ION TRANSPORT AND STORAGE IN IONIC
ELECTROACTIVE POLYMER MEMBRANES

A Thesis in

Electrical Engineering

by

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ASTRACT

A great deal of research efforts have been denoted to ionic electroactive devices such as ionic electroactive polymer (i-EAP) actuators and supercapacitors. I-EAP actuators are attractive because relatively large electromechanical actuation can be generated under low voltage (a few volts). Hence they can be directly integrated with microelectronic controlling circuits, which have operation voltage of several volts, to perform complex actuation functions, and the low operation voltage also makes them safe to use. Thus they hold promise for a broad range of applications. Supercapacitors, because of their reasonable energy density, relatively high charge/discharge time and long cycle life, provide important energy storage devices besides batteries. The performance of these ionic electroactive polymer devices all combine an understanding of the ion and charge transfer processes that occur in the systems.

For real devices, the structures can be very complicated. Yet from fundamental principle, the system can be abstracted to a simple one: metal-ionic conductor-metal sandwich structure. It provides a good study platform for ion transport and storage on ionic electroactive polymers.

In general, the response of ionic devices to external applied voltage is slow. For example, major actuation of i-EAP actuators occurs at >0.1s seconds after the application of electric stimulus. In earlier studies[1], it is observed that there is substantial non-linear increase of charge accumulated for ionic liquid (IL) of 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-TF) in Aquivion membrane. In this thesis, further
investigations are developed to determine whether the effect is limited to this combination of IL/ionomers or a more general phenomenon.

Polymer matrix and ionic liquid are always the two basic elements to build up the ionic devices. Along this train of thought, hydrophobic IL 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) is adopted, comparing with the original hydrophilic IL EMI-TF. On the other hand, P(VDF-CTFE) based polymer matrix group is characterized, which have a drastically different morphology with ionomer Aquivion previous study used.

Both the charge response and bending actuation of membrane actuators from these polymer/ILs combinations are investigated, especially at longer time scale (>0.1s). The results show that the nonlinear response of the total charge storage in i-EAPs with applied voltage also occurs in these polymer/IL systems and suggest that the nonlinear charge response at long time scale is a general phenomenon for ionic devices. The time dependence of the bending actuation vs. the charge stored is also studied and the results reveal that charge stored at different periods lead to curvature to various degree.
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Chapter 1

Introduction

Ionic electroactive membranes present a unique media to allow ion transport and conduction, thus hold promise in many applications such as supercapacitors and electromechanical actuators. The performance of these ionic electroactive polymer (i-EAP) devices all combine an understanding of the ion and charge transfer processes that occur in the systems. For supercapacitors, under applied electric field, the accumulated charge forms an electric double layer between the charged electrode and ions in the near electrode region. The separation of the layer can be of the order of a few angstroms. Then high energy densities are achievable. For electromechanical actuators, i-EAPs can generate large mechanical actuation under relatively low voltages (1-5 V). These all combine an understanding of the ion and charge transfer processes that occur in the systems. Ion transport and charge storage fundamentally determine the performance of i-EAPs. Therefore, the understanding of the role of these factors is crucial toward developing new materials with improved performance. This chapter gives a brief introduction of supercapacitor and electroactive polymer actuators with a focus on ion transport and storage.

1.1 Supercapacitor

1.1.1 Supercapacitors Background

Targeted design and fabrication of high efficiency devices for energy conversion and
storage represent a promising strategy to meet the ever increasing global exploitation of energy resources. Different kinds of energy storage device has been proposed and used in the past[2]. Traditional energy devices, such as advanced lead-acid batteries (TLA), sodium sulfur batteries (NaS), electrochemical capacitors (EC) and lithium-ion (Li-Ion) batteries remain as the state-of-art technologies [3]. Among these technologies, supercapacitors (ultracapacitors) become increasingly popular in recent years, whose early development dates back to 1957 when General Electric patented a device using porous carbon electrode and achieved an incredible high capacitance [4]. Figure 1 shows power density (vertical axis) vs. energy density (horizontal axis) so-called ‘Ragone Plot’. Traditional dielectric capacitors can output high power energy via the fast charging and discharging process. But their low energy density makes them not suitable for general energy storage applications. In contrast, batteries or fuel cells can maintain high energy density but limited in the power output. The advent of supercapacitors bridges the gap between these two to achieve both high power and energy density. Their operation is efficient under reversible charging and discharging cycles without degradation in performance. With a proper choice of electrolyte, supercapacitors can also work in a large temperature range.
1.1.2 Principles of Supercapacitors:

Supercapacitors share the same physical principles as of traditional capacitors which are constructed with two opposing conducting plates which are connected to a battery. The capacitance C is described by formula 1.1

$$ C = \frac{\varepsilon_r \varepsilon_0 A}{L} $$  \hspace{1cm} (1.1)

where $\varepsilon_r$ is the relative permittivity; $\varepsilon_0$ is the vacuum permittivity equal to $8.85 \times 10^{-12}$ F/m, A is the surface area and L is the gap between two metal plates. The energy stored inside the capacitor is given by equation 1.2, where V is the applied voltage.

$$ E = \frac{1}{2} CV^2 $$  \hspace{1cm} (1.2)

For power output, assuming the capacitor is connected with an outer impedance R. The maximum power output can be achieved when R equals the internal impedance of the capacitors (due to electrodes, dielectric materials, etc.), which is known as the equivalent...
series resistance (ESR) based on which the energy and power density can be calculated using equation 1.3. [6-8]

\[ P_{\text{max}} = \frac{1}{4ESR} V^2 \]  

(1.3)

Though a high power density can be easily obtained by reducing the ESR value, the small capacitance kills the capability of traditional capacitors to be a good energy storage device.

Figure 1.2 Supercapacitor (EDLC) structure.[9]

From formula 1.1 and 1.2, to extract more energy from the capacitor, we are supposed to get an increased surface area and extremely small gap distance. Supercapacitors integrate electrode with large surface areas and extremely small gap distance due to the formation of an electric double layer. Take the electric double layer capacitor (EDLC) as an example, the gap distance is on the order of a few nanometers that renders the system with a high capacitance and energy density. Figure 1.2 shows schematically the typical operation principle of a supercapacitor.

