

**A Novel Use for Ionic Polymer Transducers
for Ionic Sensing in Liquid**

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Abstract

Ionic electroactive polymers have been developed as mechanical sensors or actuators, taking advantage of the electromechanical coupling of the materials. This research attempts to take advantage of the chemomechanical and chemoelectrical coupling by characterizing the transient response as the polymer undergoes an ion exchange, thus using the polymer for ionic sensing. Nafion™ is a biocompatible material, and an implantable polymeric ion sensor which has applications in the biomedical field for bone healing research. An ion sensor and a strain gauge could determine the effects of motion allowed at the fracture site, thus improving rehabilitation procedures for bone fractures.

The charge sensitivity of the material and the capacitance of the material were analyzed to determine the transient response. Both measures indicate a change when immersed in ionic salt solutions. It is demonstrated that measuring the capacitance is the best indicator of an ion exchange. Relative to a flat response in deionized water ($\pm 2\%$), the capacitance of the polymer exhibits an exponential decay of $\sim 25\%$ of its peak when placed in a salt solution. A linear correlation between the time constant of the decay and the ionic size of the exchanging ion was developed that could reasonably predict a diffusing ion. Tests using an energy dispersive spectrometer (EDS) indicate that 90% of the exchange occurs in the first 20 minutes, shown by both capacitance decay and an atomic level scan. The diffusion rate time constant was found to within 0.3% of the capacitance time constant, confirming the ability of capacitance to measure ion exchange.

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Chapter 1: Introduction

The postulate of this thesis is that ionic polymers may be used for ionic sensing in liquids. This research is conducted to demonstrate that ionic polymers can sense changes in the ionic content of a solution through measurement of the chemoelectrical properties. In Section 1.1, background information will be presented on possible applications of a polymeric ion sensor. This will include an outline of bone healing research and a description of other ionic sensors. Section 1.2 will present a history and brief review of the current state of the art of ionic polymers. The motivation for this research is then presented in Section 1.3. In Section 1.4, the goals of the research are stated, and Section 1.5 states the contributions of this research. Finally, in Section 1.6 an overview of the thesis is provided for the reader.

1.1 History of Ionic Polymers

Polymeric materials that respond to an electrical stimulus came into focus in the 1970s, when Walatka showed that certain polymeric materials exhibited electronic conduction. In 1974 and 1975, Grodinsky and Melcher found that a deformable membrane was capable of producing mechanical motion when an electrical voltage is applied in a liquid electrolyte. They also showed that the converse was true; the polymer produced a voltage drop across the membrane when it was acted on by a mechanical input.

Ionic polymers are a subset of materials from the group of polymers that respond to an electrical stimulus known as electroactive polymers. In addition to the electromechanical characteristics of electroactive polymers, ionic polymers exhibit ionic selectivity due to the structure of the material. The ionic selectivity of the materials has found one of the more successful applications for ionic polymers in fuel cell technology.

One of the most widely used ionic polymers available today is DuPont®'s Nafion™. The material is a Teflon-based polymer with sulfonic acid side groups. When the material is boiled in water, the membrane absorbs as much as 38% of its dry weight in water and causing it to expand as much as 15% [6]. When immersed in water, the cations associated with the sulfonate group become mobile, leaving a sulfonate anion covalently bonded to the fluorocarbon backbone (See Figure 1.1). This property of the polymer means it is permeable to positive charge cations, but not to anions. When the polymer is hydrated, it conducts cations across the membrane, which is the suspected mechanism that allows ionic polymers to exhibit electromechanical transduction [23].

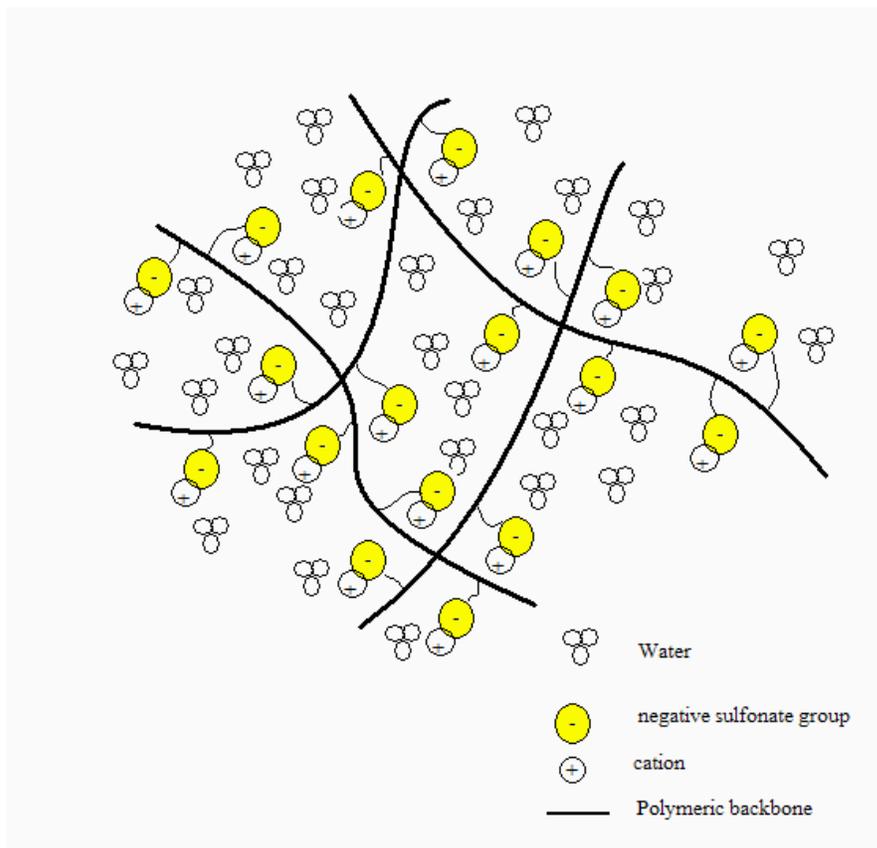


Figure 1.1: Hydrated Nafion™, with clusters of positively charge cations electrostatically attracted to negative sulfonate group, water, and polymeric backbone chain.

In order for the polymer to be useful, it needs to be able to conduct electricity. Ionic polymers are a flexible material, and most of the applications require that any electrodes applied to the material also be flexible. The most popular way of plating the polymer is an impregnation/reduction process that results in a conductive metal electrode on the surface of the polymer [24]. This process replaces the cationic groups of the polymer with a conductive metal. A reduction agent forms a network of metal particles on the surface of the polymer. Due to the intermingling of the metal electrode and the polymer, the electrode is more durable than traditional methods of attaching an electrode to the outside of the polymer. For a more detailed discussion of the plating process used, refer to Bennett's work on the manufacture of ionic polymer transducers [5].

In the 1990s, interest in ionic polymer transducers increased and the material was studied for its actuation and sensing capability. In actuation, the application of an electric field to the ionic polymer results in a rapid bending of the transducer. The performance of the transducer is measured by the unconstrained free deflection of the tip of the polymer or by the blocked force produced if the motion of the polymer is restricted [23]. The sensing capability has been demonstrated by measuring the inverse performance, the voltage produced by the transducer when a proportional motion is applied [30]. The relationship between induced current in the polymer has been shown to be proportional to the rate of motion of the mechanical deformation [23]. In both sensing and actuation, a slow relaxation of the response of the polymer is exhibited if the position or voltage is held constant [23].

A parameter that quantifies the sensing performance of the polymer is the electromechanical sensitivity of the material. In 2003, Farinholt *et al* [8] measured the sensitivity of Nafion™ when a bending, shear, or tensile force was applied. The material was found to be most sensitive to an imposed bending force. Ten 30mm X 10mm X 20mm samples were found to have an average sensitivity of $122.8\mu\text{C}/\varepsilon$ in bending, compared to $0.0242\mu\text{C}/\varepsilon$ in shear and $88.5\mu\text{C}/\varepsilon$ in tension. It was noted that the tensile

strain may need further investigation to ensure the accuracy of the tests, due to an inability of the test stand to accommodate the inducement of controlled displacements.

The bending sensitivity of the material is dependent upon several factors. The frequency of the applied force, the length of the transducer, and the ionic form of the material has an effect on the electrical response of the polymer [7]. A comparison of the polymer with different cation clusters in the material indicates that the bending sensitivity increases with the ionic size of the material. This indicates that the material is not only electromechanically coupled, but also exhibits chemoelectrical and chemomechanical coupling.

While most of the research up to this point utilizes the electromechanical coupling of the material for use in sensing or actuation, the idea of using ionic polymers as a chemical sensor by exploiting the chemoelectrical or chemomechanical properties of the material has not yet been investigated. In order to do so, the transient response of the material as cations are exchanged would need to be investigated.

1.2 Background

One of the possible applications of an ionic polymer that motivated this research is in the field of bone healing research. A biocompatible implantable sensor could greatly help in answering questions concerning the healing of bones, resulting in a different theory of bone healing applied in practice to reduce the amount of time it takes for bone to heal.

Bone is made up of an inorganic mineralized matrix consisting primarily of calcium and phosphate [29]. This inorganic matrix is combined with a nonmineralized mix of organic material that gives the bone life. When a load is applied to a bone, it causes the bone to deform. The internal forces generated by the bone causes stress in the

bone, while the deformation exhibited by the bone is known as strain [29]. It is normal for the bone to deform as it undergoes loading. For instance, at a normal gait the tibia will see a cyclic load and will respond with some cyclic deformation, the extent of which would be determined by the strength of the bone and the magnitude of the load. Normally, the magnitude of the stress in the bone is less than the yield stress of the bone, and the bone supports this regularly occurring stress cycle.

However, when bone is strained to the point that the yield stress of the bone is surpassed, the bone fractures. If the bone is subjected to very large loads and the deformation of the bone exceeds what is known as the ultimate failure point, the bone will undergo a catastrophic failure or fracture [29]. In response to this fracture, the body begins the healing process immediately. The time it takes for the bone to heal can vary significantly, depending upon the devastation caused by the break and the age of the subject. However, there are several factors that may contribute to the rate at which the bone heals, including the amount of movement in the area of the fracture that is permitted during the healing process [28].

There is much speculation as to what factors best promote the healing of the bone. If it were practical to stabilize the bone completely, the healing time would be significantly decreased because bone could reform directly along the break. However, most fracture sites see some micro movement that prevents bone from forming directly. As the bone heals, it tends to go through an intermediate cartilage phase before callus and then bone is formed [28].

Barring absolute stabilization, the subject of the best conditions to stimulate the formation of cartilage material remains open. As the bone heals, it is common practice to fixate the bone to some degree. Just how much fixation to prescribe is a point of contention amongst the medical community. While it has been common practice to fixate the bone as much as possible, new evidence suggests that allowing the bone some amount of motion actually aides bone healing.

Experiments conducted by Goodship and Kenwright [10] showed that daily application of a cyclic micromovement applied early in the callus formation resulted in the faster healing than a control group. Research on the effect of different loading patterns suggests that there is an optimum loading regimen that stimulates fracture healing. Exactly how much loading and at exactly what frequency remain unknown factors.

Another unknown is why the bone responds to such stimulation. The key may lie in streaming potentials in bone. One study has hypothesized that a complex calcium phosphate mineral in the bone generates weak electrical signals when under mechanical stress. A strong signal would tell the body to send more calcium to that location [45]. The presence of calcium would expedite quicker bone healing. This theory links the strain of the bone to the presence of certain ions to the rate of bone healing.

At this time, a suitable ionic sensor has not been found to be used in research addressing this theory. While sensing systems using reagents and spectrometers can be used for off-site, destructive testing [14, 36], it is important to develop an implantable, noninvasive, real time, multi use sensor for bone healing research. A sensor of this type would allow researchers to actively monitor the body's response to different external factors. By relating such response to the duration of bone healing required to adequately heal the bone, it can be determined what responses of the body have the greatest effect on the healing of bones and what loading regimen will stimulate those responses.

One promising approach to the sensing problem is in electrochemical sensors. Electrochemical biosensors have been developed for many uses. Chemical sensors transform chemical information, such as the concentration or presence of one component of a solution, into an analytically useful signal. This input-output relationship is made possible by some degree of sensitivity. The system translates information from the biochemical domain into a physical output signal [36]. This signal can be created by potentiometrics, measuring the potential difference between an indicator or reference electrode, or can indicate ion selective field effects.

Some results of the use of ion sensitive field effect transistors (ISFETs) indicate that they can detect a flux in Na^+ and Ca^{2+} [36]. ISFET membranes constructed of polyvinyl chloride (PVC) have been tested for possible applications for direct ion concentration measurements in blood [37]. Such a sensor has high selectivity and was proved to exhibit the required stability, sensitivity, and precision [1]. However, problems with the adhesion of the PVC to the ISFET lead to a short sensor lifetime [1].

The idea of using different ion selective membranes of a polymeric type for the quantitative determination of ions was developed by Heng et al in 2000 [13]. The sensor proposed measures a change in the electric potentiometric response to an electromotive force. Response similar to that of PVC was attained using methacrylic-acrylic copolymers.

Another polymeric material that has been used as a biosensor is a Teflon™ based DuPont® material called Nafion™. *In vivo* experiments have proved that Nafion™, a commercially available ionic polymer, is a biocompatible material [38], as it is inert and doesn't harm the subjects. One application of Nafion™ that has been studied is using it as a permeable membrane to protect implantable glucose sensors from the harsh biological environment by stretching the Nafion™ over the biosensor [19]. Initial implementation of the Nafion™ coated sensor showed that the Nafion™ was vulnerable to developing cracks due to calcification of the membrane. It is possible that this cracking occurred because the polymer was not allowed to expand. Further development of the polymer found that treating the membrane with ferric chloride (FeCl_3) greatly reduced the cracking and maintained constant permeability after the sensor had been implanted *in vivo* for four weeks [22].

1.3 Motivation for Research

A survey of the work done in the field of ionic polymers shows a lack of attention to the transient properties of the polymer as it undergoes an ion exchange. With this research, we hope to reveal characteristics of this transient response of the polymer with intentions of using the polymer for ionic sensing. The structure of the polymer includes a negatively charged sulfonate that form a covalent bond with a cation group to maintain material stability, as shown in Figure 1.1. This cation group is not a permanent fixture in the material; one cation can be exchanged for another if conditions force a change in the material. This exchange can be driven by a combination of conditions including a concentration gradient, heat, or material selectivity.

Current ionic sensing techniques generally require altering the sample solution and the test often does not offer instantaneous results. A polymeric ionic sensor could be a good solution to the problem facing researchers that would like to monitor the ionic conditions in a solution real time without altering the components of that solution.

For ionic polymers to be an effective means of determining internal ionic conditions surrounding the bone fracture, the effectiveness of the material to sense a change in ionic conditions needs to be determined. One parameter that is often used to characterize the sensing capability of ionic polymers is the electrical sensitivity of the polymer to a mechanical input. Another is the electrical capacitance of the material. Both properties can be measured in real time as an ion exchange is taking place. If the material demonstrates that a change in these properties is apparent as the ion exchange occurs, the sensing capability of the material can be established.

1.3.1 Motivation for Tensile Sensitivity Testing

We initially set out to develop an ionic sensor that could be implanted onto the tibia of a test subject. As a subject walks, the tibia is subjected to bending forces across the cross section of the bone. If an ionic polymer sensor was implanted onto the surface of the bone, it would be excited by a periodic tensile force as the subject walks.

The sensitivity of the polymer is defined as the electrical charge response of the polymer divided by the mechanical displacement of the polymer. While the sensitivity of Nafion™ to an imposed bending stress has been explored before [7], the material sensitivity to an imposed tensile stress has not been investigated nearly as well. It was a logical step in furthering the research of electroactive polymers to characterize the sensitivity of Nafion™ to an applied tensile force.

One characteristic of electroactive polymers that was demonstrated in Farinholt's research is that the sensitivity of the material is dependent on the cation that is present in the polymer. When considering the effect of different alkali metal cations on material sensitivity, Farinholt showed that the sensitivity in bending increased with cation size, with the exception of lithium [7]. There is clearly some correlation between the sensitivity of the material and the ion present in the material.

However, Farinholt only looked at the sensitivity of the material after an exchange had fully occurred. There was no consideration given to any transient changes in sensitivity as an exchange takes place. Arguably, it is this transient phase, as the material is undergoing an ionic exchange, which would be of greatest interest to us. To measure the electrical output of the material to a mechanical input while the polymer is exposed to conditions that would cause an ion exchange, the material must be mechanically excited as the exchange occurs. As the ion exchange takes place, we would expect to see some change in the sensitivity over time.

Two goals of the sensitivity testing have been established. First, we hope to establish a relationship between the tensile stress applied to the material and the electrical output of the material. Second, we hope to establish that when the material is exposed to conditions that would force the material to undergo an ion exchange, the tensile sensitivity of the polymer changes and this change in sensitivity exhibits characteristics that may be able to distinguishable for different ions.

1.3.2 Motivation for Capacitance Testing

Another way to monitor the ionic exchange process could be to measure the impedance of the material over time. The impedance of the material is the transfer function between the input voltage applied to the polymer and the current flowing to the polymer. The real component of the impedance is correlated to the resistive properties of the material, and is more a function of the properties of the electrode than of the actual polymer itself. The imaginary part of the capacitance is correlated to the capacitance of the material. The capacitance of the material is directly related to the material properties of the polymer, which is of greater interest for this research.

The goal of this test would be to determine if the polymer can be used as a real time ionic sensor in a fluid. As has been described previously, the Nafion™ material used in this test has a backbone of carbon and fluorine atoms like any polymer, but the notable characteristic of the Nafion™ is that it has covalent bonds to a cation side chain. The cation can be exchanged for other cations, driven by material preference of one ion over another, or by concentration gradient.

It is already well established that the properties of the material change when the material has fully exchanged one ion for another [7]. This is exhibited as a change in the sensitivity of the material, which demonstrated the chemomechanical coupling of the material, and as a change in the capacitance of the material, which demonstrates the

chemoelectrical coupling of the material. With this research, we are trying to determine if there is a notable transient trend in the change of the material properties as the material experiences an ion exchange.

When the sensitivity testing data was rather inconsistent, we turned to impedance testing because it eliminates a few variables from the testing, such as the mechanical properties of the material. Because the capacitance of the material is a property that is well isolated from the mechanical properties of the material, it should provide for a consistent measure of the chemoelectric coupling of the material.

By measuring the impedance of the material over time as the material undergoes a concentration driven ion exchange in a solution, we can monitor the capacitance of the material, thereby monitoring any changes to the chemoelectric properties of the material. Our hypothesis is that as the material undergoes an ion exchange, the capacitance of the material would change with some recognizable trend. The characteristics of this trend should indicate what ion or ions are present in the solution.

1.3.3 Motivation for Scanning Electron Microscopy Testing

Another concern was determining if a suspected ion exchange had taken place. The most concrete measures would look at the physical properties of the material. Other groups [44] verify that an exchange has taken place by comparing the dry weight of the material before and after an exchange is suspected to have taken place. This requires that the material be removed from the solution where the exchange would be occurring, dried, and weighted. However, there is significant room for error as the polymer rehydrates from the water vapor in the ambient air, resulting in inconsistent mass measurements.

Another way to measure that an exchange has taken place is by using a scanning electron microscope (SEM). One tool that can be implemented when using a SEM is an

energy dispersive spectrometer (EDS). This technique is discussed later in the thesis in Section 2.3, but in brief it is able to detect the presence of different ions by measuring the refraction of particles of light. However, in order to conduct this test, the samples need to be dried, plated and mounted. Again, this is not a real time measurement and would not be an applicable instantaneous measure of the ionic content of a solution.

Instead, the EDS was used to determine if any changes in capacitance could indeed be attributed to an ion exchange in the backbone of the material. The EDS is capable of identifying individual elements present in a sample. This capability will allow us to look at a freeze frame of the amount of an ion present in the polymer after the sample has been immersed in an ionic solution for a set amount of time.

In order to verify that any measured changes in capacitance were due to an ion exchange, portions of the sample were removed at designated points in time and preserved in deionized water. Following this procedure, the capacitance of the material (in mF/cm²) could be related to the ionic content of the material after it had been immersed in a solution for a certain amount of time.

1.4 Research Goals

The goal of this research is to show that ionic polymers can be used as ionic sensors and to develop a method that can be employed to sense changes in ionic conditions. Of particular interest is how this technology could be applied to biomedical sensing relating the ionic response of the body to different external stimuli. By determining a potential way to use ionic polymers as a noninvasive ionic sensor that could be applied to biomedical research, it is hoped that an ionic polymer sensor can be used to further medical research on topics including bone healing mechanisms. Other related goals of this research are to establish a reliable way to measure the rate of diffusion of different ions into the polymeric membrane and to establish the charge response of ionic polymers to tensile deformation.

1.5 Contributions

With this work, new ground was broken in the field of ionic polymer research. The transient response of the polymer as an ion exchange occurs has never been quantified before, and this work classifies that response in a way that shows the potential of ionic polymers as applied to ionic sensing. While an ion exchange exhibits a change in sensitivity, it was determined that it is better to track an ion exchange by monitoring the capacitance response over time. The capacitance change was found to consistently exhibit an exponential decay when immersed in an ionic solution, and the time constant was found to be linearly related to the size of the ion. An energy dispersive spectrometer (EDS) was used to verify that these results were due to ion exchange. By tracking the amount of diffusing ion present in the polymer, the EDS was also able to quantify the time constant of the rate of diffusion of an ion into the polymer. It was found that the time constant for the diffusion and the time constant for the rate of decay of the capacitance were very similar. This work has made significant advance towards the implementation of polymeric ionic sensors, paving the way for future research in this area.

1.6 Overview of Thesis

The purpose of this thesis is to document the transient response of ionic polymers undergoing an ionic exchange. This response can be employed to use ionic polymers as ionic sensors. This document explains the research conducted and the results obtained from this work. Chapter 2 discusses the experimental protocol followed during this research and explains experimental procedures used to obtain the necessary sensitivity and impedance data for this research, as well as a description of the scanning electrode microscope procedure used for data collection. Chapter 3 discusses the outcome of these experiments and the tangible results of the trends exhibited by the data. The thesis is summarized in Chapter 4, discussing the conclusions of the research and suggesting different directions for future work in this area.

Chapter 2: Experimental Setup, Procedure, and Protocol

Only through experimentation would we be able to prove that ionic polymers can make viable ionic sensors. A set of experiments could show that through some measurable parameter, the ionic polymer would indicate a change in the ionic content of a solution. Beyond that accomplishment, different ions could show up with different fingerprints characterizing the changes exhibited by the polymer, thereby indicating which ions are present.

We focused on two candidate properties that may indicate a change in the surroundings. Through past research [7], it is known that the sensitivity and capacitance of ionic polymers are both dependent upon what ions are infused into the polymer. What has not been investigated in previous research is the transient response of the sensitivity and capacitance change as the polymer undergoes an ion exchange. That will be the subject of this research.

Due to the fact that this research was conducted with an eye towards biomedical applications, the sensitivity of the polymer was considered first. As was discussed in Section 1.2, one area that could benefit from a sensor of this type is bone fracture healing research. A material that was chemo-mechanically coupled could provide the field with a valuable look into the conditions that may facilitate bone healing. The preliminary idea was that a section of polymer could be attached to the bone across a fracture. As the strain across the fracture changes, the polymer would be strained in tension.

The relationship between the tensile forces applied to the bone and the ionic conditions in the extracellular fluid surrounding the fracture is presently unknown to researchers, so a sensor that can track these variables would be a strong tool for researchers. This led us to first investigate the change in tensile sensitivity over time. The experiments performed for this research are described in Section 2.1.

When problems arose with the tension tests of the polymer, we looked for another way to track changes in the ionic content of a solution. This led to a series of impedance tests, which allow the capacitance of the material to be tracked over time as the material is immersed in different solutions. These experiments are described in Section 2.2.

Finally, in order to prove that any demonstrated change in the capacitance can actually be attributed to a change in the ions present in the material, an energy dispersive spectrometer test was performed using a scanning electron microscope. It was hoped that these tests would show some appreciable change in the ionic content of the polymer over time that might somehow correspond with the change in capacitance demonstrated by the material over time. The details of these experiments are documented in Section 2.3.

2.1 Tensile Sensitivity Experimental Setup and Procedure

In order to accomplish the two goals of the sensitivity testing, a test stand was designed. It was required that the test stand accommodate the following requirements in order for the test stand to be viable. In order to apply a tensile force to the polymer, the polymer needs to be firmly constrained at its top and bottom. A force would be required to pretension the polymer and keep any slack out of the polymer, keeping it from buckling. This means any axial loading applied to the polymer produces a change in the tensile stress of the material.

Due to the fact that the polymer needs to be hydrated to produce the best response, the polymer needs to be immersed in a liquid solution. If the polymer is immersed in a fluid, it also allows for an ion exchange to be induced as the tension tests are conducted. However, because the polymers are very sensitive to environment, it is important that any components of the test stand immersed in the solution be resistive to corrosion so that the solution does not become contaminated. In order to prevent a short

circuit in the system, it is also important that the electrical contact to the polymer does not become immersed in fluid.

