by using ionic liquids as the electrolyte [2], [7] or, as demonstrated in chapter 3, encapsulating them, and increasing actuation speed (resonance frequency near 1 kHz) through downsizing the thickness of each of the layers (to couple of microns) and the length of the device (to sub-millimeter) [10]. These achievements pave the way towards more vastly employing these devices into various applications and eventually commercializing them. In this regard, optimizing their design, which can be done through their modeling or simulation, is necessary. However, since their output, including the generated force and tip displacement, depends on many parameters involved with the device, it is rather difficult to find an optimized design for an intended application by just using their model. In this chapter, we demonstrate the created graphical user interface (GUI) tool, named as ActuaTool, through which modeling and design optimization of these devices based on the desired output are facilitated.
So far, trilayer conducting polymer actuators have been demonstrated in applications such as catheters [15], robotic fish [34], micro-manipulators [35], etc. Each of these applications or other potential applications such as tactile feedback interfaces [31] have different requirements from the employed actuator in terms of its key output characteristics. These output characteristics include the extent of deformation, blocking force (the force needed to return the bent tip of the actuator to its pre-actuation location), average power consumption (which is always needed to be minimized) and speed. These depend on many factors including the dimensions of the device, thickness, Young’s modulus, electronic and ionic conductivities of each of the layers, the volumetric capacitance of the conducting polymer layer, the shape and the magnitude of the applied voltage, etc. Being influenced by many parameters, the effect of one parameter on the targeted output may vary depending on the values of other parameters. Also, there is sometimes a tradeoff between the outputs as one parameter is changed [31]. For example, if we reduce the thickness of the separator layer, we expect to increase the speed of the device through reducing the path the ions need to take to move from one CP layer to the other. This, however, is not effective if the speed of the device is already limited by the thickness of the conducting polymer layer or by the length of the device. On the other hand, reducing the thickness of the separator layer causes the maximum force the device can generate to decrease and the displacement to increase [31]. This trade-off, along with the fact that many parameters are involved in determining the output characteristics of the device, makes modeling and design of these devices complicated. Creating a graphical user interface (GUI) helps the researchers in the field, to on one hand, better understand the effect of each parameter on the mentioned outputs and study the subsequent trade-off before fabrication of the device, and on the other hand, helps the designers
to select the proper material and dimensions which are suitable for their intended applications. Balakrisnan et al. [81] created a MATLAB-based GUI to evaluate the effect of layer thickness and Young’s modulus on the curvature, blocking force and work generated by multilayer actuators including dielectric elastomer, ionic polymer metal composite (IPMC), and conducting polymer actuators. Despite the wide range of actuators their GUI covers, it does not deal with the mechanism of strain generation in the active layer of the corresponding actuator, and practically has only a mechanical model behind (not an electro-mechanical or an electro-chemo-mechanical model). Hence, it does not predict the dynamic response of the actuators at frequencies larger than the cutoff. Moreover, the mechanical model they used is based on small curvature approximation; So, it is not valid for large bending actuators.

Here in this work, we present an interactive web tool, so-called “ActuaTool”, based on the electro-chemo-mechanical model of trilayer conducting polymer actuators to study and design them. ActuaTool works in three modes of operation. In “Frequency Response” mode, the tool visualizes the frequency response of the tip displacement (vertical and lateral), blocking force and average power consumption of the defined trilayer CP actuator. It also predicts the shape of the trilayer actuated to its extent at the user’s desired frequency when a defined external force is applied to its tip (free bending when the external force is zero, and maximum deflection when the frequency is below the cut-off frequency). The force-displacement graph of the device at the desired operation frequency can also be predicted. In the second mode of operation, “Parameter response”, the graph visualizations show how the bandwidth, stiffness, resonance frequency, blocking force, displacement (vertical and lateral) and average power consumption change as a function of one of the device’s parameters (for those which are frequency-dependent, the
corresponding graph will be at the desired frequency). In the third mode of operation, “Design”, the user enters all the parameters of the device except the thicknesses of the CP and separator layers and the length of the device, as well as a desired range of the selected output (including bandwidth, blocking force, maximum tip displacement, resonance frequency, average power consumption and stiffness). Actuatool then finds combinations of device dimensions and thicknesses of the CP and the separator layers which lead to the user’s desired output. This mode can hugely help the designers to find the dimensions of the actuator which is suitable for their intended application. Actuatool uses standard web technologies (HTML, CSS, JavaScript) available on all web browsers and JavaScript libraries such as d3.js and twitter bootstrap. We release Actuatool as an open-source web tool to allow researchers to extend the tool for other ionic electroactive polymer actuators such as IPMCs or Bucky gels by using the corresponding electrochemical model.

In this chapter, we first present the electro-chemo-mechanical model of trilayer conducting polymer actuators based on which Actuatool is built. We then explain its operation and how users can interact with it and demonstrate the outputs of its three modes of operation for an example trilayer actuator. Using Actuatool in “Design” mode, we demonstrate a range of dimensions which makes the employment of these trilayers feasible in a tactile feedback interface.

4.2 Modeling conducting polymer trilayer actuators

So far, there are several studies on modeling trilayer conducting polymer actuators [27]–[29]. In these, the researchers agreed to electrochemically model the separator layer as an ionic resistor and the conducting polymer layers as 2D RC transmission lines in which inserted/
expelled ions induce a positive/ negative strain in them, which, to a first order approximation, is proportional to the volumetric density of inserted/ repelled charges. Using this electro-chemo-mechanical model, separately developed by Shoa et al. [27] and Nguyen et al. [28], and considering the uniform distribution of charge and hence strain throughout the volume of the CP layers, we previously demonstrated a full study of the effect of different material properties such as ionic and electronic conductivity and Young’s modulus of the conducting polymer layer, ionic conductivity and Young’s modulus of the separator layer as well as the thickness of each of the layers and the width and length of the device on its performance in terms of its bandwidth, deflection angle and blocking force [31]. In the model used in our previous study, we neglected the effect of inertia and damping. We also neglected the part of the trilayer which is sandwiched between the two contacts as well as the corresponding contact resistance. In addition to these, we assumed the charge induced in the conducting polymer layers is distributed uniformly throughout the volume of the conducting polymer layers and hence the device has a uniform curvature. While the former assumption does not reveal its effect on the predicted output values before the actuating frequency approaches the first mode resonance frequency of the beam, the two others affect the predicted displacement and blocking force generated by the device at frequencies close to and higher than its cutoff frequency. Moghadam et al. [29] provided a non-linear mechanical model based on the rigid finite element (RFE) method, through considering the actuator beam as a system of rigid links connected by spring-damping elements (sdes) to analyze dynamic large deformation of trilayer actuators. Using this approach, the effect of inertia and damping was included to predict the displacement of the trilayer at frequencies close to and shortly beyond the resonance frequency of the beam. Even though they accounted for the effect of inertia and
damping in their dynamic mechanical model, they neglected the effect of contact resistance and the part of the trilayer which is in contact with it as well as the non-uniform distribution of ions and hence non-uniform strain generated throughout the volume of the conducting polymer layers at actuation frequencies larger than the cut-off frequency of the device.

The aim of the work presented in this chapter is to create a practical and easily accessible GUI which can quickly and conveniently predict the output characteristics of the trilayer actuators and provide design guides for different applications. Introducing the effect of inertia and damping makes the calculations complicated and results in a slower response for the tool. Hence, we sufficed to predict the frequency response of the device below its resonance frequency through using the already developed model [27], [28] and modifying it to take into account the effects of contacts as well as the non-uniform distribution of ions throughout the volume of the CP layers. This adds extra calculations to find the local charge induced to the CP layers and local curvature of the beam which can further also be used to predict the shape of the device as it actuates. Of course, the model can later be modified to include the effects of inertia and damping as well and provide a more accurate and more general response.

4.2.1 Electro-chemo-mechanical modeling of trilayer conducting polymer actuators

Trilayer conducting polymers (CPs), as depicted in figure 4.1(a), are made by sandwiching an ionically conducting film between two films of conducting polymer. When the two sides of the device are subjected to a potential difference, as shown in figure 4.1(b), being the whole structure electronically insulating but ionically conducting through the thickness, ions move from one conducting polymer layer towards the other. This causes the side with the increase of ions to expand and the other side with the decrease of ions to contract and hence, the whole structure to
bend. It is known when ions are inserted in/ repelled from a conducting polymer film, the linear tensile/ compressive strain, $\epsilon$, induced into the film, to the first order approximation, is proportional to $\rho$, the volumetric density of charge [22],

$$\epsilon = \alpha \rho,$$

where $\alpha$ is the strain to charge ratio and is related to how efficiently the electrical energy is coupled into the mechanical energy in the conducting polymer films. The value of $\alpha$ can be obtained empirically and varies from $0.3 \times 10^{-10}$ m$^3$/C to $4.5 \times 10^{-10}$ m$^3$/C for conducting polymers [82]. For a trilayer CP actuator when a sinusoidal voltage, $V = V_s \sin(2\pi ft)$, is applied through the two contact electrodes which hold the trilayer at one end, the conducting polymer films get charged/ discharged along their lengths (starting from the electric contact) and through their thicknesses (starting from their interface with the separator layer). If the frequency, $f$, of the applied voltage is smaller than the cut off frequency of the trilayer, the CP layer gets fully charged/ discharged at the peak voltage, $V_s$, and the beam demonstrates a uniform curvature.

Figure 4.1 (a) Schematic of a trilayer conducting polymer actuator. $L$ and $W$ represent the length and width of the part of the trilayer which contributes in actuation and $L_c$ and $W_c$ represent the length and width of the part of the trilayer which is sandwiched between two contact electrodes. (b) mechanism of actuation of a trilayer CP actuator with anions being mobile.
along its length. If the actuation frequency is larger than the cut off frequency of the trilayer, the conducting polymer layers do not have enough time to get fully charged/ discharged and the amount of stored/ repelled charge, and subsequently, strain, decreases along the length and through the thickness of the CP layers; So, the curvature of the beam decreases along its length. The position-dependent curvature of the beam can be calculated by knowing the local strain induced in the conducting polymer film which according to equation 4.1, depends on the local density of charge.

Here we use the 2D transmission line which has previously been developed by Shoa et al. [27] and Nguyen et al. [28] to electrochemically model trilayer conducting polymers and find the position dependent density of charge. As an extension to their model, we included the effects of contact resistance and the part of the trilayer which is sandwiched between the two contact electrodes on the impedance of the device. For trilayer actuators which are designed to work at high frequencies, the contact resistance can effectively be a rate-limiting factor.

Figure 4.2(a) shows the equivalent circuit which electrochemically models trilayer conducting polymers. In this model, we assumed that the electronic conductivity of the CP layer is independent of the oxidation state and hence, the structure is symmetric and the lateral plane passing through the midst of the separator layer has a zero potential. The length and width of the trilayer which contribute in actuation are $L$ and $W$, respectively and those of the part which is sandwiched between the two contacts are $L_c$ and $W_c$, respectively. So, the apparent contact area is $A_c = W_c L_c$. The thicknesses of the conducting polymer and the separator layers are $h_p$ and $h_g$, respectively. The separator layer is modeled as an ionic resistor through its thickness with $R_{ig} = h_g / \sigma_{ig}$, being its ionic resistance for its unit length and unit width and $\sigma_{ig}$, being its ionic
Figure 4.2 (a) Equivalent transmission line circuit, modeling the electrochemical behavior of a trilayer conducting polymer along its length. The part which is darker is fixed between the two contact electrodes. The plane laterally passing the middle of the trilayer has a zero potential since the circuit is symmetric. (b) Equivalent RC transmission line circuit of the element, $Z_i$, modeling the diffusion of ions through the thickness of the CP layers.

The conducting polymer layer through its thickness is modeled as a diffusive impedance element with the equivalent RC transmission line circuit shown in figure 4.2(b), in parallel with a double layer capacitor. Hence, its impedance per unit length and for unit width is...
\[ Z_{p(f)} = Z_{dl(f)} Z_{i(f)}/(Z_{dl(f)} + Z_{i(f)}) \]

where \( c_{dl} \) is the double layer capacitance per unit area, and its value is in the range of 10-16 \( \mu F/cm^2 \), depending on the electrolyte used [83]. \( j \) is the square root of \(-1\), and \( f \) is the actuation frequency. Solving the RC transmission line for the diffusive element shown in figure 4.2(b), its impedance per unit length and for unit width is obtained through equation 4.2.a;

\[
Z_{i(f)} = \sqrt{R_{ip} Z_{cv(f)}} \coth(\gamma(f) h_p),
\]

(4.2.a)

where \( \gamma(f) = \sqrt{R_{ip} / Z_{cv(f)}} \), \( Z_{cv(f)} = 1/2\pi f C_V \) and \( C_V \) is the volumetric capacitance of the CP layer. \( R_{ip} = 1/\sigma_{ip} \) is the ionic resistivity of the CP layer and \( \sigma_{ip} \) is its ionic conductivity. Now solving the transmission line shown in figure 4.2(a), the impedance of the deflecting part of the trilayer is obtained through equation 4.2.b;

\[
Z_{2D(f)} = W^{-1} \sqrt{R_{ep}(Z_{p(f)} + R_{ig}/2) \coth(\beta(f)L)}.
\]

(4.2.b)

where \( \beta(f) = \sqrt{R_{ep}/(Z_{p(f)} + R_{ig}/2)} \), and \( R_{ep} = 1/\sigma_{ep} h_p \), is the electronic resistance of the conducting polymer layer per unit length and for unit width, and \( \sigma_{ep} \) is its electronic conductivity. The impedance of the part of the trilayer which overlaps the contact electrodes and does not contribute in actuation is, \( Z_c = (Z_{p(f)} + R_{ig}/2)/A_c \). \( R_c = r_{ec}/A_c \), is the contact resistance between the contact electrode and the conducting polymer layer where \( r_{ec} \) is their specific contact resistance. The total impedance of the trilayer is then obtained through equation 4.2.c,
\[ Z_T(f) = R_c + \frac{Z_c Z_{2D}}{Z_c + Z_{2D}}. \] \quad (4.2.c)

And the total impedance of the trilayer is \( 2Z_T(f) \).

Now the density of charge stored at the point \((i, j)\), which as shown in figures 4.2, is located at the vertical distance \( h \) from the zero-potential plane and the lateral distance \( l \) from the fixed point of the trilayer, can simply be obtained through equation 4.3;

\[ \rho_{(i,j,f)} = C_V V_{(i,j,f)}, \] \quad (4.3)

where \( V_{(i,j,f)} \) is the frequency-dependent voltage across the capacitor at the point \((i, j)\) and is obtained by solving the 2D transmission line depicted in figure 4.1 and is equal to;

\[
V_{(i,j,f)} = \frac{h}{|h|} V_s \left( \frac{\cosh \left( y(f) \left( |h| - \frac{h_T}{2} \right) \right)}{\cosh \left( y(f) h_p \right)} \right) \left( \frac{\cosh \left( \beta(f) (l - L) \right)}{\cosh \left( \beta(f) L \right)} \right) \left( \frac{Z_{p(f)}}{Z_{p(f)} + \frac{R_{ig}}{2}} \right) \left( 1 - \frac{R_c}{Z_T(f)} \right),
\]

where \( V_s \) is the amplitude of the applied voltage and \( h_T = 2h_p + h_g \), is the total thickness of the trilayer. The details of the calculation of equations 4, 4.2.a, and 4.2.b are provided in Appendix C. In chapter 5, we will demonstrate standard measurement methods for each parameter of the device. The frequency-dependent linear strain at the point \((i, j)\) denoted as \( \epsilon_{(i,j,f)} \), is then obtained through equation 4.5;
\[ \epsilon_{(i,j,f)} = \alpha V_s C_v \left( \frac{h}{|h|} \right) \left( \frac{\cosh \left( \gamma(f) \left( |h| - \frac{h_T}{2} \right) \right)}{\cosh(\gamma(f) h_p)} \right) \left( \frac{\cosh \left( \beta(f) (l - L) \right)}{\cosh(\beta(f) L)} \right) \left( \frac{Z_{p(f)}}{Z_{p(f)} + \frac{R_{ig}}{2}} \right) \left( 1 - \frac{R_c}{Z_{T(f)}} \right). \] (4.5)

Figure 4.3 shows the generated strain, \( \epsilon_{(i,j,f)} \), at frequencies of (1, 10, 100, and 1000) Hz along the length and through the thickness of the conducting polymer layer of a trilayer actuator with parameters summarized in table 4.1, operating at 1V. These parameters belong to a typical PEDOT/PEO:NBR/PEDOT trilayer actuator which is expected to actuate at high frequencies [10]. The cutoff frequency of this device is estimated to be \( \sim 8.5 \) Hz. According to figure 4.3, the distribution of strain becomes more uniform as the frequency of the applied voltage decreases. If enough time is given to the device so one CP layer is fully charged and the other one is fully withdrawn, the strain (and consequently the curvature) will be uniform along the length and is equal to \( \epsilon_0 = \alpha (C_v + c_{dt}/h_p)V_s = 0.301\% \).

### Table 4.1 Properties of a typical fast actuating PEDOT/PEO:NBR/PEDOT trilayer actuator which is theoretically studied in this chapter

| \( h_p \) | \( h_g \) | L | W | \( E_p \) | \( E_g \) | \( \sigma_{ip} \) | \( \sigma_{ig} \) | \( \sigma_{ep} \) | \( R_{ec} \) | \( A_c \) | \( C_v \) | \( \alpha \) | \( \zeta \) | \( \rho_m \) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( \mu m \) | \( \mu m \) | mm | mm | MPa | MPa | \( \frac{S}{m} \) | \( \frac{S}{m} \) | \( \frac{S}{m} \) | \( \Omega mm^2 \) | \( mm^2 \) | \( F \) | \( cm^3 \) | \( mm^3 \) | \( g \) | \( cm^3 \) |
| 2 | 10 | 2 | 0.5 | 350 | 1 | 0.005 | 0.1 | 6000 | 10** | 2 | 30 | 0.1 | 0.1 | 1.7 |
Figure 4.3 Strain along the length and through the thickness of the conducting polymer layer in a trilayer structure with parameters described in table 4.1. \( l = 0 \) is at the fixed end and \( h = 0 \) is at the interface of the conducting polymer and the separator layers.

In order to find the curvature of the trilayer along its length, as depicted in figure 4.4(a), we divided the trilayer beam into \( m \) segments, each denoted as \( S_j \) (\( j \) varying from 1 to \( m \)) being located at the distance \( l = j \Delta L \) from the fixed point of the trilayer beam. The length, width, and thickness of each segment is equal to \( \Delta L = L/m, W \) and \( h_T \), respectively. \( F_b \) is an external force which is perpendicularly applied to the tip of the actuator. Assuming \( m \) is sufficiently large, when the trilayer actuates at the frequency of \( f \), segment \( S_j \) bends to a uniform curvature of

\[
\kappa_{(j,f)} = \frac{\theta_{(j,f)}}{\Delta L}, \quad \theta_{(j,f)}\text{ being its bending angle, and rotates to an angle of } \\
\varphi_{(j,f)} = \sum_{j=1}^{j-1} \theta_{(jj,f)}.
\]

This, as shown in figure 4.4(a), causes the tip of the segment to displace in lateral and vertical directions by \( \Delta X_j \) and \( \Delta Y_j \), respectively. \( X_{l(f)} \) and \( Y_{l(f)} \), the frequency dependent lateral and vertical displacements of the beam at distance \( l = j \Delta l \) from the fixed end of the
trilayer, respectively, is then the summation of the local lateral and vertical displacements of the segment $S_j$, and those located prior to it,

$$X_{l(f)} = \sum_{j=1}^{m} \left( \Delta L - \frac{2}{\kappa(j,f)} \sin \left( \frac{\kappa(j,f) \Delta L}{2} \right) \cos \left( \frac{\kappa(j,f) \Delta L}{2} + \sum_{jj=1}^{j-1} \kappa(jj,f) \Delta L \right) \right), \quad (4.6.a)$$

$$Y_{l(f)} = \sum_{j=1}^{m} \left( \frac{2}{\kappa(j,f)} \sin \left( \frac{\kappa(j,f) \Delta L}{2} \right) \sin \left( \frac{\kappa(j,f) \Delta L}{2} + \sum_{jj=1}^{j-1} \kappa(jj,f) \Delta L \right) \right). \quad (4.6.b)$$

Figure 4.4 (a) Schematic of an actuated trilayer conducting polymer actuator beam divided into $m$ segments with uniform curvature in each segment. Segment $S_j$ bends to angle $\theta_j$ as a result of the differential strain induced in its CP layers and rotates by $\varphi_j$ due to the bending of the segments located prior to it. (b) Segment $S_j$ with conducting polymer layers divided each into $n$ sub-segments in which the induced electrochemical strain is uniform.

The vertical and lateral displacements of the tip of the beam can then be obtained by replacing $l$ in equations 6.a and 6.b with $L$. The details on how to obtain these two equations are provided in Appendix C. Equations 6.a and 6.b suggest that by determining the local curvature of the
trilayer actuator along its length, the frequency dependent location of each point on the trilayer and hence its shape can be estimated.

Curvature of a beam with a uniform cross-section area is obtained through the familiar equation \( \kappa = \frac{M}{EI} \), where \( M \) is the bending moment and \( EI \) is the flexural rigidity of the beam [75]. To calculate the curvature of the beam along its length, as depicted in figure 4.4(b) for the segment, \( S_j \), we divided the conducting polymer layers in each segment into \( n \) sub-segments, denoted as \( SS_{i,j} \) (\( i \) varying from 1 to \( n \) for expanding CP layer and -1 to -\( n \) for the contracting one), with length, thickness and width of \( \Delta L = L/m, \Delta h = h_p/n \) and \( W \), respectively. Assuming \( m \) and \( n \) are sufficiently large, the strain in each of these sub-segments is considered to be constant and is obtained through equation 4.5 for subsegment \( SS_{i,j} \). The frequency-dependent curvature \( \kappa(j,f) \) is then obtained through equation 4.7,

\[
\kappa(j,f) = \frac{M\varepsilon(j,f) - M_F(j,f)}{EI} + \kappa_0, \quad (4.7)
\]

where \( \kappa_0 \) is the initial curvature of the beam before it actuates. \( M\varepsilon(l,f) \) and \( M_F(l,f) \) are the frequency dependent bending moments induced to the trilayer at distance \( l (= j\Delta L) \) from the fixed point of the device due to the electrochemical strain and the external force applied to the tip of the beam and are obtained through equations 4.8.a and 4.8.b, respectively.

\[
M\varepsilon(l,f) = \int_{-h_T/2}^{h_T/2} W h E(l,f) \varepsilon(l,f) \, dl
\]

\[
= \sum_{h_p/2}^{h_T/2} 2\alpha C_w W V E_p \left( \frac{\cosh(\beta(l - L))\cosh(\alpha \left( h - \frac{h_T}{2} \right))}{\cosh(\beta L)\cosh(\alpha h_p)} \right) \left( \frac{Z_p(f)}{Z_{p(f)} + \frac{R_\varepsilon}{2}} \right) \left( 1 - \frac{R_\varepsilon}{Z_{T(f)}} \right) h \Delta h, \quad (4.8.a)
\]
\[ M_{F(j,f)} = F_{b(f)} \cos \varphi_{(l,f)} \left( L - X_{(m,f)} \right) - \left( l - X_{(l-1,f)} \right) + F_{b(f)} \sin \varphi_{(l,f)} \left( Y_{(m,f)} - Y_{(l-1,f)} \right) \]  

(4.8.b)

\( EI \) in equation 4.7 is the flexural rigidity of the whole beam and is equal to the sum of the flexural rigidities of each of the layers. Assuming the ionically conducting separator and conducting polymer layers are homogeneous along their lengths and through their thicknesses, we denote \( E_g \) and \( E_p \) as the Young's moduli of the separator and conducting polymer layers, respectively. Hence,

\[ EI = \frac{W}{12} \left( E_g h_g^3 + E_p (h_r^3 - h_g^3) \right) \]  

(4.9)

### 4.2.2 Force, displacement and stiffness

When the trilayer beam undergoes a free bending, i.e. \( F_b = 0 \), equation 4.7 becomes linear and curvature of the actuator along its length and subsequently shape of the beam as well as its vertical and lateral tip displacements can simply be calculated using MATLAB. Figure 4.5 compares the frequency response of the vertical tip displacement of a free bending trilayer actuator with parameters described in table 4.1 with and without including the effect of contacts (red straight line and green dashed line, respectively) with the one obtained through the previous model (black dotted line). In the previous model, it is assumed that the charge is distributed evenly and hence the curvature of the beam is uniform along its length regardless of the operation frequency [31]. It shows while all the three models predict the same values of tip displacement at low frequencies, at frequencies higher than the cut-off frequency, if we take into account the non-uniform curvature of the trilayer but neglect the effect of contacts, the model predicts larger values compared to the previous model. When the effect of contacts is included,
as expected, the predicted displacement decreases. The amount of decrease depends on the contact area and the specific contact resistance and increases with frequency (before it reaches the resonance). Contact resistance can also cause the cutoff frequency to decrease. This will be further discussed in section 5.3.11.

