CHARACTERIZATION OF IONIC POLYMERS: TOWARDS APPLICATIONS AS
SOFT SENSORS IN MEDICINE

by

Yuta Dobashi

B.A.Sc., The University of British Columbia, 2014

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Biomedical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

October 2016

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Abstract

A phenomenon termed the piezoionic effect is described and characterized in various ionic polymers including polymer networks containing aqueous electrolytes (hydrogels) and organic electrolytes. Initial observations suggest that when an ion containing polymer is compressed, a concentration gradient is induced by the pressure differential, leading to an electrical potential difference detectable at electrodes placed at compressed and uncompressed portions of the polymer. The work focuses on the fundamental characterization of the nature of the piezoionic transduction to probe the effects of relative mobilities of the ions present in the system. The effective ion radii due to ion-solvent interactions and electrostatic ion-polymer interactions have been investigated for their contribution in dictating the piezoionic behavior by NMR measurements of the self-diffusion coefficients. The results are qualitatively correlated to the voltage response to mechanical compression of the polymer samples. Following the experiments, a numerical model is developed which incorporates a number of contributing events believed to be taking place in a concerted manner to cause the piezoionic effect. The deformation induced solvent flow is modeled by means of Biot’s constitutive equations on poroelasticity, a combination of thermodynamic equilibrium and Darcy’s law. The Darcy’s flow induced is then used as the input to model transport of dilute species. Here, the convective factor is being continuously modulated by Darcy’s flow, while Fickian diffusion concurrently takes place. The ionic species experience different displacements due to Stokes' drag experienced by the solvation spheres of the ionic species and solvent molecules and the electrostatic interactions between the charged polymer chains and the mobile ions. Furthermore, this non-homogeneous ionic charge distribution yields a voltage distribution via the Poisson’s equation. This voltage distribution is used to account for the migration of ionic species. The following chapter is dedicated to a novel electrochemical method
and modelling approach designed to probe various ionic polymers, some electronically conductive and others interpenetrated, to determine the phase-wise contributions to ionic conductivities. Finally, potential applications of the piezoionic polymers as soft sensors in medicine, particularly in unobtrusive and longitudinal monitoring of physical parameters, are discussed and some preliminary prototypes are introduced and ultimate feasibility is assessed.
Preface

All aspects of the materials appearing in this thesis have been originally drafted by the author unless otherwise noted.


A version of section 2.1 has been published in an online-only journal MRS Advances, published by the Materials Research Society. Dobashi, Y., Allegretto, G., Sarwar, M.S. and Madden, J.D.W. (2016) MRS Advances vol 1. “Mechanoionic Transduction of Solid Polymer Electrolytes Potential Applications.” Graham Allegretto and I conducted all the testing collaboratively, and we also wrote the MATLAB script for post-processing of the data acquired. The original manuscript was entirely written by myself and Graham Allegretto, and later edited by Dr. Madden.

The NMR experiments appearing in section 2.2 and 2.3 have been carried out by a Ph.D. student Yael Petel at Dr. Carl Michal’s laboratory. Dr. Michal and Yael have also greatly contributed to discussion of potential underlying mechanisms of the piezoionics, as well as planning our future collaborative experiments. I have synthesized all the samples for the NMR measurements, and Yael and I collaboratively discussed and interpreted the results.
The work presented in chapter 4 was done in collaboration with Fannir, A., Farajollahi, M., Yao, D., Usgaocar, A, Nguyen, G., and Vidal, F., all at the University of Cergy-Pontoise. The PEO/NBR-PEDOT samples were received from this group at the University of Cergy-Pontoise. A Ph.D candidate in Dr. Vidal’s group, Adelyne Fannir, has greatly contributed to this work by synthesizing the PEO/NBR-PEDOT samples and performing elemental analyses. A former post-doctoral fellow Dr. Ashwin Usgaocar has provided mentorship and guidance in synthesizing the carbon slurry samples used. An undergraduate research assistant Dickson Yao has helped set up and carry out some of the measurements and also assisted in processing of the acquired data. Dr. Vidal and Dr. Nguyen have also helped revise the draft, and provided guidance over data analysis. Dr. Madden acted in a supervisory capacity. My role was to synthesize the samples, make the measurements, perform the analysis, derive and construct an equivalent ionic impedance model, and write the paper.
Table of Contents

Abstract ........................................................................................................................................... ii

Preface ........................................................................................................................................... iv

Table of Contents ................................................................................................................................. vi

List of Tables ..................................................................................................................................... x

List of Figures ..................................................................................................................................... xi

List of Abbreviations ........................................................................................................................ xvi

Acknowledgements ............................................................................................................................ xvii

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

1.1 Initial observations and the discovery of the lateral piezoionic effect ................................. 1

1.2 Proposed overview of the mechanism of the piezoionic effect ........................................... 7

1.3 Strategy for characterization of the piezoionic effect ......................................................... 12

1.4 Piezoionic polymers: translating the discovery to applications ......................................... 14

Chapter 2  Characterization of the Piezoionic Effect ........................................................................... 18

2.1 Transduction as a function of applied pressure and frequency ........................................... 19

2.1.1 Sample Synthesis .............................................................................................................. 19

2.1.2 Experimental Setup ......................................................................................................... 21

2.1.3 Results ................................................................................................................................ 22

2.2 Transduction as a function of relative ionic mobilities – effect of ion sizes ..................... 24

2.2.1 Mechanism of ion-ion and ion-solvent interactions ....................................................... 24

2.2.2 Sample preparation .......................................................................................................... 27

2.2.3 Diffusion NMR measurements and transference numbers ........................................... 28
2.2.4 Piezoionic characterization as a function of effective ion sizes ........................................ 32
2.2.5 Ionic conductivity ........................................................................................................... 35

2.3 Transduction as a function of relative ionic mobilities – effect of polymer charge densities........................................................................................................................................................................... 38

2.3.1 Mechanism of ion-polymer interactions .................................................................... 38
2.3.2 Sample preparation ...................................................................................................... 39
2.3.3 Diffusion NMR measurements and transference numbers ...................................... 40
2.3.4 Piezoionic characterization as a function of polymer charge density ....................... 41

2.4 Discussion and conclusion ............................................................................................. 44

Chapter 3 Modeling the Piezoionic Effect ........................................................................... 48

3.1 Overview of approach in modeling the piezoionic effect in an ionic polymer .......... 48

3.1.1 Poroelastic behavior and the non-equilibrium thermodynamic theory .................. 48
3.1.2 Fluid flow and zeta potential modelling .................................................................... 52

3.2 Model implementations using COMSOL Multiphysics and MATLAB .................... 54

3.2.1 Coupled Poroelastic solvent flow – transient ionic redistribution model ............. 54
3.2.2 Electrokinetic potential across a solvent flow over a charged tube structure ......... 68

Chapter 4 Method for Determination of Ionic Conductivity in Heterogeneous and Electronically Conductive Structures ................................................................................................................. 71

4.1 Background and motivation ............................................................................................ 72

4.2 Experimental .................................................................................................................. 76

4.2.1 Materials .................................................................................................................... 76
4.2.2 Preparation of Specimens ....................................................................................... 77
4.2.3 Measurement Procedure ......................................................................................... 79
C.1 Series model .................................................................................................................. 136
C.2 Parallel model ............................................................................................................. 137
C.3 Dual Model ................................................................................................................. 139
List of Tables

Table 2-1. A list of PVDF-HFP/LiTFSI/PC polyelectrolyte samples used ........................................ 27
Table 2-2 A list of charged derivatives of polyacrylamide hydrogel samples used .................... 41
Table 3-1. A summary of the mechanical properties of polyacrylamide ...................................... 55
Table 3-2. List of variables and constants used in the computation of simulated voltage build-up across a solvent flow path ............................................................................................................. 69
Table 4-1. Summary of measured phase specific ionic conductivities ......................................... 89
List of Figures

Figure 1-1. A depiction of ionic polymer composites (EAPs and IPMCs) in (a) actuator mode operation and (b) sensor mode operation ........................................................................................................... 3

Figure 1-2. (a) the voltage responses and (b) the current responses of an aqueous 2.0M KCl swollen polyurethane hydrogels upon compression at various locations. In the middle plots the scale is much smaller, and the sensor signal is much smaller. ........................................................................... 5

Figure 1-3. A comparison of the piezoionic step response in (a) PVDF-HFP/LiTFSI/PC polyelectrolyte (0.1 M electrolyte concentration) and (b) Polyacrylamide/NaCl/Water (2.74 M electrolyte concentration) hydrogel ........................................................................................................... 6

Figure 1-4. A depiction of a compression-induced solvent flux and ion displacement within a polyelectrolyte ........................................................................................................................................... 7

Figure 1-5. A flowchart representing the proposed mechanisms and contributing factors of the piezoionic effect ........................................................................................................................................... 13

Figure 2-1. A digital photograph of the PVDF-HFP/LiTFSI/PC solid polymer electrolyte ...... 20

Figure 2-2. A depiction of the experimental setup for determination of piezoionic voltage responses ............................................................................................................................................... 22

Figure 2-3. A linearity plot of the piezoionic voltage as a function of applied force ............... 22

Figure 2-4 Bode plots for (a) complex mechanoionic transduction and (b) complex elastic modulus ........................................................................................................................................... 24

Figure 2-5. A depiction of ion-solvent (propylene carbonate) interaction for (a) lithium cation and (b) bis(trifluoromethane) sulfonamide anion. Note that the positive charge of lithium causes
the lone pairs of propylene carbonate to surround the ion, whereas the lack of H-bonding site of propylene carbonate translates to minimal interaction with bis(trifluoromethane) anion.

Figure 2-6. A depiction of the NMR experimental setup [43].
Figure 2-7. Pulse sequence employed in the PFGSE NMR measurement procedure.
Figure 2-8. Self-diffusion coefficients of Li+ ions and TFSI- ions as a function of electrolyte concentration.
Figure 2-9. Piezoionic voltage response during a sine wave compressive perturbation on PVDF-HFP hosted polyelectrolyte containing (a) 0.5 M LiTFSI/PC (b) 1.0 M LiTFSI/PC (c) 1.25 M LiTFSI/PC (d) 1.5 M LiTFSI/PC (e) 1.75 M LiTFSI/PC (f) 2.0 M LiTFSI/PC (g) 2.25 M LiTFSI/PC (h) 2.5 M LiTFSI/PC.
Figure 2-10. Peak voltage response amplitude of PVDF-HFP/LiTFSI/PC polyelectrolyte as a function of LiTFSI Concentration.
Figure 2-11. Ionic conductivity of PVDF-HFP/LiTFSI/PC polyelectrolyte as a function of LiTFSI concentration.
Figure 2-12. Chemical structure of (a) Acrylamide (b) MAPTAC and (c) AMPS.
Figure 2-13. Piezoionic voltage response during a sine wave compressive perturbation on aqueous 0.5 M NaTf polyelectrolyte hosted within (a) 100% polyacrylamide (b) 50% AMPS / 50% polyacrylamide (c) 50% MAPTAC / 50% polyacrylamide.
Figure 2-14. Peak voltage response amplitude of polyacrylamide hydrogels (in black) as a function of polymer backbone charge. The trend is compared to the change in the anionic diffusion constant (in yellow).
Figure 3-1. A graphical representation of the geometry used for gel compression test. The gel is 2cm x 2 cm x 0.5 cm, and the circular boundary with diameter of 1 cm is used to apply the displacement controlled compression. ................................................................. 55

Figure 3-2. A graphical depiction of the total displacement at t = 100. ............................. 56

Figure 3-3. A graphical representation of the pressure at t = 100....................................... 57

Figure 3-4. A graphical representation of the deformation induced Darcy’s fluid flow velocity at t = 100 ........................................................................................................................................... 57

Figure 3-5. Cross-coupling relationship between poroelasticity, transport of diluted species and electrostatics modules implemented in COMSOL Multiphysics.................................................. 60

Figure 3-6. A graphical representation of the concentration distribution at t = 0. The initial concentration was set to be 1 M. ........................................................................................................ 61

Figure 3-7. A graphical representation of the concentration distribution of species 1 at t = 100. 61

Figure 3-8. A graphical representation of the concentration difference of species 1 and 2 at t = 100................................................................................................................................................. 62

Figure 3-9. A graphical representation of the convective flux (color: magnitude, arrow: vector) at t = 100. .......................................................................................................................................................... 62

Figure 3-10. A graphical representation of the diffusive flux (color: magnitude, arrow: vector) at t = 100. ......................................................................................................................................................... 63

Figure 3-11. A graphical representation of the electrophoretic flux (color: magnitude, arrow: vector) at t = 100. ......................................................................................................................................................... 63

Figure 3-12. Voltage at various distances from the centre of the gel. Note the radius of the circular indenter was 5 mm. ......................................................................................................................................................... 65
Figure 3-13. Maximum molar convective, diffusive, and electrophoretic flux observed in the gel over time. ................................................................. 66

Figure 3-14. Average surface pressure at the site of compression as a function of time. Note the relaxation behavior due to solvent flow, the rate of relaxation decreases over time as the convective flux can also be observed to decrease in this time frame. ........................................... 67

Figure 3-15. A simulated voltage across a solvent flow path length of 0.1 mm within charged polyacrylamide having 10 nm pore sizes, as the zeta potential was varied from 0.1 V to -0.1 V (cationic gel to anionic gel), and the applied pressure across was varied from 0 to 1 kPa. ............ 69

Figure 4-1. SEM images depicting surface topologies of (a) PVDF/PPy (b) Activated carbon/Celgard® (c) PEO-NBR/PEDOT and the cross sectional views of (d) PVDF/PPy (e) Activated carbon/Celgard® (f) PEO-NBR/PEDOT ................................. 78

Figure 4-2. The diffusion cell experimental set-up. The potential difference is measured across the reference electrodes while a current perturbation is applied between the counter and working electrodes. ................................................................. 79

Figure 4-3. i-E plots representing the DC resistance of the (a) Celgard®/activated carbon sample (b) PVDF/Gold/PPy sample (c) PEO-NBR/PEDOT sample. ................................................................. 84

Figure 4-4. Magnitude Bode plots representing the complex impedances of the (a) Celgard®/activated carbon sample (b) PVDF/Gold/PPy sample (c) PEO-NBR/PEDOT sample at various PEDOT concentrations (5, 12, 19, 25, 25 wt%). Red lines represent the impedance response of the respective equivalent electrical circuit models ........................................ 87

Figure 4-5. A graphical representation describing the electronic and ionic conduction for (a) asymmetric system (electronically conductive film shown in black into which ions can travel) (b) symmetric system (electronically conductive film) and (c) symmetric system (electronically conductive film...
insulating film shown in beige), along with their corresponding equivalent electrical circuit models. Here the +’s represent electronic charges, with which there are associated anions, the –’s are also electronic charges, with associated cations (yellow spheres). At the bottom are equivalent circuit models used to represent transport in each of these cases. ..................................... 90

Figure 4-6. A comparison of the (a) series equivalent circuit (linear impedance addition), (b) parallel equivalent circuit for interpenetrating network modelling (c) dual series/parallel model using local PEDOT concentrations obtained via EDX and (d) measurements and simulations of the effect of PEDOT concentration on ionic conductivities of PEO-NBR/PEDOT samples...... 95

Figure 4-7. Flowchart representing the summary of decision criteria used in carrying out the proposed characterization protocol for an ionically conducting structure................................. 98

Figure 5-1. A Carotid Angiography taken during a coiling procedure. Note the location of an aneurysm (red arrow) and the coil being inserted (blue arrow).................................. 108

Figure 5-2. Photographs of aneurysm flow phantom with simulated fluid flow (a) before the insertion of polyacrylamide hydrogel and (b) after the insertion of polyacrylamide hydrogel .. 109

Figure 5-3. Overall experimental setup for the aneurysm flow induced piezoionic voltage measurement ............................................................................................................................... 110

Figure 5-4. (a) The voltage response of the polyacrylamide gel inserted at the simulated aneurysm site as the syringe was pumped to a displacement of 5 mm at 0.3 Hz (b) a summary of peak voltage changes detected by the gel as the magnitude of the displacement was varied from 1 to 5 mm ......................................................... 111

Figure 5-5. (a) a schematic architecture (b) a photograph of the patch type polymer electrolyte based strain sensor ................................................................. 112
Figure 5-6. The voltage response of LiTFSI/PC + PVDF-HFP polyelectrolyte attached to an index finger, while the finger was being flexed and extended cyclically.......................... 113

Figure 5-7. A proposed NMR measurement setup for acquisition of driven diffusion numbers of ions in polymer electrolyte samples........................................................................................................... 115

Figure 5-8. An example NMR pulses sequence for piezoionic driven diffusion measurement. 116

Figure 5-9. 3D models of aneurysms obtained via CT scanning................................................... 117

Figure A5-1. A depiction of the equivalent circuit model of the modified, one-sided Warburg element........................................................................................................................................ 127

Figure 5-2. PEDOT concentration profile as a function of position in the thickness of the membrane (5 wt% PEDOT sample) ................................................................................................................... 133

Figure 5-3. PEDOT concentration profile as a function of position in the thickness of the membrane (12 wt% PEDOT sample) ................................................................................................................... 133

Figure 5-4. PEDOT concentration profile as a function of position in the thickness of the membrane (19 wt% PEDOT sample) ................................................................................................................... 134

Figure 5-5. PEDOT concentration profile as a function of position in the thickness of the membrane (25 wt% PEDOT sample) ................................................................................................................... 134

Figure 5-6. PEDOT concentration profile as a function of position in the thickness of the membrane (26 wt% PEDOT sample) ................................................................................................................... 134
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>AMPS</td>
<td>2-Acrylamido-2-Methylpropane Sulfonic Acid</td>
</tr>
<tr>
<td>AP</td>
<td>Ammonium Persulfate</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl Peroxide</td>
</tr>
<tr>
<td>DCPD</td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-Ethylene(dioxythiophene)</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>IPMC</td>
<td>Ionic Polymer Metal Composite</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Poly(vinylidene fluoride-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile Butadiene Rubber</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>Bis(trifluoromethane)sulfonimide Lithium Salt</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead Zirconate Titanate</td>
</tr>
<tr>
<td>MAPTAC</td>
<td>Methacrylamidopropyltrimethylammonium Chloride</td>
</tr>
<tr>
<td>IPN</td>
<td>Interpenetrated Polymer Network</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PANi</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PFGSE</td>
<td>Pulse Field Gradient Spin Echo</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PSS</td>
<td>Polystyrene Sulfonate</td>
</tr>
<tr>
<td>RC</td>
<td>Resistor-Capacitor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to Noise Ratio</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid Polymer Electrolyte</td>
</tr>
<tr>
<td>TBAP</td>
<td>Tetrabutylammonium Hexafluorophosphate</td>
</tr>
<tr>
<td>TC</td>
<td>Templated Porous Carbon</td>
</tr>
<tr>
<td>TEABF₄</td>
<td>Tetraethylammonium Tetrafluoroborate</td>
</tr>
<tr>
<td>TEMED</td>
<td>Tetramethylethylenediamine</td>
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Acknowledgements

I would like to express my gratitude towards all personnel involved in coordinating the Biomedical Engineering – Engineers in Scrubs Fellowship and providing an optimal environment to start a career in a pioneering field of Biomedical research.

I thank all my colleagues and friends at UBC for the competitive and stimulating experience as a graduate student, and all the fun hours spent together off-campus.

I am grateful for my co-supervisors, Dr. Edmond Cretu and Dr. Victor Yang (clinical), for taking the time for various discussions to enhance the quality of my research work.

Finally, I thank Dr. John Madden for his continuous support in all aspects of the time I have spent in his group.
Chapter 1  Introduction

This thesis discusses a novel phenomenon termed the *piezoionic* effect that is found in various ionic polymers including polymer networks containing aqueous electrolytes, organic electrolytes, and ionic liquids. The initial observations revealed that when an ion-containing matrix of polymer is compressed, an ionic concentration gradient is induced by the pressure differential, leading to an electrical potential difference detectable at electrodes placed at compressed and uncompressed portions of the polymer. Motivated by this discovery, potential applications of these piezoionic polymers as robust, compliant, and biocompatible pressure/strain sensors in medicine are discussed and explored.

This chapter begins by introducing the initial observations of the voltage arising from gel deformation, leading to the discovery of the piezoionic effect. Subsequently, the postulated mechanism of the phenomenon is presented with a brief mathematical description. Based on the postulated mechanism, a strategy for empirical characterization to probe into the parameters affecting the behavior of the piezoionic effect is proposed and later implemented in chapter 2. Finally, a roadmap to translate the fundamental characterization to practical applications of the piezoionic effect is presented and compared with existing technologies.

1.1  Initial observations and the discovery of the lateral piezoionic effect

Ionic polymer devices emerged as field driven actuators in 1990’s [1]–[4]. Commonly in these actuator devices, a central ion reservoir layer is sandwiched by electronically conducting layers across which one can apply an electrical potential. The working and counter electrodes will experience a differential strain as ions that balance charge on the electrodes are intercalated into
or deintercalated from the electrodes, causing a bending motion as one electrode swells and the other contracts.

A wide variety of polymers can serve as the ion reservoir, including materials ranging from polyvinylidene fluoride (PVDF), NAFION®, FLEMION®, and various co-polymers which might incorporate polymers such as poly (ethylene oxide) (PEO) and nitrile butadiene rubber (NBR) [5]–[8]. The electrode layers can comprise of a number of classes of materials including conducting polymers such as polypyrrole, poly (ethylene dioxythiophene), and polyaniline [9][10]. Actuators incorporating such electronically conducting polymers are known as conducting polymer actuators. Others distribute metals such as platinum and gold into the surfaces of ion exchange polymers [11]. These structures are typically referred to as ionomeric polymer metal composites (IPMCs).

Conducting polymer actuators and IPMCs have been of interest as candidates for actuators employed in soft robotics as well as human to computer interfaces (i.e. haptic feedback). For example, polypyrrole based microgrippers have been reported by Bar-Cohen et al [12]. Braille cells driven by electroactive polymer actuators have also been reported [13], [14]. With the recent emergence of flexible, stretchable and wearable devices, many skin-like tactile interfaces have been developed utilizing the flexible nature of the polymer [15]–[17].

On the other hand, reverse operation of these multilayered ionic polymers as mechanical sensors were reported [10], [18]–[21]. Here, a bending strain applied to the polymer has been found to generate a voltage across the electrode layers. The polarity of the strain induced voltage
corresponds with the polarity when it is operated in the actuator mode. Namely, Wu et al. have shown that polypyrrole films doped with dodecyl benzene sulfonate (DBS) ions as well as ones doped with perchlorate ions produced in-phase and out-of-phase voltage response respectively, when a sinusoidal bending strain was applied. It had been known that doping of polypyrrole with bulky DBS ions and a relatively smaller perchlorate ions resulted in cation and anion dominant systems respectively, and as such, they were known to bend in the opposite directions when the same potential was applied. This characteristic behavior of ionic polymer sensing suggested a common underlying mechanism that is referred to here as the piezoionic effect.