Supercapacitor usually consists of three parts: two electrodes made of porous carbon,
organic electrolyte with ions inside and a separator which prevents direct electric contact between electrodes but allowing ionic permeation. During the charging process, ions are attracted to electrodes, transport into pores and form the electrical double layer at the electrode-electrolyte interface. These double layers are the places where electric energy are stored and function as capacitors. A simple equivalent circuit model will be given in latter study, where two capacitors are in series connection with one resistance.

1.1.3 Electrical Double Layer Capacitors

In general, supercapacitors can be divided into three categories based on the working mechanisms [10]. They are Faradaic, non-Faradaic and hybrid [11]. Electric Double Layer Capacitor (EDLC) is the typical non-Faradaic supercapacitor. The charging and discharging cycles only involve physical adsorption of ions onto the electrodes surfaces. High energy and power densities can be achieved with EDLC supercapacitors. The EDLC has the higher charge and discharge stability since no chemical reactions occur between electrodes and electrolytes.

In this study, Our EDLCs consist of electroactive polymers and ionic liquids (ILs). Many factors critically impact the performance of EDLCs, such as the surface area[12], pore size and distribution of electrode materials [13], as well as, the electrolyte compositions [14], ILs[15] etc. The high demands from industries for high energy density from EDLC require more research work for EDLC. Fundamentally, ion transport and storage in the EDLC is always of primary concern whatever the material is chosen as electrode, polymer matrix as
the supporter, or ionic liquid as the carrier.

1.2 Electroactive Polymer (EAP) Actuators

1.2.1 EAP Principle and Classification

Electroactive polymers (EAPs) are materials that respond mechanically to electrical stimulation. Its potential applications include drug delivery, artificial muscle, robot, etc. When they are stimulated to respond with shape or dimensional changes, they can served as actuators, while when they exhibit the inverse effect, they can be utilized as sensors or even power generators. The attractive properties of EAPs include low weigh, easy-shaped, fracture tolerances which meet a broad range of requirements in different areas. [16]

In general, EAPs can be divided into two major categories based on their activation mechanism including ionic EAPs and field-activated EAPs. Coulomb forces drive the latter one, which include electrostritive, electrostatic, piezoelectric and ferroelectric. This type of EAP materials can be made to hold the induced displacement while activated under a DC voltage, allowing them to be considered for robotic applications. Field-activated EAP materials have usually a high energy density, fast actuation speed and they can be operated in air with no major constraints. However, field-activated EAP require a high activation fields (> 50 V/μm). In contrast to the field-activated EAP, ionic EAPs are materials that involve mobility or diffusion of ions and they consist of two electrodes and electrolyte. The activation of the ionic EAP can be made by as low as 1-2 Volts. Examples of ionic EAP include gels, polymer-metal composites, conductive polymers, and carbon nanotubes. The disadvantages of
ionic EAP are that the polymer matrix must be in wet and it is difficult for ionic EAP to sustain constant displacement under activation of a DC voltage.

In this thesis, the system combining electroactive polymer matrix and ILs is investigated, which presents a typical structure of ionic electroactive devices.

1.2.3 Ionic Electroactive Polymer Actuators

In general, the performance of i-EAP devices depend on the transport of ions in the devices, includes polymer matrix as well as excess ion storage at the electrodes as shown in Figure 1.4 (a) (b). In this thesis, I will focus on the ion transport and storage in an electroactive polymer membranes with ILs as electrolyte. These simplified cases are shown schematically in Figure 1.4 (c) (d). When an external potential is applied across the polymer, ions move within the polymeric matrix toward the opposite electrode respectively and lead to mechanical deformation. Shown in Figure 1.3 is one of the ionic electroactive polymers structures studied in this thesis. The polymer matrix is sandwiched by two planar electrodes, containing ILs within the membrane.

![Figure 1.3 schematic of an i-EAP](image)

Figure 1.3 schematic of an i-EAP ionic liquid polymer matrix electrode

Ionic electroactive polymer actuators are a class of electromechanical devices that function based on ionic electroactive polymers. In the presence of an electric field, cations,
anions or the clusters formed based on them accumulated at opposite electrodes. The volume effect drives these i-EAP actuators, that is, the accumulation or depletion of ions with different sizes cause volume changes near electrodes, hence leading to bending actuation.

![Diagram showing initial and charged states of i-EAP actuators](image)

Figure 1.4 (a) (c) the initial state of i-EAP actuator when no electrical potential is applied (b) (d) the charged state when external field added

The backbone structure of i-EAP actuators is an electroactive polymer membrane which is permeable to either or both cations and anions, depending on its chemical structure and physical properties. The importance of the polymer matrix chosen is of patency. In this study, we compare two type of polymer matrix, ionomer of Aquivion and P(VDF-CTFE) based polymer matrix, which will be discussed in more detail in the following two sections.

1.2.3.1 Ionomeric Membrane of Aquivion
Aquivion, also named Hyflon, is one of the typical ionomeric membranes used in i-EAP actuators. It’s originally developed by the Dow Chemical Company in early 80s and obtained the commercial name of Aquivion by Solvay Solexis.[16-19] As illustrated in Figure 1.5, Aquivion consists of a polytetrafluoroethylene (PTFE) backbone and double ether perfluoro side-chains terminating with a sulfonic acid group. The flexible side chains facilitate the aggregation of hydrophilic clusters. When swelled with ILs, the clusters expand to connect with narrow channels forming percolation. The flexible side chains contained in Aquivion structure provide a mechanical coupling between the ions and the membrane, resulting in popular adaption of Aquivion in many recent studies.[19]

![Molecular structure of Aquivion](image)

Figure 1.5 (a) The molecular structure of Hyflon (b) the cluster network morphology model by Gierke et al[20]

1.2.3.2 P(VDF-CTFE) Based Polymer Matrices

In this thesis, we also investigated polymer matrices without side chain, such as Poly[(vinylidene difluoride)-co-(chlorotrifluoroethylene)] (P(VDF-CTFE)) and its blends or partial crosslinked with Poly(methyl methacrylate) (PMMA). The chemical structures of P(VDF-CTFE) and PMMA are shown in Figure 1.6.
Figure 1.6 the chemical structure of (a) P(VDF-CTFE) (b) PMMA

The drastically different structure of P(VDF-CTFE) comparing with the traditional ionomer such as Nafion and Aquivion don’t obstruct their potential performance of electromechanical properties. It will be discussed in more details in Chapter 2 & 3.

Since the functionality of IEAP actuators is based on mobility of ions, it would be logical to investigate all the ions behaviors within these membrane to facilitate further performance of devices based on them.