A test stand was designed to meet all of these constraints (See Figure 2.1). This portion of the test stand was machined out of glass filled PTFE, which we chose for its resistance to corrosion in harsh environments. One of the key ideas incorporated into the test stand is a dog bone shaped cutout on one face of each deck of the stand that would mate with a dog bone shaped polymer sample, shown in Figure 2.2, to eliminate any slippage during the tension tests. The samples were 60mm long and 2mm wide across the tensioned cross section and 5mm wide at the flanges on the top and bottom. The top and bottom decks of the stand both use 1/8 in brass screws to fasten both halves of the deck tightly enough to hold the polymers in place.

The height of the top deck relative to the bottom deck is regulated by a sliding brass spring. The spring rides up and down a 1/4 in brass screw by way of a nut and washer. This allows an appropriate amount of pretension to be put on the polymer to eliminate any slack in the polymer during testing. A smooth 1/4 in brass rod on each end of the stand constrains the motion of the top deck of the stand to the axial direction. Gold electrodes were glued to the top deck of the stand to conduct the short circuit charge response of the polymer to the sensing circuit.

The entire test stand is put into a 1600mL Petri dish (See Figure 2.3). The bottom of the deck is fastened to a plywood base through the Petri dish, tying the whole fixture together securely. The top deck of the test stand is excited by a Ling Dynamic Systems 5N shaker. The shaker was hung securely over the test stand from a thick steel hanger. An input signal was specified using dSpace Control Desk and supplied to the signal from a dSpace DS2103 Digital analog converter.

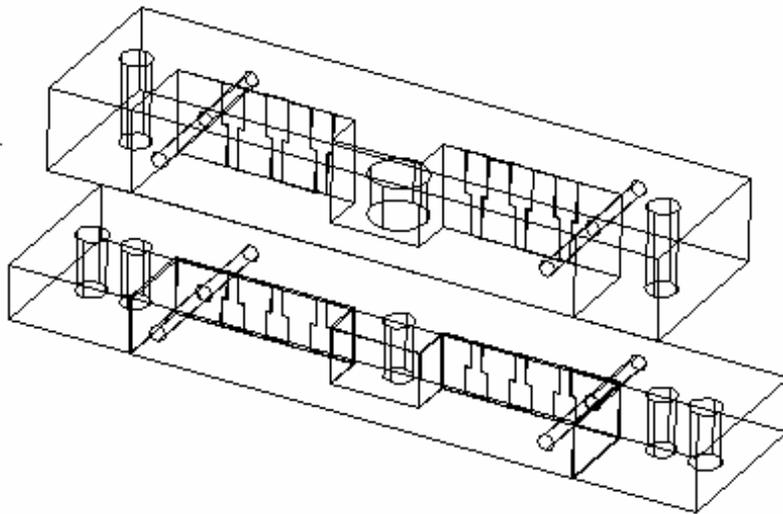
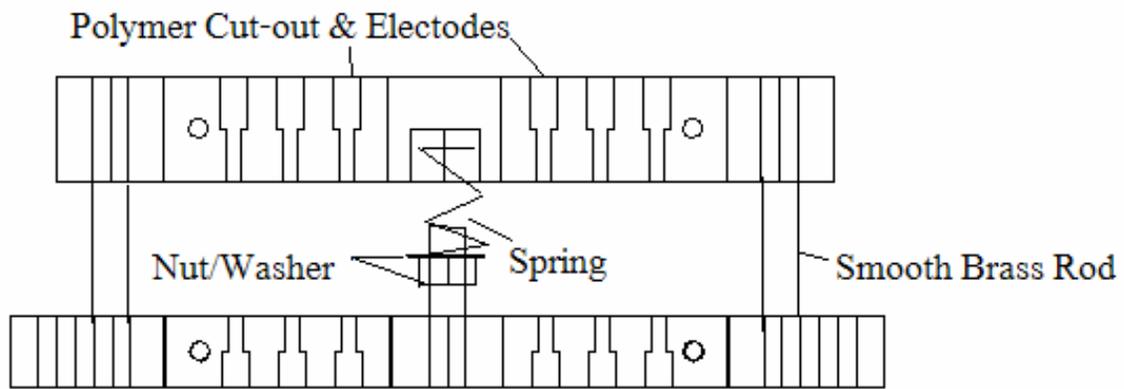


Figure 2.1: Drawing of test stand used for tension testing.



Figure 2.2: Dog bone shaped plated polymer samples.

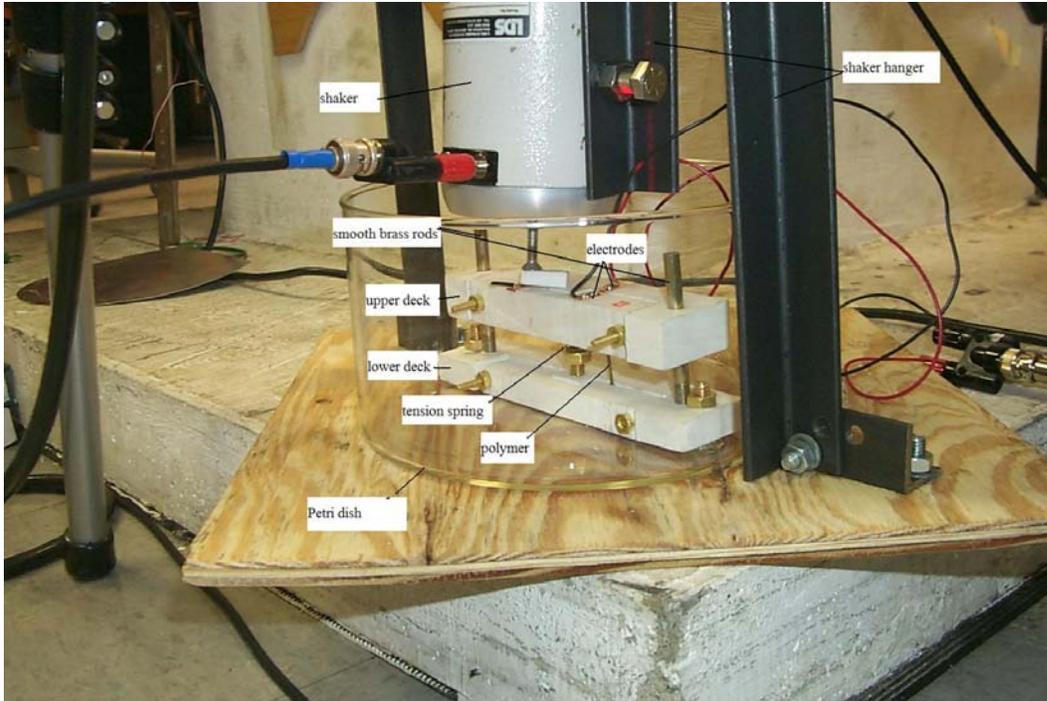


Figure 2.3: Test set up used for the sensitivity tests.

It is assumed that the motion of the top deck of the polymer is equal to the elongation of the polymer. The motion of the top deck is measured by a laser vibrometer (model Polytec OFV 303 Signal Head), and the signal was processed by a Polytec OFV 3001 vibrometer controller. A signal conditioning circuit, powered by an Agilent E368A Dual Outlet DC Power Supply, transforms the charge output of the polymer into a measurable voltage. This circuit is described in detail in Newbury's dissertation [23]. The test layout can be seen below in Figure 2.4.

The charge of the polymer and the strain of the polymer were recorded using a dSpace DS2002/DS2003 MUX AD board. The sensitivity was calculated by dividing the maximum charge displacement over five periods of motion by the maximum strain of the polymer over five periods of motion.

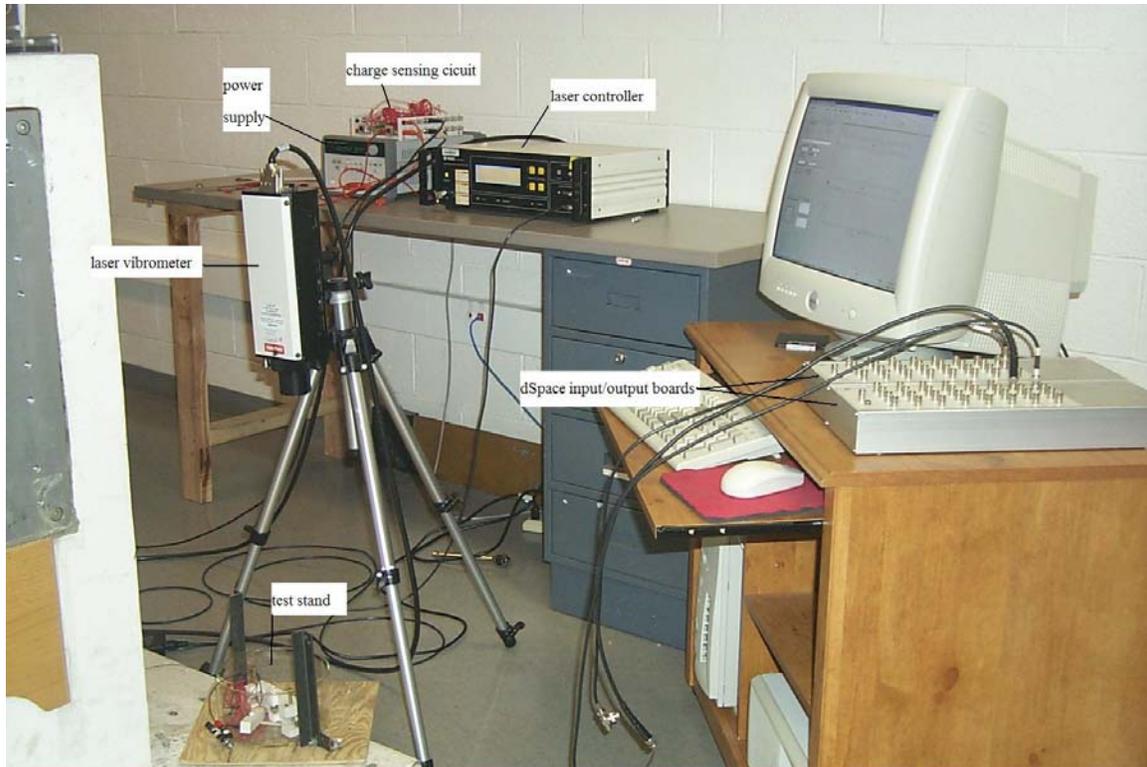


Figure 2.4: Test layout used for the sensitivity testing

The same setup procedure was followed for every test. The polymer is installed into the test stand dry, and then the test stand is firmly mounted into the Petri dish. Once the stand is secure, approximately 800mL of deionized water is poured into the Petri dish. 800 mL of water fills the Petri dish up to a point just below the top deck of the test stand, allowing the polymer to be immersed in the fluid and leaving the gold electrodes on the test stand dry. After the water is added to the Petri dish and the polymer has rehydrated, the polymer was pretensioned by adjusting the force in the spring by moving the adjustment nut by hand. The top deck of the test stand was positioned such that maximum extension of the shaker would not buckle the polymer.

A test run then ensues to ensure that all of the components were working as expected. This test includes setting the magnitude of the output signal such that the strain of the polymer is less than 5% so that the polymer is less likely to break, verifying that the polymer does not buckle over the entire stroke of the shaker, that the laser vibrometer

maintains a strong signal over the entire displacement of the test stand, and that polymer does not slip out of its groove in the test stand.

Preliminary testing attempted to establish the baseline tensile sensitivity of the material. These tests were run with the polymer immersed in deionized water. The polymer is left in the water for approximately 30 minutes of set up time before any data is recorded. Two input signals are used for this test, a 0.15V, 1.5Hz sine wave and a 0.15V, 0.5 Hz square wave. The signal is only turned on in the vicinity of the data collection. The displacement of the polymer and the electrical charge output are measured periodically over the course of six hours. The calculated sensitivity and the time the measurement was taken are recorded for each data point.

Once a baseline result was established the sensitivity of the polymer was monitored as the polymer underwent an ion exchange. Two different ions were tested for this battery of tests, sodium and calcium. The concentration of both ions was 143mOsm/L, which is equal to the concentration of sodium in the body (See Table 2.1). This was thought to be a relevant concentration because of the possible biomedical applications of a sensor of this type. The sodium was added in NaCl form, while the calcium was added in Ca(SO₄) form. 100 mL of solution would be thoroughly mixed in order to allow the salt to be fully dissociated before it is added to the larger Petri dish solution. The solution is added to the solution at time t=0 minutes and manually stirred for one minute.

The input signal used for this test was a 2.0 Hz sine wave. The magnitude of the signal was adjusted such that the strain on the polymer was approximately 2%. The polymer was excited by the shaker for the entire duration of the test. The displacement and charge output of the polymer are recorded only at points of interest over the course of the test. The calculated sensitivity and the time the measurement is taken are recorded for each data point.

2.2 Impedance Testing Experimental Setup and Procedure

Due to the simpler nature of the tests, which offer significantly fewer variables than the sensitivity testing, the round of impedance testing was much more extensive than the tension tests. More ions were investigated, and each test was run three times to ensure a degree of repeatability.

All of the samples used throughout this battery of tests were cut from the same sheet of Nafion™. While Nafion™ is a homogenous material, the plating process has not proved to be perfectly consistent. By taking samples from a sheet of Nafion™ 117 that was all plated at the same time, all of the samples should be fairly consistent from sample to sample. Twenty 5mm X 30mm samples were cut from a 60mm X 60mm sheet of Nafion™ plated with a gold-platinum electrode. The polymer was plated using a co-reduction process developed by Bennett [5]. After the polymer was plated, it was placed in the lithium ion form due to the polymers willingness to exchange the lithium for other ions while maintaining relative stability.

We determined that it was important to characterize the response to several different cations of the alkali metal family and the alkali earth metal family. This is consistent with the cations observed by others in the field [7, 32]. A summary of the tests conducted for this portion of the research can be seen in Table 2.2. The ions we chose to exchange into from the lithium (Li^+) form in this research were sodium (Na^+), potassium (K^+), cesium (Cs^+) of the alkali metal family, and calcium (Ca^{2+}), magnesium (Mg^{2+}), and barium (Ba^{2+}) of the alkali earth family.

One complex solution was also investigated in this research to determine how the polymer would respond if it was immersed in a solution with several cations. Because of the future possibility of biological or medical applications for this material, a solution with a composition similar to that of blood was deemed desirable. Normosol-R, a product of Abbott Laboratories, was picked because of it has many of the same components of blood, as can be seen in Table 2.1 below.

Table 2.1: Electrolyte comparison of plasma and Normosol-R

| Fluid | Plasma | Normosol-R |
|--------------------------|------------------|------------------------------|
| Glucose (g/L) | 1 | 0 |
| Na ⁺ (mEq/L) | 145 | 140 |
| Cl ⁻ (mEq/L) | 105 | 98 |
| K ⁺ (mEq/L) | 5 | 5 |
| Ca ²⁺ (mEq/L) | 5 | 0 |
| Mg ²⁺ (mEq/L) | 3 | 3 |
| Buffer (mEq/L) | 24 (bicarbonate) | 27 (acetate) 23 (glucose) |
| Osmolarity (mOsm/L) | 300 | 296 |
| pH | 7.4 | 6.4 |

Source: Chew DJ and DiBartola SP: *Manual of Small Animal Nephrology and Urology*. New York, Churchill Livingstone, 1986, p. 308

Similar to blood, the concentration of sodium in the Normosol-R is significantly higher than the concentration of any other ion at 140mOsm/L. In order to enhance the comparability of all of the tests, it was decided that the concentration of each solution would maintain an ionic concentration of 140mOsm/L. All of the solutions were made from the solid salt form of the materials dissolved in deionized water. All of the salts used in this research were obtained from Alfa Aesar, and were greater than 99% pure.

A clamp plated with conductive gold foil was used to supply a charge to the polymer. The clamp applied a steady force, holding the polymer in place and maintaining contact between the polymer and the gold foil. Leads wires were soldered onto the gold foil to transmit the signal via BNC chords.

Table 2.2: Designation and Description of Impedance Tests

| Test Designations | Ion | Concentraion | Number of Tests |
|-------------------|------------------|---------------|-----------------|
| DI | None | 143mOsm/L | 3 |
| Na | Na ⁺ | 143mOsm/L | 3 |
| K | K ⁺ | 143mOsm/L | 3 |
| Cs | Cs ⁺ | 143mOsm/L | 4 |
| Ca | Ca ²⁺ | 143mOsm/L | 3 |
| Mg | Mg ²⁺ | 143mOsm/L | 2 |
| Ba | Ba ²⁺ | 143mOsm/L | 4 |
| N-R | Normosol-R | See Table 2.1 | 3 |

All of the measurements taken during this experiment were taken using a Tektronics model 2630 Fourier analyzer. The Fourier analyzer was set to take 4096 samples over a range of 200Hz. The system averaged three measurement for each data point. The Fourier analyzer is able to measure the transfer function, in this case the impedance of the polymer, in approximately 20 seconds. Unfortunately, this means it is impossible to collect a constant stream of data for the duration of the test.

The test setup consists of the following equipment (See Figure 2.5). The Fourier analyzer sends a random signal with amplitude of 40mV to a Hewlett Packard bipolar supply amplifier (model 6824A). This signal is amplified and sent to a signal conditioning box. An Agilent model E3648A dual outlet DC power supply, with both channels set to 15V, is used to supply power to the signal conditioning box. The signal from the amplifier is split and sent to the polymer and to the Fourier analyzer as one of the inputs to the transfer function. The signal conditioner also sends the charge response of the polymer to the Fourier analyzer as the other input to the transfer function. These two inputs allowed the Fourier analyzer to measure the impedance of the polymer (See Figure 2.6).

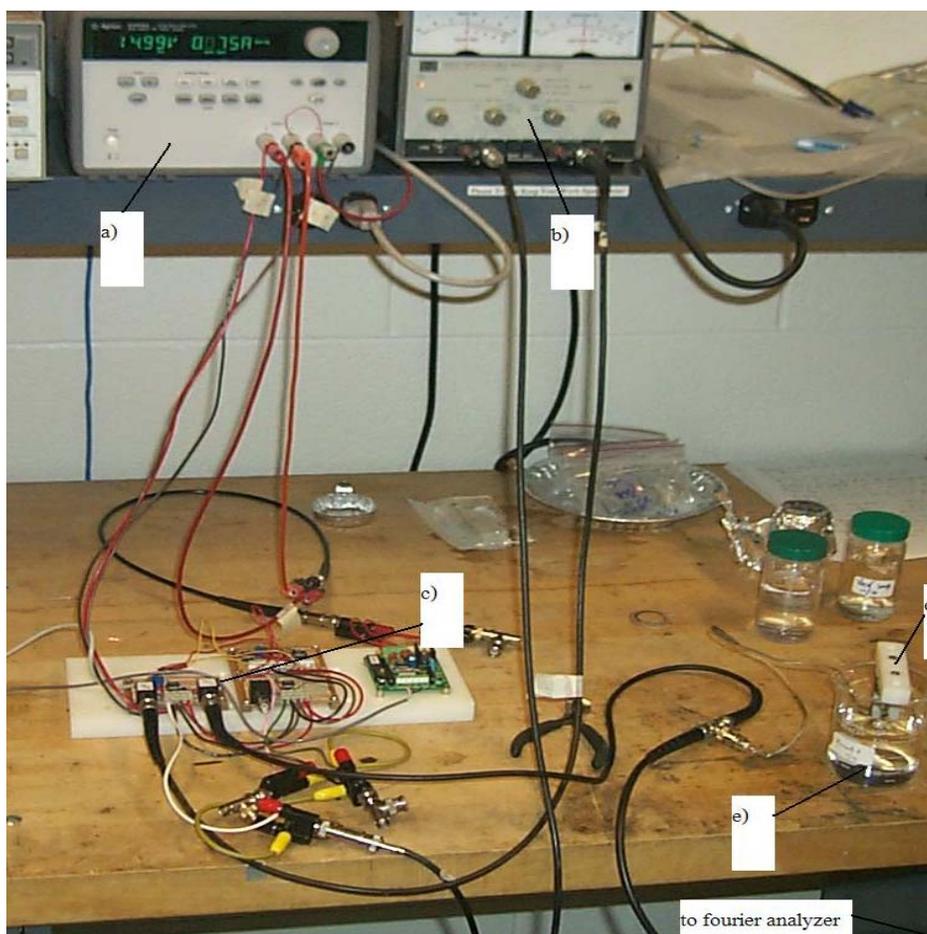


Figure 2.5: Experimental setup for impedance testing. This shows a) the power supply, B) the amplifier, c) the charge sensing circuitry, d) the clamp, e) the fourier analyzer, and f) the 250 mL beaker of solution.

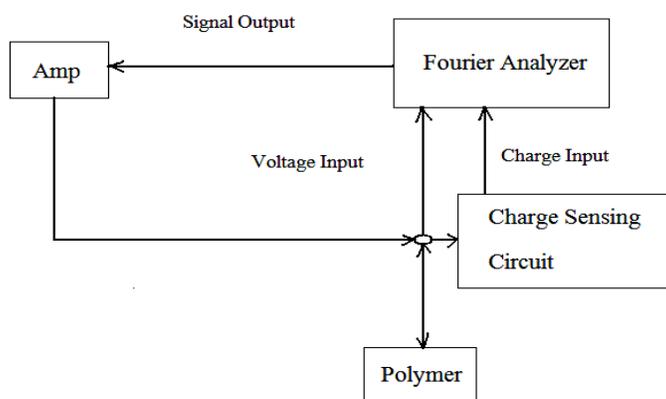


Figure 2.6: Wiring schematic of the hardware used to collect impedance data

The experimental procedure was repeated identically for each test. The samples are stored in Lithium form in a beaker of deionized water. A sample is drawn from this beaker by clean tweezers and placed into the clamp. Approximately $\frac{1}{4}$ of the length of the polymer is inserted into the clamp and placed in contact with the gold electrodes on the clamp. The impedance is measured once the polymer is situated in the clamp, shown in Figure 2.7. After one minute elapses, the polymer is placed in a beaker of ionic solution. The polymer is only immersed up to the electrode, and the electrode does not make contact with the solution. The impedance is measured approximately 5 seconds after the polymer was placed in the solution. Both of these measurements are regarded as baseline data points of the impedance of the material in the lithium form, before any exchange took place. These two data points are represented at the $t=0$ minutes line.

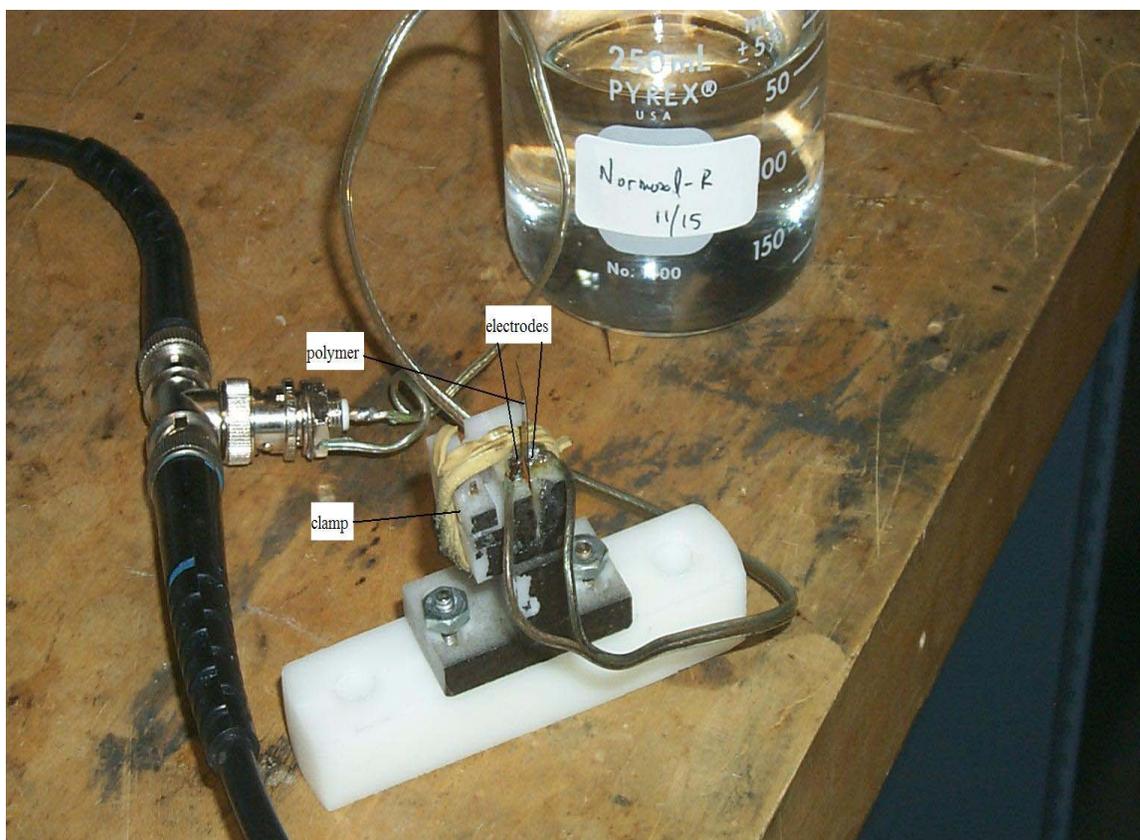


Figure 2.7: Polymer inserted into clamp

The polymer is left in the solution for 90 minutes. Data is collected every minute for the first 45 minutes, and then every five minutes for the next 45 minutes. Each data point consists of the measured impedance and the time (in minutes) that the polymer had been immersed in the solution when the impedance measurement was taken. When impedance is plotted over time, we hope to see some kind of trend that indicates an ion exchange has taken place. It is hoped that the characteristics of this trend differ for the exchange of different ions.