Inspired by the previous work on sensor mode operation of various ionic polymer composites, it was hypothesized that gel-like materials can act as pressure sensors, with the compression of such
a highly deformable polymer containing an electrolyte leading to ionic charge redistribution. Initial experiments were carried out using a number of candidate materials including poly(ethylene oxide) – nitrile butadiene rubber interpenetrated polymer networks, polyurethane hydrogels, and polyacrylamide hydrogels, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). These polymers were synthesized with various electrolytes (aqueous, organic and ionic liquid) and were placed on a flat glass surface with two parallel electrodes underneath the gel.

The ionic polymer samples were found to generate a voltage/current signal when a portion of the polymer was depressed. Furthermore, the polarity of the voltage signals was found to change over the location of the deformation, presumably as the direction of the induced ionic flux was altered. The results below were obtained on a polyurethane hydrogel sample containing an aqueous solution of 2.0 M potassium chloride. One can observe the negative voltage/current when the compression took place on the counter electrode, followed by a quasi-cancellation effect (a much smaller response magnitude) when pressed in the middle, and finally a positive signal at the working electrode.
Figure 1-2. (a) the voltage responses and (b) the current responses of an aqueous 2.0M KCl swollen polyurethane hydrogels upon compression at various locations. In the middle plots the scale is much smaller, and the sensor signal is much smaller.

Similar to the prior work on the electroactive polymer based sensors, it was further postulated that the polarity of the signals would be dependent on the ionic species with higher mobility. Therefore, several samples of gel were made while incorporating various salts. They were then compressed at the same location while the resultant voltage was recorded.

Figure 1-3 is a comparison of the step response of the polymer electrolyte synthesized in this study (LiTFSI) versus a polyacrylamide hydrogel containing 2.74 M aqueous sodium chloride. We observed an RC charging like response followed by a steady state voltage in the SPE sample, whereas the response quickly decayed in the hydrogel sample. The time constant in both cases is estimated to be in the order of 10’s of seconds, providing insight into the mechanisms behind the piezoionic response.
These initial results called for further investigation of the effect to understand the exact mechanism of ion redistribution upon compression of an ionic polymer gel. As the effect can be generalized to mechanically induced ion displacement regardless of the particular geometry of the sensor, the phenomenon has been termed the piezoionic effect. This phenomenon can reasonably be further divided into several factors: electrolyte flow (convection), ion diffusion and electrostatic interactions (ion-ion, ion-solvent, and ion-polymer). In the subsequent sections, an overview of the postulated mechanism of the piezoionic effect is discussed, addressing each of the contributing factors and how to empirically probe them.
1.2 Proposed overview of the mechanism of the piezoionic effect

The piezoionic effect is believed to be an inhomogeneous ionic distribution in response to an imposed deformation gradient to a gel structure. The highly deformable polymeric ion host initially at equilibrium has a uniform distribution of mobile species such that the electrochemical potential experienced by all species is equal, and the free energy of the system is minimal.

When a mechanical perturbation causes the polymer matrix to non-homogeneously deform as shown in figure 1-4, the solvent molecules as well as ionic species will experience a differential pressure locally, and displace such that the chemical potential change compensates the pressure applied which is described by the Gibbs-Duhem equation. At this polarized state, the change in chemical potential must directly correspond to the change in electrical potential measured. This electrical potential change, $\Delta E$, can be measured using electrodes that are in contact with the material.
To predict the voltage induced by deformation of an ionic polymer the electromechanical coupling must be explained using available free energy. We begin with the Gibbs-Duhem equation in a poroelastic solid [22]:

$$-\varphi V dP + s dT + \sum_i n_i d\mu_i = 0$$

(1 – 1)

where $\varphi$ is the porosity of the polymer, $dP$ is the infinitesimal pressure change within the bulk, $s$ is the entropy of the overall system, $T$ is the temperature, $n_i$ is the number of moles of species $i$, and finally $d\mu_i$ represents the infinitesimal change in the chemical potential of species $i$. Here we assume a constant temperature system, eliminating the entropy term:

$$\varphi V dP = \sum_i n_i d\mu_i$$

(1 – 2)

The term on the right-hand side is simply the partial molar Gibbs free energy, and we may now equate the mechanical pressure change applied to the polymer bulk to ion concentration distribution assuming a non-interacting system:

$$dG = \varphi V dP = RT \ln \frac{[i]_x}{[i]_{x+\Delta x}}$$

(1 – 3)

Where $[i]$ represents the concentration of the $i^{th}$ species and the subscripts represent two locations separated by a distance $\Delta x$ within the sample. To associate the ion concentration to the resultant voltage, we take the approach of solving for Donnan potential induced by inhomogeneous ion distribution across a cellular membrane in biological systems. The electrochemical potential of species $i$ can be expressed as a summation of chemical and electrical potentials as follows:

$$\bar{\mu} = \mu + zFE = RTln[i^+] + zFE$$

(1 – 4)

$z$ is the valence charge of the ion, $F$ is Faraday’s constant, and $E$ is the electrical potential. When the polymer is deformed and the mobile species attains a new equilibrium, the electrochemical
potential is constant across the system. Thus the chemical potential change induced by pressure gradient must be directly compensated by the change in electrical potential:

$$\Delta \bar{\mu} = \Delta \mu + zF\Delta E = 0$$  \hspace{1cm} (1 - 5)$$

and

$$\Delta E = \frac{RT}{zF} \ln \left( \frac{[i^+]_x}{[i^+]_{x+\Delta x}} \right)$$  \hspace{1cm} (1 - 6)$$

The equation predicts that if the concentration of a species varies by a factor of 2.718, the potential difference produced will be 25 mV at room temperature. At long times, the voltage will persist if either cations or anions are immobilized onto the polymer backbones such as seen in IPMC based configurations [23]. If both cationic and anionic species are mobile, the voltage will approach zero as a change in Gibbs energy induced by differential pressure on both cations and anions are the same. The decay behavior is dependent on the relative mobilities of these ionic species within the polymer bulk.

This is analogous to the Goldman-Hodgkin-Katz equation, which describes the Donnan potential in terms of the ion concentrations as well as their permeabilities, $P_i$, across a biological membrane:

$$\Delta E = \frac{RT}{zF} \ln \left( \frac{\sum_i^n P_{cation_i}[cation_i]_x + \sum_i^m P_{anion_i}[anion_i]_{x+\Delta x}}{\sum_i^n P_{cation_i}[cation_i]_{x+\Delta x} + \sum_i^m P_{anion_i}[anion_i]_x} \right)$$  \hspace{1cm} (1 - 7)$$

The potential drops to zero, or the original open circuit potential of the cell, over time if both anions and cations are mobile. In the gel sensors used in this work, one mobile anionic species and one mobile cationic species are present. A generation of a signal of a particular polarity is interpreted as indicating a higher permeability of the matrix to one sign or ion compared to the other.

Factors to consider in the solvent flow of polyelectrolytes are Stoke’s drag, and electrostatic interactions between polymers and ions, ions and ions, or ions and solvents. At this point, it is
noted that the mechanisms and modeling of solvent behavior within gels has been of interest to others and has been researched. In many cases, perfect incompressibility of both solvents and the polymer is assumed (Poisson’s ratio ≈ 0.5) [24]. Under this condition, a fully swollen gel containing solvent undergoing a given external mechanical or chemical stimulus undergoes a transient process involving poroelastic solvent flow solvent via chemical or mechanical interactions between the polymer chains and solvent [25].

Some linear theories have been proposed, such as the one by Tanaka et al, who treated a swollen gel system as a mixture of solids and liquids with a coefficient of friction for their interaction parameter [26]. An extension to this linear poroelasticity model was developed by Scherer et al, who treated the system as a continuum phase with solvent concentration and pore pressure [27]. However, linear theories are accurate only at small deformations. Intuitively, this is problematic in hydrogels that collect much attention due to their highly robust and deformable mechanical properties. Therefore, some efforts have been made to realize a non-linear model in which the elastic free energy change due to the chemical potential of the solvent molecules of the system is estimated, assuming the total Gibbs free energy of the system satisfies the inequality $\frac{\partial G}{\partial t} \leq 0$ [24], [25], [28]. It has been shown that upon indentation of gels, they behave initially viscoelastically, suggesting that the solid phase polymer is mechanically dominant in the short time frame. Over time, however, the initial mechanical perturbation results in solvent flow resulting in poroelastic behavior. For instance, a swollen hydrogel undergoing a step compressive load is deformed initially to a given indentation which is dependent on the speed of the perturbation (viscoelastic), and subsequently the displacement gradually creeps further under the same load as the solvent migrates to the surroundings of the perturbation site (poroelastic). Utilizing the fact that
viscoelastic relaxation is independent of the contact area of indentation, whereas poroelastic relaxation follows a quadratic trend over indentation area, Cai et al. elucidated the poroelastic behavior of an alginate hydrogel by using various indenters of different shapes and sizes [29].

Johansson has shown that bulk ionic concentration is diminished when free ions and the charge on the polymer backbone are attracted, leading to decreased diffusivity [30]. Also noted by the author was that this decrease in diffusivity is less severe if the size of the charged species is relatively larger than other charged species that are smaller because the smaller species would preferentially accumulate by the polymer chain [30]. Larger ionic species are more likely to be mainly governed via steric effects rather than electrostatic. However electrostatics still are a relevant factor [30]. In cellular biology, the concept is extended to protein mobility in gels (DNA or protein electrophoresis applications) or in biological tissues with charged or polar matrices depending on the amino acids present. For instance, a positively charged protein ribonuclease A in solutions of dextran with various charges and concentrations was investigated using fluorescence correlation spectroscopy. They showed that the diffusivity of ribonuclease A diffusivity was unaffected by positively charged or neutral dextran, but it was severely immobilized by negatively charged dextran and maximum binding of approximately 80% of all present protein were observed [31]. Other studies have also shown similar effects in positively charged β-lactoglobulin gels and negatively charged Na₂-fluorescein (strong influence on fluorescein diffusivity via electrostatic interaction and linear relationship between β-lactoglobulin concentration and binding), or myoglobin in agarose gels (myoglobin diffusivity was enhanced/hindered depending on the buffer pH) [32], [33].
Linking the idea of electrostatic interactions to the deformation induced flow, a laminar flow driven by a pressure $\Delta p$ through a cylindrical channel with a given surface charge on the wall yield a streaming potential [34], [35]:

$$V_{flow} = \frac{\varepsilon_r \varepsilon_0 \Delta p}{\eta l}$$

where $\varepsilon_r$ is the relative permittivity of the electrolyte, $\varepsilon_0$ is the permittivity of free space, $r$ is the radius and $l$ is the length of the channel through which the solvent flow takes place, $\eta$ is the dynamic viscosity of the solvent, $p$ is the pressure, and $\zeta$ is the zeta potential.

### 1.3 Strategy for characterization of the piezoionic effect

The Piezoionic effect is hypothesized to be the result of net movement of one charge species relative to its counter charge in response to an applied pressure, leading to the generation of an electrical potential difference, within the host polymer matrix. However, a number of possible mechanisms can contribute to this ionic charge separation. Solvent flow within the bulk of the polymer is induced poroelastically, while Stoke’s drag forces, and the electrostatic interactions with the backbone charges (the electrokinetics) of the polymer and with other ionic species dictate the initial distribution. Subsequently, back diffusive flux and migration take place, arriving at an equilibrium at long times.

To fully understand the piezoionic effect, it is necessary to construct a series of strategic experiments to probe into each of the possible mechanisms mentioned above and determine if any one of them is a dominant mechanism or if they are taking place in a concerted manner. Below, a
flow chart is presented which depicts the possible routes via which the piezoionic effect could take place in an ionic polymer.

Figure 1-5. A flowchart representing the proposed mechanisms and contributing factors of the piezoionic effect

In chapter 2, characterization methods and results of the piezoionic effect in various ionic polymers are presented. The characterization begins by determining the range of mechanoionic transduction (generation of ionic charge separation or displacement upon a mechanical perturbation to the medium which hosts the present ions) coefficient (in V/Pa) a given ionic polymer can achieve, as well as its frequency response. The purpose of this experiment is to ensure the potential being generated from the ionic polymers are within the reasonable range as expected by Donnan ionic polarization. The frequency response is also observed. This is not only because it provides insight into what type of applications piezoionic sensors could be used. It is also because it determines the time constant of the response, which may suggest whether the mechanism is more likely due to
relatively slow self-diffusion or to a solvent flow driven effect whose time constant can be shorter, as explained in later chapters.

Subsequently, the study focuses on the most fundamental underlying assumption that the piezoionic effect is relying on. That is, that there is an ionic mobility differential between the cationic and anionic species. It is this difference in the mobilities of various species present which causes a net ionic charge separation under mechanical perturbations. A number of factors affect the ionic mobility of a given species. These include the size of ions, the nature of solvation depending on the bonding mechanism between solvent molecules and ions, the ion to ion interactions which are highly correlated to the concentration of the solution, the mesh density of the host polymer matrix, and finally the electrostatic interaction between the ionic charges and the polymer backbone charges. Here, we focus on the effect of ion size and the effect of polymer charge densities on the ionic mobilities of respective species present in the polymer matrix. It is shown that the effective ion sizes and electrostatic ion-polymer interactions have some effect on the self-diffusion coefficients of the ions present and that these changes modulate the piezoionic voltage responses to a given mechanical perturbation. The findings collectively suggest that the piezoionic effect indeed arises from the differential ionic mobilities of the cationic and anionic species present in the system, but more work is still needed to fully understand the underlying mechanisms.

1.4 Piezoionic polymers: translating the discovery to applications

At this point in the discussion, naturally, one might ask of the applicability of the piezoionic effect to any relevant technologies. It is useful to note that a multitude of polymers vastly ranging in their
chemo-mechanical properties can be used to construct a so-called piezoionic polymer. Namely in this thesis, polyurethane, polyacrylamide, and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), methylacrylamidopropyltrimethylammonium chloride (MAPTAC), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) have been employed for various characterizations. How can piezoionic polymers play to their advantages and outperform currently available pressure-sensing solutions?

Transducers capable of sensing pressure are ubiquitous. Conventional sensing technologies include piezoresistive [1]–[3], piezoelectric [4], [5], capacitive [6]–[8], optical [9], and magnetic [10] methods. The well-established sensors are not generally highly stretchable or transparent – properties that are increasingly sought after in the emerging fields of wearable technologies, soft robotics and augmented reality with highly complex perception of various surfaces.

As a part of the endeavors to meet this desirable requirement, sensors are being incorporated onto thermoplastic (bendable) and elastomeric (stretchable) substrates. Promising capacitance based technology is shown to be highly sensitive [11], stretchable by up to 150% [12] [13], and relatively transparent [12] [13]. However, these promising approaches still have some limitations for widespread use as they either employ poorly stretchable electrodes [11], or materials such as carbon nanotubes (CNT) and silver nanowires (AgNW) that are still considered exotic. Sun et al [14] employ electrolyte containing tough gels to show very highly stretchable (2000%) and transparent (98.9%) capacitive sensors. It is a capacitive sensor formed by a trilayer composed of a transparent elastomer forming the dielectric, between ionically conductive transparent polymer
layers which act as stretchable electrodes. These, in addition to other sensor technologies being developed currently, face challenges such as cost and power requirement or complexity of readout circuit, and have to settle for trade-offs between transparency, flexibility, complexity and cost.

Piezoionic sensors can employ tough, compliant, and transparent polymers such as cross linked hydrogels including polyurethane, polyacrylamide, and polyalginate. Cross-linked hydrogel materials have been used in many applications such as separation membranes, biosensors, valves, artificial muscle [15], [16], drug delivery devices [17], super-adsorbent nano-composites [18] and actuators for optics and fluidics [19]. Hydrogels are very soft and wet materials with low sliding friction [20] and high solute permeability [21]. In many cases where the sensor directly interfaces with human tissue, it is highly desired that the mechanical impedance of the sensing material is matched to that of, for example, human skin which has a Young's modulus of 4.5 kPa to 8 kPa [36]. Hydrogels have been used as scaffolds hosting progenitor or stem cells in the rapidly advancing field of tissue engineering, as they exhibit little cytotoxicity, and their mechanical properties are compatible with many soft tissues in a human body [37]. Finally, it is noted that piezoionic sensors can act as active elements (actively generating voltage/current signals upon perturbation) unlike piezoresistive or capacitive sensors, allowing a relatively simpler readout circuitry design without any continuous expenditure of power on excitation signals. To summarize, piezoionic sensors are an attractive candidate for the next generation of soft pressure sensing solution as they are i) highly flexible, stretchable, and mechanically compliant ii) transparent iii) biocompatible (chemically and mechanically) and iv) capable of actively generating signals. Exactly how attractive a candidate is a piezoionic pressure sensor? This thesis aims to answer a
select few aspects of this major question. In short, the sensitivity of the piezoionic polymers under study have been shown comparable to that of piezoelectrics. While it is much more flexible and stretchable than conventional piezoelectric materials such as ceramics or PVDF, it suffers from frequencies above 10 Hz, perhaps due to the lossy aspect of soft polymers or the latency related to the solvent flux within the polymer to transport the ions. Along with the fundamental characterization of the piezoionics, a future work could potentially be a tuning of polymer materials such that mechanical compliance, pressure sensitivity, and frequency response are optimized.

With this in mind, this work proposes and demonstrates several device level implementations of piezoionic pressure sensors. In the final chapter, a patch-type piezoionic sensor is fabricated and attached to an index finger for extension and flexion monitoring to demonstrate good mechanical flexibility against human tissues and its practical functionality. Another demonstration shows a so-called intra-aneurysm pressure sensing using a hydrogel based piezoionic sensor. The sensor is embedded in a flow phantom, mimicking an aneurysm while a pulsatile flow is being applied across, and the voltage is measured at two points within the implanted gel, which has shown to linearly correspond to the flow profile. The motivation for this particular application lies in the rupture risk of an aneurysm is relatively unpredictable in the current clinical state of art. It is discussed in more details in chapter 5. Here, not only the mechanically compliant nature of the hydrogel is utilized, but also the high in vivo biocompatibility of the material enables the use of piezoionic sensing among others to be employed in this particular case.
Chapter 2  Characterization of the Piezoionic Effect

With the initial discovery of the piezoionic effect and the postulates made on the underlying mechanisms of this phenomenon briefly outlined in chapter 1, a series of experiments were designed and carried out to verify the theory. Materials appearing in section 2.1 have been published in an online-only journal MRS Advances (Dobashi, Y., Allegretto, G., Sarwar, M.S. and Madden, J.D.W. (2016) MRS Advances vol 1. “Mechanoionic Transduction of Solid Polymer Electrolytes Potential Applications.”). In section 2.1, the so-called Piezoionic or mechano-ionic transduction coefficient (in units of V/Pa) was determined as a function of perturbation frequency in a solid polymer electrolyte sample. This experiment enables a preliminary evaluation of the order of magnitude of voltage being generated via the piezoionic mechanism. Application of constitutive equations based on a Donnan-like effect to estimate the extent of ionic charge separation to yield the empirically measured voltages. Secondly, a qualitative correlation between the effective ion sizes (with consideration of solvation effects) and the change in the voltage response behavior of piezoionic effects is made. This is achieved by employing solvents to selectively form solvation spheres around cations and varying the solvent/solute ratios. Finally, to evaluate the interaction between the ionic species and the polymer backbone via electrostatic forces, NMR self-diffusion measurements were made in various polyacrylamide hydrogels with varying backbone charge densities. It is hypothesized that, other than the different ion sizes, the permanent charges on the polymer backbone could also influence the ionic mobilities by inhibiting the motion of oppositely charged ions by attraction and promoting the motion of like charged ions by repulsion. From this, various mechanisms through which the ionic charge separation could take place (i.e. solvent flow, electrostatic drag, size effect, and diffusion) are individually investigated, and the initial postulates are further refined into numerical modeling as presented in chapter 3.
2.1 Transduction as a function of applied pressure and frequency

In this section, ionic polymer gels based on Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) co-polymer were synthesized in situ to incorporate an organic electrolyte consisting of bis(trifluoromethane)sulfonimide lithium salt in propylene carbonate. With two electrodes placed under the gel, the samples were subjected to a sinusoidal mechanical force while the open circuit voltage was measured to determine the relationship between electrical signal and mechanical input. The voltages generated are in the range of 10’s of mV in magnitude at 1 kPa. Results suggest a maximum sensitivity of 25 µV/Pa at 10 mHz, comparable to the voltages expected in piezoelectric polymers such as PVDF (44 µV/Pa for similar dimensions). The new mechanism of sensing provides an alternative to the more rigid and less stretchable piezoelectric sensors.

The piezoionic effect is a discovery. However, the underlying mechanism may be related to effects seen in ionomeric polymer metal composites [38], although there are differences in electrode configurations and the manner in which the force is applied. This section aims to fully understand the capabilities of the proposed sensor by measuring the complex transduction coefficient such that the sensitivity as a function of frequency can be used to evaluate potential uses in various applications.

2.1.1 Sample Synthesis

Solid polymer electrolytes based on PVDF-HFP copolymer were synthesized with predetermined salt using a solution cast technique. PVDF-HFP copolymer pellets were purchased from Sigma-Aldrich (427187) and used as received. A polymer stock solution was made by dissolving PVDF-
HFP in acetone at a ratio of 0.25 g/mL. Subsequently, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Aldrich, 205281) was dissolved in propylene carbonate (Aldrich, 310318) at 0.1 M. The electrolyte was then mixed with the host polymer solution at a volume ratio of 1:2 (electrolyte/polymer stock). To ensure complete mixing, the mixture was sonicated for 2 hours with occasional stirring. The mixture was poured over a glassy carbon substrate and covered with a perforated lid to allow gradual evaporation of the acetone at room temperature. The resultant thickness of the films was approximately 200μm. Figure 2-1 shows an example solid polymer electrolyte film.