Figure 4.5 Frequency responses of the vertical tip displacement of a trilayer beam with parameters described in table 4.1, obtained through the uniform bending model without considering the effect of contact electrodes (black dotted line), varying curvature without considering the effect of contact electrodes (green dashed line) and varying curvature with considering the effect of contact electrodes (red straight line).

In a restricted bending \( F_b \neq 0 \), equation 4.7 becomes nonlinear and numerical methods are required to calculate the curvature of the beam along its length. Here we used an iterative method to solve equation 4.7 and reported the results within 0.5% error. Figure 4.6(a) show the resulting shape of the beam which is bent to its extent at 0.1 Hz, under different values of external force, \( F_b \), which are perpendicularly applied to its tip and figure 4.6(b) shows the force-displacement graph of the trilayer. To obtain these, first, the shape of the free bending beam \( (F_b = 0) \) is calculated through solving equation 4.7 (the beam with the lightest color shown in figure 4.6(a)). The force then increases step-wise (until the desired force, \( F_b \), is reached) and the shape of the
beam is calculated in each step. The step-size is chosen to be small (e.g., \( \sim 0.01F_b \)), so the angle
with which the force is applied in each step is approximately equal to \( \pi/2 + \varphi_{(m,f)} \), where
\( \varphi_{(m,f)} \left( = \sum_{j=1}^{m} \theta_{(j,f)} \right) \) is obtained through the shape of the beam in one step before. As
demonstrated in the inset in figure 4.6(b), \( D \) is the linear distance the tip of the beam travels after
a force, \( F_b \), is applied to it. The slope of this graph which can vary depending on the value of the
applied force (specially for large bending beams), is an indication of the stiffness of the trilayer
actuator. For the trilayer studied in this work with properties shown in table 4.1, the graph is
approximately linear with a slope of \( \sim 10.3 \text{ µN/mm} \) which is close to the value obtained through
the familiar equation for the stiffness of a cantilever beam,

\[
K = \frac{3EI}{L^3},
\]

being equal to \( 9.55 \text{ µN/mm} \).

Blocking force of an actuator is defined as the force needed to return the actuator to its un-
actuated position and is an indication of the maximum force the actuator can generate. For

Figure 4.6 (a) Estimated shape of the trilayer beam actuator, with parameters described in table 4.1, at its extent
at 0.1 Hz under different external forces. The blocking force, \( F_b \), is 9.9 µN. (b) Force versus displacement graph of
the trilayer beam, as described in the inset image.
bending actuators, it is defined as the force applied perpendicularly to the tip of the actuated beam and compensates its vertical displacement. For actuators operating at frequencies lower than the cutoff frequency of the beam, its value is roughly obtained through equation 4.11 [81],

\[ F_B \approx \frac{3W}{2L} \alpha C_v V h_p (h_p + h_g). \]  \hspace{1cm} (4.11)

In dynamic actuation, if we assume the transferred charge is distributed evenly throughout the volume of the conducting polymer, the frequency response of force is roughly obtained by substituting \( \alpha C_v \) with the frequency dependent strain equation [31]. However, as discussed before, this assumption leads to an error in our predictions at frequencies higher than the cut-off frequency of the device. Moreover, equation 4.11 is derived by assuming that the whole beam returns to its flat position along with its tip when the blocking force is applied to its tip. According to equations 4.8.a and 4.8.b, both \( M_{e(j,f)} \) and \( M_{F(j,f)} \), vary along the length of the

![Graph](image)

**Figure 4.7** Frequency response of the blocking force of the trilayer with parameters described in table 4.1, obtained through the uniform bending model without considering the effect of contact electrodes (black dotted line), varying curvature without considering the effect of contact electrodes (green dashed line) and varying curvature with considering the effect of contact electrodes (red straight line).
beam. So, as demonstrated in figure 4.6(a), while the vertical displacement of the actuated trilayer is compensated by the blocking force, $F_B$, its lateral displacement is not zero and the beam buckles. In figure 4.7, the frequency responses of the blocking force predicted through the model explained in this work with (red straight line) and without (green dashed line) including the effect of contacts is compared with the one obtained through the previous model (black dotted line) [31]. It shows at all frequencies, the model developed in this work predicts larger values of force compared to the previous one. As depicted in the inset, the graph is magnified at low frequency to show the difference between the values predicted by the two models. Similar to the displacement response, contact electrodes cause the blocking force to decrease at frequencies higher than the bandwidth of the device. Note that the algorithm used to predict the blocking force does not work for large bending actuators where the beam bends nearly 360° or more.

4.2.3 Cutoff frequency

The cutoff frequency of the trilayer actuators defines how fast the device can actuate to close to its maximum extent and is defined as the frequency at which the trilayer bends to $1/\sqrt{2}$ of its maximum deflection. According to figure 4.5(a), while contact resistance can shift the cutoff frequency to lower frequencies, including the effect of the nonuniform distribution of ions throughout the volume of the CP layer does not have much effect on the frequency at which the response rolls off. Hence, to estimate the cutoff frequency, we use the previous model and include the effect of contacts. This can be done by drawing the $|\bar{p}(f)| - f$ graph over a range of frequencies which equation $|\bar{p}(f)| = |\bar{p}_{m(f)}|/\sqrt{2}$ takes place. Here $|\bar{p}(f)|$ is the frequency-dependent amplitude of the average charge distributed throughout the volume of the CP layer.
and $|\bar{p}_{m(f)}| = (C_v + c_{dl}/h_p)V_s$, is its maximum value which takes place at frequencies below the cutoff frequency. In order to find that range of frequency, we take advantage of the rate limiting factors in trilayer conducting polymer actuators to predict a rough value of the time constant of the device $\bar{\tau}_c$ [84]. In trilayer conducting polymer actuators, there are four mechanisms which basically limit the actuation rate of the device. These include the charge and discharge of the conducting polymers via the transport of

1. electrons through the contact between the electrode and the CP layer,
2. electrons along the length of the CP layer,
3. ions through the thickness of the CP layer, and
4. ions through the thickness of the separator layer.

The time constants associated with these four mechanisms show how fast the CP film gets charged/discharged and are defined as,

$$\tau_{cP} = r_{cP}C = C_v R_c \frac{(WL + A_c)h_p}{A_c}, \quad (4.12.a)$$

$$\tau_e = r_eC = C_v \frac{L^2}{\sigma_e}, \quad (4.12.b)$$

$$\tau_P = r_PC = C_v \frac{h_p^2}{\sigma_{IP}}, \quad (4.12.c)$$

$$\tau_g = r_gC = C_v \frac{h_p h_g}{2\sigma_g}. \quad (4.12.d)$$

$\bar{\tau}_c$ is the maximum value of these four time constants. For the trilayer actuator with parameters described in table 4.1, the values of these time constants are $\tau_{cP} = 0.024$ s, $\tau_e = 0.02$ s, $\tau_P = 0.003$ s, and $\tau_g = 0.0003$ s, and hence $\bar{\tau}_c = 0.024$ s and $f_c = 1/2\pi\bar{\tau}_c = 6.63$ Hz.
is a rough value of the cut off frequency of the device. The selected range of frequency is then equal to \((10\tilde{f}_c, 0.1\tilde{f}_c)\) and the obtained value of the cutoff frequency, \(f_c\), through the method described above is 8.35 Hz.

4.2.4 Resonance frequency

As noted previously, in the model presented in this work, we neglected the effects of mass and damping of the trilayer. This means equation 4.7 provide a good estimation of the curvature of the segment \(S_t\) only when the actuating frequency is below the damped resonance frequency of the beam. It has previously been shown that the resonance frequency of the trilayer actuators is well close to its natural frequency (within \(~\)1.5 % of the measured value) which is obtained through assuming its whole mass is concentrated at its tip [16]. The \(n^{th}\) mode damped natural frequency of a free bending trilayer cantilever beam, is estimated through equation 4.13 [85]:

\[
f_d = \frac{\alpha_n^2 h_T}{2\sqrt{12\pi L^2}} \sqrt{\frac{EI}{I_T \rho_m}} (1 - \zeta^2),
\]

where \(EI\) is obtained through equation 4.9 and \(I_T = W h_T^3/12\), is the area moment of inertia of the beam. \(h_T\), \(\rho_m\) and \(\zeta\) are the total thickness, average mass density and damping ratio of the trilayer and \(\alpha_n\) is a coefficient defining the \(n^{th}\) normal mode natural frequency and its value for the fundamental frequency (first normal mode) is equal to 1.87. For the trilayer with parameters described in table 4.1, the fundamental natural frequency is equal to 203 Hz. This suggests the frequency responses of displacement and force as shown in figures 4.5 and 4.7 at frequencies close to and after 200 Hz are not valid.

When the operation frequency is below the fundamental frequency of the trilayer beam, \(f \ll f_{n1}\), the deflection of the trilayer is controlled through the ratio of the thicknesses and the
Young’s moduli of the CP and separator layers, the total thickness of the device and the charge-induced strain. In this case, the curvature of the segment, $S_t$, can be well predicted though equation 4.7 and subsequently, the total lateral and vertical displacements of the tip of the actuator can be predicted through equations 4.6.a and 4.6.b, respectively. When the operation frequency approaches the fundamental frequency of the beam, $f \approx f_{n1}$, displacement is more controlled through the damping effect. If $\zeta < 1$, actuating amplitude increases and reaches a maximum at $f = f_{n1}$, and then decreases. After that and before the actuating frequency reaches the second normal mode natural frequency, $f_{n1} \ll f \ll f_{n2}$, the displacement of the beam decreases and is more controlled by the inertia (mass) effect.

Note that the value of damping factor depends on the viscosity of the electrolyte with which the device operates and varies as the thickness of the layers changes since the device is non-homogeneous [85]. Change of the thicknesses of the layers also causes the average mass density to vary.

### 4.2.5 Average power consumption

The average power consumption of the trilayer actuators, $P_{(f)}$, is obtained through equation 4.14 [86].

$$P_{(f)} = \frac{V_0^2}{4|Z_{T(f)}|} \cos(\angle Z_{T(f)}),$$  \hspace{1cm} (4.14)

where $|Z_{T(f)}|$ and $\angle Z_{T(f)}$ are the amplitude and phase of the half impedance of the device and can be obtained through equation 4.2.c. Figure 4.8 shows the frequency response of the average power consumption of the trilayer modeled in this chapter. It suggests at frequencies lower than the cut-off frequency at which the device is more capacitive, the average power consumption is
close to zero. As the operation frequency increases, the device becomes more resistive and the average power consumption increases. The average consumed power in the trilayer causes the device to warm up. This, depending on the heat generation rate and the heat transfer rate, subsequently causes the ionic conductivity of the electrolyte to increase [9] and the electronic conductivity of the CP layer to decrease which may causes the impedance of the device and hence its speed to change with time.

![Graph](image)

**Figure 4.8 Frequency response of the average power consumption of the trilayer with parameters described in table 4.1.**

### 4.2.1 Electrical efficiency

The electrical efficiency of an electronic circuit is defined as the ratio of the stored energy in the circuit, $U_{E,s}$, to the input electrical energy, $U_{E,in}$, which can be obtained through equations 4.15.a and 4.15.b versus frequency, respectively.

\[
U_{E,s} = \frac{1}{2} \times \int_0^L \int_0^{h_p} \frac{1}{2} C_V V^2 = \frac{WLh_pC_V}{4mn} \sum_{j=1}^n \sum_{i=1}^m V_{(i,j,f)}^2, \quad (4.15.a)
\]
\[ U_{E,\text{in}} = \int_0^{T/4} vidt = \frac{V_0^2}{8f |Z_T(f)|} \left( \frac{\cos(\angle Z_T(f))}{2} - \frac{\sin(\angle Z_T(f))}{\pi} \right), \]  

where \( V_{(i,f)} \) is obtained through equation 4.4. Figure 4.9 demonstrates the electrical efficiency versus frequency for the device with parameters provided in table 4.1, showing at low frequencies, in which the device is operating mostly capacitive, all the input energy will be stored. In real applications however, due to the parasitic resistances and the leakage current through the device (as will be shown in figure 5.13(c), the impedance phase never reaches -90') the device never shows a purely capacitive behavior even at low frequencies, and the electrical efficiency is always less than 100%. As the frequency increases, the device becomes more resistive and the energy dissipation increases.

![Figure 4.9 Electrical efficiency versus frequency of the trilayer with parameters described in table 4.1](image)

**Figure 4.9** Electrical efficiency versus frequency of the trilayer with parameters described in table 4.1

### 4.2.2 Electromechanical coupling

The electromechanical coupling factor, \( k_T^2 \), is an indicator of how effective the trilayer actuator converts the input electrical energy, \( U_{E,\text{in}} \), into mechanical energy, \( U_M \), and is obtained
through equation, 4.16.

\[
k_T^2 = \frac{\text{Stored mechanical energy}}{\text{input electrical energy}} = \frac{U_M}{U_{in,E}}, \tag{4.16}
\]

in which \(U_{in,E}\) is obtained through equation 4.15.a and for a trilayer CP actuator, \(U_M\) is described through equation 4.17,

\[
U_M = \int_0^L \frac{1}{2} M \kappa \, dx = \frac{1}{2} \frac{L}{mE} \sum_{j=0}^{n} M_{\epsilon(j,f)}^2, \tag{4.17}
\]

where \(M_{\epsilon(j,f)}\) is already defined through equation 4.8.a. Figure 4.10 shows the electromechanical coupling versus frequency for the device with parameters provided in table 4.1. Here, only the actuator part is taken into account, so the effect of contacts is neglected. As demonstrated in figure 4-10, the electromechanical coupling in the trilayer conducting polymer is very small compared to e.g., piezoelectric actuators (~ 0.1) [87].

At low frequencies, equation 4.18 describes the electromechanical coupling in trilayer CP

![Figure 4.10 Electromechanical coupling versus frequency of the trilayer with parameters described in table 4.1](image)

Figure 4.10 Electromechanical coupling versus frequency of the trilayer with parameters described in table 4.1
actuators which is equal to $4 \times 10^{-4}$ for the trilayer actuator described with parameters provided in table 4.1.

$$k_{T,0}^2 = \frac{3\alpha^2 \alpha C V E_p^2 (h_T^2 - h_g^2)^2}{2 \left( E_g h_g^3 + E_p (h_T^3 - h_g^3) \right) h_p}, \tag{4.18}$$

For a single conducting polymer film which undergoes tensile strain due to the change in its oxidation state the electromechanical coupling is obtained through,

$$k_{CP}^2 = 4E_p C_V \alpha^2, \tag{4.19}$$

which is equal to $4.2 \times 10^{-4}$ for the conducting polymer with parameters provided in table 4.1.

The small electromechanical coupling in conducting polymers is mainly due to the small strain to charge ratio in these materials. One may expect to increase the strain to charge ratio by increasing the size of the mobile ions. That is true to some extent [88]. But if the size of the ions is too large, they may not be able to enter the structure of the conducting polymer and create a strain in it. The electromechanical coupling also depends on type of the conducting polymer selected, the larger the Young’s modulus and volumetric capacitance of the CP layer is, such as in PEDOT:PSS [89] and PANi [90], respectively, the larger electromechanical coupling is obtained.

### 4.2.3 Mechanical efficiency

Mechanical efficiency, $\eta_m$, is defined as the work done by the trilayer versus the input electrical energy. Here, we study the mechanical efficiency in static operation, when the trilayer lifts a mass, $m$, as it actuates upward to the distance, $Y_t$, which is obtained through equation 4.6.b at low frequencies in which the device reaches its maximum displacement. The work done is hence equal to $mgY_t$, in which $g$ is the gravity of the earth and is equal to $9.81 \, \text{m/s}^2$. Hence,
$$\eta_{in} = \frac{\text{Mechanical work out}}{\text{Electrical energy in}} = \frac{mgY_t}{(h_pLWcV_0^2)/4}, \quad (4.20)$$

Here, the largest mass which can be just lifted by the trilayer is equal to $\sim F_B/g$, and for the trilayer described in table 4.1 (according to figure 4.7, $F_B = 9.8 \mu N$), is equal to 1 mg (the total mass of the studied trilayer is equal to $\sim 24 \mu g$). Mechanical efficiency versus the mass it can lift at its tip is demonstrated in figure 4.11 for different input voltages for the trilayer actuator described in table 4.1. It shows as the applied voltage decreases, the optimum efficiency slightly decreases and there is an optimum mass at which the efficiency is largest ($\sim 0.016 \%$ for the trilayer described in table 1).

Note that in these devices, the input electrical energy is stored in the device and can be recovered. Hence, the device can potentially demonstrate a larger electromechanically coupling or mechanical efficiency than what is demonstrated in figures 4.10 and 4.11, respectively.

![Graph](image)

Figure 4.11 Mechanical efficiency versus frequency of the trilayer with parameters described in table 4.1

### 4.2.4 Effect of encapsulation

We showed in chapters 1 and 2 the importance of using encapsulation for trilayer CP
actuators with solvent-based electrolyte to increase their operation lifetime. This added layers, however, cause the flexural rigidity of the structure to increase, which consequently affects the stiffness, displacement, blocking force, and the resonance frequency of the device. Effect of encapsulation can be included through substituting the flexural rigidity, $EI$, in equations 4.7, 4.10, and 4.13, with equation 4.21,

$$EI = \frac{W}{12} \left( E_g h_g^3 + E_p (h_T^3 - h_g^3) + E_e (h_{Te}^3 - h_T^3) \right) + \frac{t_s}{6} E_e h_T^3,$$  

(4.21)

where $h_{Te} = h_T + 2t_s$, $t_s$ is the thickness of the encapsulating layer and $E_e$ is its young’s modulus. The $\frac{t_s}{6} E_e h_T^3$ term in equation 4.21 demonstrates the effect of encapsulation on the sides of the device.

The resonance frequency of the device is hence obtained by substituting $h_T$ and $I_T$ with $h_{Te}$ and $I_{Te} = \frac{W h_{Te}^3}{12}$. Note that the damping factor of the device also changes due to the added layers.

Figure 4.12 compares the shape of the trilayer described in table 4.1, freely bending to its extent (light colors) and blocked through the application of a force to its tip (dark colors), before (green) and after (orange) encapsulation with 10 µm thick encapsulant (e.g. SIBSTAR) with Young’s modulus of 10 MPa and average mass density of 1 g/cm$^3$. It shows, as expected, the extent of bending of the trilayer decreases due to the increased stiffness. It also shows that a smaller blocking force is needed to return the tip of the encapsulated trilayer back to its initial (zero) vertical position. This is accompanied by a smaller buckling along the length of the beam.

4.3 ActuaTool

The model explained in section 2 was implemented in MATLAB to predict the output of the
device, as shown in figures 4.5 to 4.12. This powerful software can also be used to design the

Figure 4.12 Comparison of the shape of trilayers, with parameters described in table 4.1, at 0.1 Hz, freely bending to their extent (light color) and blocked (dark color), without encapsulation (green) and with encapsulation (orange). Note that the value and direction of the blocking force are different for the two trilayers.

intended graphical user interface (GUI), similar to what Balakrisnan et al. [81] carried out. However, all the researchers may not have access to this software without the MATLAB license. Here, we designed a web-based GUI, so-called “ActuaTool”, to implement the model. ActuaTool uses standard web technologies (HTML, CSS, and JavaScript) and can run on all web browsers, which makes it accessible for everyone. This tool enhances the practicality of the model and facilitates the design of the conducting polymer actuators for various applications. In addition to that, having an online web-tool, we can anonymously log user interactions with it which is necessary for future usability studies and further improvements on it. We release ActuaTool as an open-source web tool which allows researchers to further modify the model, e.g., through including the effect of oxidation-state on the electronic conductivity and Young’s modulus of the
CP layer, the effect of temperature on the ionic conductivity of the electrolyte and the electronic conductivity of the CP layer, as well as the effect of inertia and damping. Researchers can also include other desired output parameters and graph visualizations or extend the tool for other ionic electroactive polymer actuators or other structures such as tubular actuators.

ActuaTool works based on the model explained in section 2 and the algorithms behind all the calculations are the same as those described there. As demonstrated in figures 4.13, 4.15, and 4.17, ActuaTool runs in three modes of operation: “Frequency response”, “Parameter response” and “Design”, providing three sets of outputs. In all three modes, there are four categories of inputs which are common and titled as “Conducting polymer parameters”, “Separator parameters”, “Device parameters” and “Encapsulation parameters”. The detailed list of inputs which falls within each of these categories is shown in the figure corresponded to each mode of operation. There are also other specific sets of inputs in each mode of operation. In case the device is encapsulated, value boxes holding the encapsulation parameter values will be activated by clicking on the “ON” button. By clicking the “OFF” button next to it, the values boxes will be deactivated and ActuaTool assumes no encapsulation is applied to the trilayer. In all three modes, by clicking on the “Set Default Values” button, all the value boxes will be filled with a set of already defined ones. The user can change the values to their desired ones. In all the frequency response graphs, the minimum frequency is $0.01\tilde{f}_c^\ast$ (obtained in section 1.2.3) and the graphs are plotted for four decades. For all the graphs and calculations, the step size of frequency is 0.02 on the log-scale.

After the graph visualizations in “Frequency Response” and “Parameter response” modes, the user can save each graph and the corresponding raw data by clicking on the “Save data” and
“Save graph” buttons located below each graph. Here are the outputs that each mode of operation of ActuaTool provide along with the input they obtain:

4.3.1 “Frequency response” mode

**Input** (figure 4.13): Values of all the parameters of the device, the value of the external force applied to the tip of the beam (free bending if it is zero) as well as the frequency at which the shape of the beam and its force-displacement curve are desired, are obtained as input. They are both categorized in a column titled as “shape of the beam” in figure 4.13. The values shown for the parameters of the trilayer are default values which are inserted by clicking on “Set Default Values” button and are the same as those shown in table 4.1. By clicking on the “Draw Plots” button, ActuaTool starts calculating the results and visualizes them in separate graphs.

**Output** (figure 4.14): Frequency responses of maximum tip displacement (vertical and lateral), blocking force, and average power consumption of the trilayer beam, shape of the actuator bent to its extent at the defined frequency when an external force with the defined value is applied to its tip as well as the force-displacement curve of the actuator at the defined frequency, are the output of ActuaTool in “Frequency response” mode of operation. The values of the maximum induced strain \(= \alpha(C_v + c_{dl}/h_p)V_s\), the cutoff frequency of the actuator, its stiffness (obtained through equation 4.10) as well as the resonance frequency of the beam (obtained through equation 4.13) are also demonstrated.

Note that the frequency response of the blocking force shown in figure 4.14(b) is obtained based on the uniform curvature model [31], which assumes transferred charges are uniformly distributed throughout the volume of the conducting polymer and the beam bends to a uniform curvature along its length. After this graph is plotted along with other graphs, the user is asked
**Figure 4.13** Screenshot image of the input interface of ActuaTool in the “Frequency Response” mode.
Figure 4.14 Screenshot image of the graph visualization of ActuaTool in “Frequency Response” mode demonstrating frequency response graphs of (a) vertical displacement (“m” on the vertical axis values indicates 0.001), (b) lateral displacement, (c) blocking force, (d) average power consumption, and (e) shape of the freely bending beam and (f) force-displacement at 0.1 Hz.
force-frequency response. By clicking on the “Yes” button, the corresponding graph will be
updated to a more accurate one which is obtained through the method explained in section 4.2.1.
In this graph, while the frequency range is kept unchanged, its step-size is increased to 0.2 in log-
scale to reduce the processing time.

This mode of operation is available through the following link:

https://saeedehebr.github.io/ActuaTool/study/index.html

4.3.2 Parameter response mode

Input (figure 4.15): A range of values of a selected parameter along with its corresponding
step size, the values of all other parameters of the device and the voltage and frequency at which
the changes of the outputs are of interest, are obtained as the input in this mode of operation.
In figure 4.15, we assumed the trilayer is encapsulated and as mentioned before, by clicking on
the “ON” button, the corresponding value boxes are activated. Here, we study the effect of
encapsulating layer’s thickness on the output characteristics of the device. All other parameters
are the default values which were inserted by clicking on the “Set Default Values” button and are
the same as those shown in table 4.1. The encapsulating layer parameters are the same as the one
studied in section 1.2.6. By clicking on the “Draw plots” button, ActuaTool starts calculating the
values of outputs for versus the varying parameter.