2.3 Scanning Electron Microscopy

A scanning electrode microscope (SEM) was used to determine the characteristics of the ion exchange. (See Figure 2.8) Due to the limitations of the energy dispersive spectrometer (EDS) equipment, we decided to conduct this test with the cesium salt solution. The EDS is more accurate when used to detect larger ions, and cesium, with an ionic radius of 181pm [40], is the largest ion tested.

In order to promote an ion exchange consistent with the conditions of the capacitance testing, the polymer was immersed in a 140mOsm/L CsCl solution at $t=0$ minutes. The sample was removed from the solution after 30 seconds in the solution, and a 5mm X 5mm section was removed from the sample and solitarily preserved in deionized water. The rest of the polymer was reinserted into the solution, and this procedure was repeated at 1 minute, 2 minutes, and 5 minutes. A second sample was needed to produce 5mm X 5mm sections of polymer in similar fashion after the sample had been in the bath for 10 minutes, 15 minutes, 20 minutes, and 30 minutes.



Figure 2.8: SEM used for EDS tests.

Three other samples were included in the EDS testing. One fresh sample that was not exposed to an ionic solution replicated the sample at time $t=0$ minutes, and samples that had been immersed in the cesium solution for 2 hours and 24 hours were included to show what the composition of a polymer is once a full exchange has occurred.

Once all of the samples were collected, they had to be prepared for examination. It is important to produce a clean edge for viewing under the SEM that is used in conjunction with the EDS. This clean edge was produced by freeze fracturing the polymer. Liquid Nitrogen was used to freeze the polymer and simultaneously cool the tweezers used to hold the polymer. These cooled tweezers could then grab the polymer, one on each side, and with a slight applied torque, cleanly fracture the polymer.

This smaller sample was then mounted onto a sample holder, with the fractured edge protruding slightly beyond the edge of the holder (See Figure 2.9). In order to increase the reflectivity of the sample, the surface was coated with approximately 8nm of gold plating. Seven samples at a time could then be loaded into the test chamber, which was evacuated to about 10^{-7} torr.

A Leo 1550 Field Emission Scanning Electron Microscope in the back scatter mode with an accelerating voltage of 10-20kV captured the surface images. All of the images are fed through a Robinson RBL 1500 back scatter detector. The images are magnified to approximately 10,000 times the original size, showing an area that was approximately 25 μ m X 25 μ m.

The X-rays coming off of the sample are measured by the EDS, which was manufactured by IXRF. The EDS is able to detect the amount of fluorine, sulfur, and cesium atoms present in the material. While significant amounts of carbon would also be present in the material, the EDS was unable to detect carbon at the time of the test because of its small size. Lithium is also too small for the EDS to detect, although it would have made for an interesting comparison to the presence of cesium.

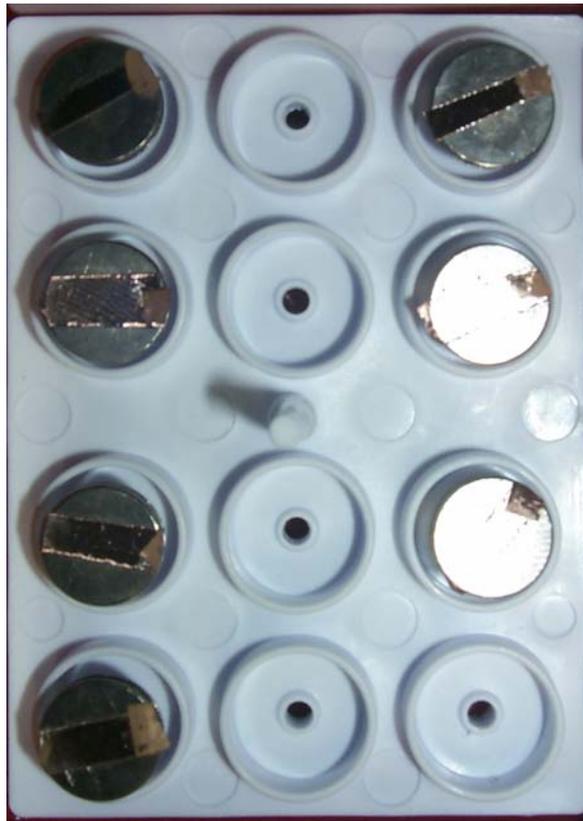


Figure 2.9: Prepared samples mounted for examination under SEM

With the data collected by the EDS, it is possible to track the amount of cesium in the sample. Knowing that the structure of the polymer yields a ratio of 17 fluorine atoms to each positive cation present in the polymer when the polymer is fully permeated with that ion, the data can be used to track the progress of the cesium.

Chapter 3: Discussion of Data and Results

The data collected from the experiments described in Chapter 2 will allow us to determine if and how ionic polymers can be applied to ion sensing. Section 3.1 discusses the results of the tension tests that were conducted, including shortcomings of the tension testing method.

In Section 3.2, the transient response determined by the impedance testing in an ionic salt solution is qualified versus the baseline response of the polymer in deionized water. These results yield a comparison of the transient response of the polymer to different ionic solutions, developing a possible way to use the results of an impedance test for ion sensing.

An energy dispersive spectrometer (EDS) was used to verify that the results of the impedance testing were due to an ion exchange. A discussion of the change in ion content of the polymer when it is immersed in an ionic solution can be found in Section 3.3.

3.1 Tension Testing Results

The tension testing that was conducted for this thesis revealed several characteristics of ionic polymers. While extensive testing has been conducted to characterize the sensitivity of ionic polymers, much of it has been in the area of the polymers sensitivity in bending [7, 8]. Further investigation into the electrical response of ionic polymers to tensile strain is developed in this section.

The test setup used for the tensile sensitivity tests conducted for this research is discussed in Section 2.1. A test stand was designed to allow a tensile force to be applied to the polymer across a 0.0008mm^2 cross section. All the tests are conducted with the polymer fully hydrated and immersed in fluid.

Baseline testing showed that the polymer exhibited a charge response in tension similar to the response it has in bending. The tensile sensitivity calculated is approximately the same order of magnitude as the bending sensitivity when the same stress is applied in both tests. These results are discussed in Section 3.1.1.

When the sensitivity is tracked over time in a deionized fluid, the sensitivity is found to within $\pm 2\%$. When the test is repeated with the polymer immersed a salt solution, we saw a change in the sensitivity of the polymer. However, the nature of these changes is not very consistent. These results are discussed in Section 3.1.2.

3.1.1 Baseline Sensitivity Tests

In order to establish the baseline response of the ionic polymer to an applied tensile force, experiments were conducted with the polymer immersed in deionized water. In theory, if the polymer is immersed in deionized water, no ion exchange will occur and the sensitivity of the polymer should remain constant.

Two different input waves are used for these experiments, a square wave at 0.5Hz and a sine wave at 2Hz. The Nafion™ was in either the lithium form or the hydrogen form for all of the baseline testing. The polymer samples used for this test are dog bone shaped pieces that have a narrow 1mm cross section, 31.75mm (1.25in) in length, where the polymer will absorb the applied strain (See Figure 2.2).

As described in Section 2.1, a Polytec laser vibrometer measured the movement of the polymer and a signal conditioning circuit measured the charge output of the polymer. The conversion factors applied for data conversion can be seen in Table 3.1. A dSpace A/D converter allowed us to record the signals from the laser vibrometer and the signal conditioner.

Table 3.1: Experimental Equipment Conversion Factors

| Laser Vibrometer | Signal Conditioning Circuit |
|----------------------------|------------------------------------|
| 320 $\mu\text{m}/\text{V}$ | 68nC/V |

When the polymer is given a step force input, the charge output of the polymer spiked and slowly returned towards zero charge output (See Figure 3.1). This is consistent with the results found in similar experiments examining the sensing capability of an ionic polymer to an applied bending force [7]. When a higher frequency sine wave of force is applied to the polymer, the polymer responds with a sinusoidal charge response (See Figure 3.2).

The sensitivity is calculated from the results of these experiments. The sensitivity of the polymer is defined by the following equation

$$S = \frac{Q}{\Delta\varepsilon} \quad \text{Eq. (1)}$$

Where S is the sensitivity of the polymer, Q is the change in the charge output of the polymer in microcoulombs, and $\Delta\varepsilon$ is the change of strain on the polymer in percent strain (mm/mm). $\Delta\varepsilon$ can be calculated by

$$\Delta\varepsilon = \frac{\max(\varepsilon) - \min(\varepsilon)}{l} \times 100\% \quad \text{Eq.(2)}$$

where l is the length of the polymer that is in tension. The magnitudes of Q and $\Delta\varepsilon$ are found by taking the average difference between consecutive peaks during 10 seconds of data collection. This gives a good representative magnitude of the average charge displacement and the average tensile displacement of the polymer to calculate the sensitivity.

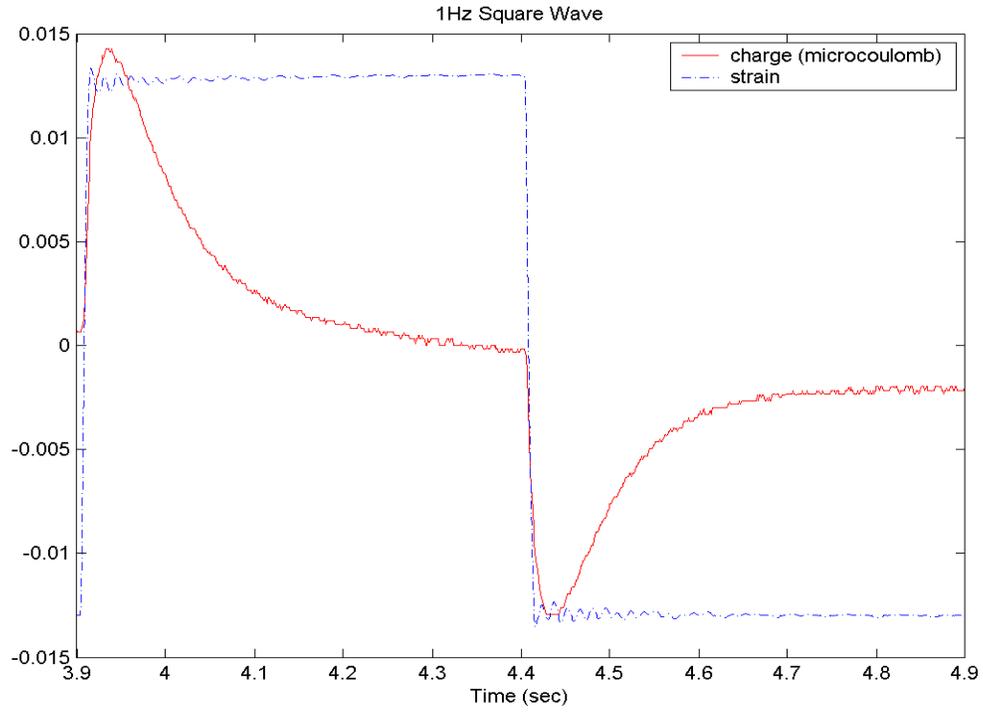


Figure 3.1: Experimental charge response of a polymer excited by a 1Hz square wave imposing a 2.5% tensile strain.

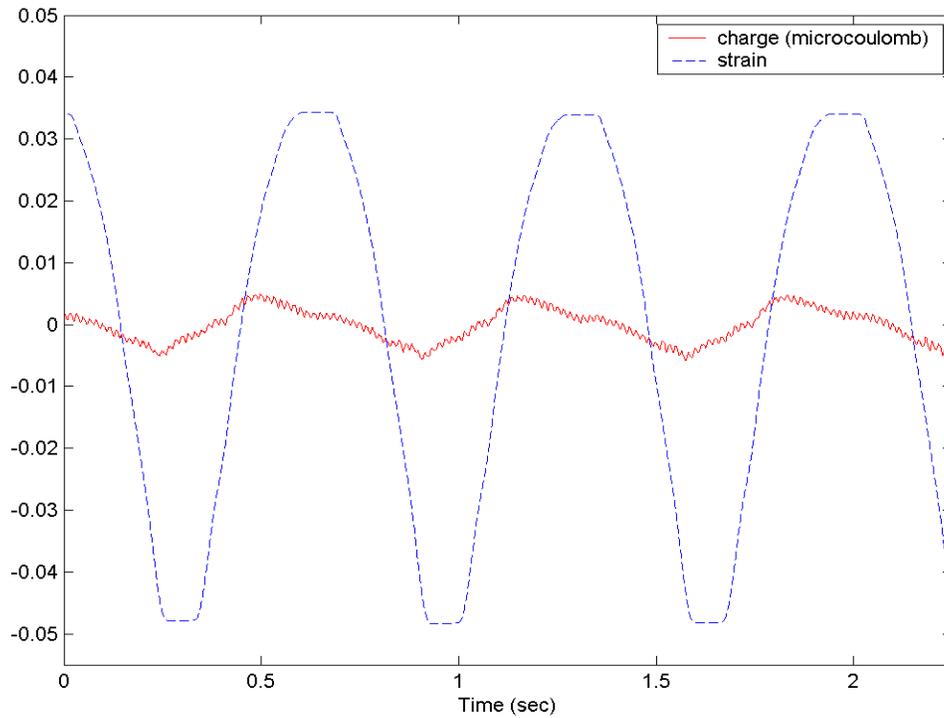


Figure 3.2: The experimental charge response of a different polymer when subjected to an 1.5Hz sine wave imposing an 8% tensile strain.

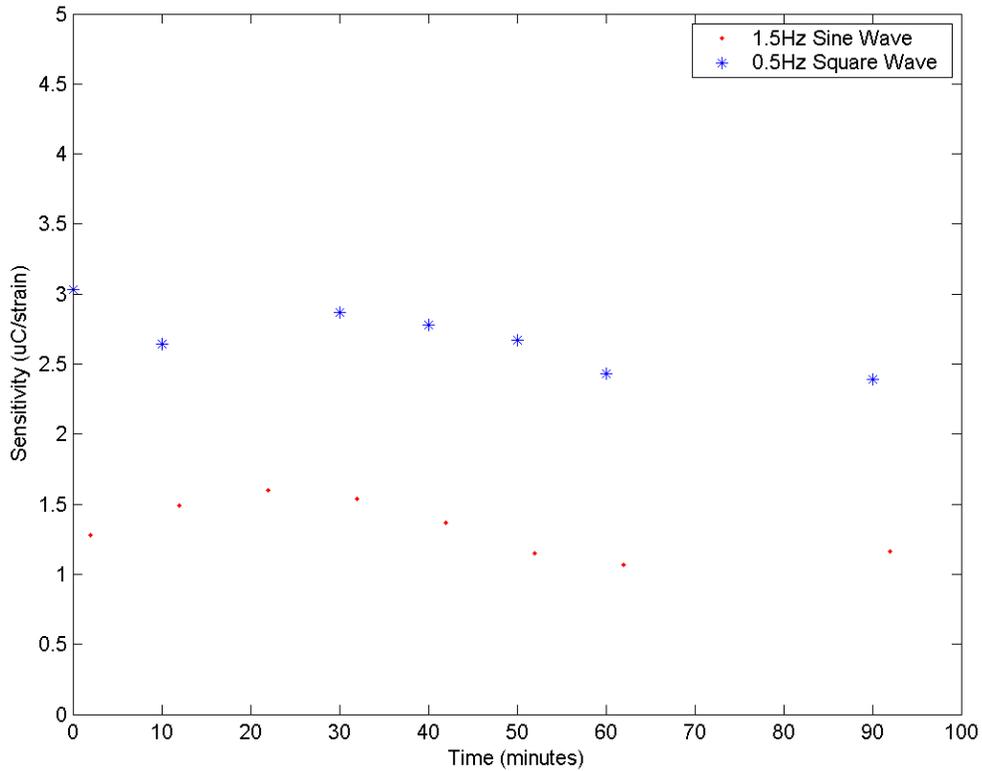


Figure 3.3: The baseline sensitivity of the polymer when immersed in deionized water

The result of the baseline testing is that the polymer does not exhibit a great change in sensitivity when tested in deionized water (See Figure 3.3, above). With no ion present to force an ion exchange in the polymer, there is no reason we would expect to see change in the sensitivity of the polymer. The slight variation of the data over time can likely be attributed to the standard deviation of the data.

The baseline tests provide three significant results for this research. The results demonstrate that the polymer exhibits the same type of charge response to an applied tensile force as it does to an applied bending force. This suggests that that a similar mechanism is in place for tension as has been purported by Farinholt to enact a response to bending strain [7]. We verified that the approach being used to measure the sensitivity of the polymer to an applied tensile force is valid by showing that the sensitivity is the same order of magnitude as the sensitivity exhibited in bending that is found by other researchers, $\sim 2.5 \mu\text{C}/\epsilon$ for a step input compared to $0.885 \mu\text{C}/\epsilon$ reported by Farinholt et al

[8]. We also showed that the sensitivity of the polymer does not significantly change if the polymer is not subjected to conditions that produce an ion exchange within the polymer.

3.1.2 Change of Tensile Charge Sensitivity in Ionic Solutions

When the polymer is subjected to conditions that drive an ionic exchange within the polymer, the sensitivity response of the polymer does exhibit a change. As described in Section 2.1.1, the polymer is immersed in a bath of deionized water until $t=0$ minutes, when an ionic solution is added to the bath. The final concentration of the bath is 0.143mOsm/L. The osmolarity (Osm) of a simple solution is equal to the number of moles dissolved being dissolved into the solution times the number of particles per molecule. For example, table salt, NaCl, has two particles per molecule.

A sinusoidal input force at 2Hz is used to excite the polymer for this set of tests. An applied step function is deemed less applicable to real world sensing application, is less consistent because it allowed the polymer to relax every cycle, and fractured the polymer during testing more often.

Figure 3.4 is the result of a test where the polymer started out in the lithium form and sodium chloride is added to the bath at $t=0$ minutes. The sensitivity of the polymer shows a change in sensitivity of an order of magnitude, notably greater than the variation in the sensitivity documented for the polymer immersed in deionized water. The sensitivity decreases in what looks like an exponential decay, with the greatest change in sensitivity taking place in the first fifteen minutes.

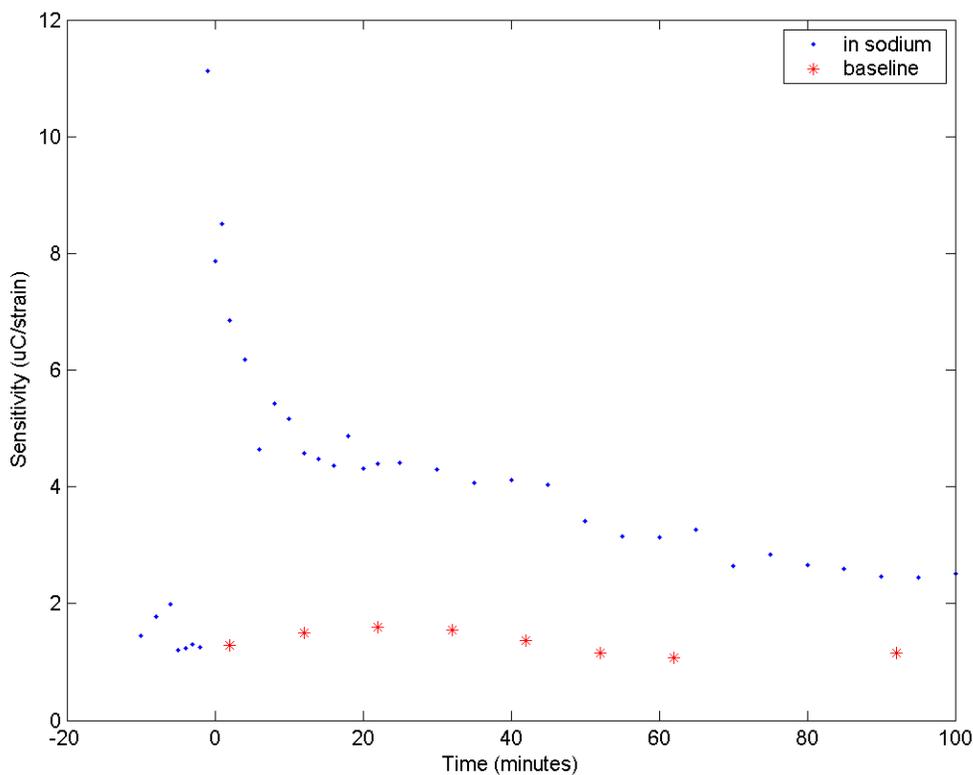


Figure 3.4: The sensitivity of the polymer to a 2Hz sine wave over time when immersed in a 143mOsm/L NaCl solution (.) and when it is immersed in deionized water (*).

However, the change in sensitivity was not repeatable from test to test. Some tests indicated that the sensitivity response took hours to reach steady state. Other tests exhibited a slow increase in sensitivity followed by a slow decrease in sensitivity. Figure 3.5 demonstrates the inconsistency of the sensitivity response, including magnitude, settling time, and the general trend exhibited by the data.

The problem is exacerbated by using samples that were initially in the hydrogen form. In its hydrogen form, the polymer demonstrates a lower sensitivity, and it is thought that any changes that occur due to an ion exchange would be amplified if the polymer started in the hydrogen form. However, the hydrogen form of Nafion™ is very unstable, as the polymer seeks out any other cation to replace the hydrogen that is in it.

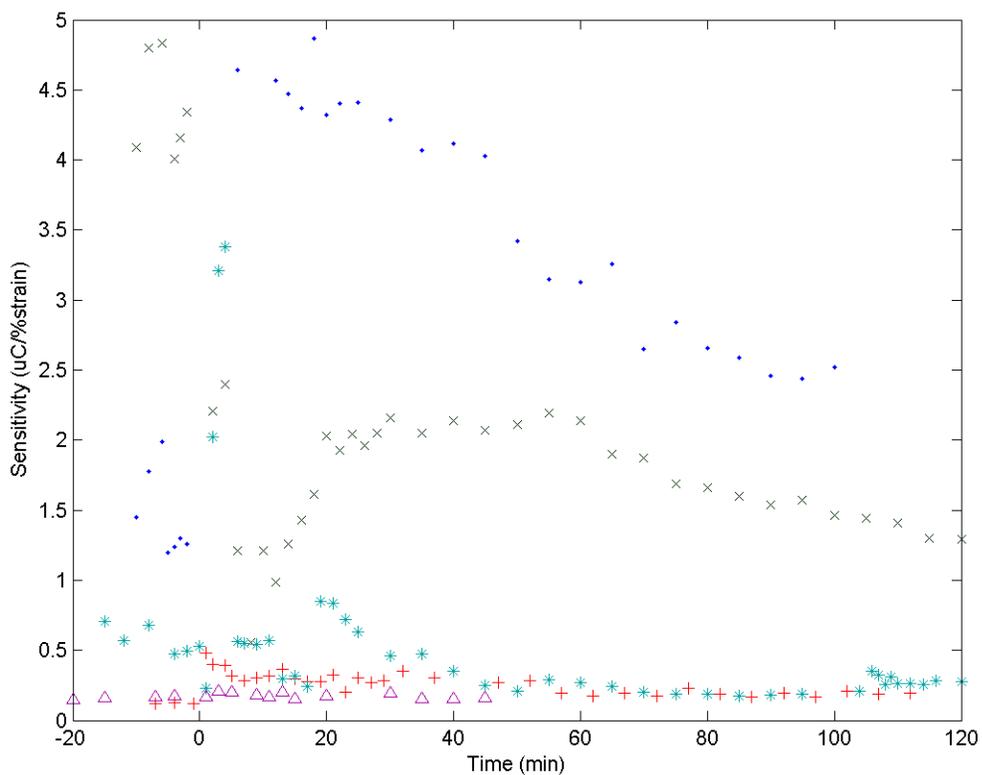


Figure 3.5: The sensitivity responses of different tensile tests showed great variability.

This lack of consistency seemed to add another variable to the experiments. The polymer would exhibit changes in sensitivity before any ions are added to the bath. Once ions are added to the bath, the response of the polymer became very jumpy. The sensitivity changed in a similarly unpredictable manner, not showing enough coherence to depict anything meaningful (See Figure 3.5, above).

3.1.3 Problems with Tensile of Testing Ionic Polymers

Due to the lack of repeatability found in this set of tests, we determined that it is not feasible to use the polymers to detect ionic content by tracking the tensile sensitivity of the polymer. There are several reasons for this conclusion.

Perhaps the biggest source of variability in the tensile sensitivity experiments is the experimental setup. The test stand did not allow fully consistent execution of the setup procedure. Once the polymer is secured into the test stand, enough tension needed to be applied to the polymer such that the polymer would not buckle at the maximum extension of the shaker. The amount of pretension could not be consistently controlled for each separate test.

This inconsistency in applying the pretension could have contributed to the number of polymers that failed during testing. A large fraction of the polymers tested would break before any significant data could be collected. This high rate of failure indicates that sensitivity testing of these materials in tension is not a very practical method for measuring a time dependent response.