![Figure 2-1. A digital photograph of the PVDF-HFP/LiTFSI/PC solid polymer electrolyte](image)

The ionic conductivities of the films were determined by clamping the samples between stainless steel plates and performing electrochemical impedance spectroscopy at an amplitude of 0.1 mA, swept from 50 kHz to 10 mHz. From the high-frequency component, the ionic conductivity of the solid polymer gel samples was found to be 0.10 S/m.
2.1.2 Experimental Setup

The films were then subjected to a mechanoelectrical transduction test using the Bose ElectroForce® 3000 series with DMA (Dynamic Mechanical Analyzer) in conjunction with the Metrohm Autotlab® 100 series potentiostat/galvanostat which was measuring the output voltage. The overall setup is depicted in figure 2-2. First, a linearity test was performed to check that the sensor signal was linear with increasing force amplitude. This was performed at 0.1 Hz perturbation. Then each gel sample was subjected to a swept sinusoidal stress perturbation with amplitudes of 1 - 5 kPa. The perturbation was load controlled with a maximum displacement of 2 mm (the hardware limit of the tensiometer), and depending on the Young’s modulus of the specimen, the stress amplitude was adjusted. The electrodes in contact with the polymer samples were connected to the Autolab® PGSTAT101 potentiostat/galvanostat system such that the voltage and current responses of the gel were captured as a function of the amplitude and the frequency of the mechanical perturbation. As PVDF-HFP can also show a piezoelectric response, similar tests were performed on dry PVDF-HFP films to confirm piezoelectric response was not observed. Results were as expected given that the film had not been poled [39].
2.1.3 Results

Figure 2-3. A linearity plot of the piezoionic voltage as a function of applied force

The sensor was found to be linear with input force amplitude, as shown in figure 2-3. This is assumed to be true within the force range where the gel behaves elastically, without much hysteresis. Future work could investigate exactly where this ideal range ends, however in the
following experiment the samples behaved mostly elastically over the force and frequency range applied. Figure 2-4 is the resultant Bode plot of the complex tensile modulus as well as the complex piezoionic transduction function of the solid polymer gel sample. The sensitivity was found to be 25 μV/Pa at 10 mHz, which decayed to approximately 3% in amplitude by 10 Hz. The Young’s modulus of the gel varied over the frequency range and was found to be mostly elastic (i.e. phase difference of displacement and load near zero). The cutoff frequency observed in the sample was between 0.1 and 1 Hz for both cases, suggesting that the decaying of the signal response is partially correlated to the mechanical limitations of the soft polymer sample. This correlation might be expected, as an increase in stiffness reduces the extent of deformation and hence perhaps the generation of the voltage. For example, a reduction in the deformation of the gel will reduce the induced concentration gradient and the extent of solvent flux. The decrease in the mechanical response is only about a factor of three, whereas the sensor response decays by a factor of 30. Thus the mechanical response does not appear to explain the entire drop in sensor response. One possible explanation is that some latency or retardation effects come from the low diffusion coefficient of the ion species present in the system. This will be further investigated using NMR technique in later sections.
2.2 Transduction as a function of relative ionic mobilities – effect of ion sizes

Piezoionic transduction is thought to take place due to an ionic charge separation when the polymer gel is under compression, which arises from the differential ionic mobility between the cationic and anionic species as described in chapter 1. This section includes a series of experiments to determine the correlation between the relative ionic mobilities and the piezoionic responses. Namely, various samples of LiTFSI/PC swollen PVDF-HFP polymer electrolytes were synthesized at different salt concentrations and were subjected to the piezoionic transduction characterization using the setup seen in figure 2-2.

2.2.1 Mechanism of ion-ion and ion-solvent interactions

To begin the discussion, let us first consider a single ion present in an electrolyte. Each ion will impose an electric field on its surrounding which dictates the distribution of counter charges and polar solvent molecules around the ion.
Debye length, $\lambda$, is a measure of the electrostatic environment surrounding a charged species, and is defined as the distance from the location of charge, where the potential decays by a factor of $1/e$ (the zeta potential). The Debye length is expressed as follows:

$$\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_BT}{2N_Ae^2I}}$$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the medium, $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, $N_A$ is Avogadro’s number, $e$ is elementary charge, and $I$ denotes the ionic strength of electrolyte. The potential of a given ionic species is said to be screened by the accumulation of counter ions and solvent molecules within the dimension described by Debye length. The expression arises from the Poisson-Boltzmann equation solved for a spherical charge in a homogeneous medium [40].

In sufficiently dilute conditions (less than 1 mM ionic strength), a given ionic species is much more likely to be in ion-solvent interaction regime rather than ion-ion interaction within the Debye length associated with it. Hence the layer comprising the Debye length is termed solvation layer. The size of the solvation sphere dictates the ion’s effective size, mass, chemical reactivity such as nucleophilicity, and the likelihood of aggregating with other ions present. The effective ion size due to Debye length is then translated to diffusion and mobility via the Stokes-Einstein relation as follows [41]:

$$D = \frac{k_BT}{6\pi\eta R}$$

where $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, $b$ is a boundary condition factor dictating whether the ion is inert (4) or strongly interacts (6) with surrounding ions, $\eta$ is the
viscosity of the electrolyte, and R is the radius of the effective ion size. Commonly known as Stokes Law in the strong interaction boundary condition case, this relationship provides a direct correlation between the ionic sizes and their respective diffusion.

The main rationale behind these experiments is the solvation effect of the ionic species. Polar aprotic solvents, such as propylene carbonate used in this experiment, are not hydrogen bond donors. What this entails is that polar aprotic solvents rely on their lone pairs to stabilize ionic species present in the solution. This lone pair interaction only takes place with cations, however not with anions [42]. Along with Stokes Law, this solvation effect partially explains how the relative ion sizes of the cations and anions and their respective mobilities might change as a function of solvent/solute ratio when one uses polar aprotic solvents – as will be shown. Figure 2-5 below depicts a comparison between the interaction of LiTFSI salt with propylene carbonate and water to picture this concept better. As will be seen in the following section, the presented experiments are carried out in dilute conditions as well as concentrated conditions, and therefore some ion-ion interactions are also expected to play a role.
Figure 2-5. A depiction of ion-solvent (propylene carbonate) interaction for (a) lithium cation and (b) bis(trifluoromethane) sulfonamide anion. Note that the positive charge of lithium causes the lone pairs of propylene carbonate to surround the ion, whereas the lack of H-bonding site of propylene carbonate translates to minimal interaction with bis(trifluoromethane) anion

2.2.2 Sample preparation

Samples prepared in this section are the same as those in section 2.1, with different salt concentrations of the electrolyte. The same synthesis protocol was applied to prepare the following samples.

<table>
<thead>
<tr>
<th>Host polymer</th>
<th>Electrolyte</th>
<th>Concentration</th>
<th>Polymer: electrolyte weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>0.5 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>1.0 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>1.25 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>1.5 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>1.75 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>2.0 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>2.25 M</td>
<td>1:2</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>LiTFSI/PC</td>
<td>2.5 M</td>
<td>1:2</td>
</tr>
</tbody>
</table>

Table 2-1. A list of PVDF-HFP/LiTFSI/PC polyelectrolyte samples used
2.2.3 Diffusion NMR measurements and transference numbers

Diffusion NMR measurements were carried out in the setup depicted in figure 2-6 on all the specimens prepared to deduce the diffusion constants of the ions present. Namely, the pulsed field gradient spin echo (PFGSE) method was employed in the measurements. The depiction of the pulse sequence is shown in figure 2-7.

Figure 2-6. A depiction of the NMR experimental setup [43]

Figure 2-7. Pulse sequence employed in the PFGSE NMR measurement procedure
A pulsed magnetic field gradient, $B(z)$, was applied across the gel samples in the Z-direction, aligning the magnetic spins of the species inside the polymer matrix. This allows the spatial encoding of magnetic spin by modulating the Larmor frequency as a function of location,

$$\omega_z = \gamma B(z) = \gamma (B_0 + g z) = \omega_0 + \gamma g z$$  \hspace{1cm} (2 - 3)

where $\gamma$ is the gyromagnetic ratio of a given isotope, $g$ is the magnetic field gradient (T/m), and $B_0$ is the static magnetic field (T).

As the Larmor frequency is spatially encoded, a given species will develop a phase shift if it experiences diffusion. The pulse sequence above, commonly referred to as pulse field gradient spin echo sequence, allows diffusion measurements by looking at the extent of decay in total magnetization due to this phase shift caused by diffusion. The first pulse at 90° orients the magnetization to the x-y plane, from which isotopes will begin to precess at their unique Larmor frequencies around the z-axis. The short gradient pulse of length $\delta$ yields phase shifts unique to Larmor frequencies:

$$\varphi = \omega_z \delta$$  \hspace{1cm} (2 - 4)

At this point, the spatial information for species pre-diffusion is encoded in the magnitude of phase shift, once again thanks to space dependent Larmor frequency. We can express the total magnetization at the end of the first time constant, $\tau$, as:

$$M_e^- = M_0 e^{-i\omega_\delta t} e^{-i\omega_0 \tau} e^{-\frac{\omega_\delta \tau^2}{2}}$$  \hspace{1cm} (2 - 5)

At $t = \tau$, a $\pi$ pulse is applied which then re-orient the spin to an out-of-phase direction by 180-degree rotation, yielding the magnetization of:

$$M_{\tau^+} = M_0 e^{i\omega_\delta \tau} e^{i\omega_0 \tau} e^{\frac{i\omega_\delta \tau^2}{2}}$$  \hspace{1cm} (2 - 6)
Now, by applying an identical gradient pulse as the first one, there will arise a phase difference between the total magnetization after the first versus the second gradient pulse due to the location change of species in the Z-direction.

\[ \Delta \varphi = \delta (\omega_{z_1} - \omega_{z_2}) = \omega \delta y g (z_1 - z_2) \]  

(2 - 7)

Therefore, the change in the phase due to diffusion is dependent on the gradient pulse strength, length, and the time interval between the two pulses. Integrated over the entire sample, the total magnetization at \( t = 2\tau \), can be expressed as follows:

\[ M_{2\tau} = M_0 e^{\left( \frac{A}{\pi^2} \sqrt{D} \delta (z) \right)} e^{\left( -\frac{2\tau}{\tau_c} \right)} \]  

(2 - 8)

The phase shift caused by the diffusion in the direction of the magnetic field gradient is reflected as the attenuation of the total magnetization, and therefore the diffusion path length during this time const can be deduced. The diffusion constant is computed by sweeping the pulse gradient strengths and fitting a Gaussian curve over the resultant magnetization as can be understood from equation 2-8.
Presented in figure 2-8 is the transition of the diffusion coefficients of Li+ ions and TFSI- ions as the electrolyte concentration was varied from 0.5 M to 2.5 M. The results suggest that at 0.5 M concentration Li+ has a lower diffusion coefficient than that of TFSI- ions as expected due to solvation effects. As the ionic strength increases, Li+ diffusion increases while TFSI- diffusion diminishes, with the crossover point located between 1 and 1.5 M. From this, it is expected that during the mechanical perturbation tests in the subsequent section, the polarity of the piezoionic response would change around this cross-over point.
2.2.4 Piezoionic characterization as a function of effective ion sizes

Each sample was subjected to a sine wave mechanical perturbation as well as step perturbation tests using the setup shown in figure 2-2 to observe the open circuit voltage responses to determine the effect of ion sizes on the behavior of the mechanoionic transduction.

In the sine wave perturbation tests, all samples underwent compressive displacement of 0.04 mm (0.01 mm of pre-compression, and 0.05 mm of maximum displacement), at a frequency of 0.1Hz. The compression was applied on half of the top surface of the samples, and it was at all times ensured that this side is the positive electrode. As the cathodic side of the polyelectrolyte gets compressed, the redistribution of the electrolyte should take place such that the flux will direct from cathodic to anodic sides. If the net flux of ionic charge is positive, this would indicate that the cations have greater mobility and are displaced by the solvent flux to a greater extent than anions. Consequently, a decrease in potential should be observed as the net positively charged flux leaves the cathodic side. Conversely, if the flux is anion dominant, one would observe an increase in potential. The voltage responses from the samples are presented in figure 2-9.
Figure 2-9. Piezoionic voltage response during a sine wave compressive perturbation on PVDF-HFP hosted polyelectrolyte containing (a) 0.5 M LiTFSI/PC (b) 1.0 M LiTFSI/PC (c) 1.25 M LiTFSI/PC (d) 1.5 M LiTFSI/PC (e) 1.75 M LiTFSI/PC (f) 2.0 M LiTFSI/PC (g) 2.25 M LiTFSI/PC (h) 2.5 M LiTFSI/PC

One can clearly observe that at 0.5 M LiTFSI/PC, the response of the voltage as the sample is compressed at the cathodic side is positive. The amplitude of this response decreases until a crossover point, which is found to be at 2.0 M. Beyond this point, it is found that the response of
the voltage as the sample is compressed at the positive electrode is negative. The indication of this trend is that at lower concentrations of LiTFSI, the net ionic flux away from the positive electrode is negative (i.e. TFSI- dominant), making the voltage response positive. At low LiTFSI concentration, the number of propylene carbonate molecules available per given lithium ion is high, making the effective ionic radius large and decreasing the mobility as confirmed by NMR measurements. This response decays towards the 2 M crossover point as the solvation effect changes and the relative mobilities of Li+ and TFSI- become more similar. Above 2 M concentration, the solvation around lithium becomes small enough such that they become the more dominant flux while the gel is being compressed. Figure 2-10 summarizes the piezoionic behavior and shows that it is correlated to the relative ionic mobilities of the Li+ and TFSI- ions, which are varied via ion-solvent interactions as a function of salt concentration. It should be noted here, that there is some discrepancy between the NMR results which suggested that the crossover point lies between 1.0 to 1.5 M and this current experiment which suggest that the crossover point lies at 2.0 M. Although further investigation is necessary to explain this discrepancy, one possible explanation is that self-diffusion coefficients which describe the ions’ tendency to follow the Brownian motion and the so-called driven diffusion, which describes ion displacements upon external perturbations including electrical and mechanical, behave differently. Therefore, a continuation of this work may entail measurements of driven diffusion coefficients of ions present in a polyelectrolyte in response to mechanical compression using a specially designed setup. This is discussed more in detail in chapter 5.

Similar effects have been observed by Woehling et al. where PEO-NBR interpenetrated polymer network was swollen with an ionic liquid EMITFSI which has been diluted with PC at different
ratios. When this ionic gel was used similarly as a sensor (PEDOT layers on top and bottom of the membrane was present to act as electrodes), a crossover point was observed to be between 3.0 and 2.5 M [44].

![Graph showing response voltage as a function of LiTFSI concentration](image)

**Figure 2-10.** Peak voltage response amplitude of PVDF-HFP/LiTFSI/PC polyelectrolyte as a function of LiTFSI Concentration

### 2.2.5 Ionic conductivity

Ionic conductivity measurements were carried out on all the samples. All of the polymer electrolytes were cut out in rectangles of 2.5 cm by 1 cm, and clamped between two stainless steel plates, and swept sine voltage was applied from 1 MHz to 0.1 Hz. The gel resistance was recorded at high frequency where the metal/gel interfacial capacitances were effectively shorted. In the figure below, a summarized graph of ionic conductivity as a function of LiTFSI concentration in the polyelectrolyte is presented. The uncertainty of the measurements were calculated based on dimensional uncertainties of the samples, as well as the resolution of the impedance measurements.
It can be seen that the ionic conductivity significantly peaks at 2.0 M, which is interestingly also the crossover point of the piezoionic response behavior.

![Comparison of directly measured and diffusion derived ionic conductivity in PVDF-HFP/LiTFSI/PC polyelectrolyte as a function of LiTFSI concentration](image)

**Figure 2-11.** Ionic conductivity of PVDF-HFP/LiTFSI/PC polyelectrolyte as a function of LiTFSI concentration

According to Nernst-Einstein relation, the ionic mobility is expressed in terms of diffusion constant as follows:

\[ D = \frac{k_B T}{Z_{\text{eff}} e \mu} \]  

(2 – 9)

where \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, \( Z_{\text{eff}} \) is the effective charge number, \( e \) is the fundamental charge, and \( \mu \) is the mobility of species. The ionic conductivity of a given electrolyte system is the sum of the specific conductivity of all of the charge carrying species present:
\[
\sigma = \sum_i C_i F z_{eff,i} \mu_i \quad (2-10)
\]

Transference number is a parameter describing the contribution of current carried by cationic (\(t^+\)) and anionic (\(t^-\)) species:

\[
t^+ + t^- = 1 \quad (2-11)
\]

From the trend of the diffusion constants of Li\(^+\) and TFSI\(^-\) as a function of concentration, we expect that as the concentration increases, Li\(^+\) mobility also increases whereas TFSI\(^-\) mobility is in a diminishing trend. The summation of the Li\(^+\) derived conductivity and TFSI\(^-\) derived conductivity yields the overall conductivity estimated via diffusion coefficients.

The apparent discrepancies between the directly measured and diffusion derived ionic conductivity values should be addressed. This is partially explained by the fact that Nernst-Einstein equation does not account for the formation of ion pairs and other aggregates. In other words, the effective charge number, \(Z_{eff}\), cannot necessarily be assumed to be identical to the ion’s valence charge, which is the stem of this discrepancy. Ion pairs, based on self-diffusion, do contribute to increase the measured diffusion coefficients. However, they will never migrate under the influence of electric field and hence will not contribute to conductivity. This agrees with the observation that the diffusion derived numbers continue to rise whereas experimentally at higher concentration the severe aggregation diminishes the conductivity. A possible way to resolve this issue is to extend the NMR studies to incorporate an active application of electric fields during the pulse sequence.
2.3 Transduction as a function of relative ionic mobilities – effect of polymer charge densities

The diffusion constants, $D$, were measured in a charged polyacrylamide hydrogel crosslinked with positively charged monomers [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), and negatively charged 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) at various densities to observe the effect of electrostatic interactions between the backbone charge of the polymers and the ionic species. The initial postulate was that the ionic species oppositely charged from the backbone charge would be hindered due to attractive forces whereas the species carrying like charges to the backbone charge would be promoted in mobility due to repulsive forces. This postulate is addressed and verified in analyzing the results.

2.3.1 Mechanism of ion-polymer interactions

Polyelectrolytes, including those containing aqueous, organic or molten salt phases, are a class of materials which exhibit duality between the solid polymer phase and the respective liquid phases. This is macroscopically prominent as the superposition of viscoelastic and poroelastic behaviors in gels have been reported as introduced in section 1.2. Compared to the ion diffusion rate of the liquid phase alone, the presence of polymer mesh network suspending the bulk electrolyte retard the diffusion. Electrostatic interactions can pose a certain degree of effect onto the diffusivity of ionic species. Some previous work on characterization of the mobility of various charged molecules under the influence of backbone polymer charge was introduced in section 1.2.

Although the exact mechanism is subject to an extensive area of ongoing research, and will depend highly on the particular polymer (mesh density, charge density, hydrophobic interactions, etc.),
there are several notable models that have been proposed previously. Namely, the three prominent models to note are hydrodynamic, average free volume, and obstruction models [45].

2.3.2 Sample preparation

The gel synthesis protocol was based on reference [46], with modifications to accommodate desired electrolytes in the host matrix as well as to vary the backbone charge densities. Polyacrylamide hydrogels with various charge densities were synthesized in an aqueous electrolyte containing the sodium trifluoromethanesulfonate (NaTf) salt at 0.5 M concentration. This salt was chosen as the incorporation in the polymer network was empirically deemed successful, whereas other candidates such as LiTFSI, NaPF$_6$ tended to inhibit the polymerization of the polyacrylamide. The polymer density was fixed at 0.15 g/cm$^3$ during synthesis to minimize confounding factor related to available spaces for solvent flow, solvent flow path lengths, and tortuosity. Acrylamide, MAPTAC, and AMPS were polymerized in situ which yielded the hydrogels with neutral, positive, and negative charges. The charge densities for MAPTAC and AMPS polymers synthesized are 0.684 M and 0.724 M, respectively. N,N’-methylene bis(acrylamide) was added as the crosslinker at 5 wt% of the polymers, and ammonium persulfate (AP) was also added as initiator at the same weight ratio. After thoroughly mixing the solution and degassing, N,N,N’,N’-tetramethylethylenediamine (TEMED) was added at 1µL/mL of the precursor solution to accelerate the polymerization process. The precursor solution was then poured into a mold and allowed to polymerize at room temperature for approximately 30 minutes to one hour.

Shown below are the three types of monomer units that are under investigation (Acrylamide, MAPTAC, and AMPS). At neutral pH, acrylamide exists in an electrically neutral state as the
amide group of the acrylamide monomer would have a pKa of around 17. The amide group of MAPTAC, on the other hand, is susceptible to base hydrolysis beyond its pKa of around 9, over which it exists in a zwitterionic neutral state. The hydroxyl group of AMPS unit becomes deprotonated around the pH of 3, and thus it maintains its negative charge beyond this point. During the experiments described in subsequent sections, the samples were ensured to have pHs of around 7.0 using Litmus papers. When polymerized, each monomer unit is oxidized as they lose the π-electrons in the alkene group extending from the α-carbon, resulting in a saturated carbon chain with the carbonyl and amide groups branching off.

![Figure 2-12. Chemical structure of (a) Acrylamide (b) MAPTAC and (c) AMPS](image)

2.3.3 Diffusion NMR measurements and transference numbers

The results from the measurement protocol described in section 2.2 on the gel samples with various charge densities is shown below. The diffusion constants of the trifluoromethanesulfonate ions exhibited a characteristic trend, whereby the mobility was inhibited by the positively charged MAPTAC samples due to attractive forces between the ions and the polymer backbone, and the negative charges on the backbone of the AMPS acted to increase the diffusion constants of these species via repulsive forces. The magnitude of these respective charge densities on the polymer backbones also modulated the magnitude of changes in the diffusion constants as compared against
that of the neutral polyacrylamide gel. The summary of the measurement results is presented below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge state</th>
<th>Electrolyte</th>
<th>Polymer density (g/cm$^3$)</th>
<th>Diffusion constant of trifluoromethanesulfonate ion (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPTAC</td>
<td>Positive</td>
<td>0.5 M NaTf (aq)</td>
<td>0.15 g/cm$^3$</td>
<td>4.012 $\cdot$ 10$^{-10}$</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>Neutral</td>
<td>0.5 M NaTf (aq)</td>
<td>0.15 g/cm$^3$</td>
<td>4.492 $\cdot$ 10$^{-10}$</td>
</tr>
<tr>
<td>AMPS</td>
<td>Negative</td>
<td>0.5 M NaTf (aq)</td>
<td>0.15 g/cm$^3$</td>
<td>6.366 $\cdot$ 10$^{-10}$</td>
</tr>
</tbody>
</table>

Table 2-2 A list of charged derivatives of polyacrylamide hydrogel samples used

The uncertainty in the above measurements was 3 ~ 5%, and the difference in the diffusion coefficients in all three samples was deemed significant. Some of the confounding factors can include morphological changes in the polymer structure in the context of obstruction model of ion-polymer interaction. Although the polymer density was fixed to 0.15 g/cm$^3$ in all the samples to partially mitigate this problem, this does not guarantee the conformation each polymer assuming similar configurations. Future work might investigate further into the specific polymer morphological configuration.

2.3.4 Piezoionic characterization as a function of polymer charge density

Each sample was subjected to a sine wave perturbation test using the setup shown in figure 2-2 to observe the open circuit voltage was to determine the effect of polymer-ion interaction on the behavior of the mechanoionic transduction. In the sine wave perturbation tests, all samples underwent compressive load of 0.03 N, at a frequency of 0.1Hz. During the measurements, a constant gain of 50 was used for all trials, and the result is presented without scaling down the voltage. Similar to the experiments in section 2.2, it was at all times ensured that the cathodic side
of the gel was compressed. As the cathodic side of the polyelectrolyte gets compressed, the redistribution of the electrolyte should take place such that the flux will direct from cathodic to anodic sides. If the net flux of ions is positive, this would indicate that the cations have greater mobility and are displaced by the solvent flux to a greater extent than anions. Consequently, a decrease in potential should be observed as the net positively charged flux leaves the cathodic side. Conversely, if the flux is anion dominant, one would observe an increase in potential. The voltage responses from the samples are presented below.