1.3 Ionic Liquids

1.3.1 Basic concept

Ionic liquids (ILs) are salts in liquid form, which consists of positively and negatively charged ions only, whereas water and organic solvents, such as toluene and dichloromethane, contain only molecules [21]. In the broad sense, ionic liquids could include all the molten salts, whose melting point may be higher than 800°C. However, nowadays the term “ionic liquid” generally describes the salt whose melting point is below 100°C. [22] These salts melt at room temperature are called “room temperature ionic liquid” (RTILs).

RTILs consist of cations which are usually organic, while the anions are inorganic or organic, as shown in figure 1.4. [23]. This incompatible construction leads to low tendency to
crystallize, remaining liquid throughout a wide range of temperatures [24]. Various kinds of salts can be used to design the ILs for specifically desired properties aimed for different applications.

Various kinds of salts can be used to design the ILs for specifically desired properties aimed for different applications.

According to the compositions, ILs can be classified as protic, aprotic and zwitterionic ionic liquids; while according to the affinity with water, they can be classified into hydrophilic or hydrophobic ILs.

1.3.2 Hydrophilicity

A hydrophilic substance has the tendency to be dissolved or ionized in water. On the contrary, the hydrophobic substance often clusters in water. In the microscopic view, the hydrophilic molecules or their hydrophilic portion are polar molecules or groups, where charges are not evenly distributed inside the whole entity. These polar molecules tend to interact with water molecules in favor of thermodynamics and lower the electrochemical potential to form the steady group. Hydrophobic molecules are non-polar molecules that prefer other neutral or non-polar molecules. Typical hydrophilic materials include sugar and
salt, which are capable of absorbing water if we expose them in air. Meanwhile, greasy materials such as oil and fats are good examples of hydrophobic substances. Ionic Liquids (ILs), according to the affinity with water, can also be classified into hydrophilic or hydrophobic ILs. The anion and cation parts of ILs together decide the intimacy to the water. \( \text{Cl}^-, \text{BF}_4^-, \text{FeCl}_4^-, \text{Alkyl}^+\text{BF}_3^- \) fall into the category of hydrophilic ions; while \( \text{C}_4\text{mim}^+, \text{IM16}^+, \text{and Pyr18}^+ \) are different classes of hydrophobic ions.

As described in the previous section, anions in ILs can be inorganic or organic. In general, ILs with inorganic anions are hydrophilic, while those with organic anions are hydrophobic. In chemistry, hydrophilic ILs contain polar groups which tends to absorb the moisture, while hydrophobic ILs have non-polar group which tends to repel the water molecules. In this thesis, i-EAP actuators with either hydrophilic or hydrophobic ILs will be characterized for a comparison of study to identify the effect of moisture on the strain behavior of i-EAP actuators.

1.4 Research Motivation and thesis organization

1.4.1 Research motivation

Electroactive polymer has a lot of potential applications. A broad range of selection of structures and materials could be the candidates to fulfill the diverse requirements. When fabricated into actuators, they have low operation voltage and the potential to achieve high strain. On the other hand, they suffer from low speed and low efficiency. When utilized in
supercapacitors, how to obtain both high energy density and power density is always an issue people concern about. Ion transport and charge storage within i-EAPs fundamentally determine the performance of these devices. The understandings of the role of these factors are crucial.

These ionic devices respond to external applied voltage substantially after 1 second. It’s far beyond the charging time of electrical double layer. Dr. Junhong Lin[1] observed that there is substantial non-linear increase of charge accumulated for EMI-TF in Aquivion membrane. Further investigations are developed to determine whether the effect is limited to this combination of IL/ionomers or a more general phenomenon.

Polymer matrix and ionic liquid are two essential elements to build up the ionic devices. Hydrophobic IL (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) (EMI-TFSI) is adopted for the purpose of comparison with hydrophilic IL EMI-TF. On the other hand, new developed P(VDF-CTFE) based polymer matrix group is characterized, which have a drastically different morphology with ionomer Aquivion previous study used.

The further study goes into the bending actuation responses when these i-EAPs are fabrication into actuators. The charge accumulated in different time domain may have various extent contributions to device responses, which is another motivation for the study in the thesis. The relationship between bending actuation and applied voltage is also studied.
1.4.2 Thesis organization

This thesis contains four Chapters. Following introduction in Chapter 1, some important parameters, sample preparation process, characterization methods and equipments set-ups are presented in Chapter 2, which also include electrical properties, mechanical properties, electromechanical properties of the new P(VDF-CTFE) based polymer matrix for comparison with previous study of the ionomer group of Aquion. Their bending curvatures under 4V also are presented for the purpose of comparison of device features. In Chapter 3, ion transport and storage with respect to time and voltage will be discussed. It’s observed that regardless of the type of polymer matrix and ILs, the linear effect (charge density verse voltage) within electrode double layer relaxation time and the nonlinear effect as time elapsed into diffusion part are universal phenomena. The efficiency of ion transfer and accumulation which may contribute to bending curvature is another topic discussed in Chapter 3. The cancelling effect and formation of clusters lead to the unequal bending curvature response as time elapse. Chapter 4, the last chapter, consists of the conclusion and some suggested future work.
Chapter 2

Electroactive Polymer Development For Potential i-EAP

2.1 Sample Preparation

2.1.1 Ionic Liquid

Ionic Liquids of 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITF) and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) are purchased from Merck EMD Chemical. The former one is hydrophilic while the latter one shares the hydrophobic property. They are a good comparison pair for the study of effect of hydrophility in i-EAPs. Figure 2.1 are the schematic of EMI-TF and EMI-TFSI. Some of their properties are list in Table 2-2.

![Figure 2.1 Molecular Structure of ILs utilized in the thesis](image)

(a)EMI-TF

(b)EMI-TFSI

<table>
<thead>
<tr>
<th>Name</th>
<th>Hydrophility</th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Density (g/ml)</th>
</tr>
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<tbody>
<tr>
<td>EMI-TF</td>
<td>Hydrophilic</td>
<td>260.23</td>
<td>-12</td>
<td>1.387</td>
</tr>
<tr>
<td>EMI-TFSI</td>
<td>Hydrophobic</td>
<td>391.31</td>
<td>-15</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Table 2-1: Properties of the ILs
The membranes are soaked with ionic liquids at 70°C (stated in later parts of chapter). Through adjusting the soaking time, specific target weight percentage values of ILs can be achieved.