Output (figure 4.16): cutoff frequency, displacement (vertical and lateral), blocking force,
average power consumption, stiffness and resonance frequency of the actuator versus the varying
parameter. Those parameters which are frequency-dependent, are drawn at the defined
frequency. Blocking force values are estimated through the modified method explained in
section 1.2.1.
As shown in figures 4.16(a) and 4.16(e), increasing the thickness of the encapsulating layer has no effect on the cut-off frequency and the average power consumption since both of them are obtained using the electrochemical model of the trilayer and we assumed the encapsulation process does not change the electrochemical properties of the device. As shown previously in section 3.4.3.2 and figure 4.9 and as demonstrated in figures 4.16(b) and 4.16(c), encapsulation of the beam causes the device to deflect less and the vertical and lateral displacements to decrease. This is because the device becomes stiffer as shown in figure 4.16(f). According to the uniform curvature model, the encapsulating layer does not affect the blocking force generated by the trilayer, since it is a mechanically passive layer sitting on the outer side of the device. Using the modified method described in section 1.2.2, we showed that the encapsulating layer can cause the blocking force to slightly decrease. Note that as the thickness of the encapsulating layer increases, the observed buckling in the trilayer when it is blocked by a force applied to its tip decreases (demonstrated in figure 4.12). As shown in figure 4.16(g), as the thickness of the encapsulating layer increases within the specified range, the resonance frequency initially slightly decreases and then increase. Note that the damping factor of the device also changes with the thickness of encapsulating layer which is neglected in our calculations. That can significantly affect the actuation behavior of the trilayer at resonance.

This mode of operation comes with the previous operation mode and is available through the following link:

https://saeedehebr.github.io/ActuaTool/study/index.html

### 4.3.3 Design mode

**Input** (figure 4.17): Values of all the parameters of the device except the thicknesses of the
Figure 4.15 Screenshot image of the input interface of ActuaTool in the “Parameter response” mode. Thickness of the encapsulating layer is selected as the varying parameter
Figure 4.16 Screenshot images of graph visualization of ActuaTool in “Parameter Response” mode demonstrating graphs of (a) displacement-determined cut-off frequency, (b) vertical displacement, (c) lateral displacement, (d) blocking force, (e) average power consumption, (f) stiffness and (g) resonance frequency versus encapsulating layer’s thickness. Operating voltage and frequency are 1V and 0.1 Hz, respectively.
conducting polymer and separator layers and the length of the device, a desired range of the selected output (titled as “ Desired output” ) and a range of values for the thicknesses of the conducting polymer and separator layers as well as the length of the device over which the desired output range is possible, are obtained as the input in the “ Design” mode of operation. This set of inputs are titled as “ Range of dimensions” and can roughly be estimated through using the “ Parameter response” mode of the tool. The desired selection of output includes bandwidth, maximum displacement (vertical and lateral), maximum blocking force, average power consumption, stiffness, and resonance frequency. The user should also define the voltage and frequency of the applied voltage at which the desired output is expected. Same as the two other modes of operation, if the device is encapsulated, the user needs to first activate the corresponding value boxes and then enter the parameter values. In figure 4.17, we filled the input value boxes with the pre-defined values through clicking on the “ Set Default Values” button and select a range of cutoff frequency within which the cutoff frequency of the trilayer actuator ((8.5 ± 0.5) Hz) which is modeled in this work occurs. As the user clicks on the “ Find Dimensions” button, ActuaTool starts calculating values of the selected output for the devices designed using the set parameters and combinations of dimensions already specified in “ Range of dimensions” column. It then filters those designs which their selected output values fall within the specified range and calculates other outputs for them.

Output ( figure 4.17 ): The combinations of the dimensions of the device ( thicknesses of the conducting polymer and separator layers and the length of the device) that leads to a value of the selected output which sits within the range specified by the user as well as the values of other outputs for each combination at the defined operation voltage and frequency.
The best results in this mode are obtained through the interaction between the user and the tool. It is recommended that the user first select a wide range of dimensions and further refines it and alter the resolution they want the output at, to ensure they obtain the optimum results. If the desired output does not occur using the selected ranges of dimensions, the tool returns an error message and asks the user to alter the selected range of dimensions. The results are shown in a table in the browser (figure 4.18) and the user can sort them based on any of the outputs to navigate the data easier. The operation voltage and frequency are set to be 1 V and 0.1 Hz, respectively. The obtained data in the table can be copied and pasted in an Excel file for further use.

According to figure 4.18 different combinations of dimensions of the device with material and device properties shown in figure 4.17 can lead to a cut off frequency of (8 ± 0.5) Hz. Each set is suitable depending on the intended application of the actuator and the second priority of the designer in terms of output (the first one is the cutoff frequency). For example, if a large displacement is needed (first row), a longer beam (up to 2.5 mm) with a thinner separator layer’s thickness (down to 30 µm) works best. If a stiffer beam with a larger blocking force is desirable (last row), a short beam (down to 0.5 mm) with a large thickness of separator layer (up to 150 µm) should be made.

This mode of operation is available through the following link:
https://saeedehebr.github.io/ActuaTool/design/index.html

4.4 Design of trilayer conducting polymer actuators for a tactile feedback interface

Using ActuaTool we can optimize the design of trilayer conducting polymer actuators for various applications. Here, as a case study, we demonstrate design optimization for a tactile
Figure 4.17 Screenshot image of the input interface of ActuaTool in the “Design” mode. Cutoff frequency is selected as the dominant output.
Figure 4.18 Screenshot images of the table visualization including dimensions of the trilayer actuators with parameters defined in figure 4.17, which result in devices with values of cutoff frequency at $(8.5 \pm 0.5)$ Hz, along with their corresponding values of blocking force, vertical and lateral displacements, average power consumption, stiffness and resonance frequency at the defined voltage and frequency of 1 V and 0.1 Hz, respectively. The table is sorted so that the design which leads to a larger vertical tip displacement sits on top.
feedback display employing trilayer CP actuators as the active element.

Design of tactile feedback interfaces has been investigated through reproducing tactile sensations such as vibration, force, and texture as forms of feedback to the user [91]. Among those, vibrotactile displays are the most widespread and well-studied. These interfaces now have a variety of applications such as in interactive keyboards and displays e.g., in cell phones, minimally invasive surgery [92], Braille cell displays [93]–[95], etc.

An array of tactile pixels should meet several requirements to be practical in a vibrotactile display. Among those, the key requirements include being stiff enough compared to the human skin, being able to produce a perceivable displacement in it and being able to operate at a wide range of frequencies, providing the tactile feedback designer with more freedom to design various tactile sensations [96]. These three requirements are specifically dependent on the performance of active elements of the tactile display or the mechanical actuators. Figure 4.19 shows the threshold of detection by human fingertip, here denoted as $d_u$, versus the vibration frequency. It shows that as the vibration frequency increases up to 150 Hz, the sensitivity of

![Figure 4.19 Neural threshold for vibration detection. Adapted from [97]](image)
human skin increases. The minimum detectable amplitude at the most sensitive frequency range is about tens of nanometers.

Figure 4.20(a) shows the schematic of a possible design structure of a tactile feedback display using trilayer conducting polymer actuator beams. As demonstrated in figure 4.20(b), the array of CP actuators can generate lateral deformation in user’s fingertip as the two are placed in contact with each other, similar to what has been shown in [98], through using an array of piezoelectric actuators, to generate lateral skin deformation as a form of feedback. As mentioned before, in order to practically employ trilayer CP actuators in such structure, the beam has to generate the minimum detectable displacement, \( d_u \), in the fingertip (figure 4.19). This, as schematically demonstrated in figure 4.20(c), means the vertical displacement of the trilayer at a given frequency, \( D_u(f) \), should be more than the threshold of detection by the fingertip at that frequency, \( (D_u(f) > d_u(f)) \), after a force, \( F_u(f) > K_u d_u(f) \), is applied to the tip of the actuator beam. \( F_u(f) \) is the reaction force which fingertip, with the stiffness of \( K_u \), applies to the beam due to the penetration of the beam into it. The inequality above is approximately equivalent

![Diagram of tactile feedback display](image)

**Figure 4.20** (a) Top and (b) side views of the schematic of a possible design for a tactile feedback interface using trilayer CP actuators. (c) Schematic of the interaction of a trilayer CP actuator with a fingertip. \( F_u \) represent the threshold of the reaction force, which fingertip applies to the trilayer due to the threshold deformation it made into the fingertip.
to \( F_B(f) > (K_u + K)d_u(f) \), where \( F_B(f) \) is the blocking force of the trilayer and \( K \) is its stiffness. It suggests that a structure with a stiffness close to that of the fingertip (hence, \( F_B(f) > 2K_u \times d_u(f) \)) with a displacement larger than \( d_u(f) \) (\( D_u(f) > d_u(f) \)), fulfills the aforementioned requirements.

Studies on the mechanical properties of the fingertip show that the value of the stiffness of the fingertip depends on the penetration depth and the direction of the applied force. For small penetration depths (< 500 \( \mu \)m), its value is < 10 N/m and increases as the penetration depth increases (0.4 \( \times \) 10\(^3\) N/m and 1.2 \( \times \) 10\(^3\) N/m at a penetration depth of 2 mm at 15º and 60º, respectively [99], [100]). The trilayer CP actuator which is described in table 4.1 (a typically thin and short PEDOT/PEO:NBR/ PEDOT trilayer) and modeled in sections 2 and 3 has a stiffness of 9 \( \times \) 10\(^{-3}\) N/m which is ~3 orders of magnitude smaller than what is needed for the tactile feedback display, demonstrated in figure 4.20(a). According to equations 4.9 and 4.10, increasing the thicknesses and Young’s moduli of the conducting polymer and separator layers as well as decreasing the length of the actuator helps the stiffness of the structure to increase. Here we first investigate different materials to select the proper ones as the conducting polymer and separator layers and then use ActuaTool to find the optimum dimensions.

Table 4.2 shows the Young’s moduli of the polymers which are commonly used as the conducting polymer and separator in trilayer CP actuators. It suggests poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and polyvinylidene fluoride (PVDF), with the Young’s moduli of ~2 GPa [89] and ~70 MPa [3], respectively, create the stiffest structure compared to other combinations. PEDOT:PSS is made by chemical polymerization of (3,4-ethylenedioxythiophene) (EDOT) in a poly- (styrene sulfonic acid) (PSS)
Table 4.2 Young’s modulus of different conducting polymer and separators commonly used in trilayer CP actuators

<table>
<thead>
<tr>
<th>Conducting polymer</th>
<th></th>
<th></th>
<th></th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>PEDOT</td>
<td>PEDOT:PSS</td>
<td>PEO:NBR copolymer</td>
<td>PVDF membrane/film</td>
</tr>
<tr>
<td>90 MPa</td>
<td>180 MPa</td>
<td>2000 MPa</td>
<td>1 MPa</td>
<td>70 MPa</td>
</tr>
<tr>
<td>[3]</td>
<td>[8], [11]</td>
<td>[89]</td>
<td>[8], [11]</td>
<td>[3]</td>
</tr>
</tbody>
</table>

solution [101] and is commercially available as an aqueous dispersion (e.g., CLEVIOS PH 1000 from Heraeus [102]). It has key benefits over other types of conducting polymers such as being transparent and highly stable in thin oxides films [101]. By adding secondary dopants through adding some inert solvents such as dimethyl sulfoxide (DMSO) (5 w%), its electronic conductivity has been reported to reach to as high as $8 \times 10^5$ S/m [102] which is close to that of indium tin oxide (ITO) ($\sim 1 \times 10^6$ S/m)- the most widely used transparent conductor [103]. It has a large Young’s modulus of (1 to 3) GPa (depending on the relative humidity of the environment) [89], which is beneficial in the application studied here. However, this can be reduced to 55 MPa through incorporating ionic additives such as LiTFSI, which also helps its electronic conductivity to increase to as high as $7 \times 10^5$ S/m (for freestanding films), making it a promising solution towards realizing flexible transparent electronics [104]. PVDF membranes have been widely used as the separator layer in CP trilayers especially with PPy as the conducting polymer [4], [5], [16]. They are porous membranes with the main application in western blotting and are commercially available in different thicknesses (generally 125 µm thick) from MilliporeSigma [105]. Their porous structure helps them to have a larger ionic conductivity compared to solid polymer electrolytes (SPEs) such as PEO:NBR copolymers [24].
and maintain their original thickness as they store the electrolyte or withdraw it [6]. Using the spray-coating technique, in chapter 5, we will demonstrate a new method of fabrication of PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer structures.

Displacement of a trilayer actuator depends on the ratio of the Young’s moduli of the separator layer to the conducting polymer layer. Figure 4.21 compares how the maximum vertical displacement of the tip of the actuators with separator layers with Young’s modulus of 1 MPa (e.g. for PEO:NBR copolymer, indicated with red circle dots) [8], [11] and 70 GPa (e.g. for PVDF, indicated with black triangle dots) [3] change with respect to the Young’s modulus of the conducting polymer layer as it varies from 100MPa (e.g. for PEDOT or PPy) [3], [8], [11] to 2 GPa (e.g. for PEDOS:PSS) [89]. Other parameters of the device are as described in table 4.1. The data in figure 4.21 were obtained using ActuaTool in “Parameter Response” mode which

![Figure 4.21 Maximum vertical tip displacement versus young’s modulus of the conducting polymer layer for trilayers with separator’s Young’s modulus, $E_g$, of 1 MPa e.g., PEO:NBR copolymer (red circle dots) and 70 MPa, e.g., PVDF membrane without (black triangle dots) and with (green square dots) encapsulation with a 10 µm thick SIBSTAR. Other parameters of the device are as described in table 4.1.](image-url)
were then saved and replotted in a single graph. It shows the larger the ratio of the Young’s moduli of the CP layer to the separator layer is, the larger displacement is obtained. When this ratio is sufficiently large, displacement is no more dependent on it. This applies to actuators with a separator layer with small Young’s modulus (e.g., PEO:NBR copolymer) with any of the available conducting polymers. This makes these types of actuators favorable when large deflections are needed [11] as shown in chapter 2.

For trilayers with PVDF membranes, if PEDOT: PSS is used as the conducting polymer layer, the same displacement as those with PEO:NBR copolymer as the separator layer is obtained with significantly stiffer structure (over 15 times larger for the trilayer with dimensions- other than Young’s moduli of each of the layers- as described in table 4.1).

Employing trilayer CP actuators in a tactile feedback array requires them to be encapsulated because of the direct user-interactions involved. As explained before and shown in chapter 3, this added layer makes the structure stiffer which is favorable for the application which is being studied here. This is however with the expense of losing some of its displacement. Vertical displacement of an encapsulated trilayer with a separator layer with Young’s modulus of 70 MPa (e.g., PVDF) is plotted versus Young’s modulus of the CP layer in figure 4.21 (green square dots). Other parameters of the device are as described in table 4.1. Young’s modulus, thickness, and average mass density of the encapsulating layer are 1 MPa, 10 µm, and 1 g/cm³, respectively (as of SIBSTAR which was shown in chapter 3). It shows displacement of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer decreases by only 8% after 10 µm thick encapsulation is added while that of PEDOT/ PEO:NBR/ PEDOT decreases by ~70%. This suggests the stiffer the structure is, the less displacement it looses after encapsulation.
In addition to the stiff structure PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuators can provide, they benefit from the high electronic conductivity of PEDOT:PSS (as high as $8 \times 10^5$ S/m for free-standing films when 5% w/w DMSO is added as the secondary dopant [102]) and higher ionic conductivity of PVDF membrane compared to PEO:NBR copolymer films thanks to its porous structure. These both help the cut-off frequency of the device and its displacement at frequencies higher than that to increase.

Now that the suitable conducting polymer and separator layers are selected, we use ActuaTool in “Design” mode to search for possible dimensions of trilayer CP actuators which make them applicable for the tactile feedback display, schematically shown in figure 4.20(a). Table 4.3 describes properties of an example trilayer which can be made using PEDOT: PSS as the conducting polymer, PVDF membranes as the separator and SIBSTAR as the encapsulation layers. The operation voltage is set at 1.5 V since the devices may undergo electrochemical degradations after that. We carry out the optimization for the operation of the device at 150 Hz due to the highest sensitivity the fingertip has at that frequency. Using ActuaTool in “Design” mode, we look for possible dimensions which can make a structure with a blocking force within the range of $10 \times 2 \times 2 \times 20 \times 10^7 \times 20 \times 10^{-7} = 0.004 \text{ mN}$ to 4 mN. The lower and upper bounds are one and four orders of magnitude larger than the minimum detectable force by a human fingertip. The lower and higher bounds of CP layer thickness were set to 0.35 μm and 3.5 μm the thickness with the step size of 0.35 μm (this is because of the limitation of the fabrication method which will be demonstrated in chapter 5). The thickness of the separator layer is considered to be fixed and is equal to 125 μm (commercial PVDF membranes with properties compatible with the requirements of the separator layer in trilayer
actuators come at this thickness). The range of the length was set to 0.5 mm to 2 mm with the steps of 0.5 mm. Trilayers, as described with a length larger than 2 mm, have a resonance frequency below 1000 Hz which may interfere the results estimated through the tool.

Table 4.3 Properties of a PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuator to be designed for a tactile feedback interface

<table>
<thead>
<tr>
<th>$h_g$</th>
<th>$W$</th>
<th>$E_p$</th>
<th>$E_g$</th>
<th>$\sigma_{ip}$</th>
<th>$\sigma_{ig}$</th>
<th>$\sigma_{ep}$</th>
<th>$R_{ec}$</th>
<th>$A_c$</th>
<th>$C_v$</th>
<th>$\alpha$</th>
<th>$\zeta$</th>
<th>$\rho_m$</th>
<th>$t_e$</th>
<th>$E_e$</th>
<th>$\rho_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu m$</td>
<td>mm</td>
<td>GPa</td>
<td>MPa</td>
<td>$\frac{S}{m}$</td>
<td>$\frac{S}{m}$</td>
<td>$\frac{S}{m}$</td>
<td>$\Omega mm^2$</td>
<td>$mm^2$</td>
<td>$\frac{F}{cm^3}$</td>
<td>$mm^3$</td>
<td>$\frac{g}{cm^3}$</td>
<td>$\mu m$</td>
<td>MPa</td>
<td>$\frac{g}{cm^3}$</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>0.5</td>
<td>2</td>
<td>80</td>
<td>0.005</td>
<td>0.5</td>
<td>$10^5$</td>
<td>1</td>
<td>1</td>
<td>30</td>
<td>0.1</td>
<td>0.1</td>
<td>1.7</td>
<td>10</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

Amongst the designs which provide an actuator with a blocking force between 0.004 mN and 4 mN, those with a larger cutoff frequency are favorable. For the same values of displacement or force for two devices at 150 Hz, the larger the cutoff frequency is, the larger the displacement of the device is at frequencies below 150 Hz. This leaves the table with devices with $L < 1.5$ mm and $h_p < 1 \mu m$ ($h_g = 110 \mu m$). Table 4.4 shows a list of dimensions of possible designs and their corresponding values of outputs. The vertical displacement is at free bending and at 150 Hz, and for constant values of length, decreases as the thickness of the conducting polymer layer increases. For all designs, the average power consumption of the outcome device is between ~8.3 mW and 10 mW (the smaller the size of the actuator is, the smaller the average power consumption is at 150 Hz) and the resonance frequency varies from 2 kHz to ~5.7 kHz which is almost an order of magnitude larger than the frequency range of interest which is shown in figure 4.9. Note that when the user’s finger comes in contact with the trilayer, it may decrease the resonance frequency of the beam due to the added mass.
Table 4.4 A list of dimensions of a trilayer with \( h_e = 110 \, \mu m \) and described otherwise in table 4.3 which can potentially be used in the tactile feedback display shown in figure 4.13(a) along with the corresponding values of its outputs at 150 Hz with a 1 V input sinewave voltage.

<table>
<thead>
<tr>
<th>( h_p ) (( \mu m ))</th>
<th>( L ) (mm)</th>
<th>( f_c ) (Hz)</th>
<th>( F_B ) (mN)</th>
<th>( Y ) (( \mu m ))</th>
<th>( P ) (mW)</th>
<th>( K ) (N/m)</th>
<th>( f_d ) (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>1</td>
<td>58.2</td>
<td>0.11</td>
<td>5.18</td>
<td>8.27</td>
<td>20.8</td>
<td>4.52</td>
</tr>
<tr>
<td>0.35</td>
<td>1.5</td>
<td>37.4</td>
<td>0.059</td>
<td>9.54</td>
<td>8.54</td>
<td>6.16</td>
<td>2.01</td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>36.7</td>
<td>0.14</td>
<td>4.96</td>
<td>9.38</td>
<td>27.3</td>
<td>5.16</td>
</tr>
<tr>
<td>0.7</td>
<td>1.5</td>
<td>27.1</td>
<td>0.077</td>
<td>9.64</td>
<td>9.96</td>
<td>8.08</td>
<td>2.3</td>
</tr>
<tr>
<td>1.05</td>
<td>1</td>
<td>23</td>
<td>0.15</td>
<td>4.49</td>
<td>9.10</td>
<td>33.9</td>
<td>5.73</td>
</tr>
<tr>
<td>1.05</td>
<td>1.5</td>
<td>19.6</td>
<td>0.091</td>
<td>9.07</td>
<td>9.88</td>
<td>10.0</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The last step towards the design optimization is to calculate the vertical displacement of the beam after the application of \( F_u(f) = 10K_u d_u(f) \) to its tip (10 times larger than the minimum detectable force). The resulting displacement has to be larger than the minimum detectable penetration depth as shown in figure 4.9. This is done through ActuaTool in “Frequency Response” mode which also demonstrates the vertical displacement of the beam at a given frequency when a given force is applied to it along with the shape of the beam. Figure 4.15 compares the minimum detectable penetration depth into the skin with the displacement of the tip of encapsulated trilayers with \( h_g = 110 \, \mu m \), \( 0.35 \, \mu m \leq h_p \leq 1 \, \mu m \), and \( L = 1 \, mm \) (half-filled square) and \( L = 1.5 \, mm \) (empty square) and other parameters described in table 4.3 after the application of \( F_u(f) \) to its tip. The corresponding displacements are also demonstrated in table 4.5 for \( h_p = (0.35 \, \mu m, 0.7 \, \mu m, \text{and } 1 \, \mu m) \). It shows the trilayers with the proposed designs can successfully be detected by the human fingertip at frequencies within the range of 30 Hz and 300 Hz which is a common range for vibrotactile displays [106].