Figure 2-13. Piezoionic voltage response during a sine wave compressive perturbation on aqueous 0.5 M NaTf polyelectrolyte hosted within (a) 100% polyacrylamide (b) 50% AMPS / 50% polyacrylamide (c) 50% MAFTAC / 50% polyacrylamide.

Below, the polarity and the peak magnitudes of the above experiment along with the trifluoromethanesulfonate anion diffusion constants in the respective gel samples are presented. We can see that all of the samples generated a negative voltage response, which, qualitatively assessing, means that the sodium ions were dominantly traveling away from the positive electrode along with the solvent flux. One interpretation of the results below, in accordance with the initial postulate, is that the sodium-driven voltage response is enhanced by the electrostatic ion-polymer interaction with the positively charged MAFTAC matrix, which enhances the sodium mobility by
repulsion and inhibits the trifluoromethanesulfonate ion motion by attraction. Conversely, the negatively charged AMPS matrix suppresses the sodium-driven voltage response by inhibiting the sodium mobility via attraction, and promoting the trifluoromethanesulfonate ion motion via repulsion. The polar neutral acrylamide units do not have strong electrostatic interactions with the ionic species, and therefore its voltage response lies between the MAPTAC and AMPS gel samples. The voltage response results follow a decreasing trend in the magnitudes as we compare MAPTAC, polyacrylamide, and AMPS, respectively.

It is noted at this point that the electrostatic interactions and their effect on the piezoionic voltage response in this experimental case are less significant than the ion-solvent interaction and the change in the Debye length, potentially because trifluoromethanesulfonate anion was too bulky and steric hindrance dominated the piezoionic effect. This explains the fact that we do not observe the reversal of the polarity of the voltage response in this experiment as we have in the experiments described in section 2.2, meaning that the sodium ions in this case remained more mobile despite the electrostatic effects. This is in fact reflected in the measurement of diffusion coefficients of the anions in the PVDF-HFP/LiTFSI/PC polyelectrolyte in section 2.2, which varied by 3.5 times (0.5 M LiTFSI vs. 2.5 M LiTFSI) whereas the trifluoromethanesulfonate ion diffusion only varied by a factor of 1.6 between MAPTAC and AMPS.
2.4 Discussion and conclusion

The experimental results appear to suggest that, within the stress range where the mechanical properties of the gel behave ideally (i.e. elastically without hysteresis), there is a linear correlation between the electrical signal generated by the gel and the amount of stress exerted onto the gel. This can be deemed reasonable under the assumption that the piezoionic voltages arise from differential ionic mobilities under solvent flow within polymer matrices. The frequency response experiments suggest a maximum sensitivity of 25 µV/Pa at 10 mHz, comparable to the voltages expected in piezoelectric polymers such as PVDF (44 µV/Pa for similar dimensions). The cutoff frequency observed in the sample was between 0.1 and 1 Hz for both mechanical and voltage
responses, suggesting that the decaying of the signal response is partially correlated to the mechanical limitations of the soft polymer sample. While this result may discourage piezoionic gels from usage in high-frequency applications, efforts may be made to improve the frequency range by tuning the mechanical properties of the gel. For instance, one could employ stiffer polymers for high-frequency applications. In the step response experiment, the difference between the voltage responses, where the LiTFSI/PC/PVDF-HFP sample showed a rise in voltage which is subsequently sustained DC (over the time frame of measurement) while the NaCl containing polyacrylamide hydrogel showed a fast decay of the voltage build-up. This is perhaps due to the fact that LiTFSI diffusion was much slower than NaCl in the process of recovering the initial ion distribution. The amplitude ranges of the potential difference created lie in a reasonable magnitude range to be explained via a Nernstian approach - the \( \frac{RT}{nF} \) term has a magnitude 25 mV, which is of the same order as the voltage response of the sensor. The question is, how exactly is the differential pressure within the gel translated into net ionic charge separation? Here we consider two mechanisms: a solvent flow driven mechanism, where (i) Stokes drag is experienced by the ionic species\[47\], and (ii) polar groups and charges of the polymer matrix interact with the ions electrostatically \[34\], \[48\], \[49\], which together determine the differential transport rates between ions.

Section 2.2 aimed to show that the piezoionic effect is dependent on the effective ion sizes due to the change in Stoke’s drag forces experienced by individual ions. Effective ion sizes are governed by ion-solvent and ion-ion interactions and are characterized by the Debye length of the solvation layer around a given ion. Here, the relative sizes of lithium cations and TFSI anions were thought to vary by changing the ionic strength (ion-solvent ratio) in propylene carbonate solvent, hosted in
PVDF-HFP matrix. The results showed anion driven responses at low salt concentrations, a
crossover point where no signal was observed, and finally cation driven responses at high salt
concentrations. The initial postulate was that as the salt concentration shifts higher, lithium ions
attain smaller and smaller solvation spheres (because there are fewer and fewer solvent molecules
available per ion), increasing its diffusion rate. As explained earlier, TFSI anions are not expected
participate in solvation by propylene carbonate and therefore are do not follow this trend. Thus,
the shift of the piezoionic response voltages from anionic driven to cationic driven, as the
concentration is varied from low to high, agrees with this view. Further, the change in the diffusion
coefficient of lithium cations and TFSI anions followed this expected trend. Namely, lithium ions
exhibited a diffusion constant of $6.70 \cdot 10^{-11} \text{ m}^2/\text{s}$ in 0.5 M LiTFSI/PC sample, whereas it has
increased to $9.36 \cdot 10^{-11} \text{ m}^2/\text{s}$ in 2.5 M LiTFSI/PC sample. TFSI ions exhibited a diffusion
constant of $9.24 \cdot 10^{-11} \text{ m}^2/\text{s}$ in 0.5 M LiTFSI/PC sample, whereas it has decreased to $2.66 \cdot
10^{-11} \text{ m}^2/\text{s}$ at 2.5 M. (This decrease may be the result of increased ion-ion interaction and
increased segregation of ionic clouds, rather than ion-solvent interactions in the case of lithium.)
The reversal of sensor voltage sign as a function of concentration occurs in the same concentration
range where the switch occurs between Li and TFSI being more mobile. Therefore, from this
experiment, we can reasonably infer that (i) the piezoionic effect indeed is induced by differential
ionic mobilities of cationic species and anionic species present in a polymer electrolyte system and
(ii) effective ion sizes can affect the relative mobilities of the ions.

Section 2.3 aimed to present a qualitative correlation between the backbone charges of the polymer
and the mobilities of the ions present in the matrix. The postulate was that the repulsive and
electrostatic attractive forces played a role in the mobilities of ionic species and therefore would
cause the piezoionic behavior to change. The findings are consistent with this postulate, as the NMR studies on the diffusion coefficients determined the trifluoromethanesulfonate anions to increase or decrease their diffusion as compared to its baseline diffusion in a neutral matrix when the polymer was synthesized to have a negative or positive charge on their backbones respectively. Namely, the gel samples consisting entirely of negatively charged AMPS polymer matrix exhibited a trifluoromethanesulfonate ion diffusion constant of \(6.366 \cdot 10^{-10} \text{m}^2/\text{s}\), which is a 40% increase from pure acrylamide sample. Conversely, the sample consisting entirely of MAPTAC polymer matrix showed a trifluoromethanesulfonate ion diffusion constant of \(4.516 \cdot 10^{-10} \text{m}^2/\text{s}\), which is a 11% decrease from pure acrylamide samples. It was further postulated that by modulating the charge states of the polymer matrix, the piezoionic behavior of the respective ionic gels would be modulated. In the hydrogel samples containing aqueous sodium trifluoromethanesulfonate electrolyte, one can expect a sodium dominant response when considering the ion sizes of the two ionic species according to the size difference. This sodium driven ionic flux was enhanced in the positively charged MAPTAC gel via repulsion, making the response voltage 2.52 times larger than neutral polyacrylamide, whereas the negatively charged AMPS gel reduced the extent of net sodium displacement by attraction, making the response voltage 0.76 times that of polyacrylamide. As mentioned before, changing the charge state of the polymer could change the morphological configuration, and this could be a confounding factor in the ability to conclude the effect of electrostatic aspect of ion-polymer interactions. More thorough analysis is required to arrive at a definitive conclusion. Nonetheless, it is fair to state the results in this section were able to show that in addition to ion sizes (including solvation effects), polymer to ion electrostatic interactions are contributing factors in dictating the behavior of the piezoionic effect.
Chapter 3  Modeling the Piezoionic Effect

Based on the previous chapters’ discussion on the initial postulates of the mechanisms of the piezoionic effect a finite element simulation is constructed and presented in this chapter and compared against the empirical results obtained. The model incorporates the known contributing effects as of current understanding. The model was implemented using COMSOL Multiphysics V4.3b (COMSOL Inc., Stockholm, Sweden). The chapter begins by outlining the contributing effects and their governing equations, and the strategy used to model them together. The results are used to gain an intuitive understanding to the physics of voltage generation in a compressed polymer electrolyte. More work is needed to complete the model so that it quantitatively predicts sensor response, and to validate it though comparison with experimental results.

3.1  Overview of approach in modeling the piezoionic effect in an ionic polymer

Through the series of experiments in chapter 2, the piezoionic effect seems likely to be the result of the ionic mobility differential which arises from a number of factors such as ion sizes and steric effects and the presence of polymer backbone charges. Here, a model is constructed in an attempt to capture the effect of solvent flow within a polymer network, coupled with differential ion redistribution based on ion mobilities.

3.1.1  Poroelastic behavior and the non-equilibrium thermodynamic theory

Earlier in the thesis, the duality in the mechanical properties of gel materials was introduced. These are the viscoelastic behavior of the soft and lossy polymer material, as well as the poroelastic behavior which dictates the solvent flow in response to a deformation gradient imposed on the gel. Poroelasticity imposes a characteristic time-dependent mechanical property to the porous medium due to the presence of mobile fluid. In a gel, two coupled events take place: (i)
compression/deformation of a gel causes the pore pressure to increase and an immediate shape change, and (ii) an increased pore pressure induces solvent flow within the gel, and a gradual deformation. In what follows the basic equations used in deriving the poroelastic response are laid out. The result is an effective diffusion equation, the final equation of this section (3.12). This diffusion equation is the outcome of the combined fluid resistance produced by the pores of the gel and the elastic storage that comes from the springy polymer matrix as it accommodates volume change.

While there have been many models of these coupled phenomena within a poroelastic materials, as briefly introduced in section 1.2, Gibbs was the first in 1878 to introduce a theory based on thermodynamics to consider the solid and liquid phases in an equilibrium [50].

\[-\varphi VdP + sdT + \sum_i n_i d\mu_i = 0\]  \hspace{1cm} (3 - 1)

where \(\varphi\) is the porosity of polymer, \(dP\) is the infinitesimal pressure change within the bulk, \(s\) is the entropy of overall system, \(T\) is temperature, \(n_i\) is the number of moles of species \(i\), and finally \(d\mu_i\) represents the infinitesimal change in the chemical potential of species \(i\). Subsequently, Biot elaborated on this idea in 1941 by incorporating Darcy’s law to model the fluid movement in a fluid-filled poroelastic material [51]. More recently, Suo et al and Hong et al have followed up on the so called non-equilibrium thermodynamic theory [24], [52]. Here, they propose to express the free energy change as a summation of the deformation of polymer and the change in the concentration of electrolyte species.
Hong et al considered a gel subjected to a deformation gradient, which can be described as the time dependent movement of a given particle indexed by $i$ with respect to a reference point $X$ according to a function $x(X,t)$ [24]:

$$F_{ik} = \frac{\partial x_i(X,t)}{\partial X_k} \quad (3 - 2)$$

The gel undergoing active deformation is experiencing mechanical loads, $B(X,t)dV$ in volume and $T(X,t)dA$ at an interface with a rigid sliding substrate. Now the nominal stress, $s_{ik}(X,t)$, can be expressed as [24]:

$$\frac{\partial s_{ik}}{\partial X_k} + B_i(X,t) = 0 \quad (3 - 3)$$

in the volume of the gel, and

$$(s_{ik}(X,t) - s_{ik}^+(X,t))N_K(X,t) = T_i(X,t) \quad (3 - 4)$$

at the interface.

$N_K(X,t)$ is the normal unit vector at the gel/substrate interface. $+$ is defined as the direction towards the gel, away from the substrate. The contribution of deformation gradient and concentration to infinitesimal change in the free energy density can be expressed simply by summation [24]:

$$\delta W = \frac{\partial W(F,C)}{\partial F_{ik}} \delta F_{ik} + \frac{\partial W(F,C)}{\partial C} \delta C \quad (3 - 5)$$

From the above sequence of equations, we visualize the overall thermodynamic process to be broken down into two parts; the mechanical deformation of the polymer and the concentration change of the mobile species. What results from a gel deformation in terms of mobile species distribution, is largely dependent on the deformation and by the necessity for the overall free energy to either remain the same or decrease. It is reasonable to consider the free energy density to be separable [24]:

50
According to Flory, the free energy of stretching a polymer is [53]:

\[
W_{\text{deformation}}(F) = \frac{1}{2} N k T \left( \lambda_1^2 \lambda_2^2 \lambda_3^2 - 3 - 2 \log \lambda_1 \lambda_2 \lambda_3 \right)
\] (3 - 7)

where \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) are the stretches in each of the three dimensional coordinates, \( N \) represents the number of polymer chains, \( k \) is the Boltzmann’s constant, and \( T \) is the temperature. The Flory-Huggins free energy of mixing is expressed as follows [54], [55]:

\[
W_{\text{mixing}}(C) = \frac{kT}{\nu} \left[ \nu C \cdot \log \left( 1 + \frac{1}{\nu C} \right) + \frac{\chi}{1 + \nu C} \right]
\] (3 - 8)

where \( \nu \) is the volume per small molecule, and \( \chi \) is a dimensionless parameter which is related to the enthalpy of mixing. The first term in the square bracket represents the entropy of mixing, and the second term represents the enthalpy of mixing. A positive \( \chi \) value implies an unfavorable mixing condition, whereas a negative \( \chi \) value means that mixing is favored. Intuitively, \( \chi \) would be negative if an ionic species is about to enter a given pore with a low chemical potential as that is the stabilizing mass transfer.

Hong et al state that the i) local rearrangement of electrolyte molecules does not give rise to a significant free energy change and ii) the local equilibrium (intra-pore chemical equilibrium) is established at all times. Therefore, under these assumptions, the change in free energy of a gel becomes

\[
\frac{\partial G}{\partial t} = \int J_k \frac{\partial}{\partial X_k} \left( \frac{\partial W}{\partial C} \right) dV
\] (3 – 9)

where \( J_k \) is the long-range (i.e. intra-pore) solvent flux. The above equation implies that the total free energy of the system can only change via long range (inter-pore) motions of the electrolyte. Additionally, the nominal stress and chemical potential can be expressed as
This means that the nominal stress is the partial derivative of free energy density with respect to deformation gradient, and the chemical potential is the partial derivative taken with respect to concentration. Now, considering the inequality \( \frac{\partial G}{\partial t} \leq 0 \) (where \( G \) is the total Gibbs free energy of the system) must hold, we employ a kinetic law:

\[
J_k = -M_{KL} \frac{\partial \mu(X, t)}{\partial X_L}
\]

where \( M_{KL} (F, C) \) is a mobility tensor. Analogous to Fick’s first law of diffusion, the above equation predicts the molecular flux by means of chemical potential gradient. We can gain an intuitive understanding of solvent flux in a poroelastic solid as being Fickian. In general, it is non-linear, with the mobility tensor being continuously modified by the deformation gradient, as resistance to flow changes as a result of large pore size variations.

### 3.1.2 Fluid flow and zeta potential modelling

To model the solvent flow in response to a pressure differential under incompressible condition, we must consider Darcy’s law:

\[
v = -\frac{\kappa}{\eta} \nabla p
\]

Where \( q \) is the discharge velocity \((\text{m/s})\), \( \kappa \) is permeability \((\text{m}^2)\), \( \eta \) is the viscosity of the fluid \((\text{Pa} \cdot \text{s})\), \( p \) is the pressure \((\text{Pa})\) experienced by the fluid.
The electrostatic interaction between the polymer backbone and the ions is interpreted analogously to an electrical double layer (EDL) problem. Therefore, a zeta potential is set, depending on the surface charge density (polymer backbone charge density in this case), away from the channel wall by the distance of the Debye length in the simulation:

\[ \lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2N_A e^2 I}} \]  

(3 – 14)

The solvent flow driven formation of ionic charge separation due to ionic mobility differences can be seen as a reversal effect of an electroosmotic flow, and hence it is appropriate to employ the Helmholtz-Smoluchowski equation, which describes the ionic current due to solvent flow under differential pressure as follows:

\[ I_{flow} = -\frac{\varepsilon_r \varepsilon_0}{\eta} \frac{r^2 \pi \Delta p}{l} \zeta \]  

(3 – 15)

where \( \varepsilon_r \) is the relative permittivity of the electrolyte, \( \varepsilon_0 \) is the permittivity of free space, \( r \) is the radius and \( l \) is the length of the channel through which the solvent flow takes place, \( \eta \) is the dynamic viscosity of the solvent, \( p \) is the pressure, and \( \zeta \) is the zeta potential. Using Ohm’s law, the voltage built up across the channel is expressed:

\[ V_{flow} = \frac{\varepsilon_r \varepsilon_0 \zeta \Delta p}{\eta \sigma} \]  

(3 – 16)

Further, total charge is conserved within the studied field, and this is ensured by the inlet and outlet boundary conditions following Kirchhoff’s law:

\[ \nabla \cdot (-\sigma \nabla V) = 0 \]  

(3 – 17)

All other boundaries follow an insulating condition:

\[ -\sigma \nabla V \cdot n = 0 \]  

(3 – 18)

Fick’s law of diffusion is valid for the dissolved substances at all times,
3.2 Model implementations using COMSOL Multiphysics and MATLAB

In this section, two models are presented to describe the piezoionic behavior of a gel by means of coupling Biot’s poroelasticity, where an external mechanical load induces an internal solvent flow dictated by Darcy’s law. The flow velocity field is then introduced as the convective factor in the transport of dilute species module, which allows computation of a transient concentration gradient based on various constitutive parameters including the diffusion constants of ion species. This model can predict the differential ionic displacements as a function of the species’ diffusion coefficients. The factors influencing the diffusion coefficients include the steric hindrance imposed on an ion due to its bulky structure for instance, the porosity and the tortuosity of the flow path, and the ion-ion/ ion-solvent/ion-polymer electrostatic interactions as we learned in chapter 2. However in this model, it is not possible to deduce the explicit effects of the steric and charge interactions on the nature of ion distribution.

In particular, in order to explicitly investigate of the effect of charging of the polymer backbone, as in the experiments in section 2.3, a MATLAB model was implemented to model such electrokinetic flow induced voltages. In the following paragraphs a model is developed from which flow is estimated. Ion concentration is then determined. The final step of determining voltage distribution has yet to be carried out.

3.2.1. Coupled Poroelastic solvent flow – transient ionic redistribution model

Here, a geometry is defined such that there exists a square shaped gel of 2 cm by 2 cm by 0.5 cm placed at origin. The relevant mechanical properties of the gel are summarized in the table below.

\[
\frac{\partial c}{\partial t} = D \nabla^2 c
\]
A circular boundary was placed at the top of the gel, and a prescribed a displacement of 1 mm (20% strain vertically) on the top surface. The bottom of the gel was assigned a fixed boundary condition (displacement in x,y, and z directions are forced zero). All other surfaces were free to deform. A graphical capture of the geometry is shown below.

The liquid phase was set to be water. The poroelasticity module computed for the resultant Darcy’s flow within the polymer matrix in a transient analysis according to the following equations similar to those appearing in section 3.1.1.
\[ \nabla \cdot \sigma_{\text{elastic}} - \nabla \frac{\mu_{\text{chemical}}}{\Omega} = 0 \]  
\hfill (3 - 20)

and,

\[ \nu = \frac{-\kappa}{\eta} \nabla p \]  
\hfill (3 - 21)

where \( \sigma_{\text{elastic}} \) is the total elastic stress of a polymer (N/m\(^2\)), \( \mu \) is the chemical potential of an electrolyte molecules inside the gel (J/mol), \( \Omega \) is the molar volume of a solvent molecule (mol/m\(^3\)), \( \kappa \) is the permeability of a gel (m\(^2\)), \( \eta \) is the viscosity of fluid (Pa\cdot s), and finally \( \nabla p \) is the pressure gradient within a gel (Pa/m). Below, graphical representations of the (i) displacement, (ii) pressure (iii) Darcy’s flow velocities are presented.

Figure 3-2. A graphical depiction of the total displacement at \( t = 100 \).
The flow velocity output was then input into the subsequent physics, transport of dilute species, as the source of the convection. Namely, Darcy’s velocity was inserted to the \( \mathbf{v} \) term in the following equation. The constitutive equation for convection, diffusion and migration is as follows:

\[
N_i = -D_i \nabla c_i - z_i c_i \mu_i \nabla V + v_i c_i
\]  \hspace{1cm} (3-21)
Where $N_l$ is the molar current (m·mol/s), $D_l$ is diffusion coefficient (m$^2$/s), $c_l$ is concentration (M), $z_l$ is valence charge, $\mu_l$ is the electrophoretic mobility, and $v_l$ is convection velocity (m/s) of a given electrolyte species.

The experiments from chapter 2 (sections 2.2 and 2.3) attempted to show a correlation between the diffusion coefficients of the ionic species and the resultant piezoionic voltage response. The results were in agreement with the initial assumption that the poroelastic flow entrained the more diffusive species at a higher rate than the counter ions of lower diffusivity. However, as shown in the last term of equation 3-21, the diffusion coefficient does not in fact explicitly govern the convective flux of a given ionic species. The diffusion coefficient is ideally used as an implicit indicator of the degree of hindrance to the motion of ions sterically or electrostatically. These factors, in turn, can indeed affect the convection velocities of ionic species.

In this COMSOL model, a difference in diffusion coefficients between ions is being used as a modulation factor to induce a differential ionic distribution. In the future, it is desirable to fully characterize the and determine the analytical relationship between the ionic size, polymer mesh size, backbone polymer charge, and the resultant velocities at which ions are carried. In this way, it will be possible to probe into the effect of an individual parameter on the overall behaviour of a given piezoionic polymer.