In this study, we use weight percentage (\(\text{wt\%} = \frac{\text{ILs weight}}{\text{Dry weight of pure membrane without ILs}}\)) to describe the ILs uptake. Membranes with 40wt% of EMITF, 40wt% EMI-TFSI, 60wt% EMI-TFSI are prepared respectively.

### 2.1.2 Preparation of P(VDF-CTFE) polymer matrix

Fluoropolymer Poly[(vinylidene difluoride)-co-(chlorotrifluoroethylene)] (P(VDF-CTFE)) electroactive polymer matrix is prepared by solution cast, followed by hot-press. A typical procedure of preparation of polymer matrix is described as following: 1g of P(VDF-CTFE) powder (Solvay Solexis, 31508) is dissolved in 20g Acetone at 50°C. Heating helps the powders to dissolve completely. The solution is then casted onto a Teflon sheet to be dried in the vented oven at room temperature. Once the solution dried out, together with the Teflon sheet are been transferred to vacuum oven, baking at 70°C to remove residual solvent. This process takes 12 hours at least to give a guarantee that the Acetone, which could let down the quality of the film, is removed completely. The last but not least step is sandwiching the film by two sheets of Teflon, and hot-pressing the film under 240°C for continuous 2 hours. The process is supposed to make the crosslink take place. Then the compressor is cooled down to the room temperature by domestic water to help improve the morphology of the film. Shown in the Fig 2.2 are the equipments used during film fabrication process.
2.1.3 Preparation of P(VDF-CTFE)/PMMA polymer matrix

Poly(methyl-methacrylate) (PMMA) has a Young’s modulus as high as 3GPa [25]. The elastic modulus is always a prime consideration in determining the general utility of polymers. Since larger modulus is preferred in the potential electroactive polymer applications such as actuators, membranes of P(VDF-CTFE)/PMMA is also been made for expectation of better device performance. P(VDF-CTFE)/PMMA blends membrane is carried out in the similar
way as P(VDF-CTFE), except that the receipt is adjusted to a mixture of 0.48g (80wt%) of P(VDF-CTFE) powder (Solvay Solexis, 31508) and 0.12g (20wt%) of PMMA (Aldrich, 182230) are used for fabrication of the membrane. As for the crosslinked P(VDF-CTFE)/PMMA material, after the solution is cooled down to room temperature, two weight percentage (2 wt%) of initiator 2, 3-dimethyl-2,3-diphenylbutane (Bicumene) is added to the solution to be dissolved which serves as generating crossing process in the polymer film. The process is under room temperature to prevent the decomposition of the initiator. The process followed afterwards is same as that stated before.

2.2 Characterization

Before the characterization of electric properties, 50nm gold foils (L.A Gold Leaf Wholesaler) are pressed on two sides of the film to form the typical sandwich structure which act as an electrodes as shown in Figure 2.3.

![Figure 2.3 Polymer matrix sandwiched by gold electrodes](image)

The electrical measurement was carried out in a sealed metal box with desiccant inside to prevent moisture and noise. (Figure 2.4)
2.2.1 Impedance spectroscopy

The impedance spectrums are measured using the Princeton Applied Research PARSTAT® 2273. (Figure 2.5) A sinusoidal wave with 0.1V amplitude is applied to the sample. The sweep frequency ranges from 0.1 Hz to 100Hz. The value of real and imagery part of impedance versus frequency are recorded. Different membranes with IL uptake are characterized at room temperature.

2.2.2 Charging current

The transient current verse time is collected by the Princeton Applied Research PARSTAT® 2273. The samples’ dimensions vary, yet can be normalized before comparison afterwards. Before the characterization, the samples were shorted for hours so that the
samples be free of accumulated blocked charges, that is, the charges redistribute to the equilibrium state. In this study, a step voltage is applied on the membranes for 30-50 seconds, and then the voltage is set to zero. The charging current $I(t)$ versus time $t$ is integrated to obtain the stored charge at two electrode surfaces.

2.2.3 Dynamic mechanical analysis

Dynamic mechanical analysis is a technique used to study and characterize materials. It is most useful for studying the elastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus; this approach can be used to locate the glass transition temperature of the material, as well as to identify transitions corresponding to other molecular motions.[26] In this study, TA DMA 2980 dynamic mechanical analyzer (Figure 2.6) is responsible for characterization of the mechanical properties, young’s modulus for example.

![Figure 2.6 (a) TA DMA 2980 Dynamic mechanical analyzer](image)

(b) the liquid nitrogen tank associated with (a) to control temperature during the measurement
2.2.4 Electromechanical Characterization

Shown in Figure 2.7 is the set up for electromechanical characterization. The corresponding schematic drawing is displayed in Figure 2.8. The actuators fabricated based on i-EAPs with the size of 8mm in length, 1mm in width are clamped by two probes which are connected to a power supply or a function generator. The probes function to provide the actuators with both electrical connections and mechanical supports. The sample bending curvature, if applicable, are amplified by a microscope associated with a charge-coupled device (CCD) sensor recording the image with a rate of 200 frames/s. The images collected are analyzed by Labview and Matlab etc. In this way, the bending curvature can be retrieved from these images.

![Figure 2.7](image1.jpg)  
(a) Picture of bending actuation measurement set-up  
(b) Schematic of bending actuation measurement set-up

2.3 Result and discussion

2.3.1 Thermal properties

Thermogravimetric analysis (TGA) is a type of testing performed on samples that
determines changes in weight relation to change in temperature. Such analysis relies on a high
degree of precision in three measurements: weight, temperature, and temperature change. As
many weight loss curves look similar, the weight loss curve may require transformation
before results may be interpreted. A derivative weight loss curve can identify the point where
weight loss is most apparent. Shown in Figure 2.8 the TGA results of four P(VDF-CTFE)
based polymers. It would be clear seen that the involvement of PMMA change the polymer
matrix structure of P(VDF-CTFE) to some extent.