Because of the surprising volume of material that was used for this research, due to the durability problem with the polymers, it was impossible to limit the sample use to only samples from the same batch. This leads to a rather significant variation in the baseline behavior from sample to sample. Over the course of these tests, we noticed that certain batches of polymer samples were of poor quality. While this problem was eventually solved, it is possible that some of the poorer quality samples tainted the experimental results.

Further variance is exhibited in the mechanical properties from sample to sample. Some samples would seem to exhibit a higher modulus of elasticity, perhaps due to different properties of the electrodes plated onto the outside of the polymer. These

differences in mechanical properties would influence the sensitivity of the material independent of ionic conditions.

Another practical issue is that a real-time sensitivity measurement would be difficult to reproduce. In order to determine the tensile sensitivity, both ends of the polymer need to be held tightly so that neither end slips and the strain of the polymer needs to be measured, all while the polymer is immersed in a solution. This complex procedure allows too much room for error.

These shortcomings are especially impractical for the initially intended application, monitoring the ions present at the site of a bone fracture. We assume that the polymer could be surgically implanted and secured across the bone fracture. It is reasonable that the polymer could be affixed securely enough to ensure that neither end of the polymer would slip. The strain of the bone across the fracture would supply a constant motion to the polymer on the order of 1-4mm [2]. However, the force applied to polymer would probably create both bending and tensile stresses, as the majority of the stresses in the bone are bending stresses.

Our experiments also showed that the polymer is susceptible to failure over time. Because the polymer would be surgically implanted into a subject and utilized for data collection until the fracture heals over a period of a few months, it is undesirable to insert a piece of equipment that could break.

3.2 Impedance Testing Results

In the end, all of the problems encountered with the tensile sensitivity testing lead us to believe that tracking the change in capacitance is a better way to use the polymer as an ionic sensor. The impedance testing that needs to be done to monitor the capacitance has far fewer variables. The setup only involves inserting a portion of the polymer into an electrode so a low current field can be applied to the polymer. The polymer does not need to be constrained, a force does not need to be applied to the polymer, and all of the measurements needed to calculate the capacitance can be determined from the same electrical wires that send a signal to the polymer.

The capacitance method is a far more practical method of determining the ionic content of a solution, with much less opportunity for error. This is further emphasized by the fact that our data for the capacitance method is quite repeatable, while the sensitivity method did not exhibit any repeatability.

The impedance testing described in Section 2.2 is conducted to the relationship between the change in the capacitance of an ionic polymer sample as the sample undergoes an ion exchange. The goal is to find if there is any correlation between the ionic content of a solution and a change in the capacitance of the ionic polymer.

What we found is a definite trend to the change in the capacitance of the material sample. While the time dependent response of the polymer stays within 3% of the mean capacitance when it is tested in deionized water, the time dependent response of the capacitance exhibited an exponential decay when the material is tested in a solution with a high enough concentration of free cations to drive an ion exchange in the material. This is conclusive evidence that the polymer can sense a change in ionic conditions

The exponential decay is compared to the size of each ion, and a relationship between the ionic radius and the time constant is developed. Using this relationship, the

time constant of the change in capacitance can be used to calculate the radius of the ion being diffused into the membrane. This idea is tested using a complex solution, which shows the potential of the polymer to be used as an ionic sensor.

However, while some general conclusions can be drawn by the characterization of the exponential decay, more testing needs to be conducted before any certain ion sensing parameters can be drawn. Further testing is required to prove the repeatability of the data. Further testing in complex fluids needs to be conducted to determine the effects of the selectivity of the polymer.

This chapter will cover the results of the baseline tests in Section 3.2.1, where we found that the polymer shows no substantial trend in change of capacitance when immersed in deionized water. When the polymer is immersed in an ionic solution, we found that the polymer exhibited an exponential decay, and that each ion could be characterized by the time constant. The general trend of these results is discussed in Section 3.2.2. Section 3.2.3 compares the data collected for all of the ions tested and discusses how this data could be used to predict the presence of an unknown ion from the change in capacitance. In Section 3.2.4, we discuss the response of the polymer to a complex solution.

3.2.1 Baseline Tests

As a preliminary benchmark, we tracked the response of the polymer while it is immersed in deionized water. Without any factors promoting the replacement of the lithium cations present in the polymer, no changes in the ionic form of the polymer is expected. Accordingly, our hypothesis is that the polymer will not exhibit any change in capacitance over time as the polymer soaks in the water.

The Fourier analyzer measures the impedance of the material by dividing the voltage applied to the polymer by the current that flows to the polymer. A signal conditioning circuit, shown in Figure 3.6, is used to turn the current output of the polymer into a voltage. The conversion factor applied to the impedance data is shown in Table 3.2.

Table 3.2: Conversion Factors Used in Impedance Test Data

| Op-Amp Scaling Factor |
|-----------------------|
| 40.8mA/V |

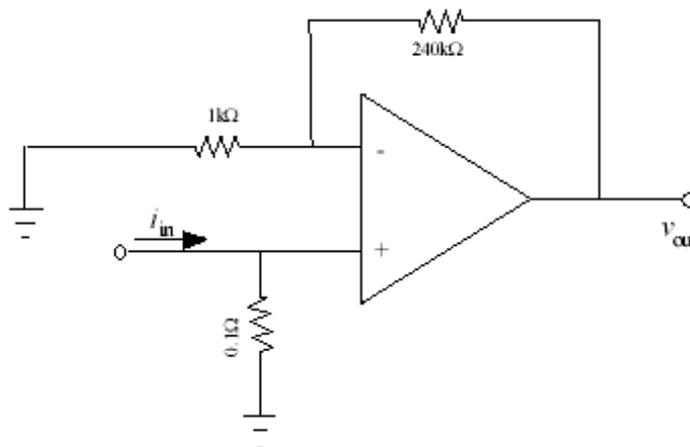


Figure 3.6: Op-Amp circuit used for sensing current. Circuit has a sensitivity of 40.8mA/V.

The magnitude and phase of the impedance measurement is separated into real and imaginary components. As stated earlier, the real component of the impedance is a function of the resistive properties of the polymer plating and polymer material, while the imaginary component of the impedance is more related to material properties than electrode properties. For the circuit used in this experiment, the imaginary component of the impedance, Z , is defined as

$$\text{Im}(Z) = \frac{1}{C\omega} \quad \text{Eq. (3)}$$

where C is the capacitance of the material in farads and ω is the frequency at which the measurement is taken in radians per second. The capacitance is then defined as

$$C = \frac{1}{\text{Im}(Z)\omega} \quad \text{Eq. (4)}$$

Given that the data for each measurement taken consists of 4096 points spread uniformly over the 200Hz range of measurement, the issue becomes the frequency at which we want to monitor capacitance. The data (Figure 3.7) shows that at frequencies below 12Hz, the imaginary component of the impedance dominates the impedance. Beyond 15 Hz, real component of the impedance dominates. In order to calculate a meaningful value of impedance, it should be calculated below 12Hz.

Another noticeable characteristic of the impedance measurement is that the imaginary component is much higher at lower frequencies. Equation 4 shows that as the frequency goes to zero, the imaginary component of the impedance approaches infinity. There is a low frequency cutoff in the signal conditioning circuit that occurs around 1Hz. Changes in the imaginary component of the impedance will be more apparent the larger the magnitude of the imaginary component. Therefore, the lowest frequency that still shows consistent data is the frequency that we will use to analyze all of the data.

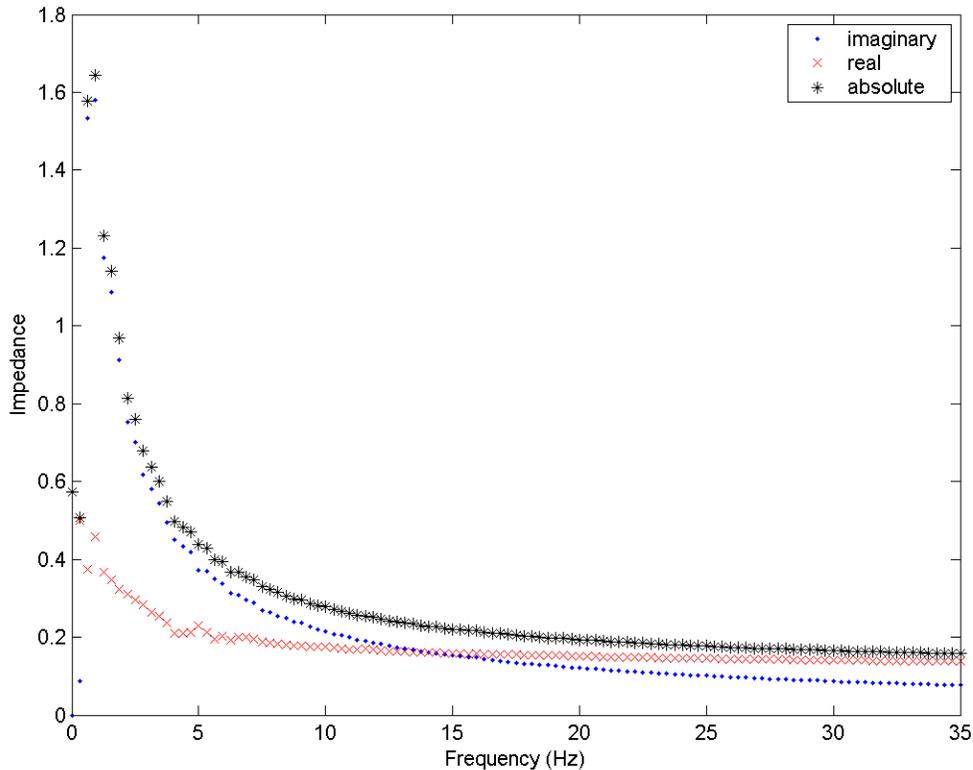


Figure 3.7: A sample of the impedance measured by the fourier analyzer separated into the real and imaginary components.

A comparison of the capacitance calculated at 5Hz with the capacitance calculated at 2Hz shows that at 2Hz the capacitance is much more consistent. When the capacitance is calculated at 5Hz, the capacitance shows significantly more scatter (See Figure 3.8). A similar comparison of the data collected from a later test where sodium chloride is added to the solution showed the same trend.

The coherence of the impedance measurements may explain these differences (See Figure 3.9). In the sample shown, the coherence of the data is a relatively low 96.0% at 2Hz, while it improves to 99.8% at 5Hz. Moreover, by 5Hz the coherence starts to flatten out and stay very close to 100%. This trend is representative of all of the data collected, thus, the impedance measured at 5Hz was used for all of the impedance analyses.

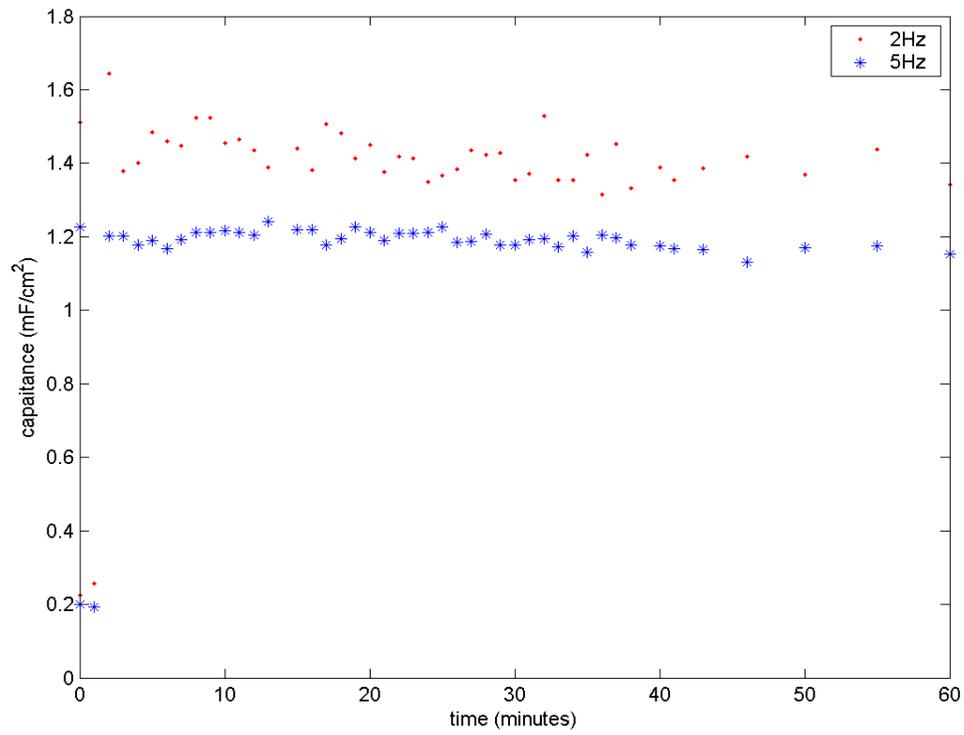


Figure 3.8: The baseline capacitance response when calculated at different frequencies.

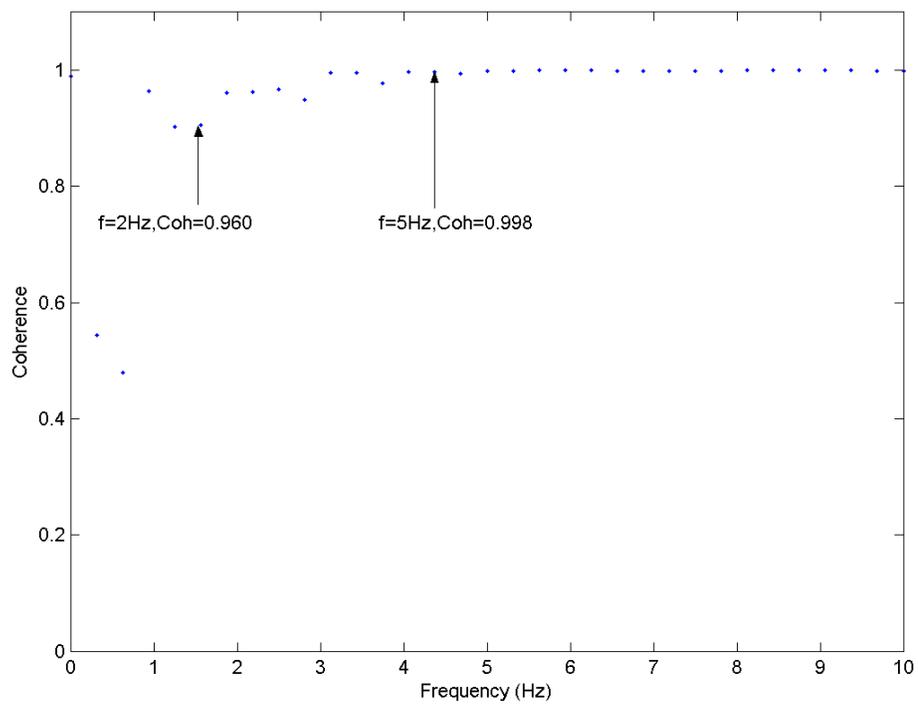


Figure 3.9: Coherence of the 3 impedance measurements making up the average impedance.

The results of the impedance tests of the material when it is immersed in deionized water does not show any change of capacitance beyond the standard deviation over time. This is consistent with our expectations that we would only notice significant changes in the capacitance of the material when an ion exchange occurs in the polymer (See Figure 3.10). Because deionized water will not drive the lithium ions out of the polymer, the capacitance of the material should remain fairly constant. The capacitance we calculated in this is in the range of 1-2 mF/cm².

A useful comparison can be made between the changes exhibited in a deionized liquid versus the change in capacitance exhibited by the polymer in an ionic solution. In order to minimize any effects of different capacitance offsets, the data is normalized by the mean capacitance value for the DI tests. The mean of the data the data has more

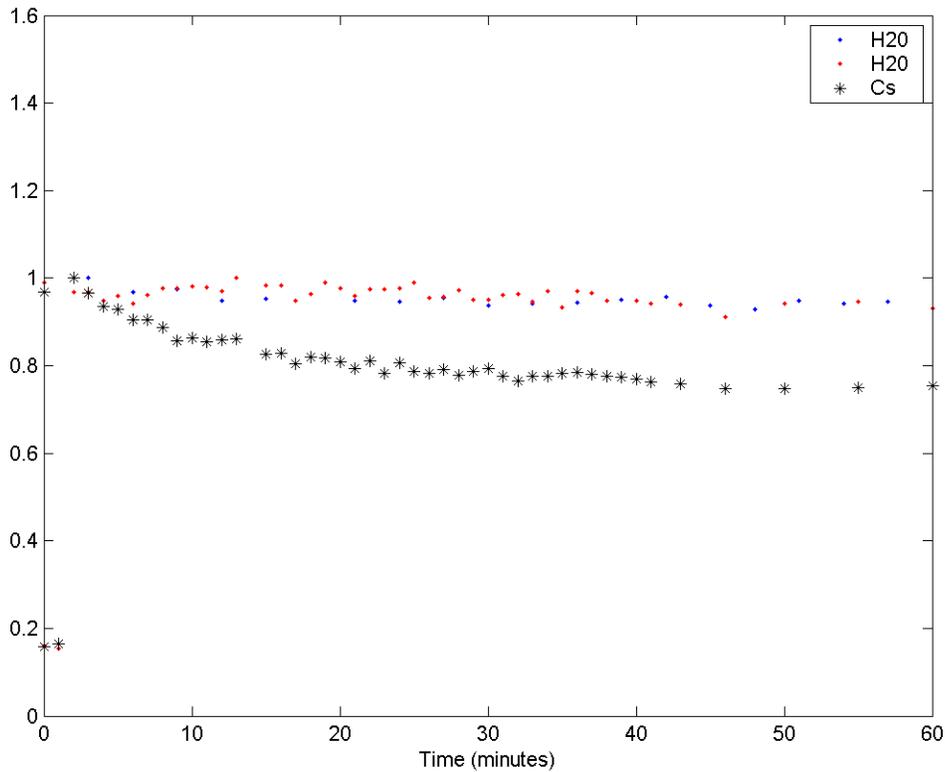


Figure 3.10: Normalized Capacitance vs. Time @ 5Hz, comparing the response in H₂O to the response in a 143mOsm/L cesium solution over time.

statistical meaning for the flat response of the DI data than does a maximum value. To determine the change in the capacitance of the data, Δ_{C_DI} , we can compare the mean to the maximum negative deviance from the mean by calculating

$$\Delta_{C_DI} = 1 - \frac{\min(C)}{\text{mean}(C)} \quad \text{Eq. (5)}$$

where C is a vector of the capacitance values for each DI test. For the tests performed in an ionic solution, the capacitance is normalized with respect to the maximum value of the capacitance. The maximum capacitance can be compared to the mean steady state value of the capacitance to quantify the decay of the data. The normalized change of the capacitance, Δ_C , can be calculated

$$\Delta_C = 1 - \frac{\text{mean}(C_{60-90})}{\max(C)} \quad \text{Eq. (6)}$$

Where C_{60-90} is a vector of steady state capacitance values calculated for $t=60-90$ minutes. Comparing the Δ_C values for the results plotted in Figure 3.10 demonstrates the flatness of the response of the DI data (See Table 3.3).

With this result, a baseline result has been established for the capacitance testing conducted for this portion of the research. With a flat response established when the polymer is immersed in deionized water, if the polymer exhibits a change in capacitance over time in ionic solutions we can infer that an ion exchange is being driven by the ionic solution.

Table 3.3: Comparison of Δ_C for DI and Cs

| Test | % Δ_C (C/C) |
|------|--------------------|
| DI_1 | 1.67 |
| DI_2 | 2.36 |
| Cs_1 | 25.8 |

3.2.2 Change of Capacitance in Ionic Solutions

When a salt is dissolved in water, the positive and negative ions that make up the salt dissociate and mix with the water to form a solution with positive and negative ions mixed into the water. An ionic polymer exposed to an ionic solution with a sufficient concentration gradient would be driven to undergo an ion exchange. All of the experiments conducted for this research start with the ionic polymer in the lithium form and are then transformed into the sodium, potassium, cesium, magnesium, calcium, or barium forms, depending upon which ionic solution the polymer is immersed in.

As the polymer is immersed in the ionic solution, the impedance of the material is measured using the process described in Section 2.2. The impedance is collected and recorded over time as the ion undergoes an ion exchange. The capacitance of the material over time could be calculated from this impedance data. With these capacitance results, we hoped to see a change in capacitance over time, unlike the flat capacitance over time that is exhibited when the polymer is immersed in deionized water.

Once the results of the first test, conducted in a CsCl solution, are compiled, it is clear that the response of the polymer is not flat. A plot of capacitance versus time (see Figure 3.11) shows that the response seems to exhibit an exponential decay. This is in line with the change of sensitivity exhibited by the polymer when it is tested in a NaCl solution. Further tests backed up this trend, with every subsequent test exhibiting an exponential decay of capacitance over time (See Appendix). Each test was run three times for each ionic solution to investigate the repeatability of the tests.

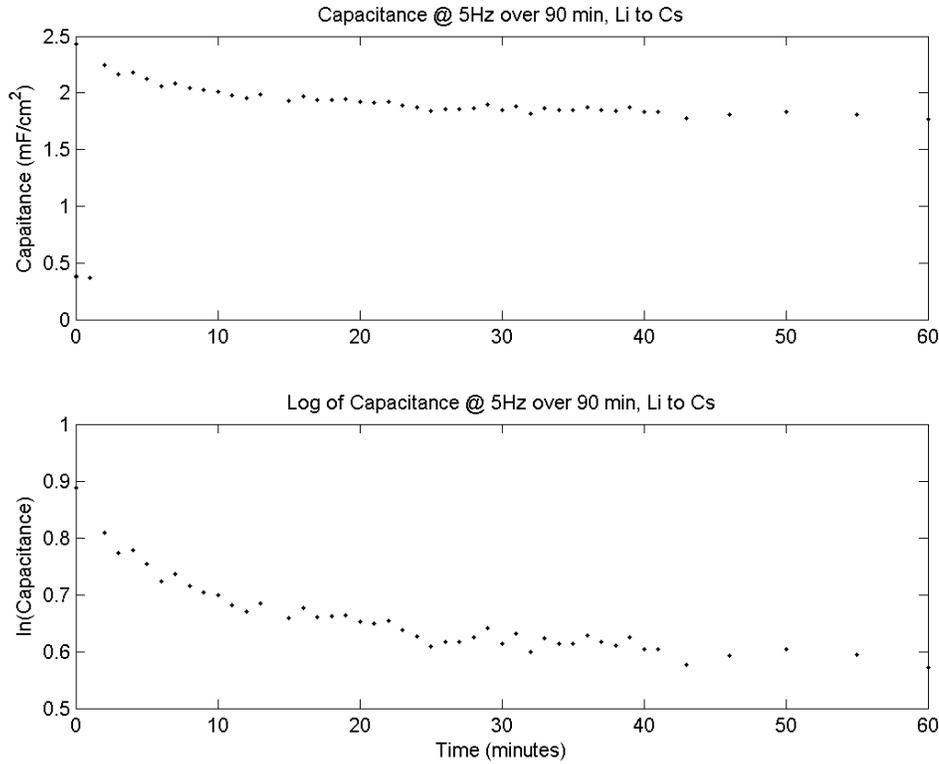


Figure 3.11: Results of one round of impedance testing of 150cm² polymer immersed in 143mOsm/L CsCl solution.

Once we had established that the response of the polymer to a strong concentration ionic liquid is an exponential decay, we characterized the response of the exponential decay in terms of the exponential time constant. An exponential fit would be of the form

$$C = Ae^{-\frac{t}{\tau}} \quad \text{Eq. (7)}$$

where C is the capacitance of the polymer, A is the scaling factor of the fit, t is time, and τ is the time constant of the fit. In trying to fit the exponential equation to the data, we tried to fit a line to the natural log of the data using the polyfit command in Matlab, set to find an appropriate first order equation with respect to time to fit to the data. This linear equation would be

$$\ln(C) = \ln(A) - \frac{t}{\tau} \quad \text{Eq. (8)}$$

A plot of capacitance versus time (See Figure 3.12) shows that the exponential decay dies out after the first twenty minutes. When the natural log of the capacitance is plotted against time, the line is found in most cases to only be linear for the first fifteen to twenty minutes. With the lines we are trying to fit the data to consistently linear only over the first fifteen minutes, we only fit the exponential decay to the first fifteen minutes of data. This means that any test to compare the time constants of the response of the polymer to an ionic solution would only need fifteen minutes to consistently collect all of the data.