Two species were assumed to be present, one was assigned +1 charge, with a diffusion coefficient of $2 \cdot 10^{-9}$m$^2$/s and the other with -1 charge and $1 \cdot 10^{-9}$m$^2$/s. This is such that the difference in the diffusivity causes a different rate of ionic redistribution upon mechanical perturbation of the
gel. Computing for the molar concentration distribution, convective flux, and diffusive flux, we can determine the gel behavior on chemically, compatible to subsequently perform an electrical voltage calculation using the electrostatics module coupled with this physics. Here, the space charge distribution is computed by taking the difference between the local cationic and anionic concentrations, and scaling it by Faraday’s constant. The electrostatic module then computes the voltage distribution in the gel using Poisson’s equation,

\[ \nabla^2 V = \frac{\rho_f}{\varepsilon} \]  

(3 – 23)

where \( V \) is voltage (V), \( \rho_f \) is space free charge density (C/m\(^3\)), and \( \varepsilon \) is the permittivity of medium (F/m). The differential entrainment of cations and anions have induced an inhomogeneous ionic charge distribution, yielding not only diffusive backflow towards chemical equilibrium but also electrophoretic migration to satisfy the electrical equilibrium. Thus, the voltage computed in this step is inserted back into the migration term of the transport of diluted species, further modulating the overall ionic distribution in the next time step. The diagram below depicts the cross-coupling relationships between each physics, enabling an iterative solving approach.
Figure 3-5. Cross-coupling relationship between poroelasticity, transport of diluted species and electrostatics modules implemented in COMSOL Multiphysics.

Presented below are graphical depictions of (i) concentration distribution of species 1 at t = 0 and 100 seconds, (ii) concentration difference (c1 – c2) computed at t =100 seconds, (iii) convective flux, (iv) diffusive flux, and (v) electrophoretic flux at t = 100 seconds.
Figure 3-6. A graphical representation of the concentration distribution at $t = 0$. The initial concentration was set to be 1 M.

Figure 3-7. A graphical representation of the concentration distribution of species 1 at $t = 100$. 
Figure 3-8. A graphical representation of the concentration difference of species 1 and 2 at \( t = 100 \).

Figure 3-9. A graphical representation of the convective flux (color: magnitude, arrow: vector) at \( t = 100 \).
One can observe qualitatively that Darcy’s fluid flux induced a convective flux carrying away the present species, from the compressed region to its surrounding, yielding a decrease in concentration within the circle in the center and an increase around the circle where the solvent is flowing towards. The net increase in the molar concentration just outside the compression site is
in the approximately 10 mM. When one takes the difference in the species 1 and species 2
distribution, it is less than 1 mM. This is in fact a sufficient concentration differential to induce a
significant voltage. For instance, consider a biological cell membrane, which maintains its internal
potential at around -70 mV with respect to its surroundings. Assuming the membrane interface to
be a relatively good representation of a parallel plate capacitor, with a capacitance of 1\mu F/cm^2.
The charge required here is only \(7 \cdot 10^{-8} \text{C/cm}^2\), and for monovalent ions about \(10^{-12} \text{ moles/cm}^2\)
to establish this voltage. Below, the voltage response yielded by this simulation is presented, at
various distances from the centre of the gel. The radius of the circular indenter used in the
simulation was 5 mm. Therefore, the polarity of the voltage is reversed about this location. The
voltage responses measured at 5 mm and 6 mm had the shortest time constant whereas the further
it is from the compressed/uncompressed interface, the time constant was longer. This provides an
insight as one can change the electrode placement within a given gel and attain an effective change
in the frequency response of the voltage. The magnitude of the voltage is in the order of a tenth of
a milliVolt, which is within a reasonable range of values expected experimentally (sub mV ~ 100
mV).
As described in the flowchart summarizing the suspected contributing factors to the piezoionic effect, the convective ion transport is thought to be the short time response whereas the diffusive backflow of ions is the source of voltage decay over time. This is reflected in the direction and the order of magnitude of molar convective, diffusive, and electrophoretic fluxes. One can assess that at the time of capture, the convective flux was dominantly carrying the ionic species outwards, while the diffusive and electrophoretic fluxes were directed inwards to cancel out the concentration field. It is believed that once the poroelastic relaxation of the polymer takes place and the solvent flux decreases, the diffusive and electrophoretic ionic fluxes become the dominant effect,
cancelling the chemical and electrical potential gradient and hence the voltage. The simulation
result shows in figure 3.13 that the maximum convection takes place at short times (<10s), whereas
the diffusive and electrophoretic fluxes peak at around 80 ~ 100 s.

Figure 3-13. Maximum molar convective, diffusive, and electrophoretic flux observed in the gel over time.
Finally, the simulated relaxation behavior due to the solvent flow of the gel is presented as a function of time. One can observe that the presence of liquid phase increases the apparent rigidity initially, perhaps as the effective frictional drag is maximum between the solid polymer phase and the electrolyte. During the mechanical tests, the mechanical relaxation of the gels due to a significant solvent flow was not observed experimentally. With 5% crosslinking of polyacrylamide, the porosity yielded was assumed to be relatively low experimentally. Namely, the volumetric swelling after synthesis was estimated to be less than 5%. This implied that perhaps this particular gel sample did not allow for significant solvent flow, explaining the absence of
relaxation. Furthermore, the step response or the square wave compression tests such as the ones presented in figure 1.3 may not have been conducted at sufficient length in time (i.e. the step load only lasted for 50 ~ 80 seconds), and a longer step test lasting for ~ 1000s is desired in the future.

### 3.2.2. Electrokinetic potential across a solvent flow over a charged tube structure

A simple geometry comprising a single channel, through which an electrolyte flow can take place, was assumed to simulate the piezoionic ionic charge separation along a given path in an ionic gel. The dimensions for this channel were decided according to reference [46], where the authors have characterized the effective pore sizes, of polyacrylamide hydrogels synthesized using the same methods as in this study, to be between 6 and 11 nm. The zeta potential in cationic and anionic polyacrylamide microbubbles were characterized by Oliveira et al, where they have reported it to range from 44mV to -93mV [59]. Here the simulation sweeps the zeta potential from -100 mV to 100 mV, ensuring that the empirically reported values are well within the range. A pressure differential can be applied as a boundary condition at the two ends of the channel, effectively driving the liquid to propagate over time. The charge distribution must be studied as the solvent travels through this channel in two ways: according to their sizes, and according to their electrostatic interactions with the charges on the polymer backbone. The lateral displacement or the flow path length was set to a value similar to the indentation depth used in experiments in chapter 2. Below, the list of parameters used to compute the simulated voltage build-up is presented.
<table>
<thead>
<tr>
<th>Parameter (variables)</th>
<th>Symbol / Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore radius</td>
<td>r (m)</td>
<td>1·10^{-8}</td>
</tr>
<tr>
<td>Path length</td>
<td>l (m)</td>
<td>1·10^{-4}</td>
</tr>
<tr>
<td>Temperature</td>
<td>T (K)</td>
<td>300</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>εᵣ</td>
<td>80.4</td>
</tr>
<tr>
<td>Pressure</td>
<td>Δp (Pa)</td>
<td>0 ~ 5·10^8</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>η (Pa·s)</td>
<td>8.94·10^{-4}</td>
</tr>
<tr>
<td>Conductivity</td>
<td>σ (S/m)</td>
<td>0.1</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>ζ (V)</td>
<td>-0.1~0.1</td>
</tr>
<tr>
<td>Charge number</td>
<td>z</td>
<td>1, -1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter (constants)</th>
<th>Symbol / Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permittivity of free space</td>
<td>ε₀ (m^{-3}kg^{-1}s^4A^2)</td>
<td>8.854·10^{-12}</td>
</tr>
<tr>
<td>Avogadro’s number</td>
<td>N_A</td>
<td>6.022·10^{23}</td>
</tr>
<tr>
<td>Elementary charge</td>
<td>e (C)</td>
<td>1.602·10^{-19}</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>k₀(m^2kg^{-2}sK^{-1})</td>
<td>1.381·10^{-23}</td>
</tr>
</tbody>
</table>

Table 3-2. List of variables and constants used in the computation of simulated voltage build-up across a solvent flow path

As can be seen in the table above, the applied pressure and the zeta potential were varied, and the resultant voltage was plotted over the simulated range. Figure 3-15 shows the voltage build-up across the channel or the ‘pore’ as a function of applied pressure and zeta potential.

Figure 3-15. A simulated voltage across a solvent flow path length of 0.1 mm within charged polyacrylamide having 10 nm pore sizes, as the zeta potential was varied from 0.1 V to -0.1 V (cationic gel to anionic gel), and the applied pressure across was varied from 0 to 1 kPa.
The resultant voltage appears to be in the reasonable range and comparable to the experimental results. Namely, the above simulation suggests approximately 1 mV/kPa, whereas the sensitivity of the charged polyacrylamide used in section 2.3 is approximately estimated to be around 1~3 mV/kPa. The major difference or discrepancy in this simulation, understandably, is the fact that the voltage yields zero at uncharged polymer state. This is because the model has yet to account for the differential ionic mobility based on effective ion sizes. Without accounting for the ion size and steric effects, the change in the polarity of polymer backbone does indeed translate to the direction of the voltage being opposite. This was initially postulated, but not in fact observed in the charged polyacrylamide samples in section 2.3, presumably because the sodium ion mobility, based on sizes, is still much greater than that of triflate anions. Nonetheless, a trend in the magnitude change of the piezoionic voltage response of the charged sample was observed in section 2.3, where the initially sodium-dominant flow is enhanced by positively charged polymer backbone and diminished by negatively charged polymer backbone. Despite the potential confounding factors such as differences in the microscopic mesh structure and change in steric hindrance on the ion mobilities, experimental results suggested and called for a more rigorous investigation of the electrostatic interaction between the polymer and ions. This current simulation is another piece of information to motivate this future inquiry.
Chapter 4  Method for Determination of Ionic Conductivity in Heterogeneous and Electronically Conductive Structures

Measurement of ionic conductivity is commonly performed by clamping ionically conducting membranes between inert metal plates and recording the impedance in the kHz frequency range. This method poses an inherent problem in specimens which are multi-phase, multi-layer, or electronically conducting, as the impedance will have phase-specific contributions. In this study, a four-electrode diffusion cell setup was employed to determine the ionic conductivity of multilayer and multiphase structures. In this approach, a swept sine or constant current is applied between two counter electrodes in solution, and the potential drop across an intervening membrane is measured using reference electrodes. At low frequencies and long times, the ionic resistive drop dominates the impedance even in electronically conductive electrodes. Ionic conductance and conductivity are deduced from this impedance. Measurements were made by sequentially adding layers or phases to a substrate membrane and estimating their contributions to determine their ionic conductivity. To demonstrate the approach, the ionic conductivities of activated carbon coated Celgard® (a typical supercapacitor construction material), polypyrrole (PPy) coated polyvinylidene fluoride (PVDF), and poly(ethylene dioxythiophene) (PEDOT) interpenetrated poly(ethylene oxide) (PEO) – nitrile butadiene rubber (NBR) co-polymer with various PEDOT concentrations were measured. Equivalent electrical circuit models were used to interpret the complex impedances within each ion conducting phase. The approach can be applied to any membrane composed of one or more ionically conductive layers or phases, and is particularly useful when electronic conductors are also present. The determination of phase-specific ionic conductivities in heterogeneous ionic conductors will find applications in the modeling and
understanding of a wide variety of devices including supercapacitors, batteries, fuel cells, ion exchange membranes, and conducting polymer actuators.

4.1 Background and motivation
Multilayered ion conductors are employed in various applications such as batteries [60]–[62], fuel cells [63], supercapacitors [64]–[68], ion exchange membranes [69], and conducting polymer based devices [1], [70]–[74]. In modeling and optimizing such structures, ionic resistances in each of the ion conducting phases can contribute significantly to the overall cell impedance. The relative thicknesses and morphologies of the individual layers are major parameters in determining the device charging speed and current density [75], [76]. In modeling and optimizing such structures, a thorough understanding of ionic conductivities in each of the ion conducting phases is of vital importance. However, it is not a trivial task to distinguish individual phases in a composite with multiple layers of ion conductors, especially in the case where phases can form an interpenetrating network with one another [8]. The direct measurement of ionic conductivity using conventional AC methods becomes impossible to even in one-layer structures when they are also electronically conductive. Here we present an approach for measuring ionic conductivities in multi-layer structures, and for estimating conductivities of individual layers or phases.

In an asymmetric configuration where the specimen is placed between a metal and an electrolyte, both ionic and electronic conduction takes place simultaneously, and it is challenging to separate the effects of the ionic and electronic transport properties. Although parameter values such as ionic resistance and volumetric capacitance can be deduced by iteratively fitting an empirical response using an equivalent circuit model, this is prone to errors as the uncertainties may propagate when
computing the ionic conductivity [77]. The ionic conductivity of electronically conducting membranes has been previously demonstrated using a four point ionic conductance diffusion cell [78], [79]. In this symmetric system, the specimen interfaces with the electrolyte on both sides, therefore limiting the system to ion transfer only, enabling direct measurement and characterization of ion transport properties [78]. This arrangement is unlike the three electrode configuration, depicted in figure 4-5 (a), where impedance measurements rely on probing distributed ionic, $R_i$, and electronic, $R_e$, resistances of an electrode, which are capacitively coupled via electrical double layers, $C$. The measurements in the 3-electrode case must find a frequency region where ionic resistance makes a dominant contribution, which may be at some intermediate frequency range. Instead in the symmetric case used here and shown in figure 4-5 (b), the ionic current conducts through the membrane parallel to the electronic current. As a result, at long times or low frequencies relative to the time constants associated with the capacitances and resistances in the circuit, the capacitors will effectively be an open circuit, and ionic resistance will dominate. The potential drop across the cell is then determined by the current, ionic resistance and the solution resistance. This approach is dependent on operating in a region of applied potential where the charge transfer resistances across the double layer are large compared to ionic resistances.

In this work, an experimental setup based on the four-electrode diffusion cell shown in figure 4-2 is used to distinguish the ion transport in each layer of a heterogeneous, multilayered ionic conductor. The four-electrode configuration in a diffusion cell was previously introduced by authors including Ehrenbeck and Jüttner to determine the ionic conductivity through polypyrrole films [78], [79], and later applied by Otero et al. for a similar purpose [80]. DC and AC analyses were performed, and ohmic and capacitive behaviors were observed respectively in free-standing
polypyrrole samples. A multiple time constant modeling of such symmetric systems has been reported by Yoo et al. for conducting polymer PEDOT: PSS membrane electrodes of non-uniform thickness [81]. Fekri and colleagues applied the four electrode configuration to measure ionic conductivity in carbon fiber paper into which varying amounts of polypyrrole are electrodeposited [77], with ionic conductivity measurements being compared with values obtained by pulse-gradient NMR [82]. Here we extend these efforts to describe multi-layered and interpenetrated structures composed of layers that are only ionically conductive and are of mixed ionic and electronic conductivity.

In all application areas under discussion, the knowledge of phase-specific properties regarding ion transport is valuable in enabling more accurate modeling and better system optimization. Construction of heterogeneous, multi-phase ionic conductors is a crucial aspect of energy storage devices as they may be tuned to selectively conduct particular ionic species, and to conduct in a certain region of the bulk. Ion transport can limit charge/discharge rate and power. Fuel cells are typically constructed of stacked layers that include ion selective membranes, as well as porous catalyst and carbon containing electrodes. Supercapacitors employ high surface area materials with micro, meso, and macro-porosity to attain high energy density. Tuning the pore sizes, densities, and morphologies is an extensively studied topic. Materials such as activated carbon (AC) [64][67], carbon nanofibers [66], aerogel [68], carbon nanotubes, graphene, and templated porous carbon (TC) [65] are commonly investigated as supercapacitor electrodes. Often the aim is to maximize capacitance and energy density, but what is the effect of pore sizing and lamination or interpenetration on ionic resistance and device time constant? Here we demonstrate a method that can be used to directly probe ionic resistance in these device components. Intrinsically
electronically conducting polymers such as polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(aniline) (PANi) have been extensively investigated for their use as electro/bio-chemical sensors [70], [71], selective ion membranes [72], energy storage devices [73], and electrochemically driven actuators [1], [74]. In such π-conjugated polymers, electrostatic compensation for free charge carriers is maintained by the insertion or removal of mobile dopant ions intra-matrix, as the conjugated backbones carry either polarons (P+) or bipolarons (P2+) [83]–[85]. Much like supercapacitor electrodes, electroactive polymers accommodate mobile ions by intercalation – in this case between polymer chains. Again it is useful to identify ionic resistance and conductivity in these electronically conductive materials, which often form part of a two or three-layer structure [5], [8].

In this work, the 4-electrode symmetric configuration is employed to estimate the layer and phase specific ionic conductivities in the multi-phase ion conducting specimens including activated carbon coated Celgard®, polypyrrole coated polyvinylidene fluoride, and poly(3,4-ethylenedioxythiophene) interpenetrated poly(ethylene oxide) – nitrile butadiene rubber co-polymer. Conductance and conductivities of individual layers are obtained either by direct 4-point measurement or after subtraction of the resistance of laminated layers. Equivalent electrical circuit models are developed to separately estimate the ionic conductivities of such multi-phase structures (i.e. multiple immiscible domains of varying morphologies and electronic properties within the same layer, such as PEDOT within the interpenetrating polymer network).
4.2 Experimental

Three composites were prepared for this study to demonstrate the applicability of this work in various fields. The composite based on activated carbon and a polypropylene based microporous membrane Celgard® was constructed to imitate similar structures found in supercapacitors, whose rate of charging can be limited by ionic resistance in the separator or electrodes. The polypyrrole/PVDF/polypyrrole composite is a popular trilayer structure of a bending actuator or sensor using electroactive polymers [5]. Since actuation speed directly correlates to the rate of ion transfer into the polypyrrole layer, it is useful to characterize the ionic conductivity within each layer of this composite. The third is the PEDOT/PEO-NBR/PEDOT interpenetrating polymer network with various PEDOT concentrations (0, 5, 12, 19, 25, and 26 wt%). It is another electroactive polymer based trilayer actuator also used as a sensor and as electrochromic windows [86][87]. In this case, the electroactive polymer PEDOT is polymerized within the host PEO-NBR copolymer matrix. Thus the ion conduction mechanism differs from specimens with discretely separate layers. The interpenetrating network macromolecular architecture is also of interest as a battery separator [88] [89].

4.2.1 Materials

Polyvinylidene fluoride (PVDF) films (thickness: 125 µm, pore size: 0.45 µm) were purchased from Millipore (Darmstadt, Germany). The Celgard® 2500 separator membrane was purchased from Celgard® (Charlotte, North Carolina). Activated carbon (PICACTIF SUPERCAP BP10) was purchased from PICA USA, Inc. (Columbus, Ohio). Carbon black (Super P Li) was purchased from Imerys Graphite & Carbon (Bironico, Switzerland). Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), Sodium hexafluorophosphate (NaPF₆), lithium
bis(trifluoromethane)sulfonimide (LiTFSI), tetraethylammonium tetrafluoroborate (TEABF₄), propylene carbonate (PC) and acetonitrile (ACN), and N-Methyl-Pyrrolidinone (NMP) were purchased from Sigma-Aldrich (St. Louis, Missouri). All reagents were used as received unless otherwise specified.

4.2.2 Preparation of Specimens

Samples of poly(ethylene oxide) (PEO) – nitrile butadiene rubber (NBR) copolymer network of thickness 250 µm, as well as samples based on the PEO-NBR copolymer and PEDOT, were synthesized following the protocol described in [8]. The PEO and NBR were crosslinked in situ using thermal initiators dicyclohexylperoxidicarbonate (DCPD) and dicumyl-peroxide (DCP) respectively while the temperature was varied to allow sequentially the crosslinking of the both polymers to take place. In the PEO-NBR copolymer, PEO primarily acts as the ion conducting phase whereas the NBR serves to improve the mechanical compliance. As the fabrication procedure involves soaking the PEO-NBR copolymer in EDOT followed by oxidative polymerization in aqueous ferric chloride, the PEDOT layer is in an interpenetrating form within the host copolymer matrix, forming a third component [8].

Celgard® 2500 polypropylene based separator film was used to construct a multilayer structure which resembles of a typical supercapacitor construction. The void fraction for this product is 55%, and the average diameter of the pore sizes is 0.064 µm according to the supplier. Activated carbon (85%wt), carbon black (5 wt%), PVDF-HFP (10 wt%), were mixed thoroughly in N-Methyl-Pyrrolidinone at 20µL/mg to form a slurry. This was empirically tuned based on prior work in [90]. The slurry was then vacuum-filtered onto the separator to form a film of
approximately 20 µm thickness [91]. The solvent was then evaporated at 50 °C for 20 hours. Before the experiment, the samples were gently washed with deionized water to remove excess carbon particulates weakly bound to the surface. From the SEM images in figure 4-1 (e), it is observed that the grains of activated carbon penetrated partially into the Celgard® film, perhaps due to the suction and compression force applied during synthesis.

Figure 4-1. SEM images depicting surface topologies of (a) PVDF/PPy (b) Activated carbon/Celgard® (c) PEO-NBR/PEDOT and the cross sectional views of (d) PVDF/PPy (e) Activated carbon/Celgard® (f) PEO-NBR/PEDOT

A PVDF film of thickness 200 µm was used to construct a multilayer film of PVDF and polypyrrole [5]. Gold was sputtered onto the PVDF film at a thickness of approximately 120 nm to form a conductive substrate on which polypyrrole was electrodeposited. Polypyrrole deposition was carried out galvanostatically in a propylene carbonate (PC) solution containing 0.06 M pyrrole and 0.05 M tetrabutylammonium hexafluorophosphate (TBAP) at current density of 0.125 mA/cm² at -40 °C, following a variation of a well-established procedure for obtaining high quality, high
capacitance, electrically conductive and mechanically robust films [92]. The properties of these films have been thoroughly studied [82]–[85], [92]. The resulting structure was stored in propylene carbonate for up to 7 days to remove any residual oligomers. The image of the polypyrrole layer showed cauliflower like features that are much more densely packed morphology than its substrate. 0.10M aqueous sodium hexafluorophosphate (NaPF$_6$) as well as 0.10M lithium bis-(trifluoromethane)sulfonimide (LiTFSI) in propylene carbonate (PC) were prepared and used for measurements of PVDF/PPy and PEO-NBR/PEDOT samples respectively. These are relatively common electrolytes in which the trilayer bending actuators are deployed. For the Celgard®/activated carbon samples, 0.10M tetraethylammonium tetrafluoroborate (TEABF$_4$) dissolved in acetonitrile (ACN) was used as it is well suited for standardized characterization of electrode materials in supercapacitor applications [93].