Figure 2.8 Thermogravimetric analysis result of four polymer matrix

2.3.2 Mechanical properties (storage modulus)

The elastic modulus is always a prime consideration in determining the general utility of
polymers. Dynamic mechanical analysis (DMA) is adopted to investigate the mechanical
properties of Polymer matrix with ILs in the study. Shown in the Figure 2.9 is the storage
modulus of polymer matrix P(VDF-CTFE), P(VDF-CTFE)/PMMA with/without initiate with 40wt% uptake ionic liquid, respectively. Each group have four curves referring to different frequencies 1Hz, 2Hz, 5Hz, 10Hz from the top one to the bottom one. It is clearly noticed that the blend-in PMMA help improve the young’s modulus of polymer matrix up to the doubled value of pure P(VDF-CTFE) without PMMA. Furthermore, due to the effect of crosslinking, the P(VDF-CTFE)/PMMA with initiate demonstrated a higher storage modulus. The typical values at 25 °C are listed in the Table 2-3.

![Graph](https://via.placeholder.com/150)

**Figure 2.9** Young’s Modulus of four polymer membranes soaked with 40wt% EMI-TF Perfluosulfonate ionomer Aquivion soaked with same amount of ILs exhibits lower The Young’s modulus, around 50MPa. In general, the young’s modulus of membranes would reduce with uptake ionic liquid, as indicated by the data in Table 2-3 demonstrate the drop in evidence. Here ionic liquid acting as plastizors which reduce Young’s modulus of membranes [28]. The polymer matrices of P(VDF-CTFE), P(VDF-CTFE)/PMMA (crosslinked) with high
modulus will be further characterized for other properties in the following sections.

<table>
<thead>
<tr>
<th>Stored Modulus</th>
<th>Polymer Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C (MPa)</td>
<td>Aquivion P(VDF-CTFE)</td>
</tr>
<tr>
<td>w/o ILs</td>
<td>410</td>
</tr>
<tr>
<td>with ILs</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2-2 Values of Young’s modulus in room temperature referring to different polymer matrices

### 2.3.3 Electrical properties

The complex impedance of an electrical system can be expressed as the formula below:

\[ Z(\omega) = Z'(\omega) + jZ''(\omega) \]

In this formula \( \omega \) is angular frequency, \( Z' \) is the real impedance, \( Z'' \) is the imaginary impedance, \( j \) is the imaginary unit. Phase angle could be expressed as \( \theta = \tan^{-1}(Z''/Z') \).
2.3.3.1 Nyquist Plot

Figure 2.10 Series of Nyquist plots of two polymer matrices with 40 wt% ILs

Nyquist plot of P(VDF-CTFE)/PMMA, Aquivion membrane with different ILs are shown in Figure 2.10 and Figure 2.11 shows their corresponding phase-angel plots. The impedance data are all normalized by sample size. The ionomers are soaked with hydrophilic EMI-TF and hydrophobic EMI-TFSI respectively. The quantity of two ILs soaked in were controlled as for the same mole percentage. In this way, the total number of carriers are the same. According to the calculation by Qian and Conway[29], the rightward shift in the Nyquist Plot indicates a more notable resistor character and a larger capacitance of ions. It’s consistent with the electric analysis in the following section. It’s stated the viscosities of two kinds of ILs are similar [30-32]. The transport of hydrophobic ionic liquid in P(VDF-CTFE) polymer
matrix is more resistive than that in P(VDF-CTFE)/PMMA. The possible reason is that the PMMA portion in P(VDF-CTFE) behave like “hydrophilic” or “less hydrophobic” than P(VDF-CTFE”).

Figure 2.11 Plot of phase angle vs. frequency in Hz corresponding to the Nyquist plot in previous figure

2.3.3.2 Impedance and Capacitance

Shown in Figure 2.12 is the capacitance and conductivity of the five IL/polymers matrices combinations studied. The molar uptake of different ionic liquid remains the same for all these samples.
The conductivity at high frequencies, that is the plateau region in Figure 2.12(c) could be regarded as the dc conductivity[1]. The ionomer Aquivion exhibits obviously high conductivity $1.3 \times 10^{-4}$ S/cm than other four polymers (e.g. $4.0 \times 10^{-5}$ S/cm for P(VDF-CTFE)/PMMA) which do not have side chains. The hydrophilic ion channels facilitate ion transport of hydrophilic liquids. With same mol percentage of different ILs, it is found the conductivity of P(VDF-CTFE) with EMI-TF is lower than EMI-TFSI. Since it is well known that both EMI-TFSI and P(VDF-CTFE) are hydrophobic, while EMI-TF is
hydrophilic, our finding suggests that the hydrophilicity of the materials significantly affects the transport of ions in polymer matrix. Ionic conductivity are enhanced when polymer and IL have similar hydrophilicity.

Similarly, hydrophilicity also affects the conductivity when 20 wt% PMMA presents in the P(VDF-CTFE) polymer matrix. Adding PMMA into P(VDF-CTFE) based polymer improved the conductivity of hydrophilic ionic liquid EMI-Tf and reduced the conductivity of hydrophilic ionic liquid EMI-TFSI. It indicates that the PMMA portion in P(VDF-CTFE) behave like “hydrophilic” or “less hydrophobic” than P(VDF-CTFE). P(VDF-CTFE) and PMMA form micro-phase separation, which behave like “ion tunnels” for hydrophilic ionic liquids while lag the transport of hydrophobic ILs.

Figure 2.13 The charge accumulation under 4 volts step voltage

The plot of charge density verse time of five polymers is shown in figure 2.13. At the
charging time 15s, the charge accumulated on Aquivion membrane surface doubled the amount of that of P(VDF-CTFE) polymer, which is consistent with the conductivity result. Besides facilitating the ion transport in the polymer matrix, the short-side chains also help the storage of ions. In the next study, we will present the relationship between charge and bending extent when those membranes are fabricated into i-EAP actuators.

2.3.3 Electromechanical properties

Under a 4 V step voltage, the bending actuation took place, as shown in figure 2.14. It can be observed, practically, under constant DC bias, actuators bend toward the anode, and later on, either saturate or relax back in the opposite direction to bend toward the cathode. Ionomer Aquivion severely bends towards cathode at a later stage. As for the other four i-EAP based on P(VDF-CTFE) polymers, the bending direction remains the same. The reverse bend phenomenon may be a combined result of two mobile ions’ speed of movement and size effect in the actuation process. It is determined by the ions near the electrodes after the diffusion process [1] [17].
Figure 2.14 Bending Curvature of i-EAPs fabricated based on five polymers.