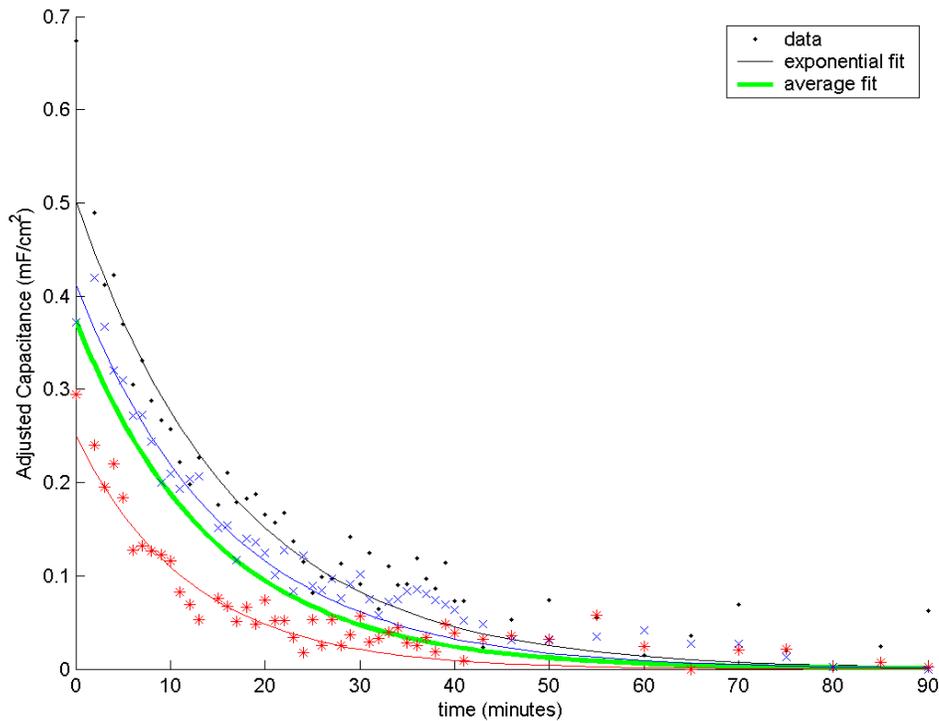


Figure 3.12: A typical exponential fit of the adjusted capacitance over time. The average fit line is an average of the three time constants (τ) and the three scaling factors (A)

Because a negative exponential equation will go to zero as time goes to infinity, all of the data is moved such that the capacitance would settle out to zero Farads. This would also eliminate any inconsistencies caused by the different offsets of each set of data. The offset of each set of data at 90 minutes is shown in Table A.1 of Appendix. There does not seem to be any trend concerning the capacitance of the polymer after an ionic exchange and the ion present in the polymer.

A line can be fit to the data if the offset in capacitance is equalized by adjusting the capacitance at $t=90$ minutes to zero. Once a line has been fit to each set of data, the parameters of each fit are averaged for each ion. A typical set of results is shown for cesium in Figure 3.12 showing that the average fit is representative of the characteristics of the data for that ion. Cesium is shown as a representative set of data, and similar results can be seen for the other ions in Appendix Figures A1-A.5.

3.2.3 Correlation of Results to Ion Size

While these results show a distinct change in the capacitance of the polymer over time when the polymer is immersed in an ionic solution, we are also interested to see if the polymer exhibits any characteristics that may be unique to each ion. If the polymer does exhibit a unique response to each ion, the notion that the polymer could be used as an ionic sensor is greatly substantiated. The polymer could then be placed into an unknown solution and tested experimentally to measure the impedance over time. From the change of the capacitance over time, one could determine what ion is in the solution.

Each test was performed exactly the same as the Cs tests described above. The polymer was immersed in a 0.143mOsm/L solution at $t=0$, and the impedance was measured every minute for the next 45 minutes and every five minutes thereafter to determine the transient capacitance response of the polymer to an ion exchange.

The response of the polymer to each ion is compared using the average fit lines for each ion. The characteristics of the average fit lines for each ion are then compiled, compared and analyzed to see if there are any notable differences between the characteristics of the response for each ion (See Table 3.4). If all six ions are plotted together (see Figure 3.13), nothing is notably apparent. While there is a definite difference between each line, no trend is readily apparent.

Figure 3.14 shows the data sorted by atomic number. Cesium and barium are right next to each other on the periodic table, as is potassium and calcium, and sodium and magnesium. When the ions are grouped this way, another interesting relationship becomes apparent. The lines appear to be parallel over the first 10 minutes, suggesting that the time constants are very similar. One distinction is that, apart from sodium, the more charged ions have a larger scalar factor.

Table 3.4: Average characteristics of change in capacitance

| Test | Ionic Radius (pm) | τ (minute) | % Δ_C (C/C) |
|-------------|--------------------------|-----------------------------------|--------------------------------------|
| DI | N/A | N/A | 2.01 |
| Na | 113 | 25.8 | 13.4 |
| Mg | 65 | 11.8 | 11.1 |
| K | 151 | 14.5 | 14.8 |
| Ca | 114 | 22.0 | 28.7 |
| Cs | 181 | 14.5 | 23.5 |
| Ba | 149 | 16.5 | 30.4 |
| N-R | N/A | 14.6 | 25.5 |

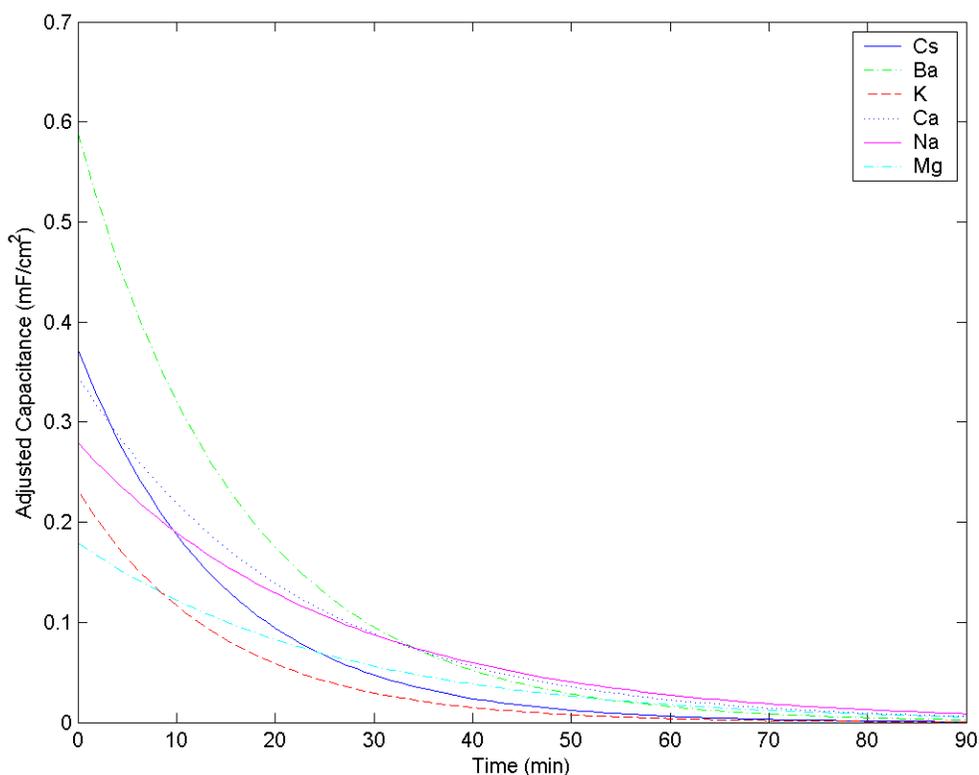


Figure 3.13: The average fit of the response of each ion shows no discernable trend.

This led us to wonder how we might be able to find a trend somewhere in the data. Our initial hypothesis was that the response of the polymer would be different for different families of ions and also for ions of different sizes. Figure 3.15 shows the data sorted by charge. What becomes apparent when the data is sorted by family is that the larger ions have a much faster decay, and the time constant τ is smaller for the larger ions. Excluding sodium, the scaling factor A is larger for the larger ions as well.

Our initial hypothesis was that the time constant of the capacitance change would be the most unique characteristic of the ion exchange. If we only consider the time constants of the exchange, a trend related to the size of the ion becomes apparent (See Figure 3.16). With the exception of magnesium, there is indeed a trend that indicates the magnitude of the time constant decreases as the ionic radius increases.

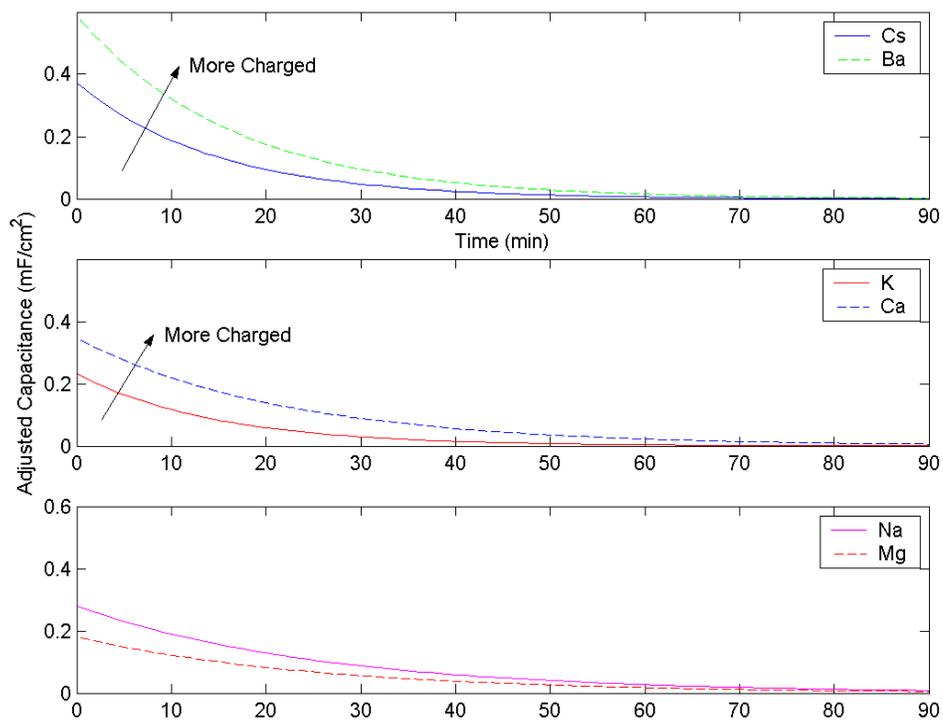


Figure 3.14: Capacitance response sorted by atomic number

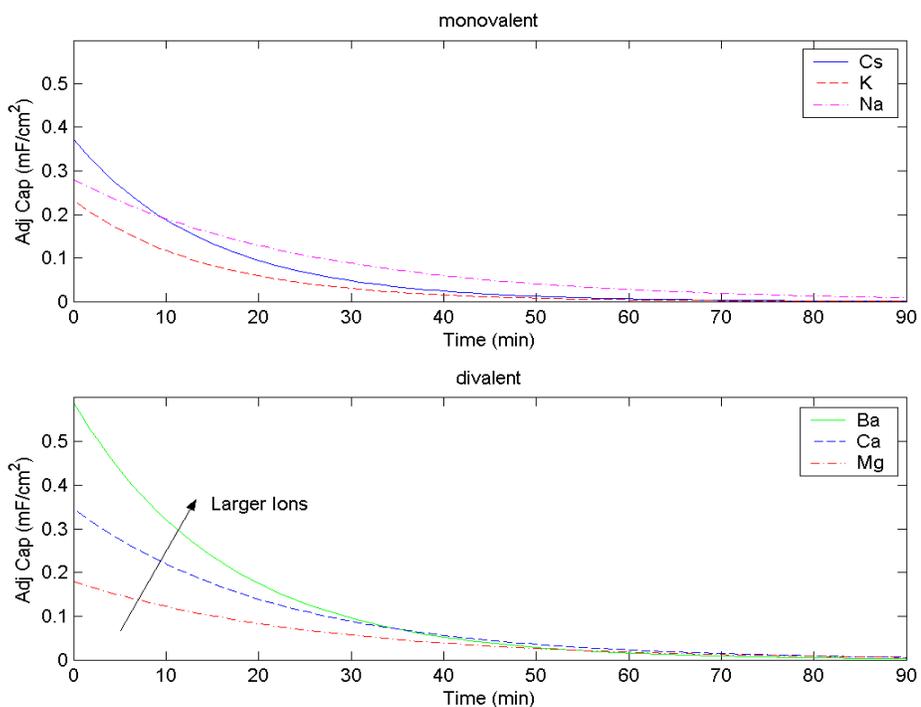


Figure 3.15: Capacitance response sorted by charge

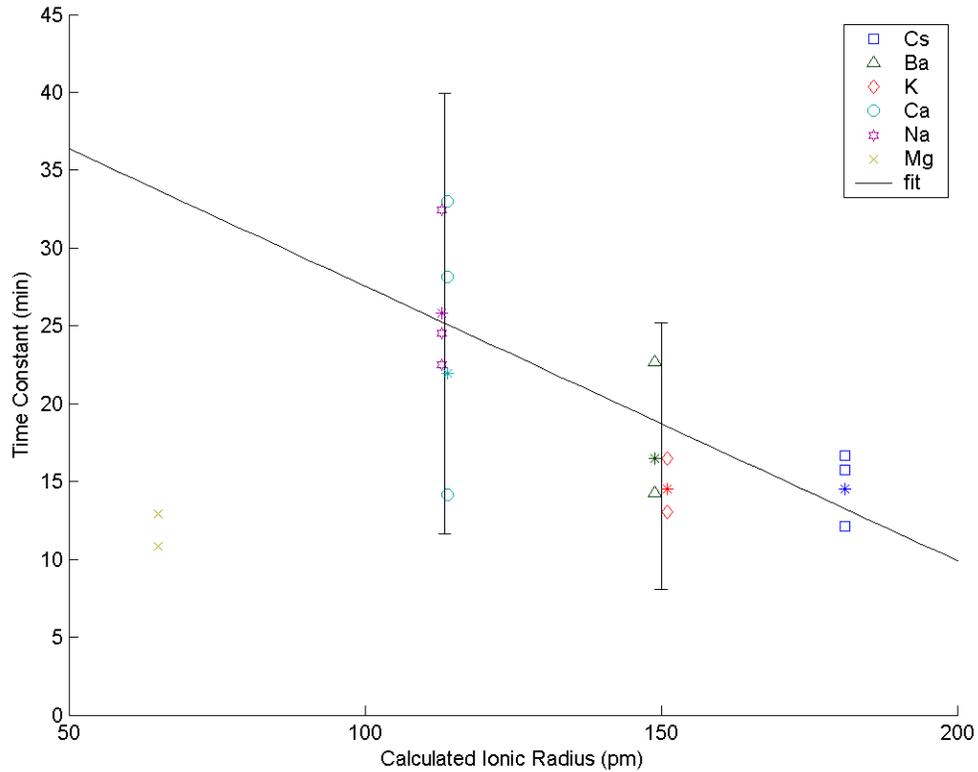


Figure 3.16: Scatter plot of time constants found in testing versus the ionic radius. The * represents the average time constant for each ion, and the vertical black lines are 2σ error bars.

The trend appeared to be linear, and a first degree polynomial is fit to the data using the polyfit command in MATLAB. The equation of the line that fits the data is

$$\tau = 45.2 - 0.177r \quad \text{Eq. (9)}$$

where τ is the time constant and r is the ionic radius in picometers (pm). If an experiment is conducted and the time constant τ is found experimentally, the radius of the ion that permeated the membrane could be calculated using the formula

$$r = -\frac{\tau - 45.2}{0.177} \quad \text{Eq. (10)}$$

While the average time constants over three tests do indeed follow the trend indicated by the fit, the scatter of the results for each ion shows overlap in the time constants of the ions tested. With the limited amount of testing conducted for this thesis, this is not unexpected. More testing would probably result in greater clustering around the average time constant for each ion. However, the fact that the average time constant for three tests generally follows the trend is a good result.

With the limited amount of testing conducted for this thesis, it is not surprising that this result is not definitive. The results exhibit an overlap of the time constants of many of the ions, and magnesium is not well represented by the fit line.

Another potential complication incurred by characterizing each ion by time constant is the clustering of the ionic size of the ions tested. The size of each ion is quantified by the radius of the atom in its ion form, defined as the ionic radii. Sodium and calcium have ionic radii of 113 and 114pm, respectively, while potassium and barium have ionic radii of 151 and 149, respectively [43]. This clustering makes it virtually impossible to predict what ion is permeating the membrane based on the time constant of the change of capacitance alone.

The scatter of the data is another factor of the limited amount of testing that could be conducted for this thesis. If we consider time constants of the clustered ions together, the spread of the data can be quantified by the standard deviation of the six points. The standard deviation of the combined sodium and calcium data is 7.08, which is 32.2% of the time constant for calcium and 27.4% of the time constant of sodium. The standard deviation of the potassium/barium cluster is 4.29, which is 29.5% of the time constant for potassium and 26.0% of the time constant for barium.

One useful prediction that can be gathered from the standard deviation is how much we can expect to see any future data scatter. If the time constants are considered to be normally distributed, 95.44% of all the time constants will be within two standard

deviations (σ) of the data. This means that we could expect that all of the time constants for a cation with an ionic radius close to sodium or calcium to be ± 14.2 min and any cations with an atomic radius in the vicinity of barium or potassium to have a time constant ± 8.58 min of the time constant predicted by the fit line (Eq. 9).

The unfortunate side effect of these 2σ error bars is that the margin of error that will cover 95.44% of the time constants for one ion exhibits enough overlap to cover the range of most of the ions tested. The error bars on the sodium/calcium data mean that the mean of any of the experimentally determined time constants could possibly be interpreted as a sodium ion diffusing into the membrane. The only ion tested whose size doesn't fit into the margin of error for barium/potassium is magnesium.

It is hoped that more extensive testing would show greater clustering around a line that is fit to the data. If this proves to be true, and the standard deviation correspondingly decreases, the time constant of the change of capacitance could prove to be a good way to predict the size of the exchanging ion.

3.2.4 Response to a Complex Solution

A decent test of the idea that one could predict the size of the exchanging ion from the time constant of the change of capacitance would be to find the time constant for the change of capacitance for a known complex solution and compare it to the fit line predicted in Section 3.2.2. Three samples of polymer are returned to the lithium form by boiling them in 1.0M sulfuric acid (H_2SO_4) for 30 minutes and then leaving the polymer to soak in 0.1M lithium hydroxide solution for 24 hours. The polymer is thoroughly rinsed before any tests are conducted on it.

The same test procedure described in Section 2.2 was conducted in a complex solution. For this test, we used a complex solution from Abbot Laboratories called Normosol-R. This solution is generally used as a stabilizing fluid for rehydration of the body due to it having a similar composition to blood. This similarity to blood will also show any potential an ionic polymer has to be used as a biological sensor used for *in vivo* research.

The three cations that are present in Normosol-R are Na^+ , K^+ , and Mg^{2+} , with respective concentrations of 140, 5, and 3 mEq/L. The total composition of the Normosol-R and plasma can be seen in Table 2.1. Because the concentration of sodium is so much greater than the concentration of the other ions, we expect that an ion exchange would be driven by the concentration gradient of sodium. Because the concentration of the sodium in Normosol-R and the concentration of sodium used for the single ion test is the same, we expect to see a result similar to the capacitance result for the polymer immersed in a sodium solution.

The results of the test showed a qualitative capacitance response of the polymer that is very similar to the response exhibited when the polymer is immersed in fluid with a single cation dissolved in it. What is seen is that the capacitance exhibits an exponential decay over time (See Figure 3.17). The majority of the decay seems to occur in the first twenty minutes. Similar to sodium, it takes a long time for the decay of the capacitance to entirely die out, and the capacitance still seems to be decaying at 90 minutes for the * set of data.

All of the calculations are executed as described above for single ion solutions. The average time constant for the three sets of data is 18.6min, the average scaling factor is $0.4785\text{mF}/\text{cm}^2$, and the average offset of the data is $0.2798\text{mF}/\text{cm}^2$. If we use the equation of the line fit of the data, we predict that the ionic radius of the ion being diffused into the polymer is 151pm, the same ionic radius as potassium, and very nearly the ionic radius of barium.

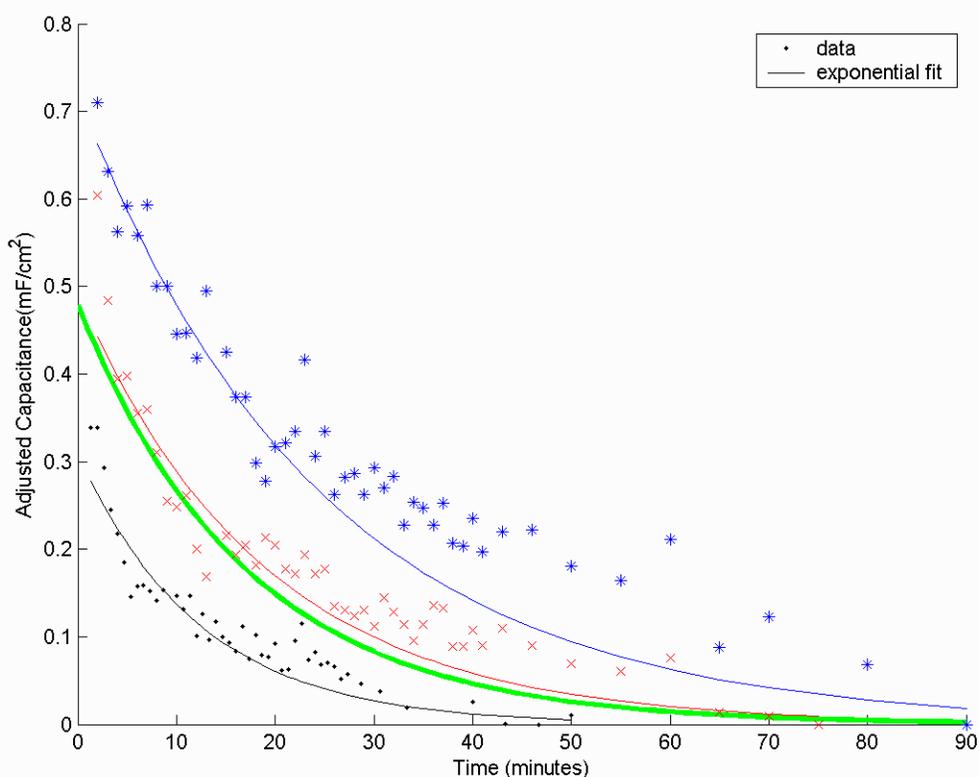


Figure 3.17: The adjusted capacitance results of the Normosol-R tests. The average fit line (green) is an average of the three time constants (τ) and the three scaling factors (A)

However, this average time constant is within 1.03σ of the predicted time constant of sodium. Here the scatter of the data we collected makes it difficult to predict which ion is actually diffusing into the polymer. It is evident when the time constant values for Normosol-R are plotted along with all the time constants for all the other ions tested verse ionic size (figure 3.18), the scatter of the data makes it very hard to predict what ion is in the solution from the time constant alone.

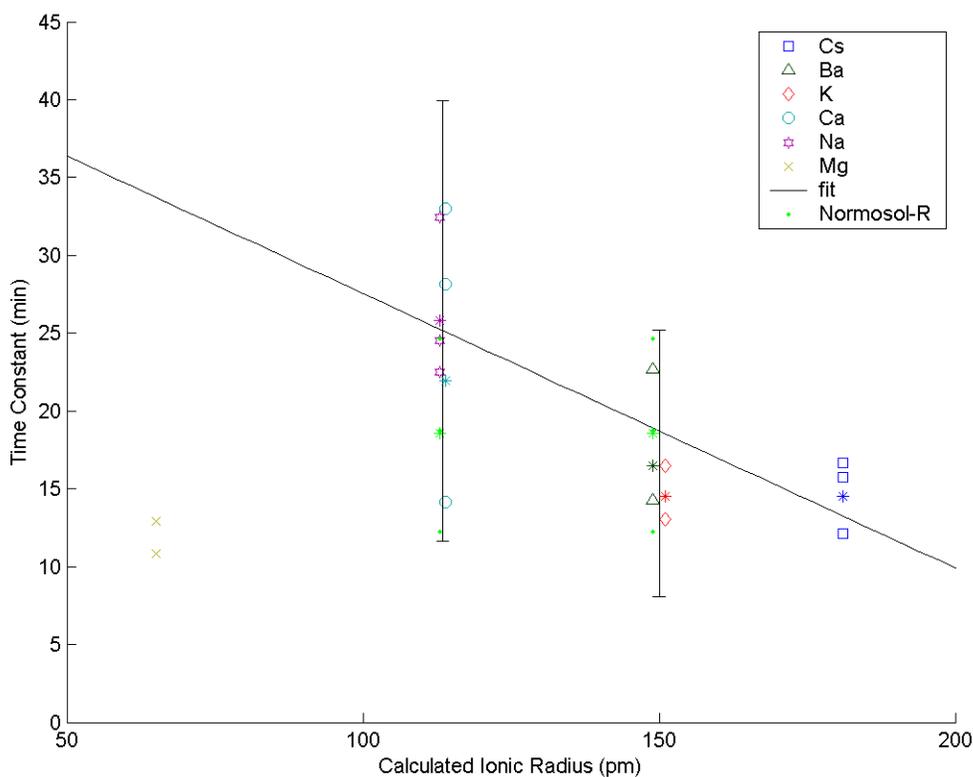


Figure 3.18: Scatter plot of time constants found in testing versus the ionic radius. The time constants for Normosol-R have no known corresponding ionic radius. The * represents the average time constant for each ion, and the vertical black lines are 2σ error bars.

Barium and potassium are considered the candidate ions being the two candidate ions that may be exchanging into the membrane. If the scaling factor is also taken into account to predict the diffusing ion, we find a very close match. When the average response of the polymer in Normosol-R is plotted along with the average response of the polymer in barium and potassium, the responses for barium and Normosol-R appear to be virtually identical (See Figure 3.19). The response of the polymer in sodium is included for comparison as well. But from this examination, it appears that barium is the ion that is diffusing into the membrane.