4.2.3 Measurement Procedure

Figure 4-2. The diffusion cell experimental set-up. The potential difference is measured across the reference electrodes while a current perturbation is applied between the counter and working electrodes.
Each film sample was immersed in selected electrolytes to for up to two weeks before measurements to ensure complete uptake of the electrolyte. In some samples including Celgard®, the wetting process was quite rapid and took several minutes, whereas combinations of a bulky electrolyte and a dense material such as PEDOT in LiTFSI/PC took up to several days. In all samples, the full swelling was confirmed by the saturation of wt% swelling ratio. After the immersion period, the specimens were clamped between the diffusion cells as shown in figure 4-2. The two cannulas extend to a very proximity (~ 1 mm) to the membrane, such that when reference electrodes are inserted, the potential immediately outside the surface of the membrane can effectively be measured. For Celgard®/activated carbon samples only, two-ply stacks were made such that the resistance due to the membrane was sufficiently higher than the fluctuations in the impedance measurement. Ag/AgCl reference electrodes (BASi, MF-2021) were used in aqueous solutions. Ag/Ag⁺ non-aqueous reference electrodes were assembled using 0.1M TEABF₄/0.01M AgNO₃/ACN for measurements in the acetonitrile-based electrolyte, and 0.1M TEABF₄/0.01M AgClO₄/PC for measurements in the propylene carbonate based electrolyte. Carbon paper of size 10.0 x 20.0 mm was used as the relatively inert counter electrodes.

To characterize the ionic impedances, each sample was subjected to a constant current input and a swept sine input using a Solartron 1287A Potentiostat/Galvanostat, Hampshire, UK, combined with a Solartron 1260A Frequency Response Analyzer in the case of swept sine. All procedures were carried out at room temperature (295 ± 2 K). The apparatus, as depicted in figure 4-2, acts as a 4-point measurement across the membrane, with the two reference electrodes detecting local potential drop. At long times and low frequencies, this drop is due to the ionic resistance of the sample and of the electrolyte between the sample and the tips of the cannulas [77].
4.2.3.1 Galvanostatic Polarization Method

DC currents of -1 mA to 1 mA at an increment of 0.1 mA were applied between the counter electrodes, including across the sample films, for 1200 s per measurement so as to stabilize the RC charging. The steady state potential across the membrane sample was recorded. The expected ohmic behavior (resistance independent of current) is confirmed by plotting the resultant potentials against applied current, with the slope providing an estimate of the resistance.

4.2.3.2 Swept Sine Impedance Spectroscopy

A sinusoidal current with an amplitude of 0.5 mA was applied, and its frequency was swept across five decades from 100 Hz to 1 mHz while measuring the phase and the amplitude of potential across the ion conducting membranes. The amplitude of the current was chosen with the purpose of attaining an appropriate signal to noise ratio (SNR), as the open circuit potential can fluctuate during the measurement while avoiding significantly modulating the oxidation levels of the specimens. Measurement of impedance relies on a linear, time-invariant response of the cell system. In samples that are also electronically conductive, the ionic resistance measurement using the impedance method is estimated by using the low-frequency value of the magnitude of impedance, which is nearly purely resistive. The remainder of the impedance spectrum provides insight into the ionic resistance of the conductive and non-conductive portions.

To determine the solution resistance between the ends of the cannulas, the same tests were performed on a setup without the membrane for each of the electrolytes. This resistance is then subtracted from the total resistance of the membrane plus external solution, to estimate the ionic
resistance, \( R_i \), of the membrane under test. The ionic conductivity was calculated using the following equation:

\[
\sigma_i = \frac{d}{R_i \cdot A}
\]

where \( d \) is the conducting layer thickness (m), \( A \) is the film area (m\(^2\)), and \( R_i \) is the ionic resistance (\( \Omega \)). The area or the samples through which the ionic current passes is 63.62 mm\(^2\). Subsequently, the ionic conductivities of layers were estimated by taking the difference in ionic resistance between specimens with or without the additional layer. For example, the difference in resistance of the Celgard\(^\circledast\) with and without a carbon coating is used to estimate the conductivities of the Celgard\(^\circledast\) and of the coating itself. SEM images of the cross sections were obtained and the thicknesses of each layer were estimated in order to compute the layer specific conductivities to use in the equation above.

### 4.3 Results and discussion

The method of estimating layer by layer ionic resistance and total ionic resistance is applied to three devices. Ionic resistances of individual device layers and the combined device ionic resistances using step current and impedance measurements are presented. The current-potential (i-E) plots produced via the DC galvanic polarization method as well as the Bode plots from the swept sine impedance spectroscopy are presented and discussed. The ionic conductivities of the phases are directly calculated according to equation 1 for the layers whose boundaries have been clearly identified via SEM imaging, or the thickness was measured using a micrometer.
4.3.1 DC Galvanic Polarization

The addition of each layer of the electrochemical device led to discrete differences in the measured ionic resistance. For non-electronically conducting samples the resistance was largely time independent. In electronically conducting samples subjected to a step current, an initial jump in potential was observed due to the resistance of the electrolyte between the reference electrodes and the sample. The electronic/ionic interfaces subsequently charge, increasing potential drop, and leading to a field that drives ionic current through the porous electronically conductive electrode. The layer-specific ionic resistances were measured, and ionic conductivities were calculated. These are compared with the results obtained via the swept sine impedance spectroscopy method.
Figure 4-3. i-E plots representing the DC resistance of the (a) Celgard®/activated carbon sample (b) PVDF/Gold/PPy sample (c) PEO-NBR/PEDOT sample.
Figure 4-3 shows the i-E plots for all DC galvanic experiments performed with each of the samples, fitted with a linear equation. All $R^2$ values were greater than 0.95, indicating a good fit and that the experiments were carried out within the linear region. The slopes of the plots highlight the increase in resistance due to the addition of ion conducting layers or phases to a given sample. Figure 4-3 (a) is the result obtained from the Celgard®/activated carbon membrane. It was deduced that the samples of activated carbon coated Celgard® exhibited ionic conductivities of $0.30 \pm 11\%$ S/m and $0.048 \pm 13\%$ S/m in the Celgard® layer and carbon layer respectively in $0.1\text{M TEABF}_4$ in acetonitrile as tabulated in Table 4-1. The uncertainties are the result of dimensional uncertainties, the accuracy limit of the instrument, temperature fluctuation, and the margin of error of the fitted slope at 99% confidence interval.

Ionic resistances of PDVF alone and polypyrrole coated PVDF were obtained from the slopes in figure 4-3 (b). The conductivity of polypyrrole was deduced to be $0.018 \pm 17\%$ S/m in 0.1 M aqueous sodium hexafluorophosphate whereas the porous PVDF layer was found to have a conductivity of $0.65 \pm 22\%$ S/m. It is evident from the results that the polypyrrole is the most significant contributor to the overall ionic resistance of the composite. From the linearity of the response seen in figure 4-3 (b), it was deemed that the measurement was effectively able to probe into the resistive component of the partially capacitive polypyrrole layer.

The conductivities of the PEO-NBR/PEDOT samples were computed using the thickness of the entire membrane, as discretely separate and individual layers were not detected via SEM imaging. The conductivity of the PEO-NBR alone was $0.20 \pm 12\%$ S/m in LiTFSI/PC whereas the addition of PEDOT decreased the conductivity to $0.023 \pm 8\%$ S/m at 26 wt% PEDOT content. The low
ionic conductivity of the PEDOT-containing layer is expected due to its stiffer, less mobile backbone compared to the electrolyte swollen PEO-NBR.

4.3.2 Swept Sine Impedance Spectroscopy

The same sequence of measurements was repeated using impedance in the four-point configuration of figure 4-2 to extract the conductivities of the specimen. As expected using the four-point method, there is no frequency dependence of the electrolyte impedance, indicating a purely resistive response. Subsequently, other films without electronically conducting phases were measured using the apparatus.
Figure 4-4. Magnitude Bode plots representing the complex impedances of the (a) Celgard®/activated carbon sample (b) PVDF/Gold/PPy sample (c) PEO-NBR/PEDOT sample at various PEDOT concentrations (5, 12, 19, 25, 25 wt%). Red lines represent the impedance response of the respective equivalent electrical circuit models.
Again, the impedances are purely resistive, with an additional membrane resistance, over a wide frequency range (1 mHz – 100 Hz). The conductivities of Celgard®, PVDF and PEO-NBR substrates were found to be 0.31 ± 9%, 0.44 ± 10% and 0.25 ± 10% S/m via this method. These match those found using the i-E curves within uncertainty. A Higher level of errors was attributed to low cell impedance. When measuring samples with low ionic resistance compared to the solution resistance, such as Celgard and the PEO-NBR, the uncertainties in the solution resistance, and slight changes in the distance between the reference electrodes during cell assembly, have a significant influence on the estimated resistance. However, this was partially mitigated by pairing samples into two-ply stacks and later dividing the resistance into half.

Capacitive impedances appeared on polypyrrole and PEDOT incorporated samples in the 1 mHz – 10 Hz range. It was not seen in the activated carbon sample within the frequency range measured due to the small RC time constant of this electrode but was expected to be seen at a higher frequency. Such responses are expected from the electronically conductive phases as the counter charge formation is readily achieved in the frequency ranges beyond kinetically governed regions. Eventually, the bulk capacitances are fully charged as the perturbation frequency lowers well below the time constant of charging. At 1 mHz, the samples exhibited nearly purely resistive behavior and the ionic resistances can be directly deduced. The conductivities of activated carbon, polypyrrole and PEO-NBR/PEDOT (at 26 wt%) were found to be 0.044 ± 10%, 0.019 ± 13%, and 0.023 ± 6% S/m and again agree with those obtained using the DC galvanic method.

According to the overall results from both characterization methods (presented in Table 1 below), it is deemed that the two methods for determination of ionic conductivities have produced
reasonably similar results within uncertainty and that they may be used to verify each other’s results.

<table>
<thead>
<tr>
<th>Conduction phase</th>
<th>Electrolyte</th>
<th>Thickness (Swollen) (m)</th>
<th>Ionic Conductivity (S/m) via DC Galvanic Method</th>
<th>Ionic conductivity (S/m) via Swept Sine Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard®</td>
<td>0.1M TEABF₄ in ACN</td>
<td>2.60 ¥ 10⁻⁵ ± 2 ¥ 10⁻⁶</td>
<td>0.30 ± 11%</td>
<td>0.31 ± 9%</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.1M TEABF₄ in ACN</td>
<td>2.60 ¥ 10⁻⁵ ± 3 ¥ 10⁻⁶</td>
<td>0.048 ± 13%</td>
<td>0.044 ± 10%</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.1M NaPF₆ (aq)</td>
<td>1.10 ¥ 10⁻⁴ ± 3.7 ¥ 10⁻⁶</td>
<td>0.65 ± 22%</td>
<td>0.44 ± 10%</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>0.1M NaPF₆ (aq)</td>
<td>2.20 ¥ 10⁻⁵ ± 1.2 ¥ 10⁻⁶</td>
<td>0.018 ± 17%</td>
<td>0.019 ± 13%</td>
</tr>
<tr>
<td>PEO-NBR</td>
<td>0.1M LiTFSI in PC</td>
<td>2.38 ¥ 10⁻⁴ ± 6.6 ¥ 10⁻⁶</td>
<td>0.20 ± 12%</td>
<td>0.25 ± 10%</td>
</tr>
<tr>
<td>PEO-NBR/PEDOT (5 wt%)</td>
<td>0.1M LiTFSI in PC</td>
<td>3.58 ¥ 10⁻⁴ ± 1.6 ¥ 10⁻⁵</td>
<td>0.16 ± 13%</td>
<td>0.21 ± 11%</td>
</tr>
<tr>
<td>PEO-NBR/PEDOT (12 wt%)</td>
<td>0.1M LiTFSI in PC</td>
<td>3.67 ¥ 10⁻⁴ ± 2.9 ¥ 10⁻⁶</td>
<td>0.071 ± 14%</td>
<td>0.079 ± 15%</td>
</tr>
<tr>
<td>PEO-NBR/PEDOT (19 wt%)</td>
<td>0.1M LiTFSI in PC</td>
<td>3.54 ¥ 10⁻⁴ ± 6.7 ¥ 10⁻⁶</td>
<td>0.042 ± 12%</td>
<td>0.039 ± 8%</td>
</tr>
<tr>
<td>PEO-NBR/PEDOT (25 wt%)</td>
<td>0.1M LiTFSI in PC</td>
<td>2.79 ¥ 10⁻⁴ ± 2.0 ¥ 10⁻⁵</td>
<td>0.022 ± 11%</td>
<td>0.022 ± 6%</td>
</tr>
<tr>
<td>PEO-NBR/PEDOT (26 wt%)</td>
<td>0.1M LiTFSI in PC</td>
<td>3.65 ¥ 10⁻⁴ ± 1.0 ¥ 10⁻⁵</td>
<td>0.023 ± 8%</td>
<td>0.023 ± 6%</td>
</tr>
</tbody>
</table>

Table 4-1. Summary of measured phase specific ionic conductivities

4.4 Analysis and discussion

Presented in this section are the equivalent electrical circuit models used to understand the layer and phase specific contributions to ionic conductivity and frequency response, as well as a discussion of the fits of these models to experimental impedance results. An RC transmission line model is proposed to describe ion transport in combined ionically and electronically conducting electrodes. The model is expanded to describe interpenetrated morphologies. For cell structures that contain discretely stacked layers, the total impedance is considered to be the sum of the ionic impedances of each layer. When a specimen consists of multiple polymers that are interpenetrated, the approach is modified by taking the volumetric fraction of the polymers from the synthesis protocol to compute the equivalent layer thickness of a given phase. This is used to predict the
impedance response as a function of PEDOT concentration in the PEO-NBR/PEDOT samples. Finally, the algorithm for determining ionic conductivities of the constituent parts is summarized in a flowchart (figure 4-7).

4.4.1 Modeling of the 4-electrode symmetric configuration

Figure 4-5. A graphical representation describing the electronic and ionic conduction for (a) asymmetric system (electronically conductive film shown in black into which ions can travel) (b) symmetric system (electronically conductive film) and (c) symmetric system (electronically insulating film shown in beige), along with their corresponding equivalent electrical circuit models. Here the +’s represent electronic charges, with which there are associated anions, the –’s are also electronic charges, with associated cations (yellow spheres). At the bottom are equivalent circuit models used to represent transport in each of these cases.

Unlike conventional two or three electrode electrochemical cells, the four electrode setup employed in this study places the specimen of interest between the two reference electrodes. The two reference electrodes are placed on either side of the film under study such that the impedance due to migration and diffusion in the film itself can be detected and distinguished from electrode charging, solution resistance, and electronic resistance.
In the absence of a specimen membrane, the four-point measurement shows a purely resistive behavior which is described by the solution resistance, $R_s$, between the reference electrodes. Electrically insulating materials such as the PEO-NBR interpenetrating polymer network, PVDF, and Celgard® are treated as an additional resistance in series with this solution resistance, configurations that are described by the circuit model of figure 4-5 (c). Capacitive/pseudo-capacitive behavior, represented by capacitance, $C$, is observed in PPy, PEDOT, and activated carbon, with electronic carriers within the bulk of these materials coupling with ionic counter charges. This interaction is modeled by an RC transmission line shown in figure 4-5 (b) and referred to here as a one-sided transmission line or a modified Warburg element. The element includes ionic and electronic resistances, $R_i$ and $R_e$. The connections are made only to the ionic phase (the top line) of the circuit, with the electronic phase capacitively coupled. This lends different boundary conditions from the typical three-electrode configuration solution to the diffusion equation, such that in this new case at either side of the membrane (position zero or $L$), $i_{ionic}(0) = i_{ionic}(L) = i_{total}$ and $i_{electronic}(0) = i_{electronic}(L) = 0$. In the continuum the frequency dependent impedance of the ladder circuit can be expressed as:

$$Z(L, \omega) = R_i L \left(1 - \frac{R_i}{R_i + R_e}\right) + \frac{2R_i^2}{(R_i + R_e)\sqrt{C_v A j \omega (R_i + R_e)L}} \left(\tan h \left(\frac{\sqrt{C_v A j \omega (R_i + R_e)L}}{2}\right)\right)$$

where $R_i$ is ionic resistance per unit length ($\Omega/m$), $C_v$ is capacitance per unit volume ($F/m^3$), $A$ is the cross-sectional area through which the current passes ($m^2$), $j = \sqrt{-1}$, $\omega$ is radial frequency (radians/s), and $L$ is the length of the ionic current path (i.e. the thickness of the membrane in meters). As angular frequency, $\omega$, approaches zero, the impedance of the ladder circuit becomes purely resistive:

$$\lim_{\omega \to 0} Z(L, \omega) = R_i L$$
It is this limiting case that is employed to estimate the ionic resistance of electronically conducting layers. In this case of high ionic resistance relative to electronic resistance the impedance in equation 2 becomes:

\[ Z(L, \omega) = \frac{2R_i}{\sqrt{C_0 A\omega R_i}} \tanh \left( \sqrt{\frac{C_0 A\omega R_i L}{2}} \right) \]  

(4 – 4)

which has the same mathematical form as the Warburg short circuit element. It is convenient in this case of negligible \( R_e \) to use a Warburg short element common in equivalent circuit fitting programs to model the impedance. The fits in figures 4-4 (b) and (c) are generated using ZPlot (Scriber Associates Inc., North Carolina). The method is generalized to multi-layer structures by a linear addition of individual layer ionic impedances that add in series. This method assumes there is little to no interpenetration between phases, but rather that each layer is physically distinct.

The results of the model fitting are presented as red lines in figure 4-4. Simple resistances are used to model layers that contain no electronically conducting phase, as seen in figure 4-4 (a). Where electronically conducting phases are present (PEDOT, PPy or carbon), a series combination of resistances representing the electronically insulating substrates and the modified one-sided transmission line of equation 2, are fit. These models are used to justify the interpretation of the data to estimate the ionic conductivities of the unknown layers. For the conducting electrodes, taking the limit of impedance at low frequency provides an estimate of \( R_i \), assuming the results continue to follow the equivalent circuit behavior in figure 4-2. These values are tabulated as conductivities in Table 1, after subtracting the resistances of other layers. The response closely followed an impedance response predicted by the RC transmission line model in the intermediate
to low frequencies as the bulk capacitance is charged and the overall resistance transitions from solution resistance of the surrounding to the internal ionic resistance of the membrane.

Particularly interesting is the observation of stepped rises in the magnitude of impedance observed in the PVDF/PPy sample and the PEO-NBR/PEDOT samples as frequency tends to zero. The plateau of the step is seen between 0.1 and 0.01 Hz and is most obvious in the PVDF/PPy response. It is also noted for all of the PEO-NBR/PEDOT samples as well as the PVDF/PPy, that the membrane is shorted at high frequencies and the cell resistances converge with that of the electrolyte alone as if there were no membrane present at all. In other words, the impedance of the separator layer (i.e. PVDF and PEO-NBR) is not seen at high frequencies in these two cases, as can be observed by the impedances dropping below the PEO-NBR only and PVDF only resistances in figures 4-5 (b) and (c) at frequencies of up to 1 Hz, and tending to equal the solution resistance at 100 Hz. This response suggests a bypassing of the resistance across the membranes, likely due to capacitive coupling of some form. The bypass may be due to the small concentrations of PPy or PEDOT known to be present even at the center of the membrane. It is known from elemental analysis (EDX) characterization of the PEO-NBR/PEDOT for example that there is PEDOT present throughout the membrane, although at much lower concentrations than near the surface [8]. In the middle section, it is low enough that it does not allow significant percolation at steady state. However, we postulate that capacitive coupling between small, closely spaced conducting regions essentially short circuits the separator layer at higher frequencies. Such effects have been observed by Cornejo et al. in carbon nanotube dispersed PDMS in the near-percolated regime [94]. To produce a short, the postulated capacitive element due to the electronically conductive phases is placed in parallel with the impedance of the substrate material, which is analogous to the
physical configuration where the conductive regions are dispersed but do not form a complete blockage.

The second RC charging corresponds to the volumetric capacitance of the PEDOT or PPy, whose frequencies lie between $10^{-1}$ to $10^{-2}$, yielding capacitances in the order of 100’s of mF. This value of capacitance is in line with expectations, given the dimensions of the polypyrrole and PEDOT layers, and their capacitances per unit volume of $5 \cdot 10^7 - 3 \cdot 10^8$ F/m$^3$ [95]. In principle, the impedance plots can be used to extract layer capacitance as well as ionic resistance. In practice, it may be best to extract these values via a three-electrode measurement as in figure 4-2 (a), as the capacitive nature will be very clear at low frequencies.

### 4.4.2 Ionic impedance modeling in interpenetrated structures

In many cases ionically conducting phases have well-defined layer structures, such as the PPy/PVDF/PPy trilayer samples used in this study, and each layer can be modeled as an electrochemical impedance in series with other layers. However, with the introduction of novel composites such as interpenetrating polymer networks (IPNs) and conductive materials dispersed in various polymer networks, heterogeneous phases exist in various fields of application [96]–[99]. In the PEO-NBR/PEDOT samples investigated here, the PEDOT phase is widely dispersed within the host matrix.
It was observed using energy dispersive x-ray spectroscopy (EDX) that the local PEDOT volume fraction approaches close to 100 % near the surface of the PEO-NBR in the samples of higher PEDOT content. Such a distribution suggests a series resistance model may be appropriate to represent the contributions to ionic resistance from the PEDOT and PEO-NBR phases. A
simulation represented by the red dashed line in figure 4-6 (d) was generated using the equivalent circuit model in figure 4-6 (a), with resistive element, $R_{i,2}$, to represent the PEO-NBR ionic contribution to impedance, and the RC transmission line described by equation 4-5 representing the PEDOT phase. In the model, which reduces to purely resistive series elements at DC, a PEDOT ionic conductivity of 8 mS/m was assumed, which is comparable to the ionic conductivity of polypyrrole measured in this study. This model, which assumes that the phase-specific impedances add in series, has a good convergence with the measured results at higher overall PEDOT contents. It, however, underestimates the effective conductivities of the membranes with lower PEDOT content. The underestimation by the model for these samples is not surprising since the local peak PEDOT concentration reaches only as high as approximately 30 vol%. At such a low PEDOT concentration, it is not expected that the PEDOT phase forms a complete blockage, which makes it unreasonable to assume that the impedance contribution by the PEDOT phase acts only in series in these cases.

In seeking to further understand the effect of PEDOT on the effective ionic conductivity, a second approach is to view the conduction through the PEDOT and PEO phases as being in parallel. In this case, the equivalent circuit consists of the phase wise impedance units linked in a parallel configuration as shown in figure 4-6 (b). At a given cross section within the membrane, the impedance is thought to be the parallel equivalent of the phase conductivities, scaled by the volumetric fraction. That is, $Z_{eq} = \left( \frac{1}{Z_1} + \frac{1}{Z_2} \right)^{-1}$ where $Z_1 = (\sigma_1 \cdot A \cdot vol\%)^{-1}$ and $Z_2 = (\sigma_2 \cdot A \cdot (100\% - vol\%))^{-1}$. This approach yields a linear decrease in the ionic conductivity as also shown in figure 4-6 (d) in the blue dashed line. It severely over-estimates the ionic
conductivities compared to the experimental results overall, however the convergence at very low PEDOT content is in fact better than the series resistance model. As might be expected, the actual response is somewhere between the series and parallel configurations. Now, a hybrid series/parallel model is considered in figure 4-6 (c) where the infinitesimal impedance of incremental thickness is integrated over the total thickness to give the overall membrane impedance given the PEDOT concentration profile as a function of position across the thickness, $C_{phase}(z)$. This model assumes that the incremental thicknesses at various positions in the membrane are individually conducting in parallel regime (phase wise), but each slice of impedance unit is connected to the adjacent ones in series regime. This allows to dynamically allocate local impedances as a function of position, as well as modulate the conduction regime (i.e. at high peaks of PEDOT concentration, close to the surface, the impedance will locally converge to the series regime whereas other parts with lower PEDOT concentration will carry ionic current mostly in parallel regime.) The simulation result of this hybrid model can be seen in the purple dashed line in figure 4-6 (d), and it has a very good convergence to the experimental data which lies between the completely series or parallel regimes discussed above. Such hybrid model may then be used for tuning purposes (i.e. a look up table for polymer ratios to synthesize specimen with desired conductivities) to further enhance and optimize the sample.