It’s also clear noticed that the non-side chain P(VDF-CTFE) polymer group enhanced the electromechanical properties of i-EAP than short side chain ionomer Aquivion as displayed in figure 2.14. In the short time period (t<5s), P(VDF-CTFE) with either hydrophilic or hydrophobic ionic liquid revealed a quicker response (50% more bending curvature than Aquivion) to external potential. At a longer time period~20s, P(VDF-CTFE)/PMMA shows larger bending. When reaching the time 30s, the bending actuation values are 0.75mm⁻¹ (P(VDF-CTFE)/PMMA with EMITF), 0.60mm⁻¹ (P(VDF-CTFE)/PMMA with TFSI), 0.45mm⁻¹ (P(VDF-CTFE) with EMITF), 0.3mm⁻¹ (P(VDF-CTFE) with TFSI), -0.5mm⁻¹(Aquivion with EMITF). The enhancement of electromechanical response by P(VDF-CTFE) based polymer group is of patency. It can be seen from Figure 2.14 that P(VDF-CTFE) based polymers with EMI-Tf show both quicker and larger response in actuation comparing with those with EMI-TFSI, although they have lower conductivity
values and charge consumptions. It can be inferred that EMI-Tf has larger cation/anion size difference or better mechanical coupling with the polymer matrices.
Chapter 3
Ion Dynamics in electroactive polymer matrix

3.1 Introduction

In classic theories of ion transport mechanism, under an external field, the cations and anions move to the opposite polarity of electrodes and polarize the electrodes. Electrode polarization in ionic conduction systems has been studied for many decades and it has been shown that it takes less than milliseconds to screen the electrodes with drifting current. These earlier studies were mostly limited to low applied voltage (<1 V) [1, 17]. To study the ion transport in ionic devices, such as ionic actuators and supercapacitors, requires an understanding of the influence of sample geometry on the ion transport and storage within the membrane sandwiched between two electrodes. The major actuation and ion stored take place within a few seconds at a higher voltage [28, 30]. Therefore it is necessary to investigate the basic ion dynamics under a broader time scale(t=ms to 10s) and voltage arrange.

3.2 Frequency domain and Time domain method

3.2.1 Electrode polarization model

To delve into the ion dynamic behavior in ionic electroactive devices, such as supercapacitors and i-EAP actuators, a complex dielectric constant measurement responding to frequency is adopted. Based on this frequency characterization method, a typical model called Electrode Polarization (EP) model is established shown in the figure 3.1[1]. It is
abstracted as a parallel-plate field. Under low applied voltage, charges and holes accumulates at the interface of electrodes. At the same time, ions with opposite polarities will be attracted to the cathode and anode through the ionic conduction process. In this way, the electrical double layer (EDL) is formed between ions and electrical conductors. The dimension of the layer is of Debye length \( L_D \) (shown in equation 3.2) on the order of nm.

\[
L_D = \left(\frac{1}{q}\right)\sqrt{\frac{ekT}{n_0}}
\]  

(3.2)

By define \( M \) as the ratio of the sample thickness to twice the Debye length equals \( L/2L_D \),

![Figure 3.1 Schematic of charge density distribution under a dc parallel-plate field.][5]

\( \tau \) as the dielectric relaxation time \( \tau = \frac{\epsilon_r\epsilon_0}{n_0q\mu} \) (3.3), it can be approximated to obtain the relaxation time of electrostatic double layer as shown in formula 3.4, the real and imaginary part of dielectric constant as repealed in formula 3.5,3.6.

\[
\tau_{EP} = \frac{L}{2L_D} \tau = \frac{L}{2\mu} \left(\frac{\epsilon_r\epsilon_0}{n_0kT}\right)^{1/2}
\]  

(3.4)
\[ \varepsilon_{EP}' = \varepsilon_R + \frac{\Delta\varepsilon_{EP}}{1 + \omega^2 \tau_{EP}^2} \]  

\[ \varepsilon_{EP}^* = \frac{\Delta\varepsilon_{EP} \omega \tau_{EP}}{1 + \omega^2 \tau_{EP}^2} \]

Where \( \varepsilon_r \) is the dielectric permittivity of the material, \( \varepsilon_0 = 8.85 \times 10^{-12} \) F/m (vacuum permittivity), \( n_0 \) is the equilibrium number density of free positive charges, \( \mu \) is the mobility, \( k \) is Boltzmann’s constant and \( T \) is temperature.

We could notice that when reaching a steady balance, the inner electrical field formed by the cation (single ion conductor in the model case) concentration gradient counteracts the external applied electrical field. The charge distribution under a DC parallel-plate field exhibits a rapid charge concentration drop within the near-plate area.

By taking the derivative of \( \varepsilon_{EP}' \) with respect to \( \omega \), it is noticed that the extreme value of \( \varepsilon_{EP}' \) taking place at \( \omega = 1/\tau_{EP} \). It also turns out that the second derivative of \( \varepsilon_{EP}' \) below zero when \( \omega = 1/\tau_{EP} \). Hence through figuring out the peak value of \( \varepsilon_{EP}' \) in the frequency domain, we could obtain this special frequency to further take in the value of \( \tau_{EP} \) (\( \tau_{EP} = 1/2\pi f \)). The schematic of \( \varepsilon_{EP}' \) response in the frequency domain is shown in figure 3.2.
3.2.2 Time domain model

A time domain approach can also be adopted to investigate the ion transportation in electroactive polymer. According to Poisson-Nernst-Planck equation (3.7) and (3.8), the charge transportation is composed of drift and diffusion.

\[
\varepsilon \varepsilon_0 \frac{\partial E}{\partial x} = \rho 
\]

(3.7)

\[
J_z = q \psi_z = \pm q \mu n_z E - qD \frac{\partial n_z}{\partial x}
\]

(3.8)

where \( \rho \) is the charge concentration, \( \varepsilon \) is the dielectric constant of the medium, \( \varepsilon_0 \) the vacuum permittivity, \( \psi \) is the ion flux density, \( \mu \) is the ion mobility, \( n \) is the ion concentration (the subscripts + and – indicate positive and negative charges), \( E \) is the electric field, and \( D \) is the diffusion coefficient following the Einstein equation, \( D = \mu KT / q \). [33-35]
When applying a step voltage to the typical sandwich structure of the electroactive polymer (figure 3.3), the initial transient current can be calculated according to formula 3.9.

It’s also modeled as an electric double layer capacitor $C_D$ in series with a bulk resistor $R$[1, 35-37], where $\tau_{dl} = RC = RC_{dl}/2$, $I_0 = qn\mu V/d = \sigma E$.

$$I(t) = I_0 \exp(-t/\tau_{dl}) \tag{3.9}$$

Figure 3.3 (a) The typical sandwich structure of electroactive polymer under a step voltage.