Because we know the actual composition of the fluid, we know that the ion that is exchanging into the polymer is not barium. Due to the selectivity of the membrane, it is possible that potassium or even magnesium is diffused into the polymer. Nafion™ is a

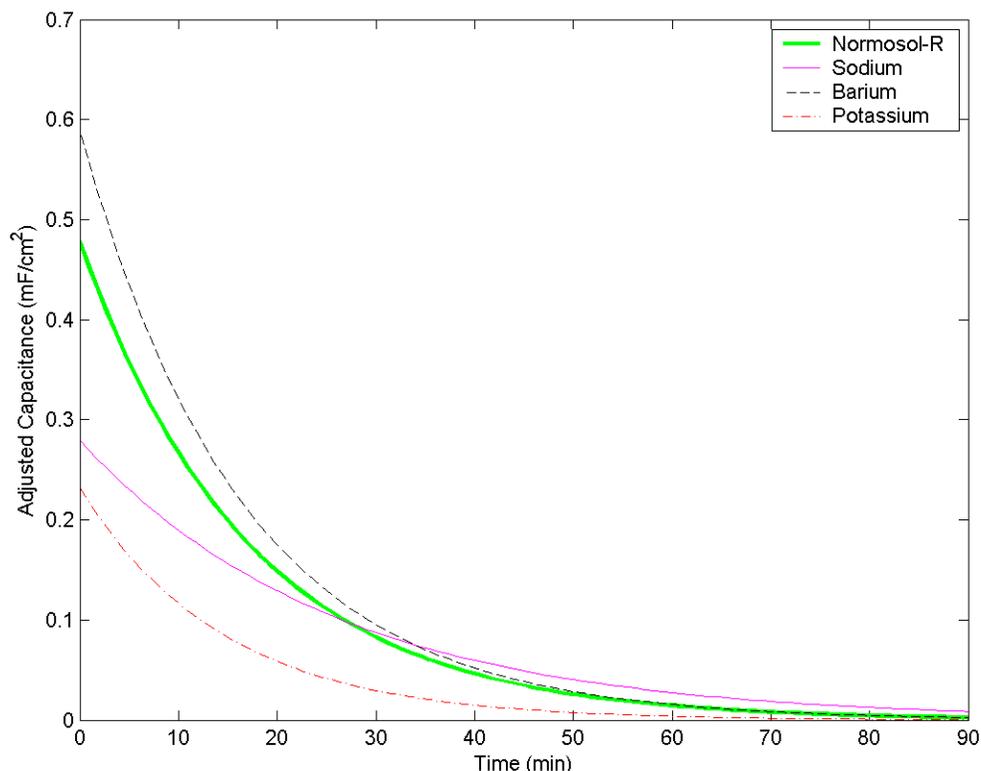


Figure 3.19: Average response of the polymer to a Normosol-R solution compared to the response to other ionic solutions.

selective membrane, and it is known to prefer larger and more highly charged ions [20]. So even though there is a significantly higher concentration of sodium in our complex solution, it is the least likely ion to be selected by the Nafion™.

What this test ultimately shows is that more testing needs to be done. More testing on each individual ion would hopefully show more repeatability and exhibit less spread in the data. This would make it easier to conclusively predict which ion is present in a solution. Also desirable is to conduct more extensive research in complex solutions. The selectivity of the Nafion™ could be further explored to determine what the effects are of a complex solution. It would also be beneficial if an EDS test could be conducted on the polymer after it has been immersed in a complex solution to determine what ions have been exchanged into the polymer.

3.3 SEM Analysis Results

Another goal of this research is to quantify the amount of time it takes for an ion exchange to take place. In doing this, we expect to show that any change of capacitance exhibited by the polymer is due to a change in the ionic conditions within the polymer, and is therefore influenced by the ionic conditions of the solution it is immersed in.

One way of determining ionic changes in the polymer is to compare the dry weight of the polymer before and after an exchange is expected to have taken place [44]. For a full exchange to have taken place, every cation would have to be replaced with a different cation, therefore changing the mass of the sample. The samples need to be fully dehydrated, which can result in a significant margin of error. As soon as the polymer is allowed in open air, the polymer will start to rehydrate due to the water vapor present in the air. We are attempting a different method that should give us a more exact measurement of the atoms present in the polymer.

The experiment described in Section 2.3 was conducted to prove our theory. As described in earlier, a sample of Nafion™ in the lithium form is immersed in a solution of 143mOsm/L CsCl. The sample was removed at 30sec, 1min, 2min, 5min, 10min, 15min, 30min, 45min, 60min, 120min, and 24hr, when a 5mm square section was removed and preserved in deionized water. These samples were then prepared and analyzed using a SEM.

The SEM uses an energy dispersive spectrometer (EDS) to measure the atomic relative composition of the sample. The EDS is capable of recognizing the fluorine, sulfur, and cesium present in the sample. However, the EDS is unable to detect the presence of lithium in the sample, as the atomic size of lithium is too small. An interesting comparison would have been to compare the amount of lithium present in the sample with the amount of cesium present in the sample. We would expect that the amount of lithium would decrease as the amount of cesium in the sample increases.

There are other ways of quantifying that an exchange is taking place. Even though the EDS is unable to detect the amount of lithium present in the sample, it does give us enough information to determine if an exchange has taken place. The structure of Nafion™ is well known (See Figure 3.20). It is known that Nafion™ is composed of a Teflon™ backbone that is interspersed with modified side chains that contain a negatively charged sulfonic acid (SO_3^-). We are interested in the presence of the positive cation that is held to the negatively charged sulfonic acid by electrostatic attraction.

The number of side chains present in the material is not constant, but varies between five and eleven Teflon™ (CF_2CF_2) links for every modified side chain present. The average ratio between a and b can be determined by comparing the amount of fluorine present in the sample to the amount of sulfur present in the sample. The amount fluorine and sulfur present in each sample should remain constant, as these two atoms make up the basic backbone of the material.

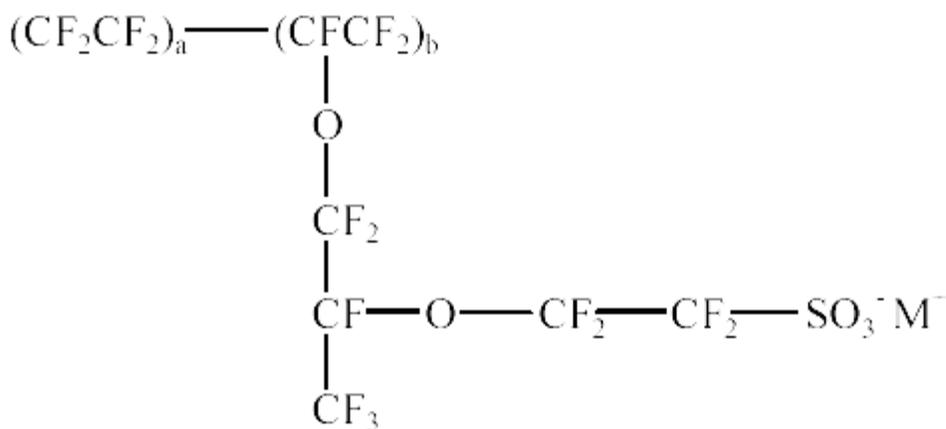


Figure 3.20: The atomic structure of Nafion™.

It is the amount of cesium that we detect that will be constantly changing. For each test, we know that there should be one sulfur atom for every cation present in the sample. There should also be a fixed ratio between the amount of fluorine present in the sample and the number of cations present in the sample. While the total amount of atoms present in the sample should not change, the number of atoms detected by the EDS scan will change as the undetectable lithium is exchanged for detectable cesium.

The amount of these atoms should remain constant, even though the results of the EDS will not show a constant atomic percentage of fluorine or sulfur present in the sample. What is changing is the total amount of atoms detected by the EDS. As an exchange occurs, there is proportionally less fluorine and sulfur and proportionally more cesium detected by the EDS (See Figure 3.21).

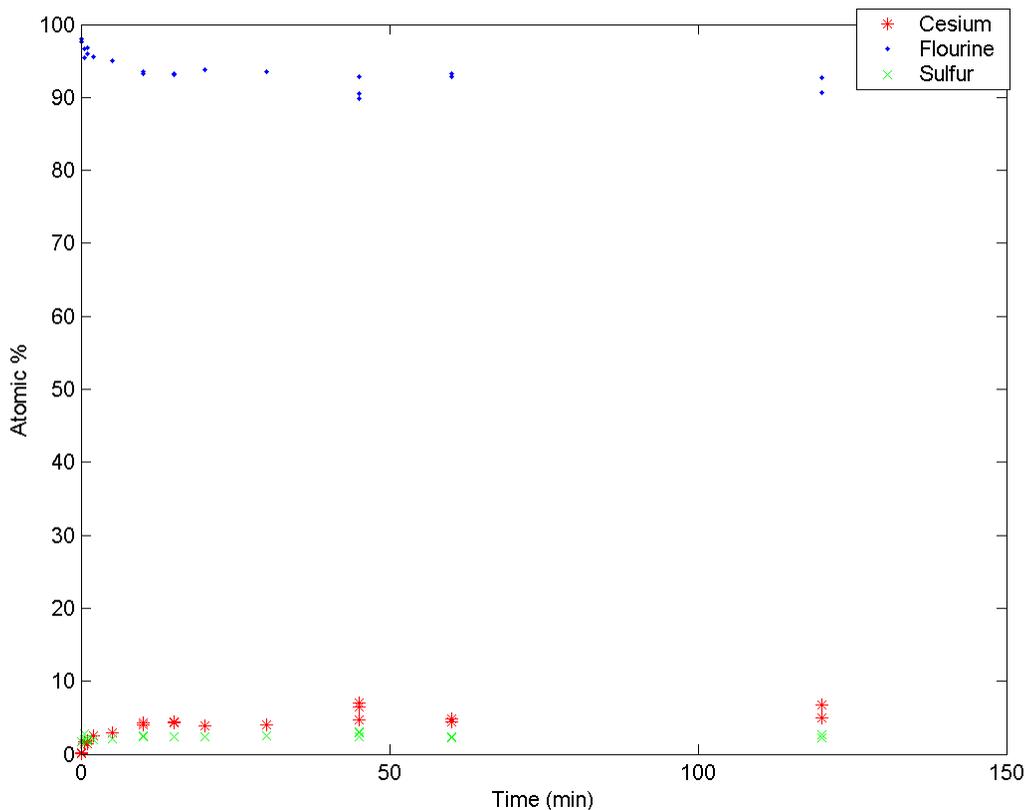


Figure 3.21: The detected atomic percentage of each atom time over time as the polymer undergoes an ion exchange from lithium to cesium.

When the atomic percent of each ion is plotted against time, it becomes apparent that the greatest changes occur in the first twenty minutes that the sample is immersed in the solution. Beyond the twenty minute mark, the percentage of each atom detected by the EDS flattens, except for a jump in the data at 45 minutes. If we consider only the percent of cesium present in the polymer, this result shows that there is no cesium present in the sample at $t=0\text{min}$ and that the amount of cesium increases to a mean final value of 4.96% (Figure 3.22).

Once the percentage of fluorine and sulfur are known, we can determine the ratio between a and b for the polymer sample we are testing. We calculated that on average there are 40.16 fluorine atoms per sulfur atom. The sulfonic acid side chain includes thirteen fluorine atoms, so the remaining 27.16 fluorine atoms belong to the Teflon™ (CF_2CF_2) chain. It can be easily calculated that there is an average of 6.79 a chains for every b chain.

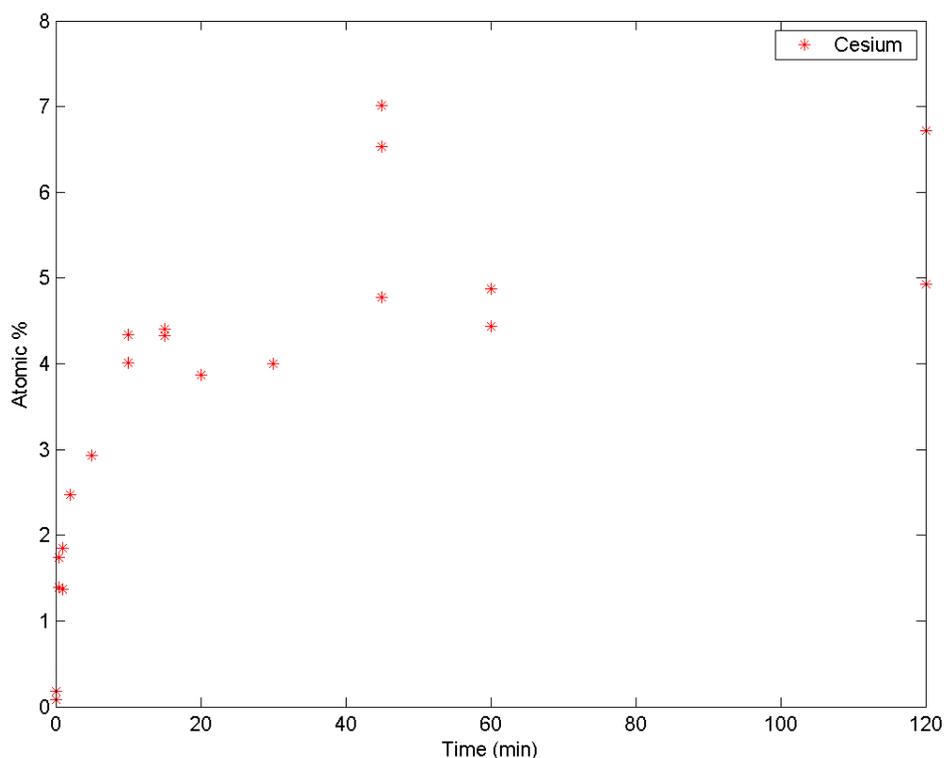


Figure 3.22: Percentage of cesium detected in polymer sample over time.

Once we know the relationship between a and b , we can determine the composition of fluorine, sulfur, and cesium that should be detected by the EDS when a full exchange has taken place. When every undetectable lithium ion that was covalently bonded to the negatively charged sulfonic acid is exchanged for a detectable cesium ion, the EDS should detect 95.26% fluorine, 2.37% sulfur, and 2.37% cesium.

The data collected at 45 minutes does not fit in with this result with or the general trend of the data. This data point is also significantly skewed when used to track the amount of cesium in the sample. The fluorine count in the 45 minute sample is quite low, and when the fluorine count is used to track the amount of cesium present in the material, there is a large spike. When the sulfur count is used to track the amount of cesium present in the material, the spike in the data at 45 minutes is missing.

The difference in the percent of the cesium exchanged when tracked by sulfur or fluorine is perhaps due to the EDS technique. An EDS sends an X-ray to the sample over the area being scanned for two minutes. Once the EDS process is finished, there is a noticeable impression left by the X-ray beam.

A test was conducted on the 45 minute sample to see what the effect of the X-ray beam may be. The results of the EDS are compared if the X-Ray beam is scanned over the same $25\mu\text{m}^2$ area for 30 seconds vs. 150 seconds. (See Figure 3.23 and 3.24) Another test is conducted where a point scan is used, and the X-ray beam is shot at just one point. The result is a noticeable alteration of the polymer at the location of the scan.

When the results of the EDS are compared, it becomes apparent that the X-ray beam is burning up sulfur and fluorine atoms, and leaving behind the metallic cesium atoms. (See Table 3.5) This is most apparent in the results of the intense point scan, where a gaping hole is made in the material and the results of the scan show nearly as much cesium present as fluorine. This would mean that the percentage of cesium in the polymer would be inflated over the true amount of cesium in the polymer at any given point in the data presented here.

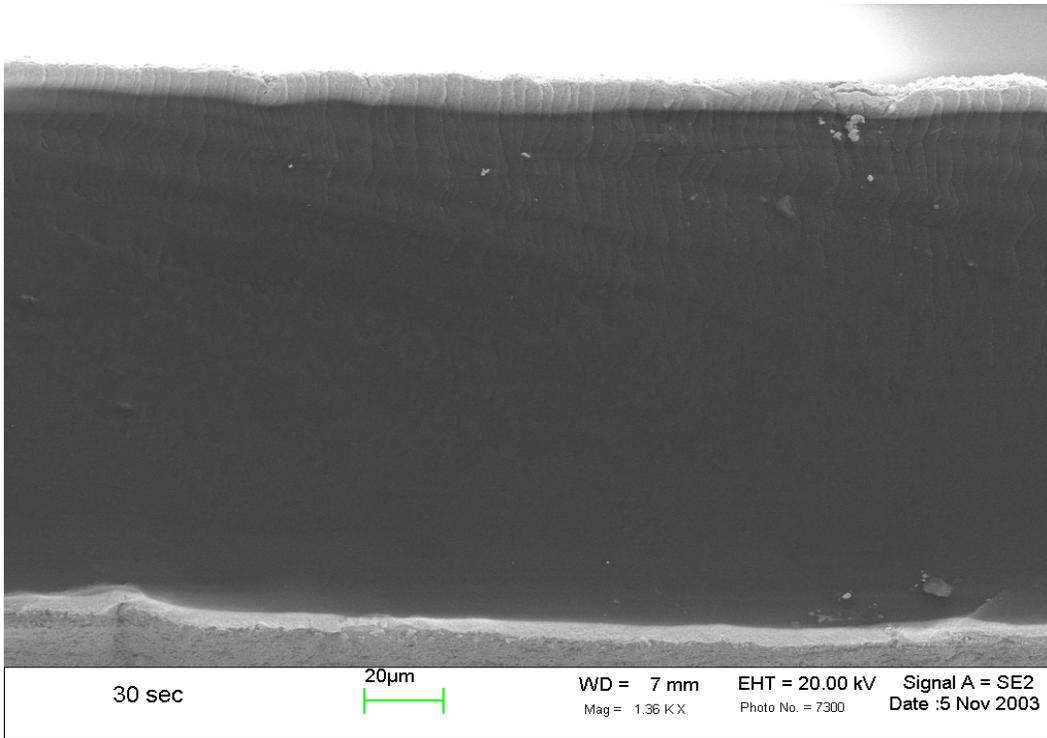


Figure 3.23: SEM image of the polymer before the material is scanned. The light area on the top and bottom of the polymer is the electrode.

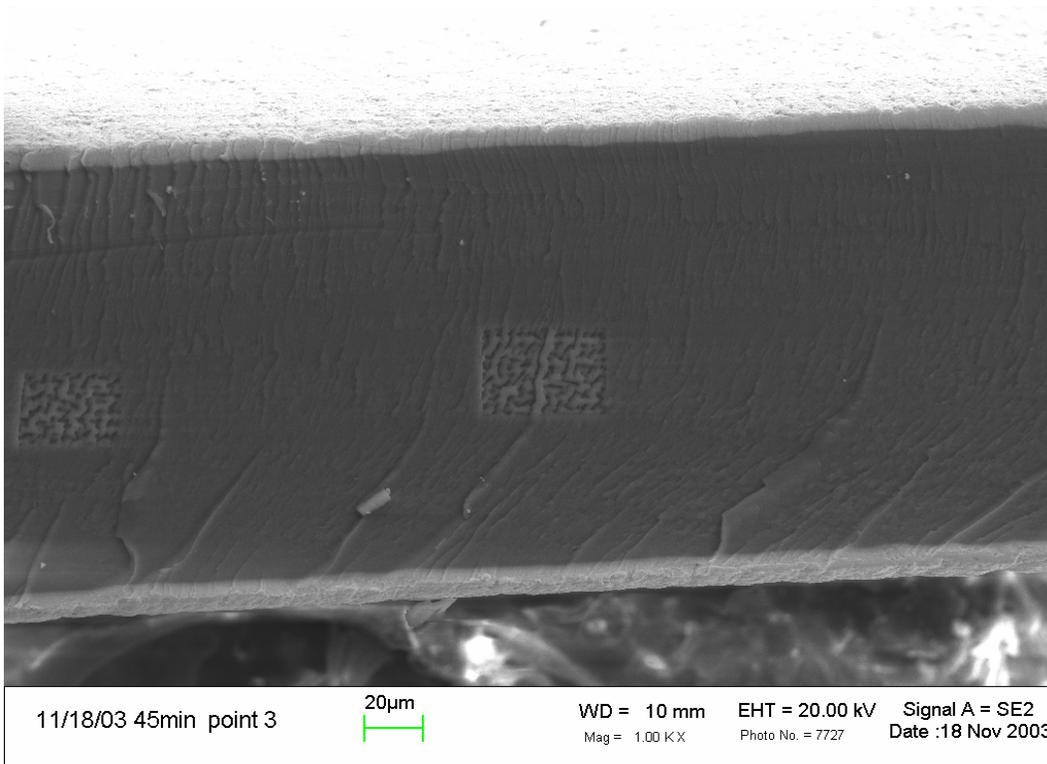


Figure 3.24: SEM image of the polymer after it has been scanned for 120 seconds showing an imprint left by the X-ray beams.

Table 3.5: Results of different EDS approaches on a Nafion™ sample immersed in 143mOsm/L CsCl for 45 minutes

| Atomic % | 30 second scan 25µm ² area | 120 second scan 25µm ² area | 150 second scan 25µm ² area | 120 second Point Scan |
|----------|--|---|---|--------------------------|
| F | 92.5 | 92.8 | 92.4 | 47.6 |
| S | 3.06 (129%) | 2.38 (100%) | 2.03 (85.7%) | 6.97 (294%) |
| Cs | 4.41 (186%) | 4.77 (201%) | 5.54 (234%) | 44.1 (1860%) |

The point scan shows the most drastic deviation from the other results. The significantly lower atomic percentage of fluorine seems to indicate that the fluorine is most susceptible to being burned off by the X-ray. The fact that the fluorine burns off during the EDS explains the spike in the results that show significantly more cesium exchanged into the polymer than we would expect to see at 45 minutes and at 120 minutes. This spike is smaller when the amount of cesium present is compared to the sulfur present in the polymer because the sulfur does not burn off as rapidly.

A more pertinent result is shown if the percent of the cesium detected in the polymer versus the percent expected in the polymer if a full exchange had taken place. The fraction of the total exchange can be calculated by dividing the percent of cesium present by the total percentage of cesium expected if a full ionic exchange had taken place. This calculation can be done as a comparison to the fluorine or sulfur present in the sample.

Two interesting results emerge from this calculation. The first is that there appears to be more cesium present in the material than predicted by the atomic formula of Nafion™. Beyond 45 minutes, there is more than double the amount of cesium detected by the EDS than we would expect. On average, 203% of a full exchange has taken place beyond 45 minutes. This may be partially explained by the EDS process burning away the sulfur and fluorine and leaving behind the atomic cesium ions (See Table 3.5).

The other interesting result is that approximately 80% of the mean final detected amount of cesium is present after the polymer has been immersed in the solution for 20 minutes (See Figure 3.25). This is consistent with the results seen in the impedance testing of the material in cesium. The capacitance results showed a large initial change in the first 10-30 minutes the polymer is immersed in an ionic solution, followed by a slow change in the capacitance towards the final capacitance of the material.

This result is consistent with previous results in the field. The concentration of the cesium chloride (CsCl) solution is 143mOsm/L, which is equal to a 0.0715M solution of cesium chloride. When studying plating techniques, Millet has studied the diffusion rate of platinum tetramine $[Pt(NH_3)_4]^{2+}$ into Nafion™ using a Camebax electron microprobe analyzer [21]. Millet found that for a stirred 0.0375M solution of platinum tetramine would fully exchange into the membrane in 20 minutes. Millet does not

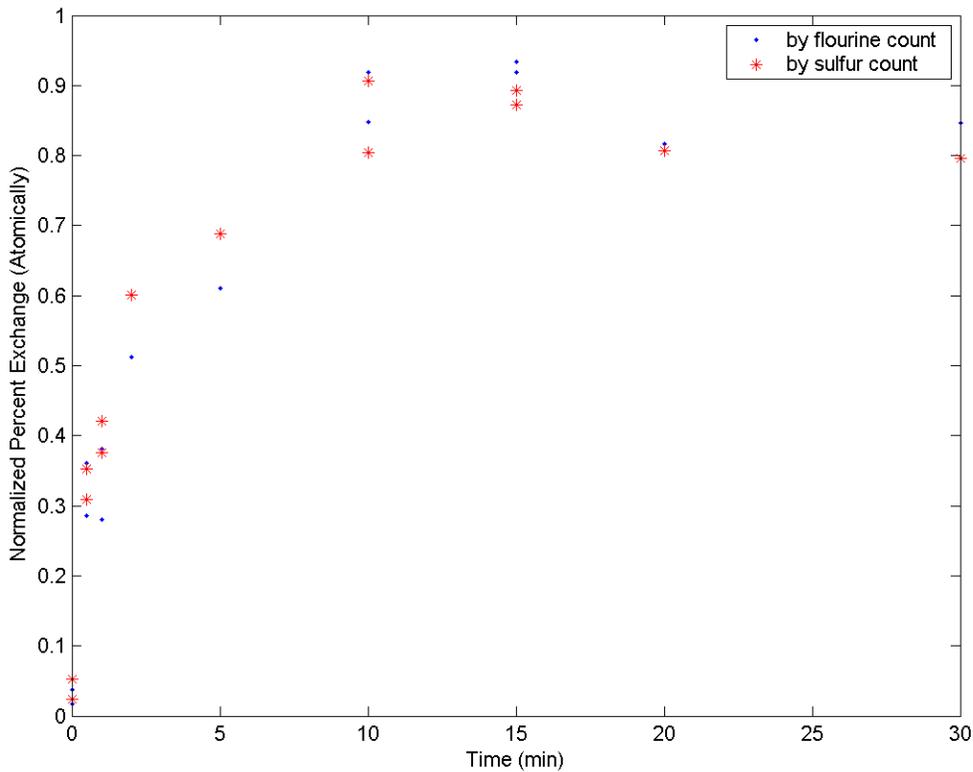


Figure 3.25: The percentage of cesium present in the material calculated by the amount of sulfur or fluorine, normalized to the average amount of cesium found in the material at $t=\infty$

mention how the membrane was prepared for this research, and the membrane is unplated, so the conditions are definitely not the same. But what can be determined by this comparison is that the exchange occurs in tens of minutes, which is the same order of magnitude of time as witnessed by others.