4.5 Conclusion
In this chapter, a modification to the already developed electro-chemo-mechanical model of trilayer conducting polymer actuators was carried out which includes taking into account the effect of the non-uniform frequency-dependent distribution of ions throughout the volume of conducting polymers which results in a non-uniform curvature along the length of the device as well as the effect of resistance and area of contact electrode. Accordingly, we demonstrated a new method of displacement and force calculations which results in larger predictions of free bending displacement at frequencies larger than the cut-off frequency of the device and blocking force at all frequencies. Based on the modified model, we created a web-based graphical user-

![Graph](image-url)

**Figure 4.22** Comparison of the minimum detectable penetration in human skin (black diamonds) with the tip displacements of encapsulated trilayers described in table 4.3 with $h_g = 110 \ \mu m$, $0.35 \ \mu m \leq h_p \leq 1 \ \mu m$, and $L = 1 \ mm$ (half-filled square) and $L = 1.5 \ mm$ (empty square) when $F_u(f) = 10K_ud_u(f)$ is applied to its tip (as demonstrated in the inset image).
interface (GUI), named as ActuaTool, to facilitate the study of trilayer conducting polymer actuators and their design for various applications. ActuaTool uses standard web technologies (HTML, CSS, JavaScript) available on all web browsers and JavaScript libraries such as d3.js and twitter bootstrap, making it easily accessible for all the researchers. It works in three modes of operation named as “Frequency response”, “Parameter response”, and “Design”. In “Frequency response” mode, ActuaTool can predict the frequency responses of vertical and lateral tip displacements, blocking force as well as average power consumption, the shape of the beam when a given force is applied to its tip, and its force-displacement graph at a given frequency. In “Parameter response” mode, at a given operation frequency, it predicts the effect of change of one parameter of the device on

Table 4.5 $D_{u(f)}$, the displacement of the beam with specified $h_p$ and $L$ after the application of $F_{u(f)} = 10K_u d_{u(f)}$ to its tip (other parameters are the device are described in table 4.3)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$h_p = 0.35 \mu m$</th>
<th>$h_p = 0.7 \mu m$</th>
<th>$h_p = 1.05 \mu m$</th>
<th>$h_p = 0.35 \mu m$</th>
<th>$h_p = 0.7 \mu m$</th>
<th>$h_p = 1.05 \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>4.73</td>
<td>9.99</td>
<td>10.7</td>
<td>0.96</td>
<td>13.8</td>
<td>16.8</td>
</tr>
<tr>
<td>40</td>
<td>7.73</td>
<td>11</td>
<td>10.4</td>
<td>11.1</td>
<td>18.9</td>
<td>18.8</td>
</tr>
<tr>
<td>60</td>
<td>8.34</td>
<td>9.59</td>
<td>8.48</td>
<td>14.2</td>
<td>17.6</td>
<td>16.2</td>
</tr>
<tr>
<td>100</td>
<td>7.12</td>
<td>6.97</td>
<td>6.09</td>
<td>12.6</td>
<td>13.2</td>
<td>12</td>
</tr>
<tr>
<td>150</td>
<td>5.53</td>
<td>5.13</td>
<td>4.6</td>
<td>9.86</td>
<td>9.68</td>
<td>9.09</td>
</tr>
<tr>
<td>200</td>
<td>4.38</td>
<td>4.02</td>
<td>3.72</td>
<td>7.71</td>
<td>7.58</td>
<td>7.31</td>
</tr>
<tr>
<td>300</td>
<td>2.96</td>
<td>2.74</td>
<td>2.6</td>
<td>4.99</td>
<td>4.86</td>
<td>4.87</td>
</tr>
<tr>
<td>400</td>
<td>4.73</td>
<td>9.99</td>
<td>10.7</td>
<td>0.96</td>
<td>13.8</td>
<td>16.8</td>
</tr>
</tbody>
</table>
the lateral and vertical tip displacements, the blocking force, average power consumption, stiffness, and resonance frequency of the beam. In “Design” mode, ActuaTool provides a list of dimensions for a trilayer with their already set parameters, which generate values of a selected output within a range which the user has previously defined. The three modes of operation of ActuaTool are available through the following links:

- “Frequency response” and “Parameter response” modes:
  https://saeedhebr.github.io/ActuaTool/study/index.html
- “Design” mode:
  https://saeedhebr.github.io/ActuaTool/design/index.html

Then using ActuaTool, we theoretically optimized the design of trilayer conducting polymer actuators to be used in a tactile feedback display. For this application, the trilayer needs to be stiff compared to human fingertip and generate a perceivable displacement in it. Its resonance frequency is also needed to be beyond the perceivable vibration range (< ~500 Hz). Here we proposed using PEDOT:PSS as the conducting polymer and PVDF as the separator layer due to their large Young’s modulus compared to other materials which are commonly used in trilayer CP actuators. We theoretically showed that sub-micron layers of PEDOT:PSS sandwiching a 125 µm thick commercially available PVDF membrane with a length of ~1 mm to 2 mm can generate perceivable displacements in the fingertip and can potentially be used in a tactile feedback display.
Chapter 5: Fabrication and characterization of PEDOT:PSS/ PVDF/PEDOT:PSS trilayers

5.1 Introduction and motivation

So far, the fabrication of trilayer conducting polymer actuators have been demonstrated through several recipes [2], [7], [10], [107]–[109]. Among these, near kHz resonance actuation with ~10 Hz cut-off frequency have been obtained through reducing the thicknesses of the conducting polymer and separator layers down to ~2.2 µm and 7.4 µm, respectively, and the length of the beam to < 1 mm [10]. This fabrication method - although it demonstrated the proof of concept of fast actuation for these devices- is still facing some obstacle to provide a reproducible and scalable recipe so the engineers can reliably apply the resulting devices in real applications.

In this chapter, we demonstrate a new fabrication process for trilayer conducting polymers through using commercially available polyvinylidene fluoride (PVDF) membranes as the separator layer and aqueous dispersion of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) deposited through spray-coating to form the conducting polymer layer. This fabrication process takes advantage of reliable commercially available already-polymerized products and uniformly coated sub-micron films of conducting polymer, which are obtained through spray coating and could eventually lead to the roll to roll fabrication of fast conducting polymer actuators.

5.1.1 Rate limiting factors in trilayer conducting polymer actuators
As discussed in section 4.2.3, there are four mechanisms which basically limit the actuation rate of conducting polymer actuators. These rate-limiting factors include the charge and discharge of the conducting polymer layers via the transport of

1. electrons through the contact between the electrode and the CP layer,
2. electrons along the length of the CP layer,
3. ions through the thickness of the CP layer, and
4. ions through the thickness of the separator layer.

In section 4.2.3, we accordingly introduced four time-constants describing each of the mechanisms mentioned above and defined a rough value of the cut off frequency of the device as 
\( \tilde{f}_c = 1/2\pi \tilde{\tau}_c \), in which \( \tilde{\tau}_c \) is the minimum value among the introduced time-constants. A fast contracting trilayer conducting polymer actuator, in other words, a device with a large cutoff frequency, can be created through the selection of proper materials (conducing polymer, separator, contact electrode as well as the ionic medium) and reducing thicknesses of each of the layers and dimensions of the device. Accordingly, improvements in their speed and strain rate have been achieved through the selection of the electrolyte [17], [88], producing thin film micro actuators [10] and increasing the rate of charge injection through increasing the magnitude of the applied voltage in PPy actuators [110].

Changing the aforementioned parameters to increase the speed of the device may also affect the maximum displacement and blocking force generated by it. Before demonstrating the developed fabrication process and reporting the corresponding results, we study the effect of each of the parameters of the device and its corresponding effect on the output characteristics of the device. We then discuss the pros and cons of different materials which have been so far used
in conducting polymer actuators.

5.1.1.1 Material properties

5.1.1.1.1 Ionic medium

The ionic conductivity of the ionic medium defines the ionic conductivity of the conducting polymer and separator layers and significantly affects the transport of ions throughout the thickness of the device, and hence its speed. In addition to affecting the speed of the device, selection of the ionic medium can influence the strain to charge ratio and hence the strain generated in the CP layer through the size and number of mobile ions [82]. Moreover, its electrochemical window (EW) can limit the operation voltage of the device, if it is smaller than the voltage range over which the conducting polymer layer is stable. Ionic medium in these devices can be a solution of a salt in a polar solvent such as water, propylene carbonate or organic ethers, or an ionic liquid such as EMITFSI.

Aqueous electrolytes have generally a large ionic conductivity; The drawback is that water easily evaporates if the device is not encapsulated. As shown in section 2.3.3, as the solvent evaporates, the viscosity of the electrolyte increases and hence the speed of the device decreases. Moreover, their electrochemical window is small (~1 V), which limits the operation voltage of the device. Other polar solvents with larger vapor pressures such as propylene carbonate (PC) or organic ethers, evaporate more slowly than water, but the ionic conductivity of their solutions are generally smaller than that of water. Ionic liquids own the benefit of having a large electrochemical window (3.5 < EW < 6) [111] and of being non-volatile at room temperature. So, they can solve the problem of solvent evaporation in air if no encapsulation is involved. However, compared to solvent-based electrolytes, they may generate a smaller strain to charge
ratio in the CP layer [88].

5.1.1.1.2 Conducting polymer

Conducting polymer as the active element of these devices can significantly influence their speed and output characteristics. The larger the volumetric capacitance it has, the more charge is stored in them and the larger strain, and hence displacement and blocking force the device can generate [14]. Its electronic and ionic conductivity needs to be high, so it can get charged faster along its length and through its thickness, respectively. Compared to the separator layer, it generally has a more dense structure and hence its ionic conductivity is lower.

Polypyrrole (PPy) is the most studied conducting polymer and its thin films can be obtained through electrochemical polymerization on a conductive surface such as gold. It has the advantage of producing large strains – 5 % typical, and ~40 % in free-standing films [112]. The ionic conductivity of $2.2 \times 10^{-3}$ S/m has been reported for it in a 1 M aqueous solution of NaPF$_6$ [113]. Its thin films with PF$_6$ as the dopant deposited on a gold-coated PVDF membrane showed electronic conductivity of $1.13 \times 10^5$ S/m (though the large electronic conductivity is mainly due to the underlying gold layer). The disadvantage of this polymer is that it is non-soluble and its mechanical properties change significantly with its oxidation state [114]. Moreover, it requires a non-reactive conducting layer such as gold to electrochemically be deposited on. This layer adds cost to the fabrication process and reduces the displacement of the device by increasing its stiffness.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is another conducting polymer which can be formed through chemical and electrochemical polymerization of EDOT. Electronic conductivity of $4.2 \times 10^4$ S/m has been reported for chemically polymerized PEDOT at the presence of
polyethylene glycol methacrylate derivatives (MPEG) (MPEG is washed with methanol after polymerization) [18]. Similar to PPy, PEDOT is insoluble in any solvent but its mechanical properties are less dependent on the oxidation state and, in general, is more stable compared to PPy. It also has the advantages of easier and more controllable synthesis process and higher stability in electrochemical reactions.

poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is obtained when PEODT is chemically polymerized in a poly- (styrenesulfonic acid) (PSS) solution. Here sulfonate anionic groups of PSS are the counterions and balance the positively doped PEDOT. As opposed to other conducting polymers, PEDOT:PSS can form water dispersion and be then later deposited through spin-coating [104], casting [107], spray-coating [115], and inkjet printing [108], etc. By adding some inert solvents such as dimethyl sulfoxide (DMSO) to the PEDOT:PSS aqueous dispersion, it gets secondarily doped, and the electronic conductivity of the resulting PEDOT:PSS film is reported to reach to as high as $8 \times 10^5$ S/m [102] which is close to that of indium tin oxide (ITO) ($~1 \times 10^6$ S/m) - the most widely used transparent conductor [103]. It has a large Young’s modulus of (1 to 3) GPa (depending on the relative humidity of the environment) [89], which can be reduced to 55 MPa through incorporating ionic additives such as LiTFSI, which also helps its electronic conductivity to increase to as high as $7 \times 10^5$ S/m (for freestanding films), making it a promising material towards realizing flexible transparent electronics [104].

5.1.1.3 Separator

The separator layer is an ionically conducting but electronically insulating layer. The larger its ionic conductivity is, the faster the ions can transfer across it and the smaller its electronic
conductivity is, the smaller the leakage current is, and the less power is dissipated.

Polyvinylidene fluoride (PVDF) in the form of commercially available porous membranes has been traditionally used as the separator layer with PPy as the conducting polymer. It is commercially available and has a relatively large Young’ modulus of ~70 MPa [3]. Being a porous membrane, it has an ionic conductivity close to that of the electrolyte [24]. Thin films of PVDF can also be synthesized in the form of solid polymer electrolyte with different thicknesses or mechanical and electrochemical properties [116].

A double network of an ionically conducting polymer such as polyethylene oxide (PEO) and a mechanically robust polymer such as NBR can also be used as the separator layer. As demonstrated in chapter 2, when EDOT is polymerized from the two sides of this film, an interpenetrated polymer network of three polymers, PEO:NBR:PEDOT, is formed which act as the conducting polymer layer. The density of PEDOT decreases through the thickness of the PEO:NBR film and eventually leaves a pure PEO:NBR layer which acts as the separator layer. This non-porous copolymer swells as it stores the ionic medium and has a lower ionic conductivity compared to that of PVDF. Its ionic conductivity is reported to be $5.37 \times 10^{-2} \text{S/m}$ and $7.83 \times 10^{-2} \text{S/m}$ when it is fully soaked with a 1 M solution of Li$^+$TFSI$^-$ in PC and EMITFSI, respectively [40].

5.1.1.4 Contact electrode

The choice of metal electrode is important in these actuators first because the contact resistance between the metal electrode and the conducting polymer can effectively limit the speed of the device and the output characteristics of those which are intrinsically fast, and second, because the metal electrode may react with the electrolyte stored in the device and the
contact resistance further increases. The latter restricts the choices to non-reactive metals and the former further restricts the choices to those which make ohmic contact with the conjugated polymer. The selection of the element for the metal electrode is decided by the work function and how close it is with respect to the HOMO level of the polymer in use. As an example, gold, having a work function of 5.1 eV, is the best choice to achieve an ohmic contact with PEDOT:PSS, which has a HOMO level at 5.1 eV [117]. In addition to that, it is important to make sure the metal electrodes hold the conducting polymer tightly and have a proper contact area.

5.1.1.2 Dimensions of the device

Downsizing the device helps electrons and ions to reach their destination faster as the distance they should take gets shorter. It also reduces the power consumption of the device. Here we briefly investigate the effect of the length of the device and thicknesses of the conducting polymer and separator layers as well as the contact area on the speed and other output characteristics of the device.

5.1.1.2.1 Length of the beam

The shorter the length of the beam is, the faster the electrons can propagate along its length and the faster its curvature becomes uniform along its length. A shorter length beam provides a stiffer structure, a smaller deformation, and a larger force, if the width of the device does not change. Reducing the length of the trilayer beam also shifts its resonance frequency to larger values.

5.1.1.2.2 Thickness of the conducting polymer layer

The thinner the thickness of the conducting polymer layer is, the faster it gets fully charged
through its thickness and reaches its extent. It, however, causes the extent of displacement of the device, the blocking force it generates, and its resonance frequency to decrease.

5.1.1.2.3 Thickness of the separator layer

The thinner the thickness of the separator layer is, the faster the ions transfer across it and move from one CP layer to the other and get charged or discharged and the trilayer bends. Reducing the thickness of the separator layer causes the extent of displacement of the device to increase and its blocking force and resonance frequency to decrease.

5.1.1.2.4 Contact area

The larger the contact area is, the smaller the contact resistance is and the less it affects the speed of the device which also helps the power consumption to reduce.

5.1.2 Challenges in fabrication towards fast trilayer conducting polymer actuators

Realizing fast trilayer conducting polymer actuators requires finely tuning the thicknesses of the conducting polymer and separator layers and micropatterning them. Maziz et al. demonstrated cut off frequency of around 10 Hz and resonance frequency of near 1 kHz for a PEDOT/PEO:NBR/PEDOT trilayer actuator through reducing the thicknesses of the separator and conducting polymer layers down to 7.5 µm and 2.2 µm, respectively, and length and widths of the device down to 690 µm and 45 µm, respectively. Thin films of PEO:NBR separator layers were obtained through spin coating the precursor solution on a glass slide and subsequently polymerizing it using the procedure explained in section 2.2.2. To form a thin layer of PEDOT on the two sides of the separator layer, the freestanding PEO:NBR films were fixed between two frames and swelled with EDOT vapor under a controlled condition. EDOT was then oxidized from the two sides of the separator layer in a 1 M solution of FeCl₃ at 40°C. The thickness of the
PEDOT layer was controlled through the oxidation time. The device was then patterned using photolithography and dry etching and then swelled with EMITFSI as the electrolyte. This method of fabrication, although could demonstrate the proof of concept of fast CP actuators and near kHz resonance, takes about 2 days to be processes and is very difficult to be repeated and in general, has a lot of material waste and is not scalable. The lack of repeatability is mainly due to the non-uniform penetration of EDOT molecules in the PEO:NBR film which subsequently leads to a non-uniform thick film of PEDOT. This is because thin films of PEO:NBR deform as they swell with EDOT and hence different parts of the film get exposed to EDOT vapor differently. Moreover, due to swelling and deswelling in solutions used in photolithography, it is difficult to reliably pattern them to get the desired dimensions.

Aiming to more precisely control the thickness of each of the layers using the same materials, Maziz et al. then developed a novel fabrication method based on sequential spin-coating and polymerization of each of the layers on a silicon wafer and then patterning them using laser micromachining [18]. This method of fabrication despite its moderate control on the thickness of each of the films, still has some disadvantages such as delamination of the films due to small penetration of PEDOT into PEO:NBR layer and significant difference in the electronic conductivities of the two PEDOT electrodes [109]. Moreover, it could not so far demonstrate an improvement in the bandwidth of such actuators; Also, there is a limit in reducing the thickness of each of the layers (to potentially increase the speed of the device), and also is not scalable, both due to the limitations of the spin coating process [109].

Doping PEDOT within a poly- (styrenesulfonic acid) (PSS) solution leads to an aqueous dispersion which can be later deposited through spin-coating, casting, spray coating, inkjet
printing, etc. By adding secondary dopants through adding some inert solvents such as dimethyl sulfoxide (DMSO) or ionic additives such as LiTFSI, both its electronic conductivity and Young’s modulus can be tuned.

There are several reports on the use of PEDOT:PSS in trilayer actuators [107], [108], [118]–[120]. Among those, Ikushima, et al. [119], and Simaite, et al. [107], demonstrated a reproducible fabrication process based on commercially available PVDF membranes and cast aqueous dispersion of PEDOT:PSS. In [107], they functionalized the two surfaces of the PVDF membrane through using argon-plasma-induced surface polymerization of poly- (ethylene glycol) monomethyl ether methacrylate (PEGMA) to make them hydrophilic. PEGMA was deposited on the two sides of the PVDF membrane using spray coating through which its thickness and hence the depth of the hydrophilic layer is defined. PEDOT:PSS aqueous dispersion, secondary doped with 1 vol % of polyethylene glycol (PEG400), was then drop cast and let dry in air in UV-reduced environment for at least 20 h. The same procedure was carried out on the other side of the PVDF membrane to form the second conducting polymer layer which is separated from the first PEDOT:PSS layer by the part of the PVDF membrane which remained hydrophobic. The membranes were then thermally annealed in the oven for 2 h at 70 °C. They showed 2 mm × 1.43 cm actuators with ~20 µm thick films of PEDOT:PSS as the conducting polymer layers, a ~125 µm thick PVDF membrane as the separator, and EMITFSI as the electrolyte, can generate peak to peak displacement of ~1 cm when a 2.25 V sine wave at 0.05 Hz is applied across the two CP layers. The actuator which they fabricated were slow due to the thick layers of PEDOT:PSS.

In this chapter, we present a novel method of fabrication of PEDOT:PSS/PVDF/PEDOT:PSS
trilayers for the purpose of fabricating fast CP actuators. PVDF is selected since its ionic conductivity is higher than solid polymer electrolytes due to its porous structure. PEDOT:PSS is selected since it has a large Young’s modulus and according to figure 4.21, when combined with PVDF membrane can generate a larger displacement compared to other conducting polymers. Moreover, when it is further doped with DMSO or ionic additives, it can provide a large electronic conductivity. More importantly, it is commercially available in the form of an aqueous dispersion, and its films with controlled thicknesses can be obtained through various solution processing methods such as spin coating, spray coating, drop casting, and inkjet printing. Among these methods, spray coating was used in this work since it can provide sub-millimeter thick uniform films of PEDOT:PSS by adjusting the flow rate of the solution and the spraying speed.

In this chapter, all the material properties of the PEDOT:PSS and PVDF membranes which contribute in the output characteristics of the resulting trilayer, such as electrical, electrochemical and mechanical properties of sprayed films of PEDOT:PSS on PVDF and mechanical and electrochemical properties of PVDF are characterized. The fabricated devices were also characterized in terms of their cutoff frequency, frequency response of displacement, resonance frequency, power consumption, and cycle life.

5.2 Experiments

5.2.1 Materials

Polyvinylidene fluoride (PVDF) membranes (hydrophilic, ~125 µm thick, 0.45 µm pore size, MilliporeSigma), PEDOT:PSS ((1.0 to 1.3) wt.% dispersed in water, CLEVIOS PH 1000, Heraeus), Dimethyl sulfoxide (DMSO, ≥ 99.7%, Sigma-Aldrich), 1-Ethyl-3-methylimidazolium Bis(trifluoromethanesulfonylimide (EMITFSI, ≥ 99%, Solvionic), Methanol (CH$_3$OH, ≥ 99.8%,
Sigma-Aldrich).

5.2.2 Trilayer Conducting Polymer actuators fabrication

5% DMSO by volume was added to PEDOT:PSS aqueous dispersion and stirred vigorously for 15 min. It was then loaded into a spray-coating syringe (Hamilton 1025 TLL, 25 ml). Spray-coating was carried out using a Sono-Tek ExactaCoat automatic spray-coating system. As already schematically depicted in figure 3.3, the spraying follows a spiral path with spacing between paths of $d = 2$ mm to deposit PEDOT:PSS aqueous dispersion on the sample. Films of PVDF membrane with the size of 6 cm × 6 cm were fixed on the spray-coating substrate using a metallic frame with the dimensions of 5 cm × 5 cm. The substrate temperature was set at 130ºC to facilitate water evaporation and prevent it from diffusing into the PVDF bulk. Water starts evaporating from the solution shortly after it sits on the PVDF membrane and leaves a thin film of PEDOT:PSS on PVDF membrane. The nozzle to substrate distance, nozzle speed, shaping air pressure and flow rate were set to 9 cm, 20 mm/s, 0.8 kPa and 0.13 ml/min, respectively. 6 set of samples, namely Pn, were prepared through spraying $n$ successive PEDOT:PSS coats with $n$ being equal to 1, 2, 4, 6, 8, and 10, on the two sides of PVDF membranes. The fabricated trilayers were then immersed in EMITFSI as the ionic medium for an adequate amount of time (~3 hours for a 5 cm × 5 cm P10 trilayer, and less for samples with a smaller area or thinner layers of PEDOT:PSS ) to ensure they are fully soaked.

5.3 Results

5.3.1 PEDOT:PSS film characterization

Thickness of the PEDOT:PSS layers spray coated on glass slides were measured using a Bruker Dektak XT profilometer (stylus diameter: 2 µm, force: 0.1 mN) and dispersion of
PEDOT:PSS sprayed on PVDF membrane were analyzed using a Nikon Eclipse LV100 polarized light microscope and an FEI/ Aspex Explorer scanning electron microscope (SEM) which is equipped with an Energy-dispersive X-ray (EDX) spectrophotometer. The samples were cut using a razor blade prior to the SEM and EDX analysis.

Figure 5.1(a) demonstrates the thickness of PEDOT:PSS films deposited on a glass slide versus the corresponding number of spray coats. It shows films as small as ~400 nm thick can be obtained using the spray coating technique, which is the minimum thickness that has ever been reported for the CP layer of a trilayer conducting polymer actuator. It also shows that thickness linearly increases with the rate, $\nu_{hp}$, of 350 nm/ coat. Top view optical images of the trilayers

![Figure 5.1(a)](image.png)

**Figure 5.1 (a) Thickness of PEDOT:PSS doped with DMSO on glass slide versus the corresponding number of coats, and (b) top view optical image of the fabricated trilayers. The underlying texts shows the corresponding number of PEDOT:PSS coats.**
placed on a sheet of paper are shown in figure 5.2(a). The written text underneath each sample indicates the corresponding number of PEDOT:PSS coats on each side of the sample. It shows the trilayers made through one and two coats of PEDOT:PSS on each side (P1 and P2, with an equivalent thicknesses of 400 nm and 650 nm, respectively), provide semi-transparent trilayers. When PEDOT:PSS dispersion is sprayed on a hydrophilic PVDF membrane, it penetrates in the bulk of the membrane through its pores. We set the temperature of the substrate to 130ºC to force water to evaporate fast and avoid a short circuit between the two CP layers. There is anyways a depth through which PEDOT:PSS is dispersed, so its apparent thickness is larger than the thickness of the film deposited on a glass slide. Figure 5.2(a) shows the optical micrograph of the cross-section of a dry PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer made through 10 coats of PEDOT:PSS on each side. The black regions on the two sides of the PVDF membrane are the sprayed PEDOT:PSS. To investigate its penetration depth, an SEM micrograph along with an EDX elemental analysis was carried out. Figure 5.2(b) shows the SEM micrograph of the cross-section of a dry PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer with PEDOT:PSS formed through 10 coats along with the EDX line scan (yellow line) of sulfur distribution along a line in the cross-section of the trilayer before being soaked in the electrolyte. It shows that the density of PEDOT:PSS is maximum at the two outer surfaces and it reduces towards the centre of the device. The depth to which PEDOT:PSS dispersion could penetrate in PVDF is ~15 µm in each side, leaving ~95 µm PVDF with no PEDOT:PSS. According to figure 5.1(a), the same amount of PEDOT:PSS forms a film with a thickness of ~3.5 µm when it is deposited on a glass slide.

5.3.2 Young’s modulus

Young’s moduli of the samples were obtained through stress-strain measurements using a
Figure 5.2 (a) Optical and (b) SEM micrographs of the cross-section (vertical orientation) and EDX line scan (in yellow) of sulfur distribution in the cross-section of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer film before being soaked in the electrolyte. PEDOT:PSS is obtained through 10 spray scans.

Bose ElectroForce®-3100 system in tension mode (a strain of 1% at 0.1 Hz). The width of all the samples was (14.5 ± 0.25) mm and the length which goes under tension was (20 ± 0.25) mm. In each measurement, the sample was unmounted from the measurement instrument and remounted to take into account human errors.

Figure 5.3 shows the stiffness of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers after being fully soaked in EMITFSI as the thickness of PEDOT:PSS layer increases through increasing the number of coats with the rate, $v_{KT}$, of $0.75 \times 10^3$ N/m. The error bars come from four measurements on the corresponding sample as well as the errors in the measurements of the dimensions. As shown in figure 5.3, the stiffness increases linearly as the number of PEDOT:PSS coats increases. The stiffness of the pure PVDF is obtained from the intercept of the linear fit to the data and is equal to $(4.4 \pm 0.15) \times 10^3$ N/m. Its Young’s modulus is then obtained through equation 5.1,
Figure 5.3 Stiffness of PEDOT:PSS/PVDF/PEDOT:PSS trilayers versus number of PEDOT:PSS spray coats. The length and width of the tested samples are 2 cm and 1.43 cm, respectively, and the thickness of the PVDF membrane is 125 µm.

\[ E_g = \frac{K_g \cdot L}{h_g \cdot W} \]  

(5.1)

where \( K_g \) is the estimated stiffness of the PVDF membrane, and \( L, W, h_g \) are its length, width and thickness, which are equal to \((20 \pm 0.25) \text{ mm}, (14.5 \pm 0.25) \text{ mm}, \text{ and } 125 \mu \text{m}, \) respectively.