4.4.3 Summary of decision criteria for experimental and analysis methods

The proposed characterization protocol of complex ionic conductors has been shown to provide accurate and reliable ionic conductivity values in all phases of the structures. At this point, it is important to indicate clearly the decision criteria, based on the specimen, to determine which of the various experimental procedures and equivalent circuit models need to be chosen for a
successful characterization of the given specimen. Shown in figure 4-7 is a flowchart of the overall characterization procedure for a given specimen.

Figure 4-7. Flowchart representing the summary of decision criteria used in carrying out the proposed characterization protocol for an ionically conducting structure

Beginning with the measurement methods, a given specimen can be subjected to up to three different ionic conductivity tests. Namely, i) two electrode, metal plate clamping method, ii) four electrode DC galvanic polarization method, and iii) four electrode swept sine impedance spectroscopy can be used. Specimens containing electronically conducting phases are not suitable for the traditional parallel metal plate clamping method as discussed earlier. It is not useful in
cases where the determination of the ion transport within porous electrodes is desired. It does, however, have the advantage of a simpler apparatus. For this reason, it may be preferable to use when there are no electronically conductive components.

The swept sine test has an advantage especially in new specimens with somewhat unknown equivalent models as it can deliver insights into the impedance behavior over a wide frequency range. This can provide evidence to justify equivalent circuit models to employ subsequently. The use of the DC galvanic method is more reasonable as it is less time consuming, and hence it is proposed in the flow chart for general use in. The swept sine approach, however, can be useful in providing additional information about the nature of the coupling between the ionic and electronic phases, and convenient for equivalent circuit model fitting.

Next in the flowchart, selection of the suitable equivalent circuit model is carried out by first classifying specimens by whether or not they contain interpenetrated networks whose phases need to be characterized separately. Interpenetrated networks will most likely require manual estimation of equivalent layer dimensions as discussed earlier. In either case (interpenetrated or discrete layers), the specimen is further classified by whether or not it contains any electronically conducting phases. Where such conductive regions are present, a modified Warburg element can be used to represent the conductive regions – though this is not strictly necessary as it is sufficient to wait long enough that the response is primarily resistive in nature. The measurement of ionic conductivity then allows for redesign of layer thickness, the density of the active materials and so on for a given application, followed by re-measurement. For instance, PEDOT content could be
optimized in the PEO-NBR/PEDOT membrane to improve power output by reducing content depending on its application such as electroactive polymer actuators and supercapacitors.

4.5 Conclusion

This work has proposed a characterization protocol for determining field driven ion transport in a wide range of ionic conductors used in various fields. The commonly practiced characterization method for ionic conductivity measurements (i.e. metal plate clamping) probes only ion conductors that are not electronically conducting. Therefore, not only is there a need for additional methodologies that encompass more complex ionic conductor structures, but also it is of importance to establish a reliable platform to be utilized as a standard approach. In this study, the practical utility of the diffusion cell based, four-electrode impedance analysis methods have been shown along with equivalent circuit models to interpret the complex impedances. Three composites were characterized including activated carbon coated Celgard®, polypyrrole coated polyvinylidene fluoride (PVDF), and poly(ethylene dioxythiophene) (PEDOT) interpenetrated poly(ethylene oxide) (PEO) – nitrile butadiene rubber (NBR) co-polymer. The proposed method has proven to be effective in analyzing multilayer or multiphase structures and those containing electronically conducting phases. It has been shown that individual probing of each phase or layer in a heterogeneous structure is possible, assuming the specimen with and without the layer or phase can be prepared. The experimental approach accompanied by the equivalent circuit models presented in this work enable decoupling of the charge transport mechanisms to help analyze the specimens in the presence of ionic species. Implications of the presented protocol for characterizing ion transport in complex ionic conductors include capabilities to optimize the
thicknesses and morphological features of battery electrodes, supercapacitor electrodes, and many other electrochemical systems.
Chapter 5 Conclusion, Applications and Future Work

The majority of this thesis has covered from the initial discovery of the piezoionic effect, stemming from an inverse operation of some of the emerging materials such as conducting polymer actuators [20], [100] and IPMCs [101], to experimental characterization and the development of numerical models for this effect. This final chapter will discuss the significance of what has been achieved in this work, the promising avenues at device level implementation through which the novel piezoionic sensors can greatly contribute, and the future work necessary to realize such solutions.

5.1 Significance of this work

With increasing interest emerging recently in soft or tissue-like sensors and actuators that are capable of interacting with humans more effectively, the initial discovery of the piezoionic effect in various gel materials provides a promising avenue to sense pressure or strain unobtrusively and seamlessly in interfaces such as flexible touch screens and wearable devices.

This work has contributed firstly to the fundamental understanding of the piezoionic effect by experimentally probing various parameters which were initially suspected to be the cause of the effect. The results of this work largely conformed to the initial postulates and revealed critical information such as some contributing factors which dictate piezoionic behavior, including effective ion sizes and electrostatic ion-polymer interactions. In summary, the contribution of this current work are:

1. The piezoionic effect in a polymer electrolyte gives rise to a voltage change that is proportional to the force or pressure applied to it.
Specifically, a LiTFSI/PC/PVDF-HFP polyelectrolyte sample of 0.1 M concentration used in section 2.1 yielded 25 μV/Pa at 10 mHz.

2. The frequency response of an LiTFSI/PC/PVDF-HFP polyelectrolyte sample of 0.1 M concentration was characterized.
   - The sensitivity at 10 mHz (25 μV/Pa) decayed to about 3% in amplitude by 10 Hz, whereas the modulus increased from 25 to 60 kPa.
   - The frequency response is partially diminished by this increasing stiffness, but other effects (such as latency due to limited ionic mobility) are also suspected to be present.

3. A correlation was observed between the electrolyte concentration of LiTFSI/PC and the piezoionic response of the LiTFSI/PC/PVDF-HFP polyelectrolytes. An NMR study was done to explore the nature of this correlation, and the resulting data suggested an inverse relationship between anionic mobility and concentration and a direct relationship between cationic mobility and concentration. It is hypothesized that the selective solvation of cations mediated by lone pair interaction plays a role in the modulation of effective ion size. This change in effective ion size is thought to be the key contributor to the changes in diffusion coefficient that result in the magnitude and frequency of charge separation in piezoionic materials.

4. An NMR study was done to relate the electrostatic ion-polymer interactions and their effect on corresponding ionic mobilities to the observed change in piezoionic behavior.
   - Trifluoromethanesulfonate anion mobility in polyacrylamide hydrogel samples containing positive, neutral, and negatively charged backbones was investigated.
The results showed that the anion mobility increased in the negatively charged matrix, whereas it decreased in the positively charged matrix.

- This is thought to be due to electrostatic attraction, hindering the ionic mobility, and in the other case electrostatic repulsion, promoting the ionic mobility.

- The piezoionic voltage response also changed to reflect the relative ionic mobilities as they were modulated.

5. An experimental protocol, comprising of a 4-electrode setup in a diffusion cell, to study ion transport in an ionically conductive membrane was introduced.

- Its utility was expanded by investigating membrane samples of heterogeneous composition (PEDOT/PEO-NBR) and devising a new equivalent circuit model (the dual series-parallel configuration) to explain the transition in the overall ionic impedance as the PEDOT content was varied.

- The method is potentially useful for tuning purposes while blending multiple polymers to synthesize an ionically conducting composite.

- The characterization and modeling can help tailor ionic composites for applications including energy storage, electroactive polymer actuators, and the piezoionic sensors.

Further, the current work also produced a U. S. patent application titled *METHOD AND SENSOR FOR PRESSURE SENSING BASED ON ELECTRICAL SIGNAL GENERATED BY REDISTRIBUTION OF MOBILE IONS IN PIEZOIONIC LAYER* (U.S. PCT patent application number PCT/CA2016/050238, filed on March 4 2016) as part of this work in collaboration with
colleagues in our group, contains many embodiments of piezoionic sensor materials in the context of tactile sensing in touch screen interfaces. Another U.S. provisional patent application titled *SURFACE SENSOR ARRAYS USING IONICALLY CONDUCTING MATERIAL* (U.S. provisional patent application number 62347601, filed on June 8, 2016) particularly focuses on the implementation of 2D grid structures of piezoionic sensors, with applications such as wearable sensors and large surface area sensing in mind.

5.2 Potential applications of piezoionic materials as soft sensors in medicine

In this section, several rudimentary feasibility tests of device level piezoionic sensor implementations in the context of physiological monitoring are performed and reported. Namely, a saline swollen polyacrylamide hydrogel is inserted to a simulated aneurysm while the flow across the phantom was changed over time. The relationship between the internal pressure and the readout voltage is reported here and the sensor resolution achieved is evaluated. Next, a LiTFSI/PC PVDF-HFP polyelectrolyte was used as a bending strain gauge to detect the flexion and extension of an index finger and the corresponding change in voltage is recorded over time. Unlike a strain gauge (at least when used in one), a piezoionic sensor provides a directional information of the mechanical perturbation such as bending due to the dominant ion flow mechanism. Both proposed applications have shown satisfactory performances at this stage of development and are concluded to be a promising bridge for further investigation.

5.2.1 Applications of piezoionic sensors – implantable in-vivo pressure sensor

Internal pressures of a human body are highly regulated by the peripheral nervous system to ideal levels according to the location. Deviation from the healthy ranges of internal pressures can result
in events including morbidity and mortality via a number of mechanisms [102]. Therefore, a convenient and accurate pressure monitoring solution is a sought after topic in emerging medical technology fields. Currently, in clinical practices, internal pressure is a parameter commonly measured. Internal pressures include blood pressure, intraocular pressure, intraabdominal pressure, intracranial pressure, and intramuscular (or intra-compartment) pressure.

In most instances, however, physicians only obtain a single pressure value representing a snapshot of a dynamic parameter which depends on a number of factors such as parasympathetic tone (i.e. increased blood pressure reading is probable in doctor’s visits due to stress experienced by patients). In some cases, catheter-based pressure monitoring of blood pressure, bladder pressure, and intracranial pressure are available for patients in justifiable situations. However, catheterization severely immobilizes patients as well as exposes them to increased risk of infection at the site of insertion. Given the current state of the art, many types of research [102], [103]. Major difficulties and challenges with the current solutions, as discussed in section 1.1.2, are their size, power requirement (including the need for on-site amplification), and biocompatibility.

Piezoionic gel based pressure sensing could potentially address the problems outlined above. As hydrogel materials such as polyacrylamide and polyurethane can be extremely soft and compliant (< 1MPa) yet very tough (> 2000% strain), the mechanical properties itself will be very much tissue-like, and less likely to be rejected. Described below is an implementation of a so-called intra-aneurysm pressure monitoring using piezoionic gels.
It is estimated that 50,000 strokes occur in Canada every year, 14,000 of which result in death [104]. This makes strokes the third most common cause of death in the country, costing $3.6 billion per annum in medical expenses [105]. Aneurysms cause approximately 20% of all stroke cases. Aneurysms are a balloon-like structure formed where blood vessel walls have weakened and are at risk of rupturing. Hemorrhagic stroke occurs when the aneurysm ruptures, exposing the surrounding brain tissue to arterial blood pressure and damage.

Currently, aneurysms are treated by either surgical clipping at the aneurysm neck or through minimally invasive endovascular coiling. Clipping is a more invasive procedure involving craniotomy and traditional microscopic surgery to directly locate and approach an aneurysm. Coiling is a minimally invasive procedure performed by inserting a catheter into the femoral artery and navigating the catheter to an aneurysm in the brain with the aid of fluoroscopy. Once at an aneurysm, a number of fine metallic coils are delivered into the aneurysm cavity and compacted into a spheroid or oblong shape. This compacted coil mass initiates thrombosis and blocks further blood from flowing into an aneurysm, stagnates the blood present, and promotes complete clotting to seal an aneurysm. Shown in figure 5-1 is an example of an angiogram taken during a coiling procedure.
One idea that is described below, complementing an ongoing research by our group in collaboration with Dr. Victor Yang’s group at Ryerson University to deliver a safer coiling procedure to combat hemorrhagic strokes due to aneurysm rupture, is to create a hydrogel based counterpart of the ‘coils’, which would occupy the aneurysm in lieu of a series of fine metallic wires. Perhaps the hydrogel can be doped with blood coagulants such as aprotinin, tranexamic acid, epsilon-aminocaproic acid, and aminomethylbenzoic acid. Furthermore, the piezoionic gel can monitor the intra-aneurysm pressure post-operatively to provide an insight to the risk of re-rupturing at the aneurysm site, and opportunity for early mitigation if the pressure is found too high.

The photographs below show the phantom, with water colored with red food dye being pumped across by hand using a syringe. They show that before and after the insertion of polyacrylamide
hydrogel, the flow of the fluid has been altered such that it no longer enters an aneurysm, virtually acting as the coils which might be used in a typical neurovascular intervention.

Figure 5-2. Photographs of aneurysm flow phantom with simulated fluid flow (a) before the insertion of polyacrylamide hydrogel and (b) after the insertion of polyacrylamide hydrogel

To measure the piezoionic voltage responses arising from the fluid pressure across the phantom, a pair of silver wires were inserted at the gel and connected to Autolab® PGSTAT101 potentiostat/galvanostat system. This time, the flow was controlled by connecting a 25 ml syringe to the Bose Electroforce Planar Biaxial TestBench Instrument, and allowing the actuator arm to push and pull on the syringe head at known displacement and frequency. The flow was maintained to have a sinusoidal profile. The outlet led to the waste fluid collection and was at atmospheric pressure at all times. The figure below depicts the overall experimental setup used in this study.
Figure 5-3. Overall experimental setup for the aneurysm flow induced piezoionic voltage measurement

Figure 5-4 below shows that the applied flow rate across the phantom is closely correlated to the voltage reading from the hydrogel. The maximum flow rate applied was approximately 1.1 ml/s as the syringe was actuated at 5 mm displacement. A phase contrast magnetic resonance technique was used previously to study flow rates of major cerebral vessels by Enzmann et al. The results showed that although the instantaneous flow rate varied over a cardiac cycle, the lower bound was around 0.5 ml/s (in right anterior cerebral artery), and the upper bound was as high as 6 ml/s [106]. This suggests that the polyacrylamide gel was experiencing the flow velocity similar to what is typically seen clinically, and encourages further investigation. For instance, hydrodynamic pressure experienced by the gel sensor inserted can be made more realistic by using a flow phantom.
that has a similar mechanical compliance as arterial vessels [107]. Plans for follow-up work on this application is discussed in section 5.3.

Figure 5-4. (a) The voltage response of the polyacrylamide gel inserted at the simulated aneurysm site as the syringe was pumped to a displacement of 5 mm at 0.3 Hz (b) a summary of peak voltage changes detected by the gel as the magnitude of the displacement was varied from 1 to 5 mm

5.2.2 Applications of piezoionic sensors – patch type strain sensor

As demands and interests emerge recently for highly discrete and skin-like devices for longitudinal monitoring of various physiological parameters, it is naturally of our interest to investigate the utility of the soft piezoionic sensor epidermally applied to monitor the local strain. This enables monitoring of Gait/motion, flexion/extension, and other micromotions such as tremor and pulsation due to the heartbeat. Here we demonstrate one use case of epidermally applied piezoionic sensors - monitoring of flexion/extension of digits.

In this demonstration, a solid polymer electrolyte containing LiTFSI/PC with PVDF-HFP polymer host was synthesized in a rectangular shape suitable for placing over the digits. The exact synthesis
protocol of the solid polymer electrolyte can be found in section 2.1, and the concentration of the salt was chosen to be 0.5 M. A layer by layer assembly as described below was made using the polymer electrolyte, copper tape electrodes, and VHB tapes or porous athletic tapes.

![Figure 5-5. (a) A schematic architecture (b) A photograph of the patch type polymer electrolyte based strain sensor](image)

The device was placed on the dorsal side of the index finger using a double-sided adhesive tape, and the finger was cyclically flexed and extended while the voltage signal was recorded. Figure 5-6 presents the voltage reading from the piezoionic sensor in response to the bending strain induced by the finger.
In this configuration, much like an IPMC based strain sensor [101], the differential strain is experienced by the film of polyelectrolyte on the top side and the bottom side. By bending, the bottom part of the polyelectrolyte will undergo relative compressive strain whereas the top part will experience elongation. Therefore, the liquid phase in the polyelectrolyte is expected to displace from the bottom towards the top, while recalling from the experimental result of section 2.2, this particular polyelectrolyte with 0.5 M LiTFSI content should yield an anion-dominant flow. As the bottom electrode was connected to the positive electrode of the potentiostat in this experiment, one would expect a rise in the voltage as the user of the sensor bends the index finger.
The experimental results indeed follow this trend, and the change in voltage consistently behaves as the bends of similar degrees are applied to the sensor by the experimenter. These preliminary results demonstrate the potential capability of the polyelectrolyte based piezoionic sensors to behave ideally as a sensor while additionally providing the polarity distinction based on the direction of mechanical perturbation applied such as bending, which is lacking in commonly available counterparts such as strain gauges when used in one.

5.3 Future work

In this newly discovered and promising area of research, there remains much work to understand exactly the piezoionic effect and what it entails to be able to harness the full capabilities of soft sensors made from polymer electrolytes. This includes a basic understanding of classical questions such as ion-ion, ion-solvent, and ion-polymer interactions in polyelectrolytes, common to many disciplines of research such as in solid-state energy storage solutions. In the present work, correlational results were obtained that relate the piezoionic effect and the self-diffusion constants of the ions in a given polyelectrolyte system. These diffusion constants were also found to be affected by ion-ion, ion-solvent (effective ion sizes), and ion-polymer electrostatic interactions. So far, the work has confirmed with high confidence that the piezoionic effect stems from ionic charge separation due to differential ionic mobilities as the liquid phase flows within the bulk of polyelectrolyte. However, the current understanding is highly qualitative, and further investigation is needed to quantify the above-mentioned parameters that have been found to each play a role in the piezoionic effect. To accomplish this, most likely a more extensive dataset of the experiments carried out in chapter 2 with a more diverse selection of salts, solvents and polymers are needed. One new experiment that is at this point worth attempting is the measurement of driven diffusion.
coefficients of ions in the sample polyelectrolytes. Unlike self-diffusion which is based on Brownian motions of molecules and continuously occur without the presence of a chemical gradient, driven diffusion represents the ability of molecules to displace in response to a particular stimulus such as solvent flow due to pressure gradient (convection), or migration of charged molecules due to an electric field (migration). Some discrepancies were found while comparing the experimental results of the piezoionic voltage responses and their corresponding NMR self-diffusion measurements in chapter 2, such as the difference in the crossover point of the piezoionic response and the self-diffusion coefficients of the lithium and TFSI ions. This could perhaps be attributed to the fact that the measured parameter was self-diffusion coefficients rather than driven diffusion due to solvent flow. Therefore, an NMR measurement setup such as the one described below may be employed to measure the driven diffusion in a piezoionic gel during deformation of the gel.

![Magnetic gradient direction](image)

**Figure 5-7. A proposed NMR measurement setup for acquisition of driven diffusion numbers of ions in polymer electrolyte samples**

Here, a pneumatic pump is used to control a cuff which surrounds the gel specimen. Inflation of the cuff causes a compression of a portion of the sample, causing displacement of ions. The
The proposed pulse sequence below may be used for example to detect the ions under driven diffusion as the cuff is released and the solvent flows back towards the site of compression. Movement of ions up or down the magnetic field gradient over time will translate to a detectable phase shift of the total magnetization, which is scaled by the gyromagnetic ratio of the specific ions present.

![Figure 5-8. An example NMR pulses sequence for piezionic driven diffusion measurement](image)

Much work is needed on the theoretical modeling of the effect as well. As of now, the poroelastic mechanics of the gel and its internal solvent flow has been successfully coupled with the ionic redistribution, based on their differences in diffusivity. However, the diffusivity needs to be empirically determined and entered manually to the current model. As we have uncovered in this thesis, the diffusivity of ionic species is strongly dependent on the steric effects, as well as the electrostatic interactions in the cases of charged polymer backbones. The future work might involve the ability to predict the effective ionic diffusivity based on such conditions, and automatically incorporate this factor to the remainder of the simulation. This will then allow thorough comparison of the empirical and simulation results.
On the device level implementation of the piezoionics, preliminary demonstrations have shown some promise in being able to convey, for example, tactile information on highly deformable and complexly contoured human skin. Suitability of the soft polymer-based piezoionic sensors for wearables and human motion monitoring has been made evident through some of the prototypes such as the digit flexion/extension monitoring case. In this avenue, the immediate goal is to fabricate and test various embodiments such as the 2D array structures and optimize for device level implementation on specific applications. Namely, these applications can be a smart bedsheet for pressure distribution sensing of a patient for ulcer prevention or generalized seizure detection, a wearable sensor for detection of limb/digit movements or Parkinson’s tremors, and many others.

Figure 5-9. 3D models of aneurysms obtained via CT scanning
The immediate follow-up to the demonstration of intra-aneurysm pressure monitoring using piezoionic gels is to set up a more rigorous and controlled experimental platform to characterize its performance. 3D models of common aneurysm cases can be obtained via CT scans such as seen in figure 5-9, from which a flow phantom of 1:1 scale can be molded out. A pulsatile flow pump controller is ideally used to along with the phantom for further studies. Subsequently, optimization for implantability and biocompatibility, the design of the readout circuitry, and commencement of \textit{in vivo} studies using porcine samples can take place.