The result of the SEM testing quantified by the fractional exchange of cesium into the polymer appears to be an exponentially increasing function of time that settles out to a 203% exchange (See Figure 3.26). A curve could be fit to these results evaluating the amount of cesium exchanged into the polymer as a function of time if the equation is of the form

$$N = 1 - Ae^{-\frac{t}{\tau}} \quad \text{Eq (11)}$$

where N is the fraction of the total exchange that has occurred, A is a scaling factor, τ is the time constant of the exchange in minutes, and t is the time that has elapsed since the polymer was immersed in the solution in minutes.

A curve is fit to this line by using the polyfit command in Matlab to fit a first degree polynomial to the natural log of the fractional exchange of cesium. The natural log of the fractional exchange of cesium is linear for the first twenty minutes, so the fit only included data from the first twenty minutes. The equation of the line fit to the results of the SEM analysis is

$$N = 1 - 0.724e^{-\frac{t}{13.95}} \quad \text{Eq. (12)}$$

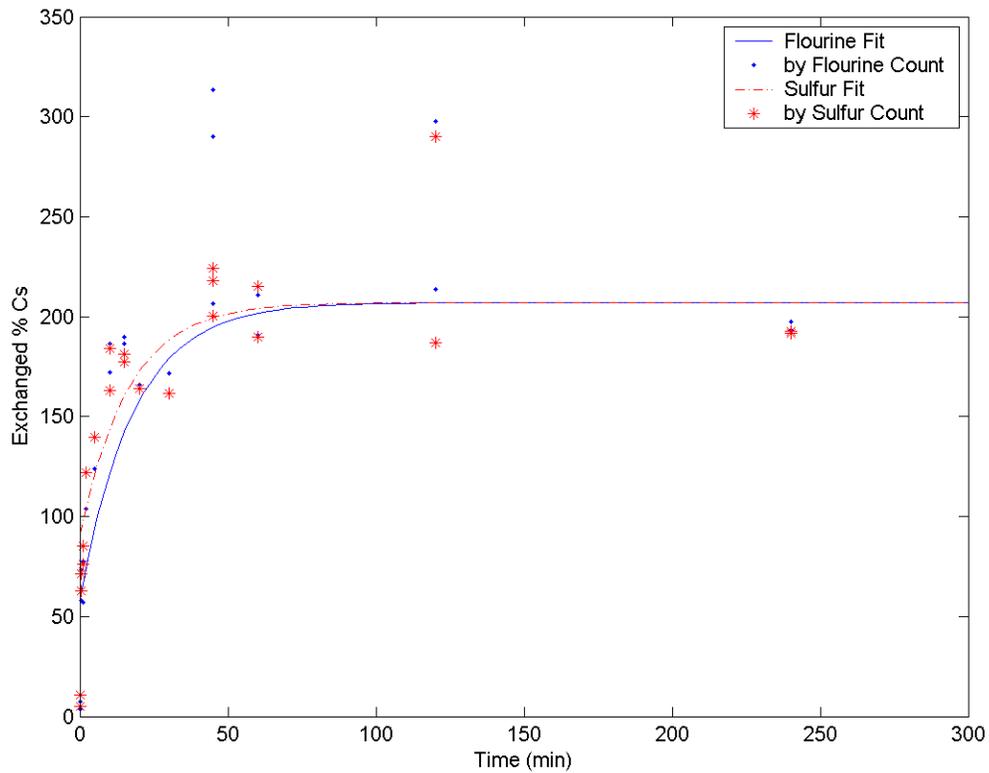


Figure 3.26: Percentage of cesium exchanged into the material

An interesting comparison between the time constant for the exchange of cesium into the polymer and the average time constant for the change of impedance of the polymer while immersed in cesium chloride reveals that the two time constants are very close. The time constant for the exchange of the cesium into the polymer is 13.95min and the time constant for the change of the capacitance of the polymer while immersed in a cesium chloride solution is 13.53min. The time constant of the change of capacitance of cesium predicted using Equation 9 is would be 13.91min.

This time constant is virtually the same as the time constant of the exchange of cesium into the polymer for the same concentration solution. That means that the rate of the exchange of the cation into the membrane is virtually the same as the rate of change of the capacitance of the polymer. This suggests a direct relationship between the change in capacitance of the polymer and the exchange of the cation into the polymer.

This EDS analysis of a plated sample of Nafion™ immersed in an ionic solution verifies that a change of capacitance during an ion exchange is caused by the ion exchange in the polymer. If the polymer is subjected to conditions that will force an ionic exchange, the polymer will be able to sense the exchange. This result validates the idea that an ionic polymer can be used to detect changing ionic conditions in a fluid by monitoring the capacitance of the polymer.

Chapter 4: Conclusions

The primary goal of this thesis is develop ionic polymers for use in a new application and demonstrate the performance of the polymers in this new role. We want to show that ionic polymers can be used as ion sensors and to develop a method that can be employed to sense changes in internal ionic conditions. Of particular interest is how this technology could be applied to biomedical sensing relating the ionic response of the body to different external stimuli.

One motivating application for a polymeric, non-invasive *in vivo* ion sensor would be to further bone healing research. A biological sensor that could be surgically implanted at the site of a fracture that could monitor the presence of ions at the fracture site as the bone heals. This would allow medical researchers to determine what conditions best facilitate bone healing. The advancement of this research would not only determine what kind of external fixator allows the bone to completely heal the fastest, but would also allow the medical community to understand the internal conditions that stimulate the bone to heal, and the external conditions that instigate these internal conditions.

The validity of the notion that an ionic polymer could be used as an ionic sensor was proved experimentally using DuPont's® commercially available material, Nafion™. Tracking the capacitance over time is an indicator of an ion exchange within the polymer. This is proved by an energy dispersive spectrometer (EDS) showing an increase of the amount of the diffusing ion present in the material the longer the material is immersed in the ionic solution.

While we were able to show the validity of the idea, more extensive testing is needed to better quantify the response of the polymer in ionic solutions. We showed the potential of the time constant of the change of capacitance being used to predict the ionic size of the exchanging ion. However, until more data is collected, the margin of error is too great to be able to know exactly what ion is present.

4.1 Key Results and Conclusions

Much of the research that has been conducted on ionic polymers concerns only the steady state ionic form of the polymer. For example, the sensitivity of ionic polymers in different ionic forms has been considered [7, 33], but the sensitivity as the polymer exchanges one cation for another has not been studied.

The major contribution of this research is defining the transient response characteristics of ionic polymers during an ion exchange. This transient response can be correlated to the ion exchange properties of the polymer. In the end, we show that ionic polymers have a great deal of potential to be used as non-destructive ionic sensors.

This potential is shown experimentally from the results of tensile sensitivity testing and impedance testing. The tension testing conducted for this thesis revealed several characteristics of ionic polymers. Baseline testing shows that the polymer exhibits a charge response in tension similar to the response it has in bending. The tensile sensitivity calculated was approximately the same order of magnitude as the bending sensitivity at approximately the same stress levels.

When the sensitivity is tracked over time in a deionized fluid, the sensitivity was found to remain flat. Distinct from this flat response, we see a noticeable change in the sensitivity of the polymer over time if it is immersed in an ionic solution. However, the nature of these changes is found to be inconsistent from test to test. There are indications that the sensitivity may exhibit an exponential decay over time, but there is not enough agreement in the data for this result to be conclusive.

Impedance testing revealed that the capacitance of an ionic polymer sample as the sample undergoes an ion exchange. We found a correlation between the ionic content of a solution and the change in the capacitance of the ionic polymer. When the Nafion™ is immersed in an ionic solution with a high enough concentration of free cations to drive

an ion exchange in the material, the time dependent response of the capacitance exhibits an exponential change as a function of time. This is in contrast to the flat time dependent response of the polymer when it is immersed in deionized water. This is conclusive evidence that the polymer can sense a change in ionic conditions.

The response of the polymer in different solutions was quantified by comparing the time constants of the experimental data to the ionic size of the ion being exchanged into the membrane. Using the relationship between ionic size and the experimental time constant of the change in capacitance, the experimental time constant of the response in an unknown fluid can be used to calculate the radius of the ion being diffused into the membrane. This idea was tested using a complex solution with several different ions dissolved in it, and the results of the test show the potential of the polymer to be used as an ionic sensor.

However, further testing is required to prove the utility of the data. While some general conclusions can be drawn by the characterization of the exponential decay, more testing needs to be conducted before any certain ion sensing parameters can be defined. With the modest amount of data collected for this thesis, the statistical deviation of the data is too great to conclusively determine the ion being exchanged into the membrane.

The idea that these changes in capacitance or sensitivity were due to an ion exchange was proved using an EDS. The results of the EDS showed that the majority of the ion exchange takes place in the first 15-20 minutes that the polymer is immersed in an ionic fluid. This is the same amount of time that the majority of the change of the capacitance of the material occurs.

When the time constant of the ion exchange is compared to the time constant of the change of capacitance for the same ion, it was found that they are within 0.280%. What can be gathered from this result is that the capacitance of the material is directly correlated to the amount of the diffusing ion present in the polymer.

All of these conclusions validate the theory that an ionic polymer would make an effective ionic sensor. Also supported is the notion that ionic polymers would make effective biosensors. The impedance testing does not require bulky equipment to take the measurements, the polymer is inert, and any testing conducted does not modify the environment the testing is being conducted in.

4.2 Future Work

The practical application of this technology in medical research is not hard to imagine. Consider the specific application of bone healing research. Three polymers with three separate electrodes could be implanted in the vicinity of a bone fracture with minimal invasiveness. The set of polymers would allow enough data to be collected simultaneously to determine a time constant for any ion exchanges that occur while data is being collected with a reasonable degree of certainty.

The researcher could conduct an experiment where the subject could walk for fifteen minutes, applying a periodic pressure to the bone. Data could be collected over these fifteen minutes to determine the capacitance response of the polymer. The characteristics of a change in capacitance could be used to determine the ionic response of the body. In conjunction with strain gauge data tracking the healing of the bone, this would greatly advance the knowledge of the bone healing process.

Backing up this biological sensor idea is testing that was conducted on several cations that are found in the body, such as sodium, calcium, potassium, and magnesium. The transient response of the polymer to each of these ions was found to be unique. Testing in a complex fluid that has a similar composition to blood was also conducted, and the response of the polymer was qualitatively the same.

However, more research needs to be conducted to ensure the repeatability of the data before the technology can be implemented for medical research. A key factor in the usability of equipment for *in vivo* medical research is repeatability. While we have established a trend relating the time constant of the capacitance to the size of the ion that could be used for ionic sensing, the standard deviation of the data is too great at this point to determine exactly which ion is exchanging into the polymer.

More experiments need to be run under these same conditions to verify that the desired repeatability can be achieved. With more testing, we would hope to determine with certainty the relationship between ionic radius and the time constant of the change in capacitance. This would be achieved if more testing showed better clustering of the time constants when plotted against ionic size. This would reduce the standard deviation of the data and would allow the ionic radius of an unknown exchanging ion to be predicted by the experimental time constant of the change in capacitance.

Another factor that would determine the effectiveness of electroactive ionic polymers as ionic sensors will be the response of the polymer in solutions with different ion concentrations. All of the tests performed for this research were conducted in solutions that had the same high concentration of ions. Experiments need to be performed in ionic solutions of different concentrations to determine how the response of the polymer changes.

There would be two attributes to look for in these experiments. One interesting result to focus on would be the sensitivity of the polymers to a relatively small change in ionic conditions. What we would hope to find out is how low a concentration gradient can drive an ionic exchange, and if an ionic exchange driven by a really low concentration gradient displays the same qualitative response to the ionic exchange as is exhibit by an ion exchange driven by a large concentration gradient.

The second result to focus on would be whether or not changing the concentration results in a great shift in the time constants of the exchange. Other research has shown

that the rate of diffusion is directly influenced by the concentration of the fluid in which the exchange is conducted [21]. One of the results of this research indicates that the time constant of the change of capacitance is directly related to the rate of diffusion of the exchanging ion into the polymer. If both of these results are true, quantifying the time constant of an ionic exchange would depend on both the concentration of the solution and the ions being exchanged. Different parameters may need to be added to correlate these two variables to specific ions.

Further work could be conducted to better determine the response of the polymer to complex solutions with several ions as well. The response of Nafion™ in complex solutions may be more intricate than its response in solutions with only one ion. It is possible that more than one ion may diffuse into the membrane at the same time, or it may be possible that the polymer is selective and prefers to bond to certain ions or certain types of ions. This may influence the transient response of the polymer when it is immersed in a complex solution. It would be interesting determine what the response is to different complex solutions, as well as to determine by SEM analysis what ions exchange into the membrane in different complex solutions.

Another variable that could be introduced is the ionic polymer that is used. Only Nafion™ was considered for this research, but there are other electroactive ionic polymers that exist. They may exhibit different, more desirable properties of selectivity than Nafion™. They may result in more drastic differences in the response of the polymer when it is exposed to different ions. Perhaps Nafion™ will be the most useful polymer certain applications as well.

Even though the hydrogen form of Nafion was deemed too unstable to produce any conclusive results in the sensitivity portion of this research, it is possible that it is a more functional form when used in impedance testing. Different ionic forms of the polymer could be used as starting points to determine the changes that occur in the transient response when the ion leaving the polymer is changed. Two different polymers in different forms would likely be able to determine the contents of an unknown solution

with more certainty due to the addition of another parameter for classifying the exchanging ion.

Further research in the area of using different forms of the polymer as a starting point could also produce meaningful results for the implementation of this technology in medical research. For example, if a sensor is developed to be used in bone healing research, it would be desirable that it be surgically implanted once and used for research for a period of months rather than hours. As such, it probably would not remain in one form over the duration of the research. It would be important to verify that it could be used as a sensor beyond just an initial exchange. This may also prove to be highly dependent on the selectivity of the membrane.

It would also be interesting to know if the polymer would be capable of sensing changes in the concentration of an ion once a full exchange has occurred. Brief experimenting conducted in the sensitivity portion of the research indicated that the sensitivity did show a slight change when additional NaCl was added to the bath. But a better controlled battery of tests would need to be conducted to verify this result and to determine if the response can be quantified and correlated to a change in ionic concentration.

As some of these additional questions brought up by this research are answered, the application of polymeric ionic sensors may become desirable. As with any new application of a technology, significant research needs to be conducted to determine how the technology will apply to its new application.

Bibliography

- [1] Abramova, N.; Borisov, Yu.; Bratov, A.; Gavrilenko, P.; Dominguez, C.; Spiridonov, V.; Suglobva, E., 2000, "Application of an ion-selective field effect transistor with a photocured polymer membrane in nephrology for determination of potassium ions in dialysis solutions and in blood plasma", *Talanta*, Vol. 52 pp. 533-538
- [2] Aranzulla, P.J.; Muckle, D.S.; Cunningham, J.L., 1998, "A portable monitoring system for measuring weight-bearing during tibial fracture healing", *Medical Engineering and Physics*, Vol. 20, pp. 543-548
- [3] Bao, Xiaoqi; Bar-Cohen, Yoseph; Lih, Shyh-Shiuh, 2002, "Measurements of Macro Models of Ionomeric Polymer-Metal Composites (IPMC)", *Proceedings of SPIE Smart Structures and Materials Symposium, EAPAD Conference, San Diego, CA, March 18-21, 2002*.
- [4] Bennet, Matthew, 2002, "Manufacture and Characterization of Ionic Polymer Transducers Employing Non-precious Metal Electrodes", M.S. Thesis, Virginia Polytechnic Institute, Blacksburg, VA
- [5] Bennet, M D; Leo, D J, 2003, "Manufacture and characterization of ionic polymer transducers employing non-precious metal electrodes", *Smart Materials and Structures*, Vol. 12, pp. 424-436
- [6] DuPont, "Nafion Membranes NE-112, NE-1135, N-115, N-117", *Product Information*.
- [7] Farinholt, K.M.; Leo, D.J., 2003, "Modelling of electromechanical charge sensing in ionic polymer transducers", 2003 SPIE Smart Materials and Structures Conference, paper #5053-3
- [8] Farinholt, K.M., Newbury, K.M., Bennett, M., Leo, D.J. (2002) "An Investigation into the Relationship between Charge and Strain in Ionic Polymer Sensors", *Proceedings of the First World Congress on Biomimetics and Artificial Muscles*
- [9] Galeska, Izabela; Chattopadhyay, Debjit; Moussy, Francis; Papadimitrakopoulos, Fotios, 2000, "Calcification-Resistant Nafion/Fe³⁺ Assemblies for Implantable Biosensors", *Biomacromolecules*, Vol. 1, pp. 202-207
- [10] Goodship A.E.; Kentwright, J., 1985, "The influence of induced micromovement upon the healing of experimental tibial fractures", *Journal of Bone and Joint Surgery*, Vol. 67B, pp. 650-655

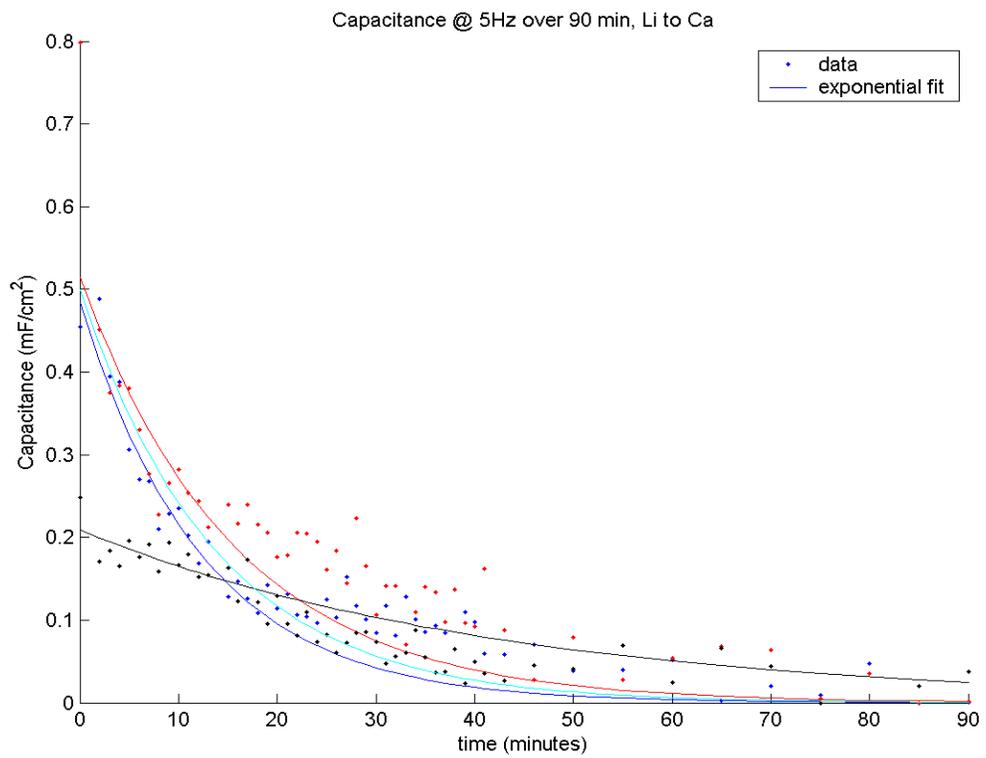
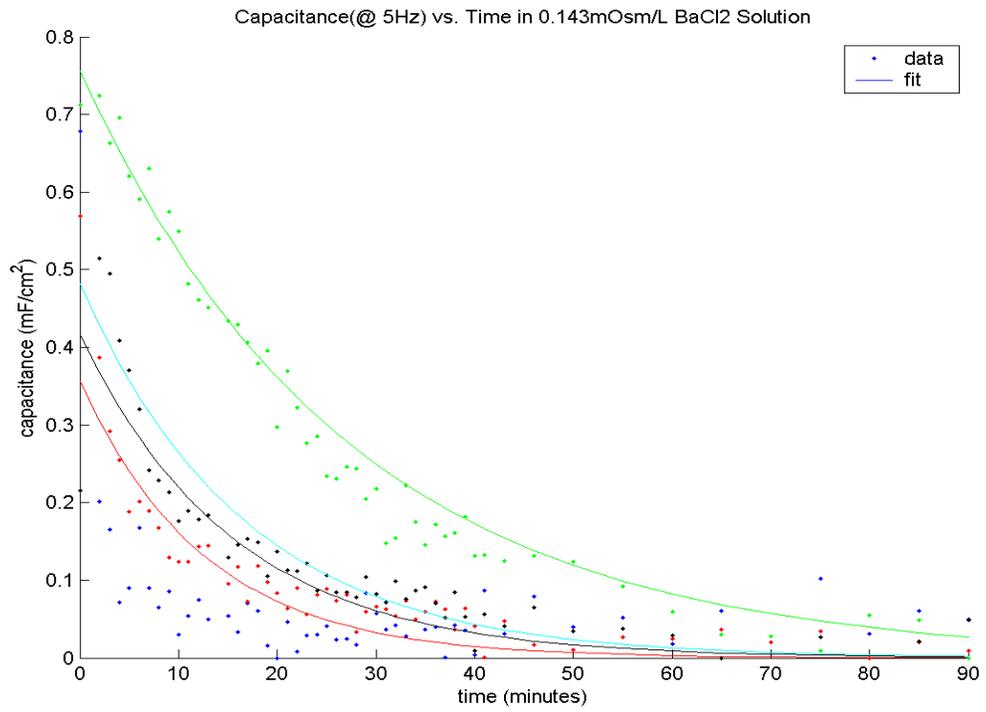
- [11] Grodzinsky, A.J.; Melcher, J.R., 1974, "Electromechanics of deformable charged polyelectrolyte membranes", Proceedings of the 27th Annual Conference on Engineering in Medicine and Biology, Alliance for Engineering in Medicine and Biology, paper 53.2, Vol. 16, pp. 485.
- [12] Grodzinsky, A.J.; Melcher, J.R., 1976, "Electromechanical transduction with charged polyelectrolyte membranes", IEEE Transactions on Biomedical Engineering, Vol. 23, No. 6, pp. 421-433
- [13] Heng, Lee Yook; Hall, Elizabeth A. H., 2000, "Producing "Self Plasticizing" Ion-Selective Membranes", Analytical Chemistry, Vol. 2, No.1, pp. 42-51
- [14] Hisamoto, Hideaki; Horiuchi, Takayuki; Uchiyama, Kenji; Tokeshi, Manabu; Hibara, Akihide; Kitamori, Takehiko, 2001, "On-Chip Integration of Sequential Io-Sensing Based on Intermittent Reagent Pumping and Formation of Two-Layer Flow", Analytical Chemistry, Vol. 73, No. 22, pp. 5551-5556
- [15] James, P.J.; Elliott, J.A.; McMaster, T.J.; Newton, J.M.; Elliot, A.M.S.; Hanna, S.; Miles, M.J., 2000, "Hydration of Nafion® studied by AFM and X-ray scattering", Journal of Materials Science, Vol. 35, pp. 5111-5119
- [16] Kamalesh, S.; Tan, P.; Wang, J.; Lee, T.; Kang, E.T.; Wang, C.-H., 5 Dec, 200, "Biocompatibility of Electroactive Polymers in Tissues", Journal of Biomedical Materials Research, vol. 52, no. 3, pp. 467-478
- [17] Kashyap, Rohit; Gratzl, Miklos, 1999, "Adjusting the Distance of Electrochemical Microsensors from Secreting Cell Monolayers on the Micrometer Scale Using Impedance", Analytical Chemistry, Vol. 71, No. 14, pp. 2255-2261
- [18] Matsumoto, T.; Ohashi, A.; Ito, N.; Fujiwara, H., 2001, "A long-term lifetime amperometric glucose sensor with perfluorocarbon coating", Biosensors and Bioelectronics, Vol. 16, pp. 271-276
- [19] Mecado, R.C.; Moussy, F., 1998, "In vitro and in vivo mineralization of Nafion membrane used for implantable glucose sensors", Biosensors and Bioelectronics, Vol. 13, No. 2, pp. 133-145
- [20] Millet, P. Andolfoatto, F.; Durand, R., 1995, "Preperation of solid polymer electrolyte composites: investigation of the ion-exchange process", Journal of Applie Electrochemistry, Vol. 25, pp. 227-232
- [21] Millet, P.; Durand, R.; Dartyge, E.; Tourillion, G.; Fantaine, A., 1993, "Preperation of Metallic Platinum into Nafion Ionomer Membranes", Journal of Electrochemical Society, Vol. 140, pp. 1373-1379