So, the Young’s modulus of the PVDF separator layer is calculated to be \((49 \pm 2) \text{ MPa}.\) The stiffness of a pure PVDF membrane with the same dimensions as those of the trilayers which are fully soaked with EMITFSI was also measured and is equal to \((7.3 \pm 0.3) \times 10^3 \text{ N/m}.\) This gives a Young’s modulus of \((80.5 \pm 3.5) \text{ MPa} \) which is within the range as what has been reported before [3]. The smaller Young’s modulus obtained from the intercept of the graph shown in figure 5.3 is probably because the PVDF membrane is placed on a hot plate at 130°C during the fabrication process of trilayers which may cause changes in its porous structure and hence its mechanical properties.

In order to find the Young’s modulus of the PEDOT:PSS layer, we used its equivalent
thickness when it is deposited on a glass slide (according to figure 5.1(a), its thickness increases with the rate of 0.35 µm/coat). The stiffness of a three-layer structure, \( K_T \), is equal to,

\[
K_T = K_g + 2K_p.
\]  

(5.2.a)

As the number of PEDOT:PSS coats increases, the stiffness of the beam increases linearly (figure 5.3), due to the increase of the stiffness of the two PEDOT:PSS layers, \( K_p \). Here the stiffness of the PVDF membrane does not undergo any changes; Hence, the rate of change of the stiffness of the CP layer, \( \nu_{Kp} \), is equal to the half of the rate of change of the stiffness of the whole trilayer, \( \nu_{KT} \), as the number of coats of PEDOT:PSS increases. So, \( \nu_{Kp} = \nu_{KT}/2 = 0.375 \times 10^3 \) N/m.

Similar to equation 5.1 for the PVDF membrane layer, we have, \( E_p = \frac{K_p L}{h_p W} \). Hence, by dividing both sides of the equation by the number of PEDOT:PSS coats, we have,

\[
\nu_{Kp} = E_p \frac{W}{L}
\]

(5.2.b)

Hence,

\[
E_p = \frac{\nu_{Kp} L}{h_p W} = \frac{0.375 \times 10^3}{0.35 \times 10^{-6}} \times \frac{2 \times 10^{-2}}{1.45 \times 10^{-2}} = 1.5 \text{ GPa}
\]

(5.2.c)

This value is within the range which has been obtained for PEDOT:PSS before ((0.9 to 2.8) GPa depending on the RH of the environment) [89].

**5.3.3 Electronic conductivity and contact resistance**

Electronic conductivity measurements were carried out on samples using a home-made four-line measurement set up as schematically shown in figure 5.4. The setup was made through depositing 5 nm/ 100 nm thick Cr/ Au films on a glass slide through thermal evaporation and
electron-beam evaporation, respectively, and patterning them using a Teflon tape as a shadow mask. Cr/ Au electrodes have a length equivalent to the width of a glass slide (~2.54 cm) and a width, $d_e$, of (2.7 ± 0.25) mm. The outer and inner electrodes are separated by (3 ± 0.25) mm and (9.7 ± 0.25) mm gaps, respectively. PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers with the size of (14.3 ± 0.25) mm × ~3 cm were cut and placed on the four electrodes. They were then pressed firmly on the electrodes by tightly holding a second glass slide on them using a clamp. A Galvano-dynamic measurement was carried out on the samples by applying a ramp current ranging from -0.5 mA to 0.5 mA with a rate of 4 μA/s, between the two outer electrodes and the change in voltage between the two inner electrodes was measured using a Solartron 1287A Potentiostat/ Galvanostat (Hampshire, UK). In each measurement, the sample was removed from the setup and reloaded to take into account the human errors during the measurement process. All the measurements were carried out subsequently and at room temperature (23 ± 1)°C.

![Figure 5.4 Schematic of the set up used for four-line electronic conductance measurement](image)

Figure 5.4 Schematic of the set up used for four-line electronic conductance measurement

Figure 5.5(a) shows I-V characteristics of the trilayers with different number of coats of PEDOT:PSS. It shows for all the samples the resistance is ohmic. The corresponding slope in each graph, $R_e$, shows the resistance of the PEDOT:PSS film between the two inner Cr/ Au
electrodes with $W \times L = (14.3 \pm 0.25) \text{ mm} \times (9.7 \pm 0.25) \text{ mm}$. Sheet resistance, $R_\square$, is then obtained through equation 5.3,

$$R_\square = R_e \frac{W}{L}. \quad (5.3)$$

Figure 5.5(b) shows the sheet resistance of the trilayers versus number of PEDOT:PSS coats. The sheet resistance of the spray-coated PEDOT:PSS on PVDF membrane decreases from 93.5 $\Omega$/sq for P2 to 7.25 $\Omega$/sq for P10. The errors coming from different measurements on a single sample as well as from the measurement of the dimensions were shown to be very small. Electronic conductivity of PEDOT:PSS film, $\sigma_e$, is obtained through equation 5.4,

$$\sigma_e = \frac{1}{R_\square h_p}. \quad (5.4)$$

Here, similar to the assumption we made in the calculation of Young’s modulus, we use the equivalent thickness of sprayed PEDOT:PSS on a glass slide as $h_p$. The calculated values of

![Figure 5.5 (a) IV characteristics and (b) sheet resistances of PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers at various number of PEDOT:PSS coats. IV characteristics demonstrate an ohmic resistance and sheet resistance decreases as the number of PEDOT:PSS coats increases.](image)
Electronic conductivity and the sheet resistance of sprayed PEDOT:PSS on PVDF membrane along with their values of thickness on a glass slide are summarized in table 5.1. It shows a unique value of electronic conductivity cannot be obtained, and it increases as the number of PEDOT:PSS coats increases. This is mainly because of the porous structure of PVDF membrane which as explained before, let PEDOT:PSS dispersion penetrate it and fill the pores. This means at initial coats of PEDOT:PSS being sprayed on the PVDF membrane, the actual area of the film is larger than the apparent one. As the number of coats increases, these two values get closer to each other since more pores are filled and hence, the calculated electronic conductivity increases.

<table>
<thead>
<tr>
<th>Trilayer</th>
<th>P1</th>
<th>P2</th>
<th>P4</th>
<th>P6</th>
<th>P8</th>
<th>P10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness on glass slide (µm)</td>
<td>0.4</td>
<td>0.65</td>
<td>1.4</td>
<td>2.12</td>
<td>2.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Sheet resistance (Ω/sq)</td>
<td>455</td>
<td>93.5</td>
<td>32.5</td>
<td>17.4</td>
<td>11.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Electronic conductivity (S/m)</td>
<td>$5.5 \times 10^3$</td>
<td>$1.5 \times 10^4$</td>
<td>$2.2 \times 10^4$</td>
<td>$2.7 \times 10^4$</td>
<td>$3.2 \times 10^4$</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>Specific contact resistance (Ωmm$^2$)</td>
<td>$1.95 \times 10^4$</td>
<td>$4.1 \times 10^3$</td>
<td>$5.3 \times 10^2$</td>
<td>$1.75 \times 10^2$</td>
<td>$1.7 \times 10^2$</td>
<td>$3 \times 10^2$</td>
</tr>
</tbody>
</table>

Comparing the calculated values of electronic conductivity in this work with what has been reported for Ppy, PEDOT and PEDOT:PSS before, shows that what is obtained in this work for a single coat of PEDOT:PSS with an equivalent thickness of 400 nm on a glass slide, is similar to what is obtained by Maziz et al. [10] for a 2.2 µm thick PEDOT chemically polymerized in PEO:NBR to form the fastest contracting CP trilayer actuator ever reported. The thickest film of sprayed PEDOT:PSS, with an equivalent thickness of ~3.5 µm on a glass slide, has an estimated electronic conductivity of ~3 times smaller than a that of a 15 µm thick PPy/TFSI electrochemically deposited on a gold-coated PVDF membrane (reported to be $(11.3 \times 10^4$ S/m))
[17], and roughly twice as much as that of a (2.2 ± 0.66) µm thick inkjet-printed PEDOT:PSS film on a PEO:NBR copolymer film (reported to be (1.92 ± 0.18) × 10^4 S/m). Note that the large electronic conductivity reported for PPy is due to the underlying gold layer (a ~6 µm porous structure).

As explained before, gold is the best metal to be used as the electrode for PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuators since it does not react with the electrolyte which the device is working at (here EMITFSI) and its work function is the same as the HOMO level of PEDOT:PSS (both are equal to 5.1 eV [117]). Specific contact resistance of PEDOT:PSS/ gold was measured through comparing the resistance obtained via a four-line measurement and a two-line measurement (between the two inner electrodes) using the same setup. The contact resistance is equal to the difference between the two measured values of resistance times the total contact area (~(80 ± 5) mm^2).

Figure 5.6 shows the average specific contact resistance versus number of PEDOT:PSS coats, demonstrating the contact resistance decreases as more PEDOT:PSS is added. This is because at the initial coats, PEDOT:PSS mostly fills the pores inside and the actual contact area is smaller than the apparent one. As more layers are added, the pores are filled with PEDOT:PSS and the actual contact area increases. The specific contact resistance obtained for P10 trilayer is however larger than what is obtained for P8 and P6. This can be due to the increased surface roughness as more PEDOT:PSS is added which causes the actual contact area to decrease again.

5.3.4 Ionic conductivity

Ionic conductivity measurement was carried out following the procedure described in [24], using an ionic four-channel diffusion set up as schematically depicted in figure 5.7(a). The
Specific contact resistance of PVDF/ PEDOT:PSS/ gold versus number of PEDOT:PSS coats. The contact area is \((80 \pm 5) \text{ mm}^2\).

trilayer samples \((1.5 \text{ cm} \times 1.5 \text{ cm})\), which have already been fully soaked with the electrolyte, were fixed between the two parts of the setup and where then loaded with the electrolyte (here, EMITFSI). The cross-section area through which the ions and solution can transfer from one side to the other is denoted as \(A\) and is equal to 0.65 mm\(^2\). Two carbon paper electrodes of size \(1 \text{ cm} \times 2 \text{ cm}\) were immersed into the solution at the two ends of the setup to serve as the working and counter electrodes and maintain current across the setup. Ag/AgCl reference electrodes (BASi, MF-2021) were placed into the two cannulas to measure the potential at the ends of their extends which are separated by a \((9 \pm 0.5) \text{ mm}\) gap. A Galvanic dynamic measurement was carried out on the samples by applying a ramp current ranging from 0.5 mA to 0.5 mA and a rate of 4 \(\mu\)A/s between the working and counter electrodes (the two outer ones) and measuring the changes in voltage between the two reference electrodes (inner ones), using a Solartron 1287A Potentiostat/ Galvanostat (Hampshire, UK). All the measurements were carried out consequently.
Figure 5.7 (a) Schematic of the setup used for four-probe ionic conductivity measurement, (b) equivalent electric circuit model of the ionic conductivity measurement setup. $R_{ls}$, $R_{ip}$, and $R_{ig}$, are the ionic resistances of EMITFISI between the samples and the closest cannula end, PEDOT:PSS layer and PVDF membrane.

and at room temperature $(23 \pm 1)^{\circ}C$.

Figure 5.7(b) shows the simplified equivalent circuit for the setup which is demonstrated in figure 5.7(a) with a PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer attached to it. $R_{ls}$, $R_{ip}$, and $R_{ig}$, are the ionic resistances of EMITFISI between the sample and the closest cannula end, PEDOT:PSS layer, and PVDF membrane, respectively.

Figure 5.8(a) shows ionic I-V characteristics of the Pn trilayers ($n$ being the number of PEDOT:PSS spray scans on each side of PVDF membrane) through their thicknesses. The error bars come from the 5 to 10 different measurements on each sample without detaching them from the setup. It shows for all the samples the resistance is ohmic, and the corresponding slope in each graph, $R_{i}$, shows the ionic resistance of the solution between the two reference electrodes which are separated through a $(9 \pm 0.5)$ mm gap, $2R_{ls}$, plus the ionic resistance of the tested PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer, $2R_{ip} + R_{ig}$. Figure 5.8(b) shows $R_{i}$ versus number of
Figure 5.8 (a) Ionic I-V characteristics and (b) ionic resistance of PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers through its thickness versus number of PEDOT:PSS coats. $n = 0$ denotes pure PVDF membrane. IV characteristics demonstrate an ohmic resistance which increases as the number of PEDOT:PSS coats increases.

PEDOT:PSS coats. Here $n = 0$ represents PVDF membrane with no PEDOT:PSS sprayed on it.

The ionic resistance of EMITFSI solution, $2R_{iS}$, was also measured through the same method and is equal to $(108 \pm 1.7) \, \Omega$. When the PVDF membrane is attached to the setup ($R_i = 2R_{iS} + R_{ig}$), the ionic resistance slightly increases to $(109.5 \pm 1.2) \, \Omega$, and as 2 coats of PEDOT:PSS are sprayed on each sides of PVDF membrane ($R_i = 2R_{iS} + 2R_{ip,2L} + R_{ig}$), it further increases to $(111.4 \pm 0.65) \, \Omega$, showing a slight increase in the resistance. The added PEDOT:PSS (an equivalent thickness of 0.65 µm on a glass slide) slightly reduces the size of the membrane pores, but it is not enough to make a significant change in their sizes. After spraying further 2 and 4 coats of PEDOT:PSS (equivalent thicknesses of 1.4 µm and 2.12 µm on a glass slide, respectively) on each side of the corresponding PVDF membrane, the ionic resistance of the trilayer significantly increases. This is mainly due to further reduction of the size of the pores on
the two surfaces of the PVDF membrane and eventually their blockage after spraying 6 layers of PEDOT:PSS on each side. After then, increasing the number of PEDOT:PSS layers on the PVDF membrane adds small changes in the ionic resistance of the film. Ionic conductivity of EMITFIS, PVDF membrane and PEDOT:PSS, denoted as \( \sigma_{ls} \), \( \sigma_{lg} \), and \( \sigma_{lp} \), respectively, can be obtained through equation 5.4,

\[
\sigma_{ij} = \frac{\Delta_j}{R_{ij}A}, (j = s, g, p).
\] (5.4)

Here \( \Delta_s \) is the gap between the two cannulas and is equal to \((9 \pm 0.5) \text{ mm}\), \( \Delta_g (= h_g \approx 125 \text{ µm}) \) is the thickness of the PVDF membrane, \( \Delta_p (= 2h_p) \) is estimated to be the equivalent thickness of PEDOT:PSS on a glass slide and \( A (= 0.65 \text{ mm}^2) \) is the cross-section area over which the ionic current is passing. These values along with the calculated ionic conductivity for each element in figure 5.8(b) are summarized in table 5.2. The ionic conductivity of EMITFISI is measured to be \((1.28 \pm 0.07) \text{ S/m} \) which is slightly larger than what is reported in the literature \((0.94 \text{ S/m} [121] \text{ and } 0.84 \text{ S/m} [122])\). The difference can be due to different measurement method or measurement conditions such as the apparatus used and ambient temperature. Also, EMITFISI, being hygroscopic, absorb humidity over time which causes its ionic conductivity to increase \([123]\). The mean value of the ionic conductivity of PVDF membrane soaked with EMITFISI was measured to be \((1.29 \pm 1.58) \text{ S/m}, \) which is slightly larger than that of the pure EMITFISI with a large standard deviation \((> 100\%) \) obtained through 10 measurements. This makes it difficult to rigorously report a value for the ionic conductivity of EMITFISI-soaked PVDF membrane. The measured ionic conductivity for PEDOT:PSS ranges from \((3.04 \pm 0.32) \times 10^{-3} \text{ S/m} \) for P6 to \((1.06 \pm 1.23) \times 10^{-2} \text{ S/m} \) for P2. The large ionic conductivity obtained for P2 is...
again because of the porous structure of PVDF membrane which roughly keeps its porous structure (the size of pores decreases) after spraying 2 coats of PEDOT:PSS on it. When 6 coats of PEDOT:PSS are sprayed, the pores are totally filled and further added layers form a pure film of PEDOT:PSS on PVDF membrane. Although these values are important to know for thin layers of PEDOT:PSS on PVDF membrane, further studies are required to more precisely report a value for the ionic conductivity of a pure film of PEDOT:PSS soaked with EMITFSI.

Table 5.2 Ionic resistance and ionic conductivity of EMITFSI, PVDF, and PEDOT:PSS at various number of layers, soaked with EMITFSI as the electrolyte

<table>
<thead>
<tr>
<th>Sample</th>
<th>EMITFSI (µm)</th>
<th>PVDF</th>
<th>PEDOT:PSS with n number of layers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 2</td>
<td>n = 4</td>
<td>n = 6</td>
</tr>
<tr>
<td>Δ_j</td>
<td>(9 ± 0.5) x10^3</td>
<td>125</td>
<td>2 x 0.65</td>
</tr>
<tr>
<td>Ionic resistance-R_{ij} (Ω)</td>
<td>108 ± 1.7</td>
<td>1.5 ± 2.1</td>
<td>1.9 ± 2.2</td>
</tr>
<tr>
<td>Ionic conductivity (S/m)</td>
<td>1.28 ± 0.07</td>
<td>1.29 ± 1.58</td>
<td>(1.06 ± 1.23) x10^-2</td>
</tr>
</tbody>
</table>

5.3.5 Cyclic voltammetry (CV) measurement

As demonstrated in figure 5.9(a), cyclic voltammetry (CV) measurement was carried out by tightly holding PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers of size 1 cm x 1 cm between two gold electrode foils (99.99 %, 0.127 mm thick, Sigma Aldrich) of the same size and applying a cycling voltage between 0 V and 1 V (ΔV = 1V) with the scan rates, θ, of (0.5, 1, 2, and 5) V/s, each for 5 times, and measuring the current using a Metrohm Autolab® potentiostat/galvanostat. Figure 5.9(b) shows the simplified equivalent electrochemical circuit, modeling the CV measurement demonstrated in figure 5.9(a). R_c is the sum of the contact resistance and any external resistance between the sample and the power supply. R_{ip} and R_{ig}, as described before,
are the ionic resistances of PEDOT:PSS and PVDF layers and \( C_p \) and \( C_{dl} \), represent the capacitance of the PEDOT:PSS layer and double layer capacitance. Figures 5.10(a-c) show the CV curves of P2, P6, and P10 trilayers at four scan rates of (0.5, 1, 2, and 5) V/s. It shows for all the measurements, the resulting CV curves are fairly symmetric and rectangular which indicates that no redox reaction is happening during the charge and discharge of the PEDOT:PSS layers over the applied range of voltage [124]. The slight slope of the graphs after the CP layers are charged indicates the leakage current passing through the PVDF membrane and has a value in the rage of kΩ. By neglecting \( C_{dl} \) (~ 20 µF) compared to \( C_p \), and assuming that the two CP layers are symmetric, \( C_p \) is obtained through the known formula, \( i = C \frac{dv}{dt} \) after the CP layers are charged (and hence the voltage across the capacitors is equal to the applied voltage).

So,

\[
C_p = 2 \frac{\bar{I}}{\bar{\theta}} \tag{5.5}
\]

where \( \bar{I} \) is the peak to peak current obtained from figures 5.10(a-c) divided by 2 and \( \bar{\theta} = \frac{dv}{dt} \)
Figure 5.10 CV curves of trilayers with PEDOT:PSS layers composed of (a) 2 (P2), (b) 6 (P6), and (c) 10 (P10) spray scans of PEDOT:PSS on each side of PVDF membrane. (d) The areal capacitance of trilayers versus number of PEDOT:PSS coats, which varies from 0.5 V/s to 5 V/s. The calculated areal capacitance, $C_A = C_p/A$, with $A$, being the area of the sample which in here is 1 cm$^2$) for each sample is demonstrated in figure 5.10(d) versus number of spray coats. It shows while increasing the scan rate does not have a consistent trend, the areal capacitance increases nearly linearly as the number of coats increases with the rate, $v_{CA}$, of $(0.846 \pm 0.15)$ mF/cm$^2$/coat. Volumetric capacitance is defined as the capacitance per unit volume of conducting polymer material. Similar to the approach we took
to estimate the Young’s modulus of the PEDOT:PSS on PVDF membrane, we have,

\[ C_V = \frac{\nu_{CA}}{\nu_{hp}}, \]

and hence, \( C_V = (24.2 \pm 0.4) \text{ F/cm}^3 \) which is within the range that has been obtained previously for PEDOT:PSS \[125\]. The mass added to the PVDF membrane per coat of PEDOT:PSS is \((42 \pm 2) \mu \text{g/cm}^2\); Hence, the specific capacitance per grams of PEDOT:PSS is \((201 \pm 3) \text{ F/g}\), which is again within the rage that is already reported in the literature \((193 \text{ F/g in [108]})\).

5.3.6 PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer characterization

A sine wave voltage was applied to the two conductive sides of the trilayer through gold electrodes using a Solartron 1287A Potentiostat/Galvanostat, Hampshire, UK, combined with a Solartron 1260A Frequency Response Analyzer. All the measurements were carried out at room temperature \((22 \pm 1)\degree\text{C}\). The trilayers were held so they actuate horizontally, and their top view actuation was captured using a Nikon D5100 DSLR Camera. Displacement was measured using a laser displacement sensor (Keyence LK-G32, repeatability of 50 nm) by illuminating the laser on a point close to the tip of the trilayer and measuring the excess of distance the laser travels to reach the trilayer surface as it actuates.

5.3.6.1 Effect of voltage on the displacement of trilayer actuators:

Before reporting the frequency response of actuation of the trilayer actuators, we investigated the maximum operation voltage at which the device does not undergo electrochemical degradation. Figure 5.11 (a) demonstrates displacement of the tip of a PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuator \(L = (10.5 \pm 0.25) \text{ mm}, L' = (10 \pm 0.25) \text{ mm}, W = (2 \pm 0.25) \text{ mm}\), with PEDOT:PSS layers obtained through 10 spray coats (P10 trilayer), versus the amplitude of
Figure 5.11 (a) Displacement and (b) impedance magnitude of a PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuator (P10) versus the amplitude of the applied sine wave voltage. The amplitude of the applied voltage was first increases (orange dots) and then decreases (green dots) to evaluate the electrochemical degradation of PEDOT:PSS.

The applied sine wave at 0.1 Hz, increasing from 0.2 V to 3 V with 0.2 V steps (orange upward triangle dots) and then decreasing from 3 V to 0.2 V with 0.4 V steps (green downward triangle dots). It shows the actuator’s displacement starts increasing linearly as the voltage increases from 0.2 V to 1 V. The rate of displacement increase versus voltage then decreases as it further increases to 1.4 V. Further increase of the voltage to 3 V, causes the displacement to decrease. After then, as the voltage decreases, trilayer’s displacement decreases as expected but the measured values of displacement are smaller than what was measured before which suggests some permanent degradation might have taken place in the PEDOT:PSS layer. To verify that, the magnitude of the impedance of the trilayer was compared as the magnitude of applied sine wave voltage ($f = 0.1$ Hz) varies. As shown in figure 5.11(b) (orange triangular dots for the increasing voltage), the impedance of the device stays within 95% of its initial value as long as the
amplitude of the applied voltage does not exceed 1 V. It then increases as the voltage increases. The increase in the impedance of the device can be due to the increase of its electronic conductivity as it gets more oxidized. As the voltage decreases, the trilayer’s impedance decreases (green triangular dots for decreasing voltage). However, similar to the trilayer’s displacement, the measured value of impedance at each voltage is smaller than what was measured before, which confirms overoxidation of PEDOT:PSS film that leads to an irreversible electrochemical degradation in it. The applied voltage in the rest of the experiments which are carried out in this chapter is selected to be 1 V to avoid the electrochemical degradation in the samples.