Furthermore, the potential of using pressure sensors made of highly biocompatible polymer matrices that can potentially be functionalized or doped to contain many secondary features is immense. For instance, many hydrogel-based drug delivery solutions have been proposed which take advantage of their sensitivity to parameters such as temperature [108] and pH [109]. How about hydrogels or polymer electrolytes that can deliver drugs based on pressure? Perhaps diuretics/antidiuretics or other means of controlling blood pressure can be released while the hydrogel detects the in vivo pressure in various parts of the body via piezoionic principle. The demonstration earlier in this chapter opens a discussion as to whether gel based soft sensors and their hybrids with various other functions can be a solution to the field of implantable sensors.
REFERENCE


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The impedance of the equivalent circuit is solved by obtaining the expression for the total voltage drop across, as well as the total current through the transmission line and applying Ohm’s law, \( Z = V/I \). First, the voltage and current expressions are written out in terms of infinitesimal impedance units within \( \Delta x \),

\[
\varphi_1(x) = -i_1 R_i \quad \quad (A - 1)
\]

\[
\varphi_2(x) = -i_2 R_e \quad \quad (A - 2)
\]

\( \varphi_1(x) \) and \( \varphi_2(x) \) are the local potentials at the top and the bottom side of the transmission line respectively. \( i_1 \) is the ionic current, whereas \( i_2 \) is the electronic current. Finally \( R_i \) and \( R_e \) are the ionic and electronic resistance per unit length (in \( \Omega/m \)), respectively. Rearranging and taking the first derivative of these equations, we have

\[
\frac{\partial i_1}{\partial x} = -\frac{1}{R_i} \frac{\partial^2 \varphi_1}{\partial x^2} \quad \quad (A - 3)
\]
\[ \frac{\partial i_2}{\partial x} = -\frac{1}{R_e} \frac{\partial^2 \varphi_2}{\partial x^2} \quad (A - 4) \]

Noticing the infinitesimal change in current as a function of position \( x \) is the leakage into the bulk capacitance \( C \) (in the units of \( \text{F/m}^3 \)), we can write

\[ \partial i_1 = -CA \partial x \frac{\partial \eta}{\partial t} \quad (A - 5) \]

and

\[ \partial i_2 = CA \partial x \frac{\partial \eta}{\partial t} \quad (A - 6) \]

where

\[ \eta(x) = \varphi_1 - \varphi_2 \quad (A - 7) \]

The direction of this leakage current is arbitrarily defined to flow from the top (the ionic side) to the bottom (the electronic side), and hence the negative sign was placed in equation s5. Now, equating s3 and s4 to s5 and s6, we get

\[ \frac{\partial^2 \varphi_1}{\partial x^2} = R_i CA \frac{\partial \eta}{\partial t} \quad (A - 8) \]

and

\[ \frac{\partial^2 \varphi_2}{\partial x^2} = -R_e CA \frac{\partial \eta}{\partial t} \quad (A - 9) \]

Taking the second derivative of the equation s7 and equating to the difference between s8 and s9, we obtain

\[ \frac{\partial^2 \eta}{\partial x^2} = \frac{\partial^2 \varphi_1}{\partial x^2} - \frac{\partial^2 \varphi_2}{\partial x^2} = R_i CA \frac{\partial \eta}{\partial t} + R_e CA \frac{\partial \eta}{\partial t} \]

\[ = (R_i + R_e) CA \frac{\partial \eta}{\partial t} \quad (A - 10) \]
Now, taking the Laplace transform of the equation $s_{10}$, the following is obtained

$$\frac{\partial^2 \eta(x,s)}{\partial x^2} = (R_i + R_e)CA\eta(x,s) \quad (A-11)$$

The solution to this equation will be of the general characteristic form as follows

$$\eta(x,s) = A(s)e^{-\gamma x} + B(s)e^{\gamma x} \quad (A-12)$$

where

$$\gamma = \sqrt{CA(R_i + R_e)} \quad (A-13)$$

The boundary conditions to solve the equation $s_{12}$ are

$$i_1(0) = i_1(L) = i_{\text{total}} \quad (A-14)$$

and

$$i_2(0) = i_2(L) = 0 \quad (A-15)$$

Now, rearranging equations $s_1$ and $s_2$ and applying the boundary conditions we have the following

$$\frac{\partial \eta}{\partial x} = \frac{\partial \phi_1}{\partial x} - \frac{\partial \phi_2}{\partial x} = R_e i_2 - R_i i_1 \quad (A-16)$$

At $x = 0$,

$$\left[ \frac{\partial \eta}{\partial x} \right]_0 = -R_i i_1(0) \Rightarrow i_1(0) = -\frac{1}{R_i} \left[ \frac{\partial \eta}{\partial x} \right]_0 \quad (A-17)$$

At $x = L$,

$$\left[ \frac{\partial \eta}{\partial x} \right]_L = -R_i i_1(L) \Rightarrow i_1(L) = -\frac{1}{R_i} \left[ \frac{\partial \eta}{\partial x} \right]_L \quad (A-18)$$

Equating $s_{17}$ and $s_{18}$ according to $s_{14}$, we have

$$\left[ \frac{\partial \eta}{\partial x} \right]_0 = \left[ \frac{\partial \eta}{\partial x} \right]_L \quad (A-19)$$
To utilize the boundary condition s19, we take the first derivative of the equation s12

\[
\frac{\partial \eta}{\partial x} = B\gamma e^{rx} - A\gamma e^{-rx}
\]  

(A - 20)

Applying the boundary condition s19 to equation s20, we have

\[
B\gamma - A\gamma = B\gamma e^{rx} - A\gamma e^{-rx} \rightarrow
\]

\[
B(\gamma - \gamma e^{rx}) = A(\gamma - \gamma e^{-rx})
\]

(A - 21)

We can express this relationship as follows

\[
A = \alpha B
\]  

(A - 22)

where

\[
\alpha = \frac{\gamma - \gamma e^{rx}}{\gamma - \gamma e^{-rx}} = \frac{1 - e^{rx}}{1 - e^{-rx}}
\]

(A - 23)

Thus, equation s12 can now be rewritten as

\[
\eta(x, s) = \frac{1 - e^{rx}}{1 - e^{-rx}}B e^{-rx} + B(s)e^{rx} = \alpha Be^{-rx} + Be^{rx}
\]

(A - 24)

Now, to obtain the expression for current, we substitute the above equation into equation s5

\[
\frac{\partial i_1}{\partial x} = -CA \frac{\partial \eta}{\partial t}
\]

\[
= -CA \alpha \eta(x, s)
\]

\[
= -CA(\alpha Be^{-rx} + Be^{rx})
\]

(A - 25)

Integrating equation s25, we have

\[
i_1 = \frac{CA \alpha}{\gamma} Be^{-rx} - \frac{CA \alpha}{\gamma} Be^{rx} + C
\]

(A - 26)
To solve for the integration constant \( C \), we take the case where \( x = 0 \), and equate the expression to \( s17 \)

\[
I_1(0) = \frac{CA}{\gamma} (\alpha B - B) + C = -\frac{1}{R_i} \left[ \frac{\partial \eta}{\partial x} \right]_0 = -\frac{1}{R_i} (B \gamma - A \gamma) \quad (A - 27)
\]

After simplifying this expression and obtaining the constant \( C \), we have the expression for \( I_1(x) \)

\[
I_1(x) = \frac{CA}{\gamma} \alpha e^{-\gamma x} - \frac{CA}{\gamma} Be^{\gamma x} + \frac{CA}{\gamma} \frac{B}{R_i}(1 - \alpha) + B \frac{1}{R_i}(1 - \alpha)
\]

\[
= \frac{CA}{\gamma} \left( \alpha e^{-\gamma x} - e^{\gamma x} - \alpha + 1 + \frac{(R_i + R_e)}{R_i} (\alpha - 1) \right) \quad (A - 28)
\]

Now, to obtain the total voltage drop across the length, \( L \), the current is integrated over the thickness from \( x = 0 \) to \( x = L \)

\[
\Delta \phi_{\text{total}} = R_i \int_{0}^{L} I_1(x) \, dx
\]

\[
= \frac{CA}{\gamma} \frac{R_i}{L} \left[ -\frac{\alpha}{\gamma} e^{-\gamma x} - \frac{1}{\gamma} e^{\gamma x} + x - \alpha x + x \left( \frac{R_i + R_e}{R_i} (\alpha - 1) \right) \right]_0^L
\]

\[
= \frac{CA}{\gamma} \frac{R_i}{L} \left( -\frac{\alpha}{\gamma} e^{-\gamma L} - \frac{1}{\gamma} e^{\gamma L} + L - \alpha L + L \left( \frac{R_i + R_e}{R_i} \right) (\alpha - 1) \right) \quad (A - 29)
\]

Finally, the expression for the impedance of the modified Warburg element is

\[
Z_{\text{modified Warburg}} = \frac{\Delta \phi_{\text{total}}}{I_1(L)}
\]

\[
= \frac{CA}{\gamma} \frac{R_i}{L} \left( -\frac{\alpha}{\gamma} e^{-\gamma L} - \frac{1}{\gamma} e^{\gamma L} + L - \alpha L + L \left( \frac{R_i + R_e}{R_i} \right) (\alpha - 1) \right)
\]

\[
= \frac{CA}{\gamma} \frac{R_i}{L} \left( \alpha e^{-\gamma L} - e^{\gamma L} - \alpha + 1 + \frac{(R_i + R_e)}{R_i} (\alpha - 1) \right) \quad (A - 30)
\]

After simplifying \( s30 \), the expression reduces to

\[
Z_{\text{modified Warburg}} = R_i \left( 1 - \frac{R_i}{R_i + R_e} \right) + \frac{2R_i^2}{(R_i + R_e)^2} (\coth(\gamma L) - \csc h(\gamma L)) \quad (A - 31)
\]
Using the trigonometric property $\coth(x) - \csch(x) = \tanh\left(\frac{x}{2}\right)$, and expanding the variable $\gamma$, the final expression (equation 2 in section 4.1) is obtained

$$Z_{\text{modified Warburg}} = R_iL \left(1 - \frac{R_i}{R_i + R_e}\right) + \frac{2R_i^2}{(R_i + R_e)\sqrt{CA_s(R_i + R_e)\L}} \left(\tanh \left(\frac{\sqrt{CA_s(R_i + R_e)\L}}{2}\right)\right)$$  \hspace{1cm} (A - 32)

We notice that it follows a hyperbolic tangent behavior, which is commonly used to describe the Warburg short element. In fact, when electronic resistances are ignored, the expression is reduced to that of Warburg short, and hence a direct comparison is possible with the Warburg coefficient, $W_{sr}$, the Nernst diffuse layer thickness, $W_{sc}$, and the impedance parameters of the membrane. Namely,

$$W_{sr} = \frac{2R_i^2}{\sqrt{CA_vAR_i}}$$ \hspace{1cm} (A - 33)

$$W_{sc} = \frac{\sqrt{CA_vAR_iL}}{2}$$ \hspace{1cm} (A - 34)
APPENDIX B  
EDX derived local PEDOT concentration data for PEO-NBR/PEDOT membranes (5, 12, 19, 25, and 26 wt%)

The following set of data presents the elemental analysis (via energy dispersive spectroscopy) derived local PEDOT concentration across the thicknesses of each of the PEO-NBR/PEDOT samples with various PEDOT concentrations used in the experimental section of this work. The sulfur atom was used as the marker for the presence of PEDOT. The molar concentration of sulfur was directly correlated to the PEDOT concentration and subsequently converted into mass and concentration using the molar mass and density.

![Figure 5-2. PEDOT concentration profile as a function of position in the thickness of the membrane (5 wt% PEDOT sample)](image)

![Figure 5-3. PEDOT concentration profile as a function of position in the thickness of the membrane (12 wt% PEDOT sample)](image)
Figure 5-4. PEDOT concentration profile as a function of position in the thickness of the membrane (19 wt% PEDOT sample)

Figure 5-5. PEDOT concentration profile as a function of position in the thickness of the membrane (25 wt% PEDOT sample)

Figure 5-6. PEDOT concentration profile as a function of position in the thickness of the membrane (26 wt% PEDOT sample)
APPENDIX C MATLAB Code to Generate the Simulated Ionic Impedances of PEO-
NBR/PEDOT Membranes using series, parallel, and dual models

C.1 Series model

% Interpenetrating/Heterogeneous Ionic Conductor Impedance Modelling
% This version assumes a SERIES configuration in calculating the
% PEO-NBR/PEDOT ionic impedance and conductivity

sigma_1 = 0.225; % ionic conductivity of the gel matrix
sigma_2 = 0.008; % ionic conductivity of PEDOT (pure free standing form)
sigma_3 = 1000; % electronic conductivity of PEDOT
Cv_PEDOT = 2*10^8; % volumetric capacitance of PEDOT
A = 0.00063617; % cross-sectional area = 0.63617cm^2
freq = 1*10^-6; % Apply low frequency to obtain the ionic resistance
omega = freq*2*pi; % Radial frequency
thickness = 0.0005; %arbitrarily defined thickness 1 mm

% PEDOT concentration range to be simulated
pedot_content = linspace(0,1,10000);

% List of experimental numbers to plot the model against
overall_vol_fraction = [0.00;0.03846;0.09231;0.14615;0.19231;0.2000];
exp_conductivity = [0.25;0.21;0.0789;0.038616;0.02479;0.023229];

% Computing the membrane resistance according to the PEDOT concentration
% Since this is a SERIES model, the concentration of PEDOT is used to
% calculate the equivalent thickness fraction of the membrane and the PEO
% and PEDOT impedances are simply added, or connected in SERIES.
for k = 1: length(pedot_content)
    R_1 = (sigma_1*A)^-1; %% Ionic resistance per unit length of PEO-NBR
    R_2 = (sigma_2*A)^-1; %% Ionic resistance per unit length of PEDOT
    R_3 = (sigma_3*A)^-1; %% Electronic resistance per unit length of
PEDOT
    C = Cv_PEDOT*A; % Capacitance per unit length
    thickness_1 = thickness*(1-pedot_content(k));
    thickness_2 = thickness*pedot_content(k);
    if(pedot_content == 0)
        impedance(k) = R_1*thickness_1;
    elseif(pedot_content == 1)
        impedance(k) = abs(R_2*thickness_2*(1 - R_2/(R_2+R_3)) + ... ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*1i*(R_2+R_3))))*... (coth(sqrt(C*1i*omega*(R_2+R_3))*thickness_2) - ... csch(sqrt(C*1i*omega*(R_2+R_3))*thickness_2)));
    else
        impedance_PEDOT = R_2*thickness_2*(1 - R_2/(R_2+R_3))... + ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*1i*(R_2+R_3))))...
impedance_PEO = R_1*thickness_1;
impedance(k) = abs(impedance_PEDOT + impedance_PEO);
end
end

%Converting the impedances to conductivities
for x = 1:length(impedance)
    ionic Conductivities_series(x) = thickness/(impedance(x)*A);
end

%Plotting the result against experimental values
plot(pedot_content,ionic Conductivities_series);
grid on;
title('Ionic Conductivity as a Function of PEDOT Content in PEO-NBR');
xlabel('Vol% PEDOT');
ylabel('Conductivity (S/m)');
hold on;
scatter(overall_vol_fraction,exp_conductivity,'r');

C.2 Parallel model

% Interpenetrating/Heterogeneous Ionic Conductor Impedance Modelling
% This version assumes a PARALLEL configuration in calculating the
% PEO-NBR/PEDOT ionic impedance and conductivity

% "Threshold" value was set, above which the PEDOT phase was considered to
% be the only phase across which the ions could flow. This is because only
% PEO is thought to conduct ions and NBR is insulating, meaning that when
% PEDOT occupies/blocks all the PEO phase (rather than both PEO and NBR),
% this is when the conductivity is dominated by that of PEDOT

sigma_1 = 0.225; %ionic conductivity of the gel matrix
sigma_2 = 0.008; %ionic conductivity of PEDOT (pure free standing form)
sigma_3 = 1000; %electronic conductivity of PEDOT
Cv_PEDOT = 2*10^8; % volumetric capacitance of PEDOT
A = 0.00063617; %cross-sectional area = 0.63617cm^2
thickness = 0.0005; %arbitrarily defined thickness 1 mm

% PEDOT concentration range to be simulated
overall_pedot_content = linspace(0,1,10000);
Threshold = 0.364;

% Apply low frequency to get ionic resistance
freq = 1*10^-6;
omega = freq*2*pi;

% List of experimental values to plot the simulated result against
overall_vol_fraction = [0.00;0.03846;0.09231;0.14615;0.19231;0.2000];
exp_conductivity = [0.25;0.21;0.0789;0.038616;0.02479;0.023229];
% The "thresholding" statement above which PEDOT will assume the whole ion
% conducting phase
for x = 1:length(overall_pedot_content)
    if(overall_pedot_content(x) > Threshold)
        pedot_content(x) = 1;
    else
        pedot_content(x) = overall_pedot_content(x)/Threshold;
    end
end

% Computing the membrane resistance according to the PEDOT concentration
% Since this is a PARALLEL model, the concentration of PEDOT is used to
% calculate the equivalent cross sectional area fraction of the membrane,
% and the PARALLEL equivalent resistance of PEO and PEDOT impedances are
% computed
for x = 1: length(pedot_content)
    R_1 = (sigma_1*A*(1-pedot_content(x)))^-1;  %% Ionic resistance per unit
    length of PEO-NBR
    R_2 = (sigma_2*A*pedot_content(x))^-1;  %% Ionic resistance per unit
    length of PEDOT
    R_3 = (sigma_3*A*pedot_content(x))^-1;  %% Electronic resistance per unit
    length of PEDOT
    C = Cv_PEDOT*A*pedot_content(x);  %% Capacitance per unit length
    if(pedot_content(x)==1)
        impedance(x) = abs(R_2*thickness*(1 - R_2/(R_2+R_3)) + ...
        ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*l1*(R_2+R_3))))*...
        (coth(sqrt(C*l1*omega*(R_2+R_3))*thickness) - ...
        csch(sqrt(C*l1*omega*(R_2+R_3))*thickness)));
    elseif (pedot_content(x) ~= 0)
        impedance_PEDOT = R_2*thickness*(1 - R_2/(R_2+R_3)) + ...
        ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*l1*(R_2+R_3))))*...
        *(coth(sqrt(C*l1*omega*(R_2+R_3))*thickness) - ...
        csch(sqrt(C*l1*omega*(R_2+R_3))*thickness)));
        impedance_PEDOT = R_1*thickness;
        impedance(x) = abs((impedance_PEDOT*impedance_PEDOT)/...
        (impedance_PEDOT + impedance_PEDOT));
    elseif(pedot_content(x) == 0)
        impedance(x) = R_1*thickness;
    end
end

% Converting the impedances to conductivities
for x = 1:length(impedance)
    ionic_conductivities(x) = thickness/(impedance(x)*A);
end
% Plotting the results against the experimental values
plot(pedot_content, ionic_conductivities);
grid on;
title('Ionic Conductivity as a Function of PEDOT Content in PEO-NBR');
xlabel('Vol% PEDOT');
ylabel('Conductivity (S/m)');
hold on;
scatter(overall_vol_fraction, exp_conductivity, 'r');

C.3 Dual Model

% Function to compute the impedance of a PEO-NBR/PEDOT membrane using the
% EDX based PEDOT concentration mapping data.
% Takes the array of concentration values along with the array of positions
% (in um) at which the concentration values were recorded.
% "Threshold" value was set, above which the PEDOT phase was considered to
% be the only phase across which the ions could flow. This is because only
% PEO is thought to conduct ions and NBR is insulating, meaning that when
% PEDOT occupies/blocks all the PEO phase (rather than both PEO and NBR),
% this is when the conductivity is dominated by that of PEDOT

function 
[new_position, impedance, conductivity, Overall_impedance, Overall_conductivity] =
IPN_Impedance_thresholding(conc_profile, position, PEDOT_content_threshold)

clear conc_by_layer;
clear layers;
clear impedance;
clear conductivity;
clear Overall_impedance;
clear Overall_conductivity;

sigma_1 = 0.225; % ionic conductivity of the gel matrix
sigma_2 = 8*10^-3; % ionic conductivity of PEDOT (pure free standing form)
sigma_3 = 1000; % electronic conductivity of PEDOT
Cv_PEDOT = 5*10^7; % volumetric capacitance of PEDOT
A = 0.000063617; % cross-sectional area = 0.63617 cm^2
freq = 1*10^-6; % apply low frequency to extract the ionic conductivity
omega = freq^2*pi; % angular frequency
density_PEDOT = 1.38; % g/cm^3

% Creating vectors containing the infinitesimal "slices" of the membrane
for n = 2:length(conc_profile)
    conc_by_layer(n-1) = (conc_profile(n) + conc_profile(n-1))/2;
end

for n = 2:length(position)
    layers(n-1) = (position(n) - position(n-1));
end

139
conc_by_layer = conc_by_layer/density_PEDOT; % Converting the concentration of PEDOT from g/cm^3 to cm^3/cm^3

% The "thresholding" statement above which PEDOT will assume the whole ion % conducting phase

for x = 1:length(conc_by_layer)
    if(conc_by_layer(x) > PEDOT_content_threshold)
        conc_by_layer(x) = 1;
    else
        conc_by_layer(x) = conc_by_layer(x)/PEDOT_content_threshold;
    end
end

% Iterating over all the "slices", calculating the infinitesimal ionic % impedance according to the PEDOT concentration

for x = 1:length(layers)
    R_1 = (sigma_1*A*(1-conc_by_layer(x)))^-1; %% Ionic resistance per unit length of PEO-NBR
    R_2 = (sigma_2*A*conc_by_layer(x))^(-1); %% Ionic resistance per unit length of PEDOT
    R_3 = (sigma_3*A*conc_by_layer(x))^(-1); %% Electronic resistance per unit length of PEDOT
    C = Cv_PEDOT*A*conc_by_layer(x); %% Capacitance per unit length

    if (conc_by_layer(x) == 1)
        impedance(x) = abs(R_2*layers(x)*(1 - R_2/(R_2+R_3)) + ...
            ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*1i*(R_2+R_3))))*...
            (coth(sqrt(C*1i*omega*(R_2+R_3))*layers(x)) - ...
            csch(sqrt(C*1i*omega*(R_2+R_3))*layers(x))));
    elseif (conc_by_layer(x) ~= 0)
        impedance_PEDOT = R_2*layers(x)*(1 - R_2/(R_2+R_3)) + ...
            ((2*R_2^2)/((R_2 + R_3)*sqrt(C*omega*1i*(R_2+R_3))))*...
            (coth(sqrt(C*1i*omega*(R_2+R_3))*layers(x)) - ...
            csch(sqrt(C*1i*omega*(R_2+R_3))*layers(x)));
        impedance_PEDOT = R_2*layers(x);
        impedance(x) = abs(impedance_PEDOT*impedance_PEDOT)/...
            (impedance_PEDOT + impedance_PEDOT));
    elseif (conc_by_layer(x) == 0)
        impedance(x) = abs(R_1*layers(x));
    end
end

% Calculating the slice wise conductivity - in general, higher the PEDOT concentration % the lower the local ionic conductivity

for x = 1:length(impedance)
conductivity(x) = layers(x)/(impedance(x)*A);
end

% Calculating the overall membrane impedance by adding all the "slices" and
% the overall conductivity is also computed

Overall_impedance = sum(impedance);
Overall_conductivity = sum(layers)/(Overall_impedance*A);

% Mapping impedance and conductivity

for x = 2:length(position)
    new_position(x-1) = 0.5*(position(x) + position(x-1));
end

end