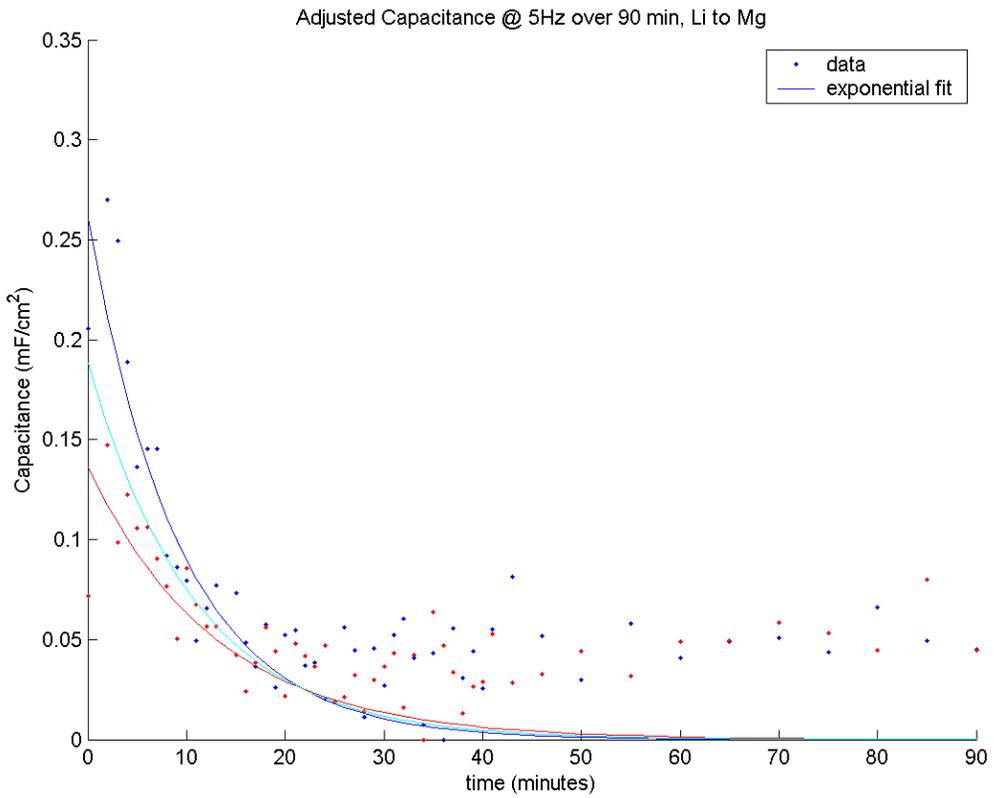
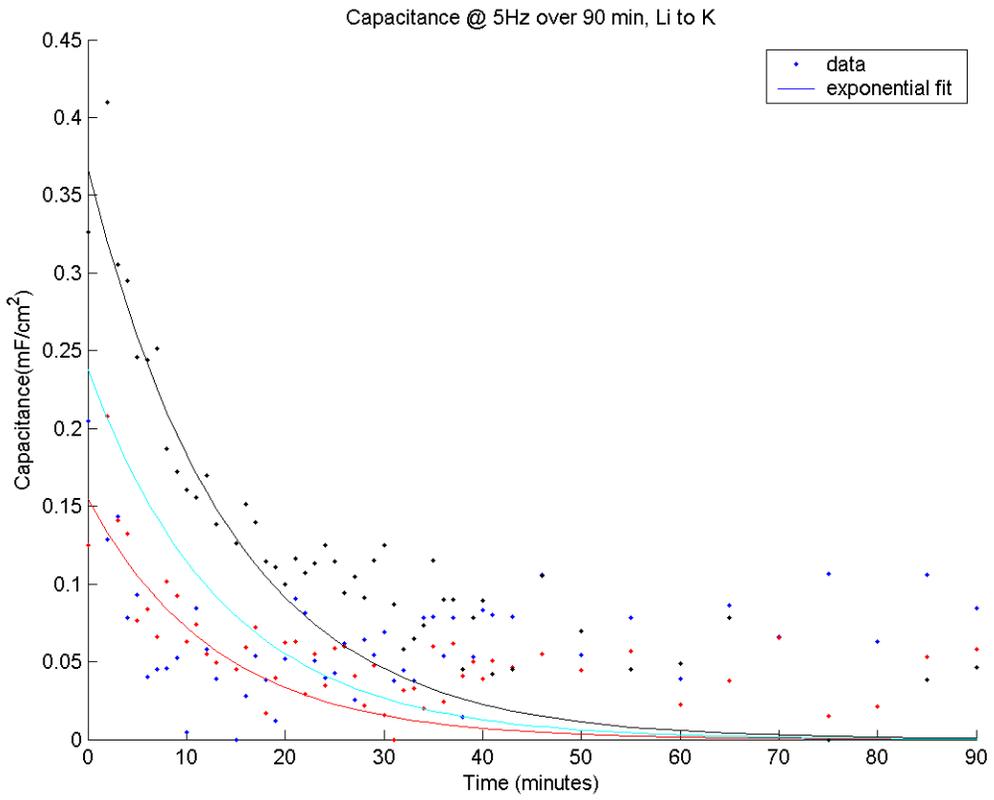
- [22] Moussy, Francis; Jakeway, Stephen; Harrison, D. Jed; Rajotte, Ray V., 1994, "In Vitro and in Vivo Performance and Lifetime of Perfluorinated Ionomer-Coated Glucose Sensors after High-Temperature Curing", *Analytical Chemistry*, Vol. 66, No. 22, pp. 3882-3888
- [23] Newbury, Kenneth, M.; Leo, Donald J., 2002, "Electromechanical Modeling and Characterization of Ionic Polymer Benders", *Journal of Intelligent Systems and Structures*, Vol. 13, No. 1, pp. 51-60
- [24] Newbury, Kenneth, 2002, "Characterization, Modeling, and Control of Ionic Polymer Transducers", PhD Dissertation, Virginia Polytechnic Institute, Blacksburg, VA
- [25] Oguro K.; Kawami, Y.; Takenaka, H., 1992, "Bending of an ion-conducting polymer film electrode composite by an electric stimulus at low voltage", *Journal of Micromachine Society*, Vol. 5, pp. 27-30
- [26] Onishi, Kazuo; Sewa, Shingo; Asaka, Kinji; Fujiwara, Naoko; Oguro Keisuke, 2001, "The effects of counter ion on characterization of a solid polymer electrolyte actuator", *Electrochimica Acta*, Vol. 46, pp. 1233-1241
- [27] Pollack, S., 2001, "Streaming Potentials in Bone," *Bone Mechanics Handbook*, pp.24-1-24-22
- [28] Prendergast, P.; Meulen, M., 2001, "Mechanics of Bone Regeneration," *Bone Mechanics Handbook*, pp. 32-1-32-13
- [29] Radasch, R., 1999, "Biomechanics of Bone and Fractures," *Veterinary Clinics of North America: Small Animal Practice*, vol. 29, no. 5, pp. 1045-1082
- [30] Sadeghipour, K.; Salomon, R.; Neogi, S., 1992, "Development of a novel electrochemically active membrane and 'smart' material based vibration sensor/damper", *Smart Materials and Structures*, Vol. 1, pp.172-179
- [31] Schong, Michael J.; Arzdorf, Michael; Mulchandani, Priti; Chen, Wilfred; Mulchandani, Ashok, 2003, "Towards a Capacitive Enzyme Sensor for Direct Determination of Organophosphorus Pesticides: Fundamental Studies and Aspects of Development", *Sensors*, Vol. 3, pp. 119-127
- [32] Segalman, D.; Witkowski, W.; Adolf, D.; Shahinpoor, M., 1992, "Theory of electrically controlled polymeric muscles as active materials in adaptive structures", *Smart Materials and Structures*, Vol. 1, pp. 44-54
- [33] Shahinpoor, Moshen; Kim, Kwang J., 2000, "Effects of Counter-ions on the Performance of IMPCs", *Smart Structures and Materials 2000: Electroactive Polymer Actuators and Devices*, *Proceedings of SPIE* Vol. 3897, pp. 110-120

- [34] Shastri, VP; Rahman, N; Martin, I; Langer, R, 1999, "Application of Conductive Polymers in Bone Regeneration", Materials Research Society Symposium Proceedings, Vol. 550, pp. 215-219
- [35] Steck, A.; Yeager, H.L., 1980, "Water Sorption and Cation-Exchange Selectivity of a Perfluorosulfonate Ion-Exchange Polymer", Analytical Chemistry, Vol. 52, No. 8, pp. 1215-1218
- [36] Thevenot, Daniel R.; Toth, Klara; Durst, Richard A.; Wilson, George S., 2001, "Electrochemical biosensors: recommended definitions and classification", Biosensors and Bioelectronics, Vol. 16, pp. 121-131
- [37] Thompson, J.M.; Smith, S.C.H.; Cramb, R.; Hutton, P., 1994, Ann. Clin. Biochem Vol. 31, pp. 12
- [38] Turner, R. F. B.; Harrison, D.J.; Rajotte, R. V., 1991, "Preliminary in vivo biocompatibility studies on perfluorosulfonic acid polymer membranes for biosensor applications", Biomaterials, Vol. 12, pp. 361-368
- [39] Valdes, T.I.; Moussy, F., 1999, "A ferric chloride pre-treatment to prevent calcification of Nafion membrane used for implantable biosensors", Biosensors and Bioelectronics, Vol. 14, pp.579-585
- [40] Yeager, H.L.; Steck, A., 1981, "Cation and Water Diffusion in Nafion Ion Exchange Membranes: Influence of Polymer Structure", Electrochemical Science and Technology, Vol. 128, pp. 1880-1884
- [41] Yeager, H.L.; Kipling, B., 1979, "Ionic Diffusion and Ionic Clustering in a Perfluorosulfonate Ion-Exchange Membrane", Journal of Physical Chemistry, Vol. 83, No. 14, pp. 1836-1839
- [42] Yeager, H.L.; Stack A., 1979, "Ion-Exchange Selectivity and Metal Ion Separations with a Perfluorinated Cation-Exchange Polymer", Analytical Chemistry, Vol. 51, No. 7, pp. 862-865
- [43] Website: <http://www.webelements.com/>
- [44] Nemat-Nasser, S.; Wu, Y., 2003 "Comparative experimental study of ionic polymer-metal composites with different backbone ionomers and in various cation forms", Journal of Applied Physics 93, 5255-5267
- [45] Baker, Andrea, June 13, 1994, " 'Bone Welder' speeds healing", Design News, Vol. 49, pp. 100-102

Appendices

Figures A.1-A.5: Compiled Capacitance Figures





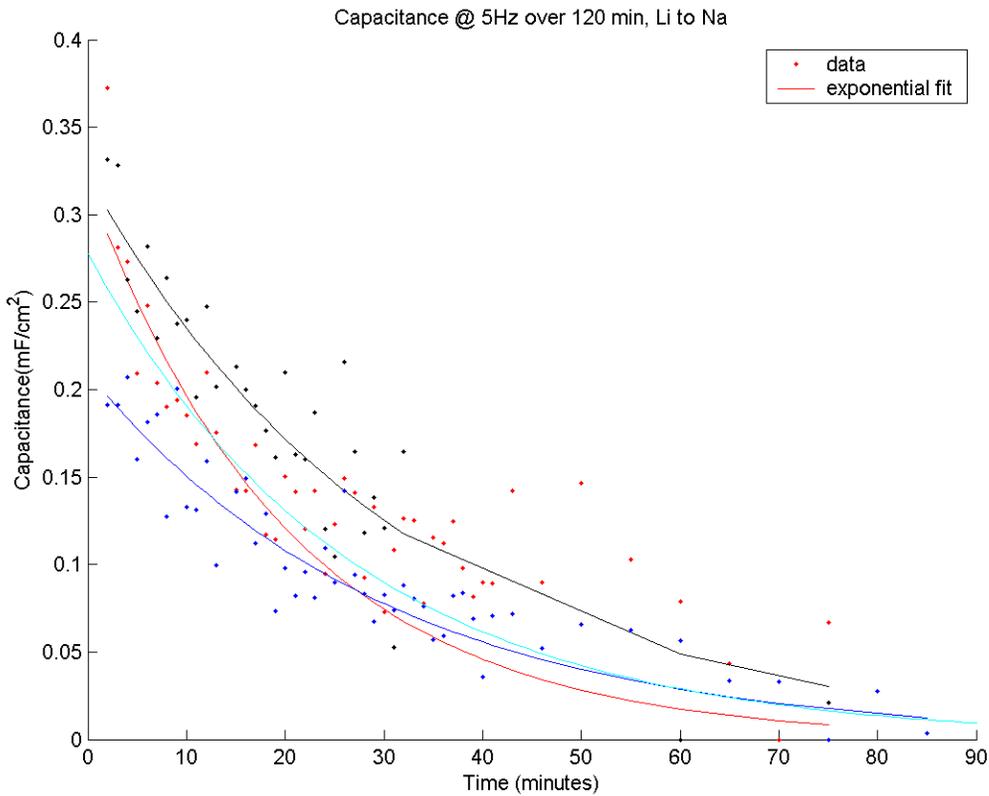
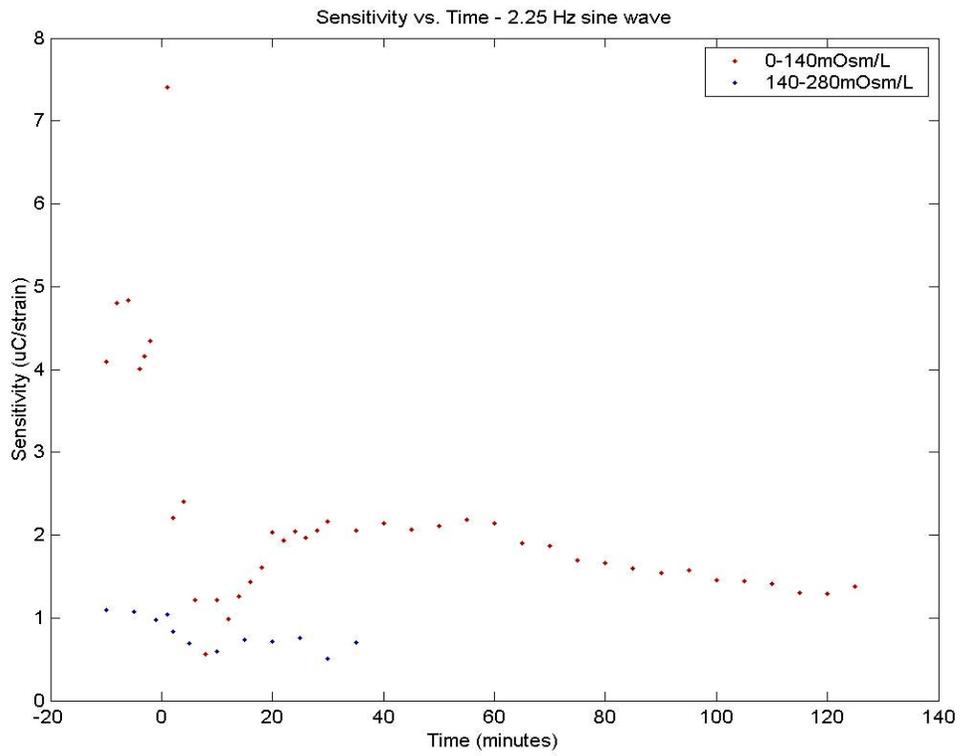
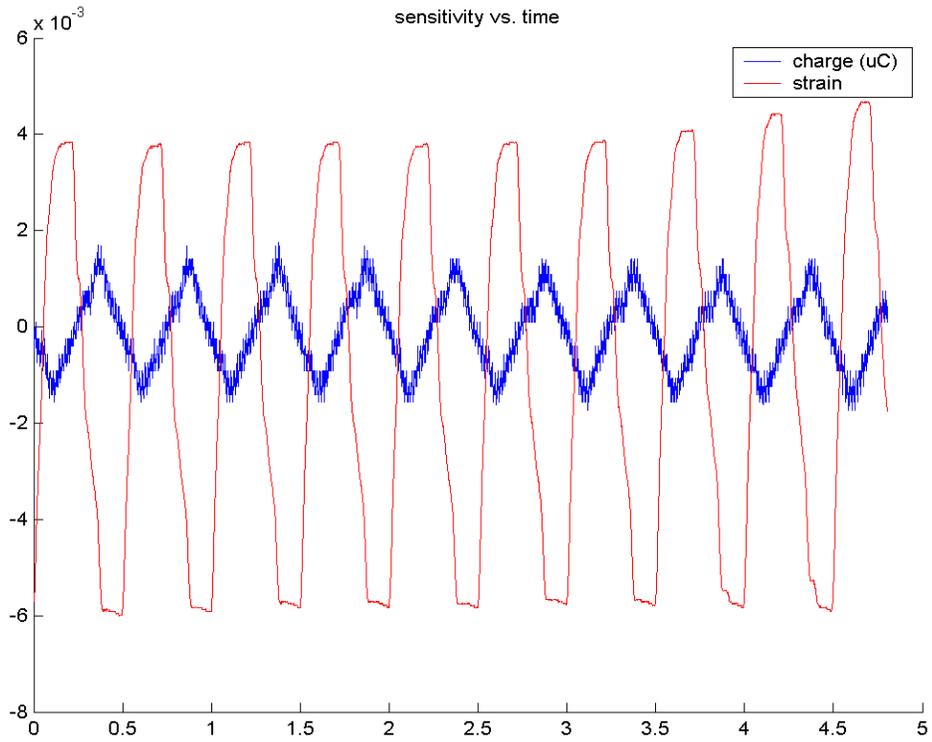
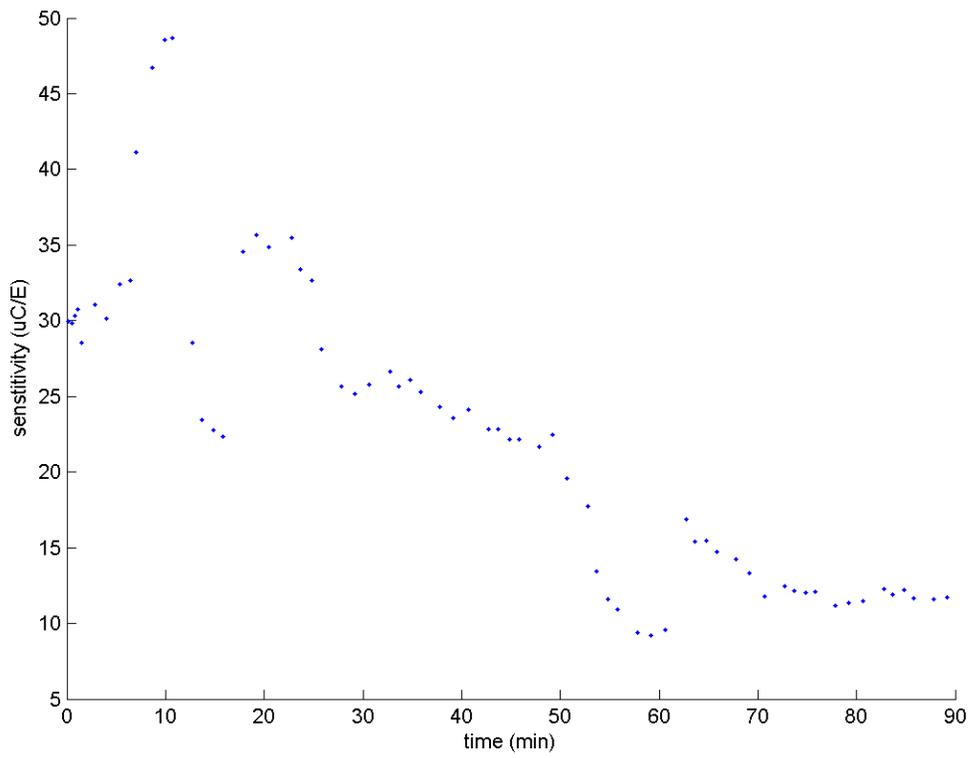
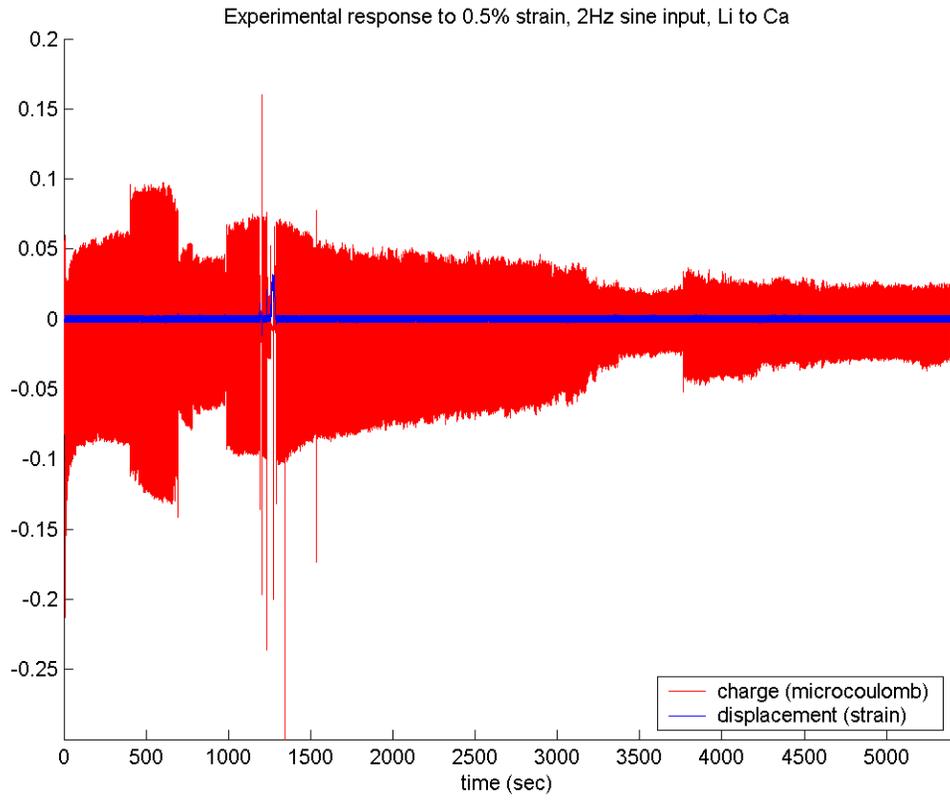


Table A.1: Capacitance values of fully exchanged polymers, measured at t=90 minutes

| Ion | Values (mF/cm²) | Avg. (mF/cm²) | Spread (mF/cm²) |
|------------|-----------------------------------|---------------------------------|-----------------------------------|
| Baseline | 1.16, 1.36, 1.32 | 1.28 | 0.2 |
| Cs | 1.67, 1.82, 1.12, 1.03 | 1.43 | 0.79 |
| Ba | 1.24, 1.10, 1.39, 1.58 | 1.33 | 0.48 |
| K | 1.51, 1.61, 1.35 | 1.49 | 0.26 |
| Ca | 1.16, 1.26, 1.71 | 1.38 | 0.55 |
| Na | 1.13, 1.62, 1.69 | 1.48 | 0.56 |
| Mg | 1.07, 1.44 | 1.26 | 0.37 |
| Nr | 1.88, 0.78, 0.66 | 1.11 | 1.22 |

Figures A.6-A.10; Sensitivity Figures





Vita*

The humbled author, Timothy C. Mudarri, was born to Richard and Mary Mudarri on July 14th, 1979, in Nashua, N.H. He grew up in North Andover Massachusetts, as the eldest among three children, two brothers and one sister, and was a guinea pig for several parenting techniques. Things turned out all right, and Tim went on to graduate from a wall-less North Andover High School in 1997. In August of 1997, he moved on to Villanova, where he studied by day and slinged ‘za by night with some shady characters at the Campus Corner and attempted to become the big man on campus. It failed in the biggest way possible. It deterred him little in his pursuit of a degree in mechanical engineering, which he earned in May of 2001, impressing faculty with his apparent disregard of any knowledge that he had been beat. The man went into hiding afterwards. Though his whereabouts were officially unknown, there is unofficial evidence that he gallivanted around the country in a horseless carriage, stealing camping and frequenting trucker haunts in the great expanses of the west. After lurking about in parts unknown, He surfaced entering the country from Mexico some time that spring, and was quickly sent to participate in top secret research at Virginia Tech. Once they were done conducting research on him, they allowed him to quench his thirst for even more mechanical engineering knowledge, and he began work on his Master’s Degree in the fall of 2002. The tomfoolery continued, tricking Dr. Don Leo to give him the opportunity to conduct the research described herein.

In the future, Mr. Mudarri is hoping to become president in 2016, running for president on a “Kung Fu Army” platform. Barring that, he would like to enter into a profitable marriage with a doctor and raise her children to be little hellions.

*-May not be entirely true. But mostly true, at least. Probably.