5.3.6.2 Actuation

Figures 5.12(a-e) show the top view optical image of the extent of displacement of the P10 trilayer through the application of a sine wave voltage with an amplitude of 1 V and frequencies of 0.1 Hz, 1 Hz, 10 Hz, 80 Hz, and 100 Hz. For figures 5.12(a-c), the images are overlaid to show the full extent of deflection at each extent of the applied voltage. The width of the device, $W$, is $(2 \pm 0.25)$ mm and as indicated in figure 5.12(e), its length, $L$, is $(10.5 \pm 0.25)$ mm. The area under the gold contacts, $A_c$, is $6 \text{ mm}^2$. From figure 5.11(a-e), the actuation of the device is fairly symmetric which indicates the symmetric deposition of the two layers of PEDOT:PSS. The displacement of the trilayer close to its tip ($L' = (10 \pm 0.25)$ mm, as shown in figure 5.12(e)) is demonstrated in figures 5.12(f-j) (gray). A sine wave function with the same frequency as that of the applied voltage was fitted to each of the graphs (red line) which indicates that the deflection follows the shape of the applied voltage (there is a phase difference between the applied voltage and the displacement as will be demonstrated in figure 5.13(b)). The y-axis of all the graphs is
Figure 5.12 Top view optical images of the peak to peak actuation of a PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuator (P10), operating through the application of a sine wave voltage with amplitude of 1 V and frequencies of (a) 0.1 Hz, (b) 1 Hz, (c) 10 Hz, (d) 80 Hz, and (e) 100 Hz, respectively. The length, $L$, and width, $W$, of the device are $(10.5 \pm 0.25)$ mm and $(2 \pm 0.25)$ mm, respectively. The corresponding displacement of a point on the trilayer located at a length, $L' = (10 \pm 0.25)$ mm from its fixed end (indicated with red arrow in each graph) when the device is operated through the application of a sine wave voltage with amplitude of 1 V and frequencies of (f) 0.1 Hz, (g) 1 Hz, (h) 10 Hz, (i) 80 Hz, and (j) 100 Hz, respectively. The red lines in is a sinusoidal curve fitted to the measured data (gray).

the same as the one shown in figure 5.12(f). As expected, the displacement of the actuator decreases as the frequency of the applied voltage increases. At ~80 Hz, the first mode mechanical resonance occurs, and displacement increases (figure 5.12(i)). As the frequency of the applied voltage further increases to 100 Hz, displacement drastically decreases (figure 5.12(j)).

5.3.7 Displacement frequency response versus PEDOT:PSS thickness

The frequency response of displacement of P2, P6, and P10 trilayers, close to their tip
\( L' = (10 \pm 0.25) \text{ mm} \) with 2, 6 and 10 coats of PEDOT:PSS, respectively, are demonstrated in figure 5.13(a). The width of the device, \( W \), and its length, \( L \), are \( (2 \pm 0.25) \text{ mm} \) and \( (10.5 \pm 0.25) \text{ mm} \), respectively, and the area under the gold contacts, \( A_c \), is \( 6 \text{ mm}^2 \). They show for all the three trilayers, as the frequency increases from 0.1 Hz, the displacement initially stays almost unchanged. It then starts decreasing (at its cut-off frequency) and as the frequency of the applied voltage reaches the mechanical resonance of the beam, a peak in displacement is observed. As the frequency further increases, displacement decreases drastically similar to the vibration of a free cantilever beam. The Bode magnitude and phase plot set of the impedance of P2, P6, and P10 trilayers are demonstrated in figure 5.13(b,c), respectively over the frequency range between 0.1 Hz and \( 10^3 \text{ Hz} \). For all devices, at high frequencies, the phase of impedance is close to zero which indicates a resistive behavior. The magnitude of the impedance at high frequencies indicates the sum of the ionic resistance of the separator layer, the electronic resistance of the two PEDOT:PSS layer and any resistance due to its contact with gold and the wires attached to the device. From figure 5.13(b), as the thickness of PEDOT:PSS increases, the resistance at high frequencies (close to 1 kHz) increases which is due to the decrease of the electronic conductivity of the PEDOT:PSS layer as discussed in section 5.3.3. As the frequency of the applied voltage decreases, the impedance phase starts decreasing which indicates the PEDOT:PSS layers are getting charged and discharged and the impedance is becoming more capacitive. As the impedance phase reaches \(-45^\circ\) (cut off frequency), the device is half resistive and half capacitive. As the frequency further increases, the impedance magnitude further increases, and the phase gets closer to \( 90^\circ \). It, however, never reaches that phase (i.e. the device never shows a purely capacitive behavior) since the separator layer is not a pure insulator and as
Figure 5.13 (a) Frequency response of the tip displacement and the Bode (b) magnitude and (c) phase plots of the impedance of P2, P6, and P10 trilayers 0.5 mm away from their tips. ($W \times L = (2 \pm 0.25) \text{ mm} \times (10.5 \pm 0.25) \text{ mm}$)

also observed in CV graphs, it has an electronic resistance within the range of kΩ. The larger phase observed for the P10 trilayer is due to the smaller electronic resistance it has which along with the series electronic resistance of the separator layer and the wires, makes the resistive part of the impedance at low frequencies.
5.3.8 Strain and Strain to charge ratio

Displacement of the tip of the trilayers when a sine wave voltage with an amplitude and a phase of 1 V and 0.1 Hz, respectively, was applied to the two gold electrodes, was measured through the same method as explained in section 5.3.6.1. The length, \( L \), and width, \( W \), of all the trilayers, are \((10.5 \pm 0.25)\) mm and \((2 \pm 0.25)\) mm, respectively, and the length at which the laser is illuminating and the displacement is measured, \( L' \), is \((10 \pm 0.25)\) mm.

Figure 5.14(a) demonstrates the measured extent of displacement of the tip of the trilayers (half of the peak to peak displacement as demonstrated in figure 5.13(a)) versus number of PEDOT:PSS coats. It shows, as expected, as more PEDOT:PSS coats are added, the extent of displacement of the device increases.

As discussed in Appendix C, for a fully actuated beam, curvature, \( \kappa \), is uniform along the length of the trilayer and is obtained through the equation,
\[
\kappa = \frac{2D}{D^2 + L'^2}.
\] (5.7)

Moreover, as discussed before in chapter 2, equation 4.6 is simplified to equation 2.2, and hence the strain induced to the CP layer can be calculated through equation 5.8,

\[
\epsilon = \frac{Dh_p(nm^3 + 6m^2 + 12m + 8)}{6(m + 1)(D^2 + L'^2)},
\] (5.8)

where \(m = h_g/h_p\) is the ratio of the separator to active polymer layer thicknesses, and \(n = E_g/E_p\) is the ratio of their Young’s moduli. Strain to charge ratio, \(\alpha = \epsilon/(C_V V)\) is then equal to,

\[
\alpha = \frac{Dh_p(nm^3 + 6m^2 + 12m + 8)}{6(m + 1)(D^2 + L'^2)C_V V},
\] (5.9)

in which \(C_V\) as discussed in section 5.3.5, is equal to 24.2 F/cm\(^3\), and \(h_p\) and \(h_g\) were assumed to be equal to the thickness of PEDOT:PSS films when sprayed on a glass slide (figure 5.1), and 125 µm, respectively. Measurement of \(E_p\) and \(E_g\) were also demonstrated in section 5.3.2. The calculated differential free strain (\(= 2 \epsilon\)), which is electrochemically induced in PEDOT:PSS with EMITFSI as the electrolyte, along with the corresponding strain to charge ratio for trilayers with PEDOT:PSS layers obtained through different number of spray coats are summarized in table 5.3. It shows, as the thickness of PEDOT:PSS increase, the corresponding obtained value for the strain to charge ratio increases. These values are within the range of the reported values for the strain to charge ratio of conducting polymers [82]. The measured values obtained here can be used for further the design of these actuators. However, further experiments are required to obtain a unique value of strain to charge ratio of PEDOT:PSS with EMITFSI as the electrolyte.
Table 5.3 Calculated strain to charge ratio, free strain, and external strain \((L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm})\)

<table>
<thead>
<tr>
<th>Trilayer name</th>
<th>P1</th>
<th>P2</th>
<th>P4</th>
<th>P6</th>
<th>P8</th>
<th>P10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain to charge ratio (mm(^3)/C)</td>
<td>0.012</td>
<td>0.017</td>
<td>0.077</td>
<td>0.098</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Differential free strain (%)</td>
<td>0.056</td>
<td>0.083</td>
<td>0.37</td>
<td>0.48</td>
<td>0.54</td>
<td>0.63</td>
</tr>
<tr>
<td>Differential external strain (%)</td>
<td>0.019</td>
<td>0.042</td>
<td>0.25</td>
<td>0.36</td>
<td>0.41</td>
<td>0.48</td>
</tr>
</tbody>
</table>

In many former publications on these types of actuators, by mistake, the bending strain at the top surface of the trilayer was reported as the “free strain” induced to the CP layers as ions are inserted in them or repelled from them, and the strain to charge ratio was calculated according to that. Here, we name this bending strain as the “external strain”, which is obtained through the equation,

\[
\varepsilon_{ex} = \frac{kh}{2},
\]

where \(h\) is the total thickness of the beam and for the case of an unencapsulated trilayer is equal to \(2h_p + h_g\). The external strain can practically be an indication of the deflection of a trilayer with a known thickness and is related to the free strain which is electrochemically induced to the CP layer through the equation,

\[
\frac{\varepsilon_{ex}}{\varepsilon} = \frac{h}{h_p} \frac{6(m + 1)}{nm^3 + 6m^2 + 12m + 8},
\]

The calculated differential external strain \((= 2 \varepsilon_{ex})\) for different devices are also demonstrated in table 5.3.

5.3.9 Resonance frequency and damping ratio

The damping ratio of the trilayer was measured by applying a small deflection to the tip of the
actuator beam and measuring its displacement. The beam starts to resonate with an angular
frequency of $\omega_d = 2\pi f_d$, and a decaying amplitude with time, which is proportional to

$$e^{-\frac{\zeta}{\sqrt{1-\zeta^2}}\omega_d t}$$

Here $\zeta$ is the damping ratio which depends on the medium in which the beam is resonating [85]. The measurement was carried out on all the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers with the floating length, $L$, and width, $W$, of $(10.5 \pm 0.25)$ mm and $(2 \pm 0.25)$ mm, respectively. Displacement was measured through the same method as explained in section 5.3.7 at length, $L'$, of $(10 \pm 0.25)$ mm.

Figure 5.15(a) shows free vibration of the P10 trilayer. The angular resonance frequency was obtained via the time between every two adjacent peaks ($\tau_d = 2\pi / \omega_d$), and the damping ratio, $\zeta$, was obtained through the decaying rate of the exponential functions which are fitted to the peaks and valleys of the displacement. The damping ratios of the Pn trilayer cantilever beams ($n = 1, 2,$

![Figure 5.15 Free vibration of P10 trilayer beam ($L \times W = (10.5 \pm 0.25)$ mm $\times (2 \pm 0.25)$ mm)](image)
6, 8, 10, indicating the number of sprayed PEDOT:PSS coats) are provided in table 5.4. It shows that the damping ratio slightly decreases as the thickness of the PEDOT:PSS layers increases. The values are, however, fairly small (< 0.1) which indicates a small mechanical damping and explains the sharp resonance peaks observed in the graphs demonstrated in figure 5.13(a).

The resonance frequency of the trilayers were also calculated from the free vibration test (figure 5.15) and was compared with the ones obtained through the frequency response of the displacement of the trilayers (as demonstrated for P2, P6, and P10 in figure 5.13(a)) and equation 4.13. Similar to the other measurements explained in this chapter, \( h_p \) and \( h_g \) were assumed to be equal to the thickness of PEDOT:PSS layer when sprayed on a glass slide through the same number of coats (figure 5.1), and 125 \( \mu \text{m} \), respectively. Measurement of \( E_p \) and \( E_g \) were also demonstrated in section 5.3.2. The values of the measured and calculated resonance frequencies are summarized in table 5.4 and also compared in figure 5.16. The errors come from the error in the measurements of frequency and dimensions of the device. It shows the resonance frequency of the trilayer actuator is well close to the resonance frequency of the free vibrating trilayer beam and ActuaTool can fairly predict their values through the assumptions made on the thicknesses of the PEDOT:PSS and PVDF layers.

<table>
<thead>
<tr>
<th>Trilayer name</th>
<th>P1</th>
<th>P2</th>
<th>P6</th>
<th>P8</th>
<th>P10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damping ratio ( (\zeta) )</td>
<td>0.061</td>
<td>0.062</td>
<td>0.055</td>
<td>0.054</td>
<td>0.04</td>
</tr>
<tr>
<td>Resonance frequency</td>
<td>Free vibration</td>
<td>41.8</td>
<td>43</td>
<td>58.8</td>
<td>64.1</td>
</tr>
<tr>
<td></td>
<td>Actuation</td>
<td>41.5 ± 0.7</td>
<td>43 ± 1</td>
<td>58 ± 1</td>
<td>60 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>ActuaTool</td>
<td>40.8 ± 2.8</td>
<td>45 ± 3.1</td>
<td>64.1 ± 4.4</td>
<td>71.6 ± 4.9</td>
</tr>
</tbody>
</table>

Table 5.4: Electronic characteristics of sprayed PEDOT:PSS on PVDF membrane with gold as the electrode \((L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm})\)
Figure 5.16 Resonance frequency of the Pn trilayer actuators versus $n$, being the number of PEDOT:PSS coats. The values were obtained through the free vibration (black triangular dots), actuation (red circular dots), and ActuaTool (green diamond dots).

5.3.10 Displacement versus length of the trilayer

Figure 5.17 shows the frequency response of the tip displacement of the P10 trilayer with the width of $(2 \pm 0.25)$ mm and lengths of $(10.5 \pm 0.25)$ mm, $(7.5 \pm 0.25)$ mm, and $(4.5 \pm 0.25)$ mm when a sin wave voltage with an amplitude of 1 V is applied. For each trilayer, the laser was illuminating on a point on the trilayer which is $\sim 0.5$ mm away from its tip.

As expected, the extent of displacement of the trilayer (here the displacement at 0.1 Hz) decreases as the length of the beam decreases. The resonance frequency of the beam increases from $(80 \pm 2.5)$ Hz to $(140 \pm 5)$ Hz when its length decreases from $(10.5 \pm 0.25)$ mm to $(7.5 \pm 0.25)$ mm. These values are the same as what is measured through the free vibration test as discussed in section 1.3.9 (80.8 Hz and 138 Hz, respectively) and close to the values which are estimated using ActuaTool ($(78.4 \pm 5.3)$ Hz and $(150 \pm 10)$ Hz. As the length of the device further decreases to $(4.5 \pm 0.25)$ mm, two peaks in the tip displacement of the actuator are
observed, one at 280 Hz and the other one at 450 Hz. The one predicted using ActuaTool is
~(410 ± 50) Hz, also the frequency response does not have the regular shape of a resonating
beam close to its resonance frequency. We could not figure out the reason behind this behavior
considering the scope of the project and further studies are required to understand it.

Figure 5.17 Peak to peak displacement of the P10 actuator with width, \( W \), of \((2 ± 0.25)\) mm and length, \( L \), of
\((10.5 ± 0.25)\) mm, \((7.5 ± 0.25)\) mm, and \((4.5 ± 0.25)\) mm. The laser is illuminating on the trilayers ~0.5 away
from their tips.

5.3.11 Cutoff frequency

As defined in section 4.2.3, for trilayer conducting polymer actuators, the cutoff frequency is
the frequency at which the trilayer bends to \(1/\sqrt{2}\) of its maximum deflection. ActuaTool predicts
this frequency by using the frequency response of the tip displacement of the beam. For an RC
electronic circuit, the cutoff frequency is defined as the frequency at which the impedance phase
of the circuit is 45° (i.e., the frequency at which the circuit is half resistive and half capacitive). Using these two definitions, cutoff frequency of trilayer actuators with total length of (10.5 ± 0.25) mm and width of (2 ± 0.25) mm were calculated through the peak to peak displacement frequency response and their corresponding Bode phase plots of the trilayer actuators, demonstrated for P2, P6 and P10 in figures 5.13 (a) and 5.13 (c), respectively are summarized in table 5.5 for the Pn trilayers (n being the number of PEDOT:PSS coats on each side of the PVDF membrane of the corresponding trilayer). To evaluate the rate-limiting factor for each of the Pn trilayers, the four cutoff frequencies based on the rate limiting factors described in section 4.2.3, were also calculated using the measured values of the volumetric capacitance, the electronic and ionic conductivities of the PEDOT:PSS layer, the ionic resistance of the PVDF membrane, as well as the contact resistance between the PEDOT:PSS and gold electrode. The calculated frequencies are summarized in table 5.5 and the values which roughly

<table>
<thead>
<tr>
<th>Trilayer name</th>
<th>Predicted cutoff frequency by ActuaTool</th>
<th>Measured cutoff frequency through the Bode phase plot</th>
<th>Measured cutoff frequency through the displacement frequency response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting frequency by the</td>
<td>Predicted cutoff frequency by ActuaTool</td>
<td>Measured cutoff frequency through the Bode phase plot</td>
<td>Measured cutoff frequency through the displacement frequency response</td>
</tr>
<tr>
<td>electronic resistance of PEDOT:PSS</td>
<td>0.37</td>
<td>0.99</td>
<td>1.79</td>
</tr>
<tr>
<td>ionic resistance of PEDOT:PSS</td>
<td>565*</td>
<td>144</td>
<td>4.57</td>
</tr>
<tr>
<td>ionic resistance of PVDF membrane</td>
<td>318</td>
<td>182</td>
<td>60.7</td>
</tr>
<tr>
<td>contact resistance between PEDOT:PSS and gold</td>
<td>1.4</td>
<td>3.2</td>
<td>25.2</td>
</tr>
</tbody>
</table>

* The ionic resistivity of PEDOT:PSS in P1 trilayer was assumed to be a value between the that of the P2 and the ionic conductivity of PVDF
define the cutoff frequency of the equivalent electronic circuit of the trilayer are bolded. The predicted values of cutoff frequency by ActuaTool are also included in table 5.5.

It shows that for all the trilayers, the actuation speed is mainly limited due to the large electronic resistance of the ~10.5 mm long PEDOT:PSS layer. This suggests reducing the length of the device may lead to a larger cut off frequency. However, for P6, P8 and P10 trilayers, the ionic resistance of the PEDOT:PSS layer also limits the actuation speed and does not let the cutoff frequency of the device to exceed a certain value, even if the length is reduced. For P1 and P2, the large contact resistance between the corresponding PEDOT and gold contact electrodes also limits the speed of the device and reducing the length of the device would not be effective unless the contact area is increased.

The calculated values of the cutoff frequency through using ActuaTool, the frequency response of displacement, and the corresponding Bode phase plots are compared versus number of sprayed coats of PEDOT:PSS in Pn trilayers and demonstrated in figure 5.18. It shows that the predicted values by ActuaTool are slightly larger than those which are obtained through their displacement frequency response. This is because, as shown in figures 5.12 (a-e), only when the device actuates at 0.1 Hz, the laser is pointing at the tip of the beam. The smaller the displacement of the trilayer actuator is (i.e., the larger the actuation frequency is before it reaches the resonance), the smaller the measured value is compared to the displacement of the tip of the actuator beam which ActuaTool predicts and accordingly predicts the corresponding cutoff frequency. Hence, the predicted values are slightly larger than what the measurement through displacement frequency response provides.
According to figure 5.18, the calculated values of the cutoff frequency through the Bode phase plots of the impedance of the devices are generally larger than those predicted by ActuaTool or calculated using the displacement frequency response. This difference is more distinguished in trilayers with thinner layers of PEDOT:PSS in which the rate is not limited by the ionic resistance of the CP layer through its thickness. In these devices, as demonstrated in table 5.5, there is a large difference between the limiting frequencies due to the migration of ions through the thickness of the PEDOT:PSS layer and the propagation of the electrons along its length which suggests that the trilayer gets charged faster through its thickness than along its length. Comparing the Bode phase plots of P2 and P10 trilayers, as demonstrated in figure 5.13(b), shows that the impedance phase of P2 trilayer changes in two steps over the range of the swept frequency, each of which corresponds to one of the rate-limiting factors mentioned above.

For an electrochemical device such as a supercapacitor in which the total amount of charge
stored in the device is important, the cutoff frequency is obtained through the Bode phase plot of the impedance of the device. However, when it comes to actuation and the stored charge is to make a change in the shape of the device, the distribution pattern of charges and hence strain throughout the volume of the PEDOT:PSS layers also determines the output characteristics (i.e., deflection) of the tip of the device and the frequency at which it rolls off.

As mentioned before, for P1 and P2 trilayers, it is expected that larger cutoff frequencies be obtained by increasing the contact area and reducing the length of the device. The impedances of the Pn trilayers which are sandwiched between the two gold foils (similar to the CV measurement setup as shown in figure 5.9(a)), were measured at 1 V and were demonstrated in figure 5.19 to evaluate the extent to which the cutoff frequency of the device reaches using these devices, if the effect of electronic resistance of the PEDOT:PSS layers are eliminated. It shows a

![Figure 5.19](image)

Figure 5.19 (a) Bode phase plot of the impedance of 1 cm × 1 cm PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers (denoted as Pn, n being number of PEDOT:PSS spray scans) sandwiched between two gold foils. (b) Cutoff frequency obtained through the Bode phase plot of impedance versus number of PEDOT:PSS coats in the corresponding trilayer.
cutoff frequency as large as ~70 Hz can possibly be obtained through reducing the length of the trilayers for P1 trilayer.

### 5.3.1 Power consumption

As explained previously in section 4.2.5, the average power consumption of the trilayers can be obtained through knowing the magnitude and phase of the impedance of the trilayers. Figure 5.20 shows the power consumption versus frequency for P2, P6 and P10 trilayers with $L \times W = (10.5 \pm 0.25) \times (2 \pm 0.25)$ mm$^2$ and $A_c = (6 \pm 1)$ mm$^2$. It shows as the number of PEDOT:PSS coats increases (i.e. $n$ increase), the power consumption increases. At lower frequencies, smaller power is consumed, since, as shown in figure 5.13(c), the devices are more capacitive ($\cos(\angle Z_T(f)) \approx 0$). The power loss increases as the frequency increases and reaches a plateau at high frequencies where the device is nearly purely resistive ($\cos(\angle Z_T(f)) \approx 1$) (figure 5.13(c)). So far, there has been no report on the average power consumption of these

![Figure 5.20 Resonance frequency of the Pn trilayer actuators versus $n$, being the number of PEDOT:PSS coats ($L \times W = (10.5 \pm 0.25)$ mm $\times (2 \pm 0.25)$ mm).](image)
types of actuators in the literature, so we could compare the results obtained here with those of other similar trilayer actuators. However, due to the large electronic and ionic conductivities obtained in this work, considering the size of the trilayers, the power consumption in the devices presented in this work probably have a lower power consumption compared to others.

5.3.2 Cycle life

Cycle life of the P10 trilayer \((L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm})\) was measured through the application of a sine wave with an amplitude of 1 V and a frequency of 2 Hz to its two sides and measuring its displacement over time through the same method as explained in section 5.3.6.1. Figure 5.21 (red line) shows the displacement of the device \((10 \pm 0.25) \text{ mm}\) away from its fixed end during \(> 7 \text{ h}\) (equivalent of \(5 \times 10^4\) cycles) actuation, normalized by the initial displacement of the trilayer beam which demonstrates \(~15\%\) decrease in the displacement during this period. The admittance of the device normalized by its initial value is also demonstrated in figure 5.21 (blue line) showing a similar behavior as the displacement. Note that since PEDOT:PSS has a very large Young’s modulus compared to the PVDF membrane (~30 times larger), a large change in its mechanical properties is needed to effectively change the displacement of the device. Also note that the power consumption in the device at 2 Hz is very small (~ 4 mW, according to figure 5.21) and considering the thickness of the device and the thermal diffusivity of polymers \((10^{-3} \text{ cm}^2/\text{s}\ [126])\), the generated heat will be transferred to the surrounding air. However, the PEDOT:PSS may electrochemically degrade over time and cause its volumetric capacitance or strain to charge ratio to decrease. The change in admittance and hence displacement can also be due to the delamination of PEDOT:PSS over time, although no visible signs of delamination were observed after \(5 \times 10^4\) cycles of actuation at 2 Hz.
Figure 5.21 Displacement and admittance of P10 trilayer ((\(L \times W = (10.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm})\)) versus time normalized by the corresponding initial values as indicated in the legend. The input voltage is a sine wave with an amplitude and frequency of 1 V and 2 Hz, respectively. The distance at which the displacement was measured is (10 \pm 0.25) mm away from the fixed end of the device.

5.3.3 ActuaTool prediction vs measurement

Figure 5.22 compares the free bending tip displacement of P10 actuator (\(L \times W = (7.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm}\)), predicted by ActuaTool (black line) and the measured using laser displacement sensor (pink diamond dots) as described in section 5.3.6.1. The measurement was carried out at \(L' = (7 \pm 0.25) \text{ mm}\). The amplitude of the sine wave input voltage was 1 V. It shows ActuaTool can fairly predict the tip displacement up to frequencies below the resonance frequency of the beam. Note that the predicted values by ActuaTool are all at the tip of the beam and hence are larger than the measured ones, specially at larger frequencies, whereas the laser illuminates at the tip of the beam only when the device is fully actuated. As the frequency increases, the displacement decreases, and the laser measures the displacement of the beam at a...
point further from the tip of the beam, hence the measured values are smaller than what ActuaTool predicts.