(b) Fitting $I(t)$ curve in the form of exponential decay to obtain the value of $\tau_{dl}$ [1]

As the time elapse, the charges/ions diffuse from the bulk to the double layer region. It leads to a power law decay of diffusion current.[38, 39]

Hence, by fitting experimental transient current $I(t)$ using formula 3.9, we could get the
electrical double layer charging time $\tau_{dl}$, $\sigma, n, \mu$ can be also be calculated when $\varepsilon$ is known from the impedance spectroscopy characterization.

### 3.2.3 The consistency of $\tau_{EP}$ and $\tau_{dl}$

As a fact of matter, the electrode polarization can be expressed as a RC circuit (figure 3.4), where $R=L/\sigma A$, $C=1/2C_\parallel = \varepsilon_\parallel \varepsilon_0 A/2L_D$. $L, A$ are the distance between two electrodes, the area of the electrode respectively. $\sigma$ is the conductivity ($\sigma=qn\mu$) in electroactive polymer matrix.

![Figure 3.4 the equivalent RC circuit of electrode polarization](image)

Then it’s easy to obtain that RC constant,

$$
\tau_{dl} = \frac{RC}{2L_D qnA} \frac{\varepsilon_\parallel \varepsilon_0 A}{2L_D qnA} = \frac{L \varepsilon_\parallel \varepsilon_0}{2L_D qn A}.
$$

(3.11)

$$
\tau_{dl} = \frac{L \varepsilon_\parallel \varepsilon_0}{2n_0} \left( \frac{n_0}{\varepsilon_\parallel \varepsilon_0 kT} \right)^{1/2}
= \frac{L}{2\mu} \left( \frac{n_0}{\varepsilon_\parallel \varepsilon_0 kT} \right)^{1/2}.
$$

(3.12)

Taking the expression of Debye length $L_D = (1/q)\sqrt{\varepsilon kT / n_0}$ into the expression of RC
time constant (3.11), we could see that the time constant of electrical double layer (3.12) has the same expression with the relaxation time of electrostatic layer in EP model, that said, $\tau_{dl}$ derive by time domain method equals $\tau_{EP}$ based on frequency domain analysis. In this way, by fitting the image part of dielectric constant, we could know how long it may take to charge the electrical double layer.

3.3 Experiment process

![Lecroy wavesurfer 42Xs-A Oscilloscope](image)

Figure 3.5 Lecroy wavesurfer 42Xs-A Oscilloscope

The sample preparation is similar with Chapter 2. Only when referring to charge measurement, the fast charging process of the electrical double layer we care about in this chapter completes within microseconds. The sampling rate of PARSTAT 2273 Potentiostat cannot meet the requirement. Therefore, a Lecroy WaveSurfer oscilloscope (Figure3.5) with adjustable sampling rate (500M/s in this study) is adopted for observing fast charging part of electrical double layer.
3.4 Results and Discussion

3.4.1 Charge transportation in ionomer Aquivion

Under an external step voltage, the behavior of changes could be regarded as the combination of two parts in the configurable ionomer system: drift and diffusion. Specifically, the charges drift towards electrodes to form electric double layers within ms or even shorter, which leads to the ion compact regions near the two electrodes. The induced charge concentration gradient drives the charges from the bulk to the near electrode regions. This current is regarded as diffusion current. It is negligible during the initial double layer charging, yet it becomes dominant at longer times because it decreases much more slowly than the exponential decay [40, 41]

Using time domain method, previous studies found that[1] that, within drift part, the charge density stored increase with applied voltage linearly. That said, the double layer capacitance \( C = \frac{\Delta Q}{\Delta V} \) remains constant with the applied voltage up to 4V. In contrast, when reaching diffusion part, a rapid increase of charge density took place as applied voltage goes beyond 1v. (Figure3.6)

The mechanism behind the nonlinear effect is beyond understanding. One possible reason is that electrochemical reaction contributes to this nonlinear effect cause up to 4V voltage is applied. The involvement of proton due to the the structure of Aquivion is another pending arguable statement.
Figure 3.6 linear and nonlinear effect of charge density when voltage increase in Lin’s Study[1]

3.4.2 Charge transportation in PVDFCTFE based polymer matrix

The polymer matrix in Lin’s study is based on Aquivion. As discussed in Chapter 2, Aquivion is a perfluorinated ionomer with short side chain. This material consists of a hydrophobic poly(tetrafluoroethylene) backbone with perfluorovinyl ether short side chains terminated by sulphonic acid (-SO$_3$H). It’s been noticed the existence of proton in the structure. It may also absorb water over time due to the hydrophilic property[42]. It’s hard to avoid moisture when characterization due to this property of Aquivion. Further, the role of proton played on the charge density is indistinct. The intent of the following work is to investigate polymer matrices without proton to avoid the impact of either H$^+$ or H$_2$O$^+$. Furthermore, instead of hydrophilic ILs, the adoption of hydrophobic ILs would improve the aridity.

Fluoropolymer Poly[(vinylidene difluoride)-co-(chlorotrifluoroethylene)] (P(VDF-CTFE))
is a random non-side chain matrix copolymerized by difluoroethylene and trifluorovinylchloride [43, 44]. There is apparently no proton in the structure. At the same time, the backbone is of hydrophobic property. The ionic liquid soaked in the polymer matrix is replaced by EMI-TFSI which belongs to the hydrophobic ionic liquid group to avoid moisture more effectively.

The current responses for this prepared polymer matrix under various step voltages are presented in Figure 3.7. These charging current I(t) verse time t is integrated to obtain the stored charge at two electrode surfaces based on formula \( Q(t) = \int I(t) \, dt \).

The permittivity \( \varepsilon_{ep} \) responding to frequency is shown in Figure 3.8. Based on the analysis in Chapter 3.3, the typical frequency related to \( \tau_{dl} \) equals 788Hz so that \( \tau_{dl} = 1/2\pi f = 2E-4s \).

Figure 3.7 Current density of P(VDF-CTFE) with EMI-TFSI in frequency domain
Figure 3.8 Imaginary part of permittivity of P(VDF-CTFE) with EMI-TFSI in frequency domain

This typical time is chosen as one upper limit of the integration of current with respect to time. It then could be obtained the charge density within charging process for electrical double layers under different voltages. Shown in figure 3.9 is the plot of charge density as a function of time as for several external potential applied.