Figure 5.22 Measured peak to peak displacement of P10 trilayer actuator ($L \times W = (7.5 \pm 0.25) \text{ mm} \times (2 \pm 0.25) \text{ mm}$) (7 ± 0.25) mm away from the fixed end of the trilayer (pink diamond dots) and the tip displacement of the beam with the same geometry predicted by ActuaTool (black line). The input voltage is a sine wave with amplitude of 1 V.

5.4 Conclusion

Uniformly thick films of PEDOT:PSS doped with DMSO with thicknesses as small as 400 nm were obtained through spray-coating technique. Thicker films of PEDOT:PSS can be achieved through increasing the number of coats or the flow rate of the sprayed PEDOT:PSS dispersion. Using this technique, PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuators with controlled thicknesses of PEDOT:PSS/ DMSO were fabricated. A thorough study on the electrical, electrochemical and mechanical properties of each of the layers, which affect the output characteristics of these types of actuators, was carried out on the fabricated trilayers with various amount of PEDOT:PSS on each side of a PVDF membrane with an equivalent thickness.
on a glass slide ranging from 0.4 µm to 3.5 µm. In addition to the ability to control the thickness of the deposited PEDOT:PSS, these trilayers benefit from a large ionic conductivity that the porous PVDF membrane and the small thicknesses of PEDOT:PSS offer (close to that of the electrolyte and ~0.01 of it for PVDF membrane and PEDOT:PSS layer obtained through 2 sprayed coats), and the large electronic conductivity of PEDOT:PSS (as high as $4 \times 10^4$ S/m for PEDOT:PSS layer obtained through 10 sprayed coats), thanks to the added DMSO which secondarily dopes PEDOT. As the thickness of the PEDOT:PSS on PVDF membrane increases, its ionic conductivity decreases, and electronic conductivity increases. This is because at small thicknesses, the PVDF pores on its two surfaces are not yet blocked and ions can freely move through the PEDOT:PSS dominated layers. As the thickness of PEDOT:PSS increases, the pores get filled which makes it difficult for the ions to move across it. This is however accompanied by the decrease of the actual surface area of the film, which causes the measured electronic conductivity to increase.

A resonance frequency of ~400 Hz was obtained using a 4.5 mm trilayer beam. A larger resonance frequency can be achieved by reducing the length of the trilayer. By using a submillimeter length trilayer with a submicron thick film of PEDOT:PSS, trilayers with cutoff frequencies as high as 70 Hz can be achieved.

The electrical, electrochemical and mechanical properties of the PEDOT:PSS at various thicknesses (provided through a different number of spray scans), along with the measured output characteristics of the corresponding trilayers are summarized in table 5.6.
Table 5.6 Calculated material properties of the fabricated PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, namely Pn (n being the number of PEDOT:PSS spray scans). For the actuator’s characterization, the length and width of the device are (10.5 ± 0.25) mm and (2 ± 0.25) mm, respectively, unless otherwise is stated.

<table>
<thead>
<tr>
<th>Trilayer name</th>
<th>P1</th>
<th>P2</th>
<th>P4</th>
<th>P6</th>
<th>P8</th>
<th>P10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of PEDOT:PSS spray scans (n)</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Equivalent thickness of PEDOT:PSS on glass (µm)</td>
<td>0.4</td>
<td>0.65</td>
<td>1.4</td>
<td>2.1</td>
<td>2.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Electronic conductivity (S/m)</td>
<td>5.5 × 10³</td>
<td>1.5 × 10⁴</td>
<td>2.2 × 10⁴</td>
<td>2.7 × 10⁴</td>
<td>3.2 × 10⁴</td>
<td>4 × 10⁴</td>
</tr>
<tr>
<td>Ionic conductivity (mS/m)</td>
<td></td>
<td>10.6 ± 12.3</td>
<td>4.12 ± 0.85</td>
<td>3.04 ± 0.32</td>
<td>3.76 ± 0.58</td>
<td>4.64 ± 0.49</td>
</tr>
<tr>
<td>Volumetric capacitance</td>
<td></td>
<td>24.2 ± 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strain to charge ratio (mm³/C)</td>
<td>0.012</td>
<td>0.017</td>
<td>0.077</td>
<td>0.098</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Damping ratio</td>
<td>0.061</td>
<td>0.062</td>
<td>-</td>
<td>0.055</td>
<td>0.054</td>
<td>0.04</td>
</tr>
<tr>
<td>Peak to peak displacement at 0.1 Hz (mm)</td>
<td>0.15</td>
<td>0.333</td>
<td>1.996</td>
<td>2.9</td>
<td>3.49</td>
<td>4.35</td>
</tr>
<tr>
<td>Differential free strain (%)</td>
<td>0.056</td>
<td>0.083</td>
<td>0.37</td>
<td>0.48</td>
<td>0.54</td>
<td>0.63</td>
</tr>
<tr>
<td>Differential external strain (%)</td>
<td>0.019</td>
<td>0.042</td>
<td>0.25</td>
<td>0.36</td>
<td>0.41</td>
<td>0.48</td>
</tr>
<tr>
<td>Resonance frequency (Hz)</td>
<td>41.5 ± 0.7</td>
<td>43 ± 1</td>
<td>-</td>
<td>58 ± 1</td>
<td>60 ± 2.5</td>
<td>80 ± 2.5</td>
</tr>
<tr>
<td>Cutoff frequency (Hz)</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>1.8</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Cutoff frequency (Hz) (1 × 1 cm², sandwiched)</td>
<td>71</td>
<td>44</td>
<td>20</td>
<td>12.6</td>
<td>7.9</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Chapter 6: Conclusion

6.1 Summary and Conclusions

The presented research had three major areas of focus:

1. Encapsulating trilayer conducting polymer actuators using sprayed films of \((\text{styrene-block-isobutylene-block-styrene})\) (SIBS):

   Selection of a proper encapsulating material requires to know how the performance of the device changes when operates without encapsulation. We first carried out a thorough study on the operation of a 360 µm thick bare PEDOT/PEO/PEDOT trilayer actuators with a 1 M solution of \(\text{Li}^+\text{TFSI}^-\) in PC as the electrolyte, as the PC evaporates from the device. We investigated the behavior of the device both in occasional use and continuous cycling in open air and in water. We showed that the trilayers lose all their solvent within 8 days, with \(~40\%\) loss within a day, when stored in an environment with controlled temperature and relative humidity of \((23 \pm 2)^\circ C\) and \((50 \pm 3)\%\), respectively. The speed of the device slows as the PC evaporates (staying within \(10\%\) of their initial value after losing \(~20\%\) of its PC content). Intermittent testing shows displacement of the device actually increases until only \(~14\%\) of the PC content remains, which would take almost 4 days if the device is stored in the controlled conditions mentioned above. This is largely due to the reduction of thickness in the trilayers, which then leads to a higher curvature. Cycling in open air or in water leads to immediate displacement decrease: dropping \(60\%\) over one hour cycling in air and over 12 min cycling in water – likely due to the reduction of charge transfer rate. Overall, we expect that encapsulation will be
beneficial for these types of actuators to maintain the intermittent operation of the device and its speed beyond 4 days and 12 hours respectively. It is also necessary to obtain a stable displacement amplitude when the device is cycling in air or in water.

Metals and glass are excellent for containing electrolytes and liquids in general but their rigid mechanics limits their application for mechanically active ionic actuators or flexible/stretchable electrochemical devices such as batteries and supercapacitors. Electrolyte evaporation, chemisorption of chemicals, and absorption of moisture are some of the key challenges in the endurance of these electrochemical devices. Non-volatile ionic liquids (e.g., EMITFSI) addresses some of the mentioned issues, but these do not prevent absorption of water and salts from the outside. In this work, we evaluated the performance of spray-coated Poly (styrene-block-isobutylene-block-styrene) (SIBS) as a stretchable encapsulant through examining the drying time of 360 \( \mu \)m thick encapsulated PEDOT/PEO:NBR/PEDOT trilayer conducting polymer actuators operating with a 1 M solution of Li\(^+\)TFSI in propylene carbonate (PC). It is estimated that a 100 \( \mu \)m thick SIBSTAR encapsulation helps these devices to retain 80\% of their stored PC for more than 1000 times longer compared to when there is no encapsulation (from less than 0.5 day to over 1.5 years), when stored in an environment with controlled temperature and relative humidity of \((23 \pm 2)\)\(^\circ\)C and \((50 \pm 3)\)%, respectively. We showed that the operation lifetime of the device (time to lose \(~86\%\) of the stored propylene carbonate), which is around 4 days when there is no encapsulation, is estimated to be extended to \(~2400\) days (6.5 years or 600 times improvement). This gain in the lifetime is at the expense of losing some bending amplitude — \(~55\%\) of the initial maximum deflection of the device because of the added stiffness.

Trilayers with no encapsulation cycling in flowing air are shown to lose their displacement with
an initial rate of 55 %/h. This value reduces to an initial 13% /h and after ~1.5 h to 2 %/h when a 100 µm thick SIBSTAR film is used to encapsulate the device after. For a bare trilayer, having a 1 M solution of Li⁺TFSI⁻ in PC and cycling in deionized water (DI) water, after ~1.5 h (2.7 × 10³ cycles at 0.5 Hz), only ~12% of the initial displacement is retained. When a 190 µm thick SIBSTAR encapsulating layer is applied to the trilayer, 90 ± 5 % of the initial displacement is retained even after 2.5 h of actuation (4.5 × 10³ cycles at 0.5 Hz) in water.

To the best of our knowledge, this work presents the best performance of an elastic encapsulating material reported for an ionic device. The outstanding results combined with the low Young’s modulus of the SIBSTAR film, its biocompatibility, biostability, and being FDA approved, as well as ease of fabrication, makes this thermoplastic elastomer a promising candidate as an encapsulant for flexible ionic devices such as flexible batteries and supercapacitors, ionic-electrode capacitive sensors as well as other types of ioni
cally electroactive actuators. This paves the way towards using these devices in implantable and in vivo applications.

2. Creating ActuaTool, a web-based GUI for modeling and designing trilayer conducting polymer actuators:

Current electro-chemo-mechanical models for trilayer conducting polymer actuators do not take into account the non-uniform distribution of charges throughout the volume of the CP layer over time. They also lack in considering the effect of contact resistance and the area of the trilayer which is sandwiched between the two electrodes. In addition to these, the models employed to predict blocking force only apply to small bending beams. In this work, we included both of the aforementioned considerations to the already developed 2D transmission line model of trilayer conducting polymer actuators and then introduced a mechanical/ geometrical solution to accurately
find the shape of the beam when a force is applied to its tip. It subsequently provides the shape of
the trilayers freely actuating, the shape of the beam when a blocking force limits the vertical
displacement of its tip and the required amount of force to carry that out and the displacement of
the tip of the device as it actuates. The model can take into account the effect of encapsulation as
well. Based on the developed model, we created a web-based Graphical User Interface (GUI),
namely ActuaTool, to facilitate the design and study of these actuators and push further their
realization in real applications.

ActuaTool operates in three modes:

In the “frequency response” mode, the user enters the material properties, dimensions of the
device and the amplitude and frequency of the operation sine wave voltage. ActuaTool predicts
the frequency response of displacement, blocking force and power consumption of the device. It
also predicts the shape of the beam at a defined operation frequency when a defined force is applied
to its tip. Moreover, it demonstrates the force-displacement graph of the trilayer at the defined
operation frequency. The values of the cut-off frequency, stiffness, resonance frequency and the
free strain induced in the CP layer are also predicted for the defined trilayer actuator.

In the “Parameter response” mode, the user enters the material properties, dimensions of the
device and the amplitude and frequency of the operation sine wave voltage. Encapsulating layer’s
parameters can also be included if the device is encapsulated. For one of the inputs, the user selects
a range of values. Actuatool then predicts the cutoff frequency, blocking force, tip displacement,
power consumption, resonance frequency, and stiffness of the beam versus the varying parameter.

In the “Design” mode, the user enters the material properties, the width of the device and the
amplitude and frequency of the operation sine wave voltage. She/ he also defines a range of values
of her/ his desired output and a range of values of thicknesses of the conducting polymer and separator layers as well as the length of the device (these ranges can be roughly obtained through the two other modes of operation of the device). ActuaTool then predicts the combinations of length and thicknesses of each of the layers through which the desired range of output by the user is obtained. This mode of operation helps the researchers in the field to design these devices for various applications.

3. Development of a reliable and scalable fabrication method for trilayer conducting polymer actuators:

A novel fabrication method based on spray-coating PEDOT:PSS aqueous dispersion, secondarily doped with DMSO, on the two sides of a PVDF membrane is presented. Films of PEDOT:PSS/ DMSO as thin as ~400 nm could be obtained. We carried out a thorough study on the material properties and device characterization of these types of actuators including the Young’s modulus, electronic and ionic conductivities of each of the layers, the volumetric capacitance of the CP layer and its strain to charge ratio, damping ratio, and free vibration resonance. A ~10 mm long PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer with conducting polymer layers composed through 10 spray passes of PEDOT:PSS, can generate a peak to peak displacement as large as ~4.5 mm, with a cutoff frequency of ~ 2.2 Hz and free and external differential strains of ~0.63% and ~0.48%, respectively. At small thicknesses of PEDOT:PSS, by eliminating the length of the beam (sandwiching the device between two electrodes), cut off frequencies as large as ~70 Hz can be achieved. We showed that ActuaTool can well predict the cut-off frequency and resonance frequency of the device, hence it can further be used for designing these devices for different applications such as in a vibrotactile feedback interface in
which fast actuators are required.

Table 6.1 compares the pros and cons of different fabrication processes for trilayer conducting polymer actuators which have been most investigated so far.

6.2 Future work

In this work, a reliable, reproducible and scalable method of fabrication of trilayer conducting polymers with little material waste, along with an effective encapsulation technique, were presented. In addition to these, a web-based graphical user interface (GUI), namely, ActuaTool, was created to facilitate the design and study of these types of actuators.

These three main achievements pave the way towards realizing these types of actuators in different applications, more importantly in those which require fast actuation. In addition to that, other applications for the fabricated PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer structures, such as supercapacitors or electrochromic devices, can be considered. Here we briefly discuss each of these:

6.2.1 Further studies on PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers

6.2.1.1 Force measurement

Using ActuaTool and the material properties obtained in chapter 5 for PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, it is predicted that a P10 trilayer with a length and width of ~10 mm and ~2 mm, respectively, can generate a maximum force of ~ 1 mN. Measurement of this amount of force and smaller values requires precise force sensors and delicate measurements. Using the same apparatus, the bending stiffness of these trilayer actuators can also be measured.
<table>
<thead>
<tr>
<th>Fabrication Process</th>
<th>Ionic conductivity of the separator</th>
<th>Electronic conductivity of the CP layer</th>
<th>Electrochemical stability</th>
<th>Patterning</th>
<th>Delamination</th>
<th>CP thickness control</th>
<th>Fast actuation</th>
<th>Fabrication process time/complexity/reproducibility</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy/ PVDF/ PPy</td>
<td>Close to that of the electrolyte</td>
<td>Large due to the gold layer</td>
<td>poor</td>
<td>reliable</td>
<td>yes</td>
<td>poor</td>
<td>Not reported</td>
<td>~ one day/ straight forward/ not reproducible at small thicknesses of PPy</td>
<td>Needs a gold layer/ chance of short circuit between the two PPy layers</td>
</tr>
<tr>
<td>PEDOT/ PEO:NBR / PEDOT: Fabrication of the separator layer through sequential polymerization of NBR and PEO to form an interpenetrated polymer network. EDOT is then polymerized on the two sides of the PEO:NBR film to make an interpenetrated polymer network of PEDOT:PEO:NBR. [7]–[10], [88]</td>
<td>~0.1 that of the electrolyte</td>
<td>Relatively small</td>
<td>good</td>
<td>Chemical patterning is not reliable due to swelling/deswelling Laser machining is possible</td>
<td>No/ PEDOT is interpenetrated in PEO:NBR</td>
<td>poor</td>
<td>Possible through decreasing the thickness of the device (demonstrated the proof of concept of fast operation of CP actuators)</td>
<td>2- 3 days/ includes multiple steps/ not reproducible at small thicknesses for fast actuation</td>
<td>large material waste due to multiple washing steps</td>
</tr>
<tr>
<td>Layer-by-layer fabrication process (PEDOT/PEO:NBR/PEDOT) sequential spin-coating and polymerization of each of the layers on a silicon wafer</td>
<td>≈0.1 that of the electrolyte</td>
<td>Very small</td>
<td>good</td>
<td>Chemical patterning is not reliable due to swelling/deswelling Laser machining is possible</td>
<td>Yes/ the interpenetration of PEDOT in PEO:NBR is poor</td>
<td>Fair</td>
<td>No</td>
<td>2 days/ includes multiple steps/ no report on reproducibility</td>
<td>The two CP layers have different material properties</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PEDOT:PSS / PVDF (hydrophobic)/PEDOT:PSS Casting PEDOT:PSS aqueous dispersion on the two sides of PVDF membrane. [107], [119]</td>
<td>Close to that of the electrolyte</td>
<td>Large</td>
<td>good</td>
<td>reliable</td>
<td>No</td>
<td>poor</td>
<td>No</td>
<td>2-3 days/ relatively simple fabrication process/ reproducible</td>
<td>Aqueous electrolytes can’t be used</td>
</tr>
<tr>
<td>PEDOT:PSS PVDF (hydrophilic)/PEDOT:PSS spray-coating PEDOT:PSS aqueous dispersion on the two sides of PVDF membrane [this work]</td>
<td>Close to that of the electrolyte</td>
<td>Large</td>
<td>good</td>
<td>reliable</td>
<td>Probable (needs further studies)</td>
<td>Excellent (&lt;0.4µm)</td>
<td>Yes</td>
<td>Very fast 2 min/layer (0.4 µm) for a 5 cm × 5 cm sample</td>
<td>Fast evaporation of PEDOT:PSS is essential/ Aqueous electrolytes can’t be used</td>
</tr>
</tbody>
</table>
6.2.1.2 Patterning

Miniaturizing trilayer conducting polymer actuators requires them to be patterned. Patterning PEDOT/PEO:NBR/PEDOT trilayers fabricated on a silicon wafer has been demonstrated through photolithography and reactive ion etching (RIE) using Tetrafluoromethane/Oxygen (CF$_4$/O$_2$) plasma [10]. Other patterning methods such as laser micromachining have also been used to shape the trilayer actuators [35]. For the PEDOT:PSS/PVDF/PEDOT:PSS trilayer actuators fabricated in this work, the laser micromachining may often be preferred since the devices are relatively thick and the laser micromachining process is simple, fast, and costs less.

For patterning the PEDOT:PSS/DMSO layer on PVDF membranes, here we suggest three methods to be examined:

(1) Shadow mask during deposition: Patterning using a shadow mask while spray coating the PEDOT:PSS dispersion on the PVDF membrane. This process is quite easy to operate however its resolution is probably limited mainly due to the lateral penetration of the solution underneath the shadow mask.

(2) Electron Beam Lithography (EBL) [127]: Patterning after deposition using Electron Beam Lithography (EBL) technique through which an electron beam removes the conductive PEDOT:PSS layer based on the defined path for it. Compared to the previous method, it owns a smaller resolution with the expense of cost and time.

(3) Shadow mask and RIE: Reactive ion etching (RIE) using Tetrafluoromethane/Oxygen (CF$_4$/O$_2$) plasma has been shown to be effective to pattern thin PEDOT/PEO:NBR/PEDOT trilayer conducting polymer actuators [10]. The same plasma can be tested to pattern PEDOT:PSS on PVDF membrane. Similar to the EBL method, it adds cost to the fabrication process and probably offers a better resolution compared to what a shadow mask while spraying
PEDOT:PSS/ DMSO offers.

6.2.1.3 Encapsulation

We showed in chapter 2 that sprayed films of SIBS work excellently as an encapsulation to protect the solvent form evaporation from the device. The electrolyte used in chapter 5 was EMITFSI which is nonvolatile and does not evaporate or degrade at room temperature. Its ionic conductivity was measured to be ~1.3 S/m which is fairly good but still smaller than some of the solvent-based electrolytes. Hence, encapsulation can help them operate with other types of electrolytes as well.

It is expected that the displacement of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayer actuators does not vary much after encapsulation with 10 µm thick SIBS due to the large Young’s modulus of PVDF and PEDOT:PSS layers and their thick structure (The Young’s modulus of PVDF and PEDOT:PSS were measured to be ~50 MPa and 1.5 GPa whereas that of SIBS is just 11 MPa).

6.2.1.4 Investigating the performance of the device with other electrolytes

The larger the ionic conductivity of the electrolyte is, the larger the ionic conductivity of the PEDOT:PSS layer becomes and the faster the trilayers with thicker PEDOT:PSS can actuate. Aqueous electrolytes offer large ionic conductivities but they cannot be used with PEDOT:PSS since it disperses in water. The type of the electrolyte used can also affect the strain to charge ratio of the CP layer, depending on the size of the migrating ions. A systematic study, hence, is necessary to evaluate the performance of these actuators with different electrolytes. Thanks to the low permeability of SIBSTAR and the stiff structure of the PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, the devices can be further encapsulated to increase their lifetime and practicality.
6.2.1.5 Efficiency limitation and energy storage

As discussed before the electromechanical coupling and mechanical efficiency of trilayer conducting polymer actuators is small compared to other types of bending actuators such as piezoelectric actuators. However, in these devices, the input electrical energy is stored in the device and can be recovered. Accordingly, further studies on this aspect of these devices are required when we consider using them in real applications.

6.2.2 PEDOT:PSS/PVDF/PEDOT:PSS trilayer structure, used in other application

6.2.2.1 Supercapacitor

As demonstrated in section 5.3.5, the fabricated PEDOT:PSS/DMSO films can demonstrate a fairly large specific capacitance (~200 F/g) which combined with the large cutoff frequency of the trilayer structure (as high as 36 Hz, without the use of a metal electrode being entirely in contact with the device) can provide a large power density with a fairly large work density through a low-cost, scalable fabrication process. Further measurements and calculations are required to fully evaluate the performance of these devices as supercapacitors.

6.2.2.2 Electrochromic displays

As shown in figure 5.1(b), thin sprayed films of PEDOT:PSS/DMSO on PVDF membrane can provide a semi-transparent film. In thin films of conducting polymers, as the oxidation state changes, the color varies from semi-transparent to dark blue. Figure 6.1(a,b) and 6.1(c,d) show the top view optical image of P1 and P2 trilayers before and after application of a 0.5 V square wave voltage to them, respectively. It clearly shows as the PEDOT:PSS layer is oxidized, its color changes and it becomes more opaque. The larger the applied voltage is, the opaquer the beam becomes. This, along with the patterning the PEDOT:PSS layer on PVDF membrane, can help to create fast-switching electrochromic displays.
Figure 6.1 PEDOT:PSS/ PVDF/ PEDOT:PSS trilayers, (a) (P1) and (c) (P2) before the application of voltage and (b) (P1) and (d) (P2) after application of a 0.5 V square wave voltage, demonstrating the electrochromic behavior of thin films of PEDOT:PSS/ DMSO.

6.2.3 Feasibility study of different applications for trilayer conducting polymers using ActuaTool

Modeling trilayer conducting polymer actuators has been studied since their invention. However, practical design of this device for different applications has been a challenge due to the numerous parameters which are involved with defining the output characteristics of these devices. We created ActuaTool to visualize all the input and output characteristics of the devices to subsequently increase the practicality of the model. We even took further steps and used the tool to design these devices based on the intended application and the desired output. So far, they have been explored in applications including catheters [15], robotic fish [34], micro-manipulators [35], etc. Knowing the performance which different fabrication methods of conducting polymer actuators provide, as well as knowing the desired specifications of different applications for them, by taking advantage of ActuaTool, we can run a feasibility study on using these devices for different applications.

In section 4.4, using ActuaTool and the specifications which PEDOT:PSS/ PVDF/ PEDOT:PSS actuators offer, we investigated a range of dimensions which provide proper trilayer actuators to be used as a vibrotactile feedback tacton (tactile icon). Fabrication of such
device in terms of the thickness of PEDOT:PSS has already been demonstrated in chapter 5. By applying patterning methods, actuators with the specified size can be obtained to be integrated into an array of tactile feedback, such as the one demonstrated in figure 4.10(b). Further psychophysical studies on human users are needed to be carried out to evaluate the practicality of the device.
References


Styrene-Isobutylene block copolymer,” presented at the Thermoplastic Elastomers, 

Smithers Rapra, 2012.


[69] C. Girotto, B. P. Rand, J. Genoe, and P. Heremans, “Exploring spray coating as a 
deposition technique for the fabrication of solution-processed solar cells,” *Solar Energy 

[70] K. A. Perevosnik, “Investigation pf the mechanical and thermal properties of poly(styrene-
block-isobutylene-block-styrene) (SIBS) and its blends with thymine-functionalized 
polystyrene,” University of Akron, Akron, OH, 2008.

[71] L. Suo et al., “‘Water-in-salt’ electrolyte enables high-voltage aqueous lithium-ion 

[72] P. Shao and R. Y. M. Huang, “Polymeric membrane pervaporation,” *Journal of 

the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 97, no. 685, 


Appendices

Appendix A : PEDOT and PEO:NBR thickness estimation

As discussed in section 2.2.2, PEDOT is formed on the two sides of the as-prepared PEO:NBR films with the initial thickness of 245 µm, through swelling it in EDOT and then oxidizing EDOT to form an interpenetrated polymer network of PEDOT:PEO:NBR, using a 1.5 M aqueous solution of FeCl₃. EDOT is then washed away with Methanol and leaves a trilayer structure with the cross-section optical and SEM micrographs as shown in figures 2.2.2(c), and 2.2.2(e), respectively, and the EDX elemental analysis on sulfur atoms as shown in figure 2.2(f). The dimensions of PEDOT-dominated layers stay unchanged after washing EDOT and the excess of FeCl₃ solution from it, leaving the PEO:NBR separator layer stretched in the x-y plain. This is because the Young’s modulus of PEDOT is significantly larger than that of PEO:NBR (~100 times larger). The following calculations are to estimate the thicknesses of the PEDOT and PEO:NBR dominated regions.

$L$ and $W$ are the initial length and width of PEO:NBR film before being swollen in EDOT, respectively, and $C_1$ is defined as the swelling ratio along one direction when PEO:NBR IPN stores EDOT (It is assumed to be the same in all three directions. So, the volumetric swelling ratio is $C_1^3$). Hence, from figure 2.2(a), the thickness of PEO:NBR after being swollen in EDOT is 245 µm $\times$ $C_1$. From the EDX elemental analysis on sulfur atoms, demonstrated in figure 2.2(f), the thickness of PEDOT and PEO:NBR layers are estimated to be $(24 \pm 0.5)$ µm in dry state (demonstrating sulfur density $> 50\%$) and $(132 \pm 1)$ µm, respectively. This, as explained above, is also the thickness of PEDOT electrode after EDOT formation. Hence, the thickness of
PEO:NBR layer after PEDOT formation while it is still swollen in EDOT is equal to 245 μm × $C_1 - (48 \pm 1)$ μm. When EDOT is removed, the dimensions of the PEDOT dominated layer stays unchanged due to its large Young’s modulus. This causes the PEO:NBR layer stay stretched after EDOT is removed. Knowing the fact that PEO:NBR is non-compressive (Poisson ratio of 0.5), equation A.1 applies,

$$\frac{245 \mu m \times C_1 - 2 \times 24 \mu m}{C_1^3} = 132 \mu m.$$  \tag{A.1}

Solving equation A.1, $C_1$ is obtained to be equal to 1.25.

The width and length of the trilayer (or the PEO:NBR layer) are now, 1.25 × $W$ and 1.25 × $L$, respectively. When the trilayer stores the electrolyte (1 M solution of Li+TFSI- in PC), both PEDOT and PEO:NBR layers swell. While their swelling ratio is considered to be almost the same in the $x$-$y$ plain (being equal to the swelling ratio of PEDOT layers), they have different swelling ratios towards the $z$-axis direction (along their thicknesses). $C_2$ is defined as the swelling ratio of PEDOT along one direction when it is swollen in the electrolyte (We assume PEDOT swells equally in the three directions). The swelling ratio of PEO:NBR IPN along its length and width are the same as those of PEDOT and are equal to $C_2$. $C_3$ is defined as the swelling ratio of PEO:NBR along the $z$-axis when it is swollen in the electrolyte. Now the following equations apply,

$$2 \times 24 \times C_2 + 132\mu m \times C_3 = 360\mu m \tag{A.2}$$

$$1.25W \times C_2 \times 1.25L \times C_2 \times 132\mu m \times C_3 \tag{A.3}$$

$$= 1.6W \times 1.6L \times 1.6 \times (245 - 2 \times 24)\mu m$$

Equation A.2 shows the total thickness of the trilayer after being swollen in the electrolyte and equation A.3 shows the total volume of the PEO:NBR layer (1.6 is the swelling ratio of the
pure PEO:NBR IPN in the electrolyte). Solving these equations, $C_2$ and $C_3$ were obtained to be equal to 1.32 and 2.24, respectively, which subsequently, leads to estimated thicknesses of $(31.5 \pm 0.6) \, \mu m$ and $(297 \pm 1.2) \, \mu m$ for PEDOT and PEO:NBR layers, respectively.

Appendix B : Estimation of PC mass loss from the experiment’s raw data
In Appendix B, the details on how to obtain the data presented in figures 3.7 and 3.9 are provided. In order to study the effectiveness of SIBSTAR encapsulation in protecting propylene carbonate from being evaporated from the trilayer conducting polymers, four sets of trilayers including 3 in each set were prepared. No encapsulation was applied to the first set including three samples named as $S_i$, where $i = 1, 2, 3$. The rest were names as $S_i$ with $50 \mu m$ ($i = 4, 5, 6$), $100 \mu m$ ($i = 7, 8, 9$) and $190 \mu m$ ($i = 10, 11, 12$) thick spray-coated SIBSTAR encapsulations. Bare and encapsulated trilayers were hung over a rod using a paper clamp as demonstrated in figure 3.4(a). The whole setup was then placed into a container with a lid to prevent dust from settling on the samples, as shown in figure 3.4(b). The whole setup was then stored in a Controlled Temperature and Humidity (CTH) room with the set temperature and relative humidity, RH, of $(23 \pm 2)^\circ C$ and $(50 \pm 3)\%$, respectively. The mass of each of the encapsulated trilayers along with the paper clamp holding it was measured over time and recorded. Figures B.(2-4) show the corresponding measured data for samples $S_5$ ($t_s = 50 \mu m$), $S_8$ ($t_s = 100 \mu m$) and $S_{10}$ ($t_s = 190 \mu m$), respectively. These samples were selected since their rate of PC mass loss was smallest compared to the two other samples with the same encapsulating layer’s thickness. Knowing the fact that the mass of propylene carbonate in the trilayer decays linearly with time (equation 3.3), the initial mass of toluene was estimated through subtracting the $y$-intercept of the trendline fitted to the linear region of the measured mass data versus time (demonstrated in each figure) from the initial mass of the corresponding whole setup (including the paper clamp and the encapsulated trilayer). The masses of the trilayers were measured before encapsulation and according to the results obtained in chapter 2, the mass of the stored PC in each trilayer was estimated to be $\sim 0.45$ of it. The initial mass of the volatile components of each sample is the sum of the initial mass of PC and toluene in it. Any measured change in the mass of the setup and the
encapsulated samples is due to the evaporation of the trapped toluene or the stored PC in the device. Tables B.(1-3) show the measured data and estimated values of the masses of the components corresponding to samples $S_5 (t_s = 50 \, \mu m)$, $S_8 (t_s = 100 \, \mu m)$ and $S_{10} (t_s = 190 \, \mu m)$, respectively. Their results were compared in figure 3.9. Note that, here we neglected the build-up period over which PC molecules are penetrating the encapsulating layer and have not yet escaped from the sample. Calculating this period requires knowing the diffusion coefficient of propylene carbonate molecules in spray-coated films. This involves more advanced experiments which are beyond the scope of this work. Of course, the assumption we made here does not have an impact on the rate of mass loss, $a$, and the estimated TR$_{PC,n}$. Making this assumption causes the time to lose 20% of the stored PC in the trilayer as well as the operation lifetime of the device, presented in table 3.2, to be underestimated (those values which were tagged with a *).

![Figure B.1 Mass of the setup + encapsulated sample, $S_5 (t_s = 50 \, \mu m)$ (measured data).](image)

Table B.1 Measured and estimated masses of the components of the set-up measurement for sample $S_5 (t_s = 50 \, \mu m)$

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Mass of Setup + encapsulated trilayer (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.628</td>
</tr>
<tr>
<td>50</td>
<td>2.626</td>
</tr>
<tr>
<td>100</td>
<td>2.624</td>
</tr>
<tr>
<td>150</td>
<td>2.622</td>
</tr>
<tr>
<td>200</td>
<td>2.620</td>
</tr>
<tr>
<td>250</td>
<td>2.618</td>
</tr>
<tr>
<td>300</td>
<td>2.616</td>
</tr>
</tbody>
</table>

$y = -2E-05x + 2.625$

$R^2 = 0.9926$
<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Mass of clamp + encapsulated trilayer (measured data) (mg)</th>
<th>Mass of toluene + PC (estimated data) (mg)</th>
<th>Normalized mass of toluene + PC, relative to the initial mass of PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.6267</td>
<td>0.0101965</td>
<td>1.157837961</td>
</tr>
<tr>
<td>4</td>
<td>2.6262</td>
<td>0.0093965</td>
<td>1.066995969</td>
</tr>
<tr>
<td>7</td>
<td>2.626</td>
<td>0.0087965</td>
<td>0.998864475</td>
</tr>
<tr>
<td>8</td>
<td>2.6252</td>
<td>0.0086965</td>
<td>0.987509226</td>
</tr>
<tr>
<td>12</td>
<td>2.6251</td>
<td>0.0085965</td>
<td>0.976153977</td>
</tr>
<tr>
<td>18</td>
<td>2.6249</td>
<td>0.0083965</td>
<td>0.953443479</td>
</tr>
<tr>
<td>22</td>
<td>2.6248</td>
<td>0.0082965</td>
<td>0.94208823</td>
</tr>
<tr>
<td>27</td>
<td>2.6246</td>
<td>0.0080965</td>
<td>0.919377732</td>
</tr>
<tr>
<td>32</td>
<td>2.6245</td>
<td>0.0079965</td>
<td>0.908022483</td>
</tr>
<tr>
<td>35</td>
<td>2.6244</td>
<td>0.0078965</td>
<td>0.896667234</td>
</tr>
<tr>
<td>39</td>
<td>2.6243</td>
<td>0.0077965</td>
<td>0.885311985</td>
</tr>
<tr>
<td>42</td>
<td>2.6242</td>
<td>0.0076965</td>
<td>0.873956737</td>
</tr>
<tr>
<td>47</td>
<td>2.6241</td>
<td>0.0075965</td>
<td>0.862601488</td>
</tr>
<tr>
<td>53</td>
<td>2.624</td>
<td>0.0074965</td>
<td>0.851246239</td>
</tr>
<tr>
<td>63</td>
<td>2.6237</td>
<td>0.0071965</td>
<td>0.817180492</td>
</tr>
<tr>
<td>71</td>
<td>2.6235</td>
<td>0.0069965</td>
<td>0.794469994</td>
</tr>
<tr>
<td>82</td>
<td>2.6233</td>
<td>0.0067965</td>
<td>0.771759496</td>
</tr>
<tr>
<td>103</td>
<td>2.623</td>
<td>0.0064965</td>
<td>0.737693749</td>
</tr>
<tr>
<td>117</td>
<td>2.6226</td>
<td>0.0060965</td>
<td>0.692272753</td>
</tr>
<tr>
<td>140</td>
<td>2.6221</td>
<td>0.0055965</td>
<td>0.635496508</td>
</tr>
<tr>
<td>193</td>
<td>2.6213</td>
<td>0.0047965</td>
<td>0.544654517</td>
</tr>
<tr>
<td>248</td>
<td>2.6202</td>
<td>0.0036965</td>
<td>0.419746778</td>
</tr>
<tr>
<td>288</td>
<td>2.6197</td>
<td>0.0031965</td>
<td>0.362970533</td>
</tr>
<tr>
<td>319</td>
<td>2.6195</td>
<td>0.0029965</td>
<td>0.340260035</td>
</tr>
</tbody>
</table>

Table B.2 measured and estimated masses of the components of the set-up measurement of sample $S_8$ ($t_e = 100 \mu m$)
<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Mass of clamp + encapsulated trilayer (measured data) (mg)</th>
<th>Mass of toluene + PC (estimated data) (mg)</th>
<th>Normalized mass of Toluene + PC, relative to the initial mass of PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.9862</td>
<td>0.014039</td>
<td>1.272859</td>
</tr>
<tr>
<td>4</td>
<td>2.9836</td>
<td>0.011439</td>
<td>1.037128</td>
</tr>
<tr>
<td>7</td>
<td>2.9835</td>
<td>0.011339</td>
<td>1.028061</td>
</tr>
<tr>
<td>8</td>
<td>2.9834</td>
<td>0.011239</td>
<td>1.018995</td>
</tr>
<tr>
<td>12</td>
<td>2.9834</td>
<td>0.011239</td>
<td>1.018995</td>
</tr>
<tr>
<td>18</td>
<td>2.9834</td>
<td>0.011239</td>
<td>1.018995</td>
</tr>
<tr>
<td>22</td>
<td>2.9834</td>
<td>0.011239</td>
<td>1.018995</td>
</tr>
<tr>
<td>27</td>
<td>2.9833</td>
<td>0.011139</td>
<td>1.009928</td>
</tr>
<tr>
<td>35</td>
<td>2.9831</td>
<td>0.010939</td>
<td>0.991795</td>
</tr>
<tr>
<td>42</td>
<td>2.983</td>
<td>0.010839</td>
<td>0.982728</td>
</tr>
<tr>
<td>47</td>
<td>2.983</td>
<td>0.010839</td>
<td>0.982728</td>
</tr>
<tr>
<td>53</td>
<td>2.9829</td>
<td>0.010739</td>
<td>0.973662</td>
</tr>
<tr>
<td>63</td>
<td>2.9829</td>
<td>0.010739</td>
<td>0.973662</td>
</tr>
<tr>
<td>71</td>
<td>2.9829</td>
<td>0.010739</td>
<td>0.973662</td>
</tr>
<tr>
<td>82</td>
<td>2.9828</td>
<td>0.010639</td>
<td>0.964595</td>
</tr>
<tr>
<td>103</td>
<td>2.9828</td>
<td>0.010639</td>
<td>0.964595</td>
</tr>
<tr>
<td>117</td>
<td>2.9827</td>
<td>0.010539</td>
<td>0.955528</td>
</tr>
<tr>
<td>140</td>
<td>2.9826</td>
<td>0.010439</td>
<td>0.946462</td>
</tr>
<tr>
<td>193</td>
<td>2.9824</td>
<td>0.010239</td>
<td>0.928329</td>
</tr>
<tr>
<td>248</td>
<td>2.9822</td>
<td>0.010039</td>
<td>0.910195</td>
</tr>
<tr>
<td>288</td>
<td>2.982</td>
<td>0.009839</td>
<td>0.892062</td>
</tr>
<tr>
<td>319</td>
<td>2.9819</td>
<td>0.009739</td>
<td>0.882996</td>
</tr>
</tbody>
</table>
Figure B.2 Mass of the setup + encapsulated sample, \( S_8(t_s = 100 \, \mu m) \) (measured data).

Table B.3 Measured and estimated masses of the components of the set-up measurement of sample \( S_{10} \) 
\( (t_s = 100 \, \mu m) \)

<table>
<thead>
<tr>
<th>Initial mass of trilayer</th>
<th>23.31 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial mass of stored PC</td>
<td>10.4895 mg</td>
</tr>
<tr>
<td>Initial mass of trapped toluene</td>
<td>8.14 mg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Mass of clamp + encapsulated trilayer (measured data) (mg)</th>
<th>Mass of toluene + PC (estimated data) (mg)</th>
<th>Normalized mass of Toluene + PC relative to the initial mass of PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3889</td>
<td>0.01974</td>
<td>1.701724</td>
</tr>
<tr>
<td>5</td>
<td>1.383</td>
<td>0.01384</td>
<td>1.193103</td>
</tr>
<tr>
<td>11</td>
<td>1.382</td>
<td>0.01284</td>
<td>1.106897</td>
</tr>
<tr>
<td>21</td>
<td>1.3812</td>
<td>0.01204</td>
<td>1.037931</td>
</tr>
<tr>
<td>29</td>
<td>1.3808</td>
<td>0.01164</td>
<td>1.003448</td>
</tr>
<tr>
<td>40</td>
<td>1.3807</td>
<td>0.01154</td>
<td>0.994828</td>
</tr>
<tr>
<td>61</td>
<td>1.3804</td>
<td>0.01124</td>
<td>0.968966</td>
</tr>
<tr>
<td>75</td>
<td>1.3803</td>
<td>0.01114</td>
<td>0.960345</td>
</tr>
<tr>
<td>98</td>
<td>1.3801</td>
<td>0.01094</td>
<td>0.943103</td>
</tr>
<tr>
<td>153</td>
<td>1.3798</td>
<td>0.01064</td>
<td>0.917241</td>
</tr>
<tr>
<td>208</td>
<td>1.3794</td>
<td>0.01024</td>
<td>0.882759</td>
</tr>
<tr>
<td>248</td>
<td>1.3792</td>
<td>0.01004</td>
<td>0.865517</td>
</tr>
<tr>
<td>279</td>
<td>1.379</td>
<td>0.00984</td>
<td>0.848276</td>
</tr>
</tbody>
</table>
Figure B.3 Mass of the setup + encapsulated sample, $S_{10} (t_s = 190 \, \mu m)$ (measured data).
Appendix C : 2D transmission line-related formulas derivations

C.1 Impedance of trilayer CP actuator and local frequency-dependent voltage

Figures C.1(a,b) shows the simplified equivalent electric circuit model of the trilayer conducting polymer actuators.

![Equivalent transmission line circuit](image)

Figure C.1 Equivalent transmission line circuit which models the electrochemical behavior of a trilayer conducting polymer along its length. (b) equivalent RC transmission line circuit of the element, $Z_i$, modeling the diffusion of ions through the thickness of the CP layers.

For the transmission line along the length of the CP layer we have,

$$i_j = \frac{dV_j}{R_e \, dl} \quad \text{(C.1.a)}$$
\[
\frac{dV_j}{dl} = \frac{V_j}{Z_p}
\]  
(C.1.b)

\[
\frac{d^2V_j}{dl^2} = \frac{R_e}{Z_p}V_j
\]  
(C.1.c)

\[
V_j = V_1e^{\beta l} + V_2e^{-\beta l}
\]  
(C.2.a)

\[
Z_p = Z_{dl}Z_i/(Z_{dl} + Z_i).
\]  
(C.2.b)

\[
Z_{dl} = 1/j2\pi f c_{dl}
\]  
(C.2.c)

\[
\beta = \sqrt{\frac{R_e}{Z_p + \frac{R_{ig}}{Z}}}
\]  
(C.2.e)

\[
i_j = \frac{1}{2\beta R_e}(V_1e^{\beta l} + V_2e^{-\beta l})
\]  
(C.3.a)

\[
V_{(l=0)} = V_s \Rightarrow V_1 + V_1 = V_s
\]  
(C.3.b)

\[
i_{(l=0)} = 0 \Rightarrow V_1e^{\beta L} + V_2e^{-\beta L} = 0
\]  
(C.3.c)

\[
V_1 = \frac{V_0e^{-\beta L}}{(e^{\beta L} + e^{-\beta L})}
\]  
(C.3.d)

\[
V_2 = \frac{V_0e^{\beta L}}{(e^{\beta L} + e^{-\beta L})}
\]  
(C.3.e)

\[
V_j = V_0\left(\frac{e^{-\beta(L-l)} + e^{\beta(L-l)}}{e^{\beta L} + e^{-\beta L}}\right) = V_0\left(\frac{\cosh(\beta(L - l))}{\cosh(\beta(L))}\right)\left(\frac{Z_p}{Z_p + \frac{R_{ig}}{2}}\right)
\]  
(C.4)

And for the transmission line describing the diffusive element, \(Z_i\), shown in figure C.1(b), we have,

\[
i_{(i,j)} = \frac{dV_{(i,j)}}{R_i dh}
\]  
(C.5.a)
\[
\frac{di_{(i,j)}}{dl} = \frac{V_{(i,j)}}{Z_{CV}}, \tag{C.5.b}
\]
\[
\frac{d^2V_{(i,j)}}{dh^2} = \frac{R_e}{Z_{CV}}V_{(i,j)}, \tag{C.5.c}
\]
\[
V_{(h,l)} = V_{h1}e^{\gamma h} + V_{h2}e^{-\gamma h}, \tag{C.6.a}
\]
\[
Z_{CV} = \frac{1}{j2\pi f C_v}, \tag{C.6.b}
\]
\[
\gamma = \sqrt{\frac{R_i}{Z_{CV}}}. \tag{C.6.c}
\]
\[
i_{(i,j)} = \frac{1}{\gamma R_i}(V_{h1}e^{\gamma h} - V_{h2}e^{-\gamma h}), \tag{C.7.a}
\]
\[
i_{(h=g/2)} = 0 \Rightarrow V_{h1}e^{\gamma g/2} - V_{h2}e^{-\gamma g/2} = 0, \tag{C.7.b}
\]
\[
V_{(h=gT/2)} = V_l \Rightarrow V_{h1}e^{\gamma gT/2} + V_{h2}e^{-\gamma gT/2} = V_l, \tag{C.7.c}
\]
\[
V_{h1} = \frac{V_le^{-\gamma gT/2}}{(e^{\gamma h_p} + e^{-\gamma h_p})}, \tag{C.7.d}
\]
\[
V_{h2} = \frac{V_le^{\gamma gT/2}}{(e^{\gamma h_T} + e^{-\gamma h_T})}. \tag{C.7.e}
\]
\[
V_{(i,j)} = V_l \left(\frac{e^{\gamma (h-h_T/2)} + e^{-\gamma (h-h_T/2)}}{e^{\gamma h_p} + e^{-\gamma h_p}}\right) = V_l \left(\frac{\cosh(\gamma (h-h_T/2))}{\cosh(\gamma h_p)}\right). \tag{C.8}
\]

Then \(Z_{2D}\) and \(Z_i\), impedances of the transmission lines shown in figures C.1(a) and C.1(b) are obtained as follow,
\[
Z_i = \frac{V_l}{i_{(h=0)}} = \sqrt{R_{lp}Z_{CV(f)}} \coth(\gamma(f)h_p), \tag{C.9}
\]

211
\[ Z_{2D} = \frac{V_0}{i_{(l=0)}} = W^{-1}\sqrt{R_{ep}(Z_{p(f)} + \frac{R_{ig}}{2}) \coth(\beta(f)L)}. \quad (C.10) \]

Now combining equations C.4 and C.8 and including the impedance of the part of the trilayer which is sandwiched between the two contact electrodes, we have,

\[ V_{(i,j,f)} = \frac{h}{|h|} V_{S} \left( \frac{\cosh \left( \gamma(f) \left(|h| - \frac{h_T}{2} \right) \right)}{\cosh(\gamma(f)h_p)} \right) \left( \frac{\cosh(\beta(f)(l-L))}{\cosh(\beta(f)L)} \right) \left( \frac{Z_{p(f)}}{Z_{p(f)} + \frac{R_{ig}}{2}} \right) \left( 1 - \frac{R_c}{Z_{T(f)}} \right), \quad (C.11) \]

\section*{C.2 Displacement of a uniformly bent beam under rotation}

Figure C.2 shows the schematic of a beam (orange) bent to a uniform angle, \( \theta = \kappa L \) (green) and rotated to an angle, \( \varphi \) (blue). \( \kappa \) is the curvature of the beam and \( L \) is its length.

\[ \sqrt{\bar{Y}^2 + (L - \bar{X})^2} = \frac{2}{\kappa} \sin \left( \frac{\kappa L}{2} \right). \quad (C.12) \]
And from the one highlighted in green, we have,

\[ \sin \left( \frac{\kappa L}{2} + \varphi \right) = \frac{\bar{Y}}{\sqrt{\bar{Y}^2 + (L - \bar{X})^2}} \]  
(C.13.a)

\[ \cos \left( \frac{\kappa L}{2} + \varphi \right) = \frac{\bar{X}}{\sqrt{\bar{Y}^2 + (L - \bar{X})^2}} \]  
(C.13.b)

Now combining equations C.12 and C.12.a, we have,

\[ \kappa = \frac{2\bar{Y}}{\bar{Y}^2 + \bar{L}^2} \]  
(C.14)

where \( \bar{L} = L - \bar{X} \). If \( \kappa \) is known, we have,

\[ \bar{Y} = \frac{2}{\kappa} \sin \left( \frac{\kappa L}{2} + \varphi \right) \sin \left( \frac{\kappa L}{2} \right), \]  
(C.15.a)

and by combining equations C.12 and C.13.b, we have,

\[ \bar{X} = L - \frac{2}{\kappa} \cos \left( \frac{\kappa L}{2} + \varphi \right) \sin \left( \frac{\kappa L}{2} \right). \]  
(C.15.b)