Therefore, Figure 3.10 is generated when applied voltages were used as the abscissa, meanwhile, charge density at $\tau_{dl}$ and long time region (20s) as the ordinate individually. The linear and non-linear effect is plain to see.
Figure 3.9 The charge density of P(VDF-CTEF) membrane with EMI-TFSI under different applied step voltage

Figure 3.10 The transient current of P(VDF-CTEF) membrane with EMI-TFSI under different applied step voltage
3.4.3 Charge transportation in PVDFCTFE /PMMA with both hydrophobic and hydrophilic ILs

For the purpose of broadening the horizon into diverse materials, the charge response in the P(VDF-CTFE)/PMMA is also investigated. It’s reported that poly(methyl-methacrylate) (PMMA) has a Young’s modulus as high as 3GPa [25], It’s also known in Chapter 2 that with the involvement of PMMA affects, both conductivity and curvature response of actuators improved. This miscible morphology of this partial crosslinking polymer matrix seems to exhibit more ion channel. Meanwhile, the hydrophobicity of PMMA further obviates the influence of moisture.

Figure 3.11 provides the value of $\tau_{dl}$, while Figure 3.12 exhibits the charge density with respect to time and voltage respectively.

Figure 3.11 Imaginary part of permittivity responding to frequency of P(VDF-CTFE)/ PMMA with both EMI-TF and EMI-TFSI
Up to now, it may be noticed that the nonlinear charging response occurs at high applied voltage (>1V) and longer times, where the substantial strain appears, is a universal phenomenon in these electro-active polymer matrix (Figure 3.6, Figure 3.10, Figure 3.12). The mechanism of the phenomena still remains question and needs further exploration. What for sure that it is not related electrochemical reaction, the existence of proton, or the moisture, but originates from certain intrinsic property of the interaction between electro-active polymer matrix and ILs.
3.4.4 Charge Storage and Bending Curvature

Shown in Figure 3.13 that P(VDF-CTFE), P(VDF-CTFE)/PMMA exhibit higher Curvature/C values than ionomer Aquivion, regardless of their different mechanical properties. It illustrates each charge stored in P(VDF-CTFE) based polymer generate larger bending curvature than Aquivion. One possible reason is that the flexible sulfonic acid side chains of the ionomer act as a cushion layer to buff the generation of curvature.

![Figure 3.13 Curvature/Charge in time domain](image)

Figure 3.13 Curvature/Charge in time domain

It repeals that, the charges accumulated in the short period, that is < 1s, make an efficient contribution to bending curvature. By contrast, in long time arrange, charge have little domination effect on bending actuation. (The value of vertical axis nearly remains the same).

These may due to the leakage current which not related to ion transport in the polymer matrix. It may also result from the cancellation effect between the cations and anions in
longer diffusion time. Another probability is the formation of cluster (e.g. EMI⁺TFEMI⁻) and their participation in the actuation process. From this point of view, the adoption of AC voltage for the generation of actuation would be much wiser.

It’s also noticed that hydrophobic ionic liquid has a larger ratio that hydrophilic ionic liquid in the longer time range. Maybe the election of a proper hydrophobic ionic liquid with higher electrical chemical window is another way to improve both charge storage and bending actuation in electroactive polymers.
3.4.5 Bending Curvature and applied voltage

![Bending Curvature Graph](image)

Figure 3.14 Bending Curvature of the actuators based on P(VDF-CTFE) soaked with 40mol% EMI-TFSI under different voltage

Shown in Figure 3.14 is the bending curvature of P(VDF-VTFE) based actuators under different voltages. Under the applied voltage 2.5 V or smaller, the actuator reveals no bending actuation within two hours. At 18 s, the curvatures under 3.5 V, 3 V, and 2.7 V are 0.3 mm\(^{-1}\), 0.075 mm\(^{-1}\) and 0.02 mm\(^{-1}\) respectively. It is of patency that the increase speed of bending actuation does not in accordance with the increase speed of applied voltage. There seems to be a switch voltage, only beyond which the corresponding curvature could rapidly roar when we apply higher voltage.
Chapter 4

Conclusion

EAP is a group of polymers that responds to the applied electric energy. It has a lot of potential applications, such as drug delivery, artificial muscle, robot, etc. I-EAP actuators and supercapacitors are among them. From the fundamental view, the complicated structures in the real devices can be abstracted to a MIM structure. This thesis has presented the work related to electroactive polymers with the MIM structure which provides a good study platform for ion transport and storage on ionic electroactive polymers. Polymer matrix and ionic liquid are always two essential elements building up the ionic devices. Two classes of polymer matrix were studied in the thesis. They are ionomer short-side-chain Aquivilon and non-side chain P(VDF-CTFE) based polymer groups. Also two classes of ionic liquids, hydrophilic ILs EMI-TF and hydrophobic ILs EMI-TFSI were adopted to be investigated. Beyond all the different structures of the supporters and carriers, it turned out that, fundamentally, the charge transport shared the same nonlinear effect in the ionic system.

Under an external electric field, the ion/charge transport in polymer matrix can be divided into two parts, that is, drift and diffusion. The drift process completed within milliseconds to charge the electrical double layer on the length of Debye Length while, by contrast, the diffusion process was slow after one second. Frequency domain was adopted to set the electric double layer charging time $\tau_{dl}$. It turned out that within the $\tau_{dl}$, charge density was linearly proportional to the applied voltage. In the longer time region (diffusion part)
nonlinear effect between charge density and applied voltage would take place. This effect was not limited to the certain combination of ILs and ionomer. It was a general phenomenon. The mechanism of the phenomena still remains a question and needs further exploration.

As for the bending curvature the actuators fabricated based on the electroactive polymers we investigated exhibit, high modulus PMMA improved the performance. It also turned out that hydrophilic ILs paired with crosslinked P(VDF-CTFE)/PMMA gave out the best electromechanical properties.

The charges accumulated at different charging period had different efficiency of contribution to the bending curvature. In the longer time diffusion part, probably due to the cancellation effect, ion/charge movement did have more effect on generating strain. Ideally, if we can synthesize a single mobile ion ionomer with enough mobile ion concentration, the cancellation effect might be reduced to facilitate the performance as i-EAP actuators.

The bending actuation did not response in accordance with the increase speed of applied voltage. There may exist a switch voltage, only beyond which the corresponding curvature could rapidly roar when applying a higher voltage.
Bibliography


