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NANOSTRUCTURED ELECTROACTIVE POLYMER ACTUATOR MATERIALS

A Dissertation in

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by

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ABSTRACT

This dissertation investigates nanostructured materials, including the nanorods of Field Activated Electro Active Polymer (FEAP) and Ionic Electro Active Polymer (IEAP) systems. As one of the most important FEAPs, the large electromechanical responses in the ferroelectric relaxor poly(vinylidene fluoride trifluoroethylene chlorofluoroethylene) P(VDF-TrFE-CFE) terpolymers make them attractive to nanoelectromechanical systems (NEMS), as well as nano-actuator and nanosensor applications. This dissertation develops the fabrication process for the nanorod array of P(VDF-TrFE-CFE) relaxor ferroelectric terpolymer using an anodic aluminum oxide (AAO) template. Nanorod arrays in the rod diameter have been fabricated down to 25 nm.

In the relaxor ferroelectric terpolymers, the bulky CFE monomers act as the random defects that break the long range polar-ordering in the ferroelectric P(VDF-TrFE), and the freezing of the random dipoles leads to the relaxor behavior. Making use of the nanorod arrays, the evolution of the relaxor ferroelectric behavior of the P(VDF-TrFE-CFE) terpolymers was investigated for nanorods with diameters reduced from 200 nm to 25 nm. It was observed that all the nanorods exhibited relaxor ferroelectric behavior, as characterized by the dielectric peak shifting toward high temperatures with frequency. The frequency-permittivity peak temperature characteristics fit well with the Vogel-Fulcher-Tammann (VFT) relation. Moreover, the freezing that the reduction of the nanorod's diameter influences the relaxor ferroelectric behavior of the terpolymer. The existence of ferroelectric relaxor properties in terpolymer nanorods as small as 25 nm suggests the possibility of terpolymers for NEMS and nanoactuator applications. It also provides an interesting ferroelectric material system with which to study the finite size effect in ferroelectric relaxor.

In the IEAPs, the ions transport through the ionic systems under an applied field and the subsequent accumulation and depletion of excess ions at the electrodes determine the response behavior of the electroactive devices, such as IEAP actuators and supercapacitors. Moreover, recent experimental results reveal the potential of ionic liquids (ILs) in enhancing the IEAP device performance. For instance, the vapor pressure of ILs is negligibly low and as a result they will not evaporate out of the IEAP devices when operated in ambient conditions. Their wide electro-chemical window (~4 V) allows the IEAP to utilize higher applied voltages than the dilute water solution electrolyte. ILs also offer the possibility of achieving high mobile ion concentration and high ion mobility. This dissertation investigates the charge dynamics of ILs in two kinds of nanostructured IEAPs, which possess distinctively different polymer nanomorphologies, and it is of great interest to know how these morphologies affect the charge dynamics of ILs:

- (i) Aquivion ionomer, which forms percolating nanostructured ionic clusters above a critical uptake of ILs for fast ion transport. In addition, its shorter side chain (in comparison to Nafion) could also lead to better IEAP actuator performance, owing to superior coupling to the polymer backbone.
- Poly(dimethylaminoethyl methacrylate-*co*-diethylene glycol methylether methacrylate) P(DMAEMA-*co*-DiglymeMA) copolymer, which was synthesized by Prof. Tim Long's group at Virginia Tech as a new class of IEAP.

A time domain electrical characterization method was developed and employed to systematically study the charge dynamics of ILs in these IEAPs. Compared with the frequency domain method, this method offers the possibility of probing the charge dynamics over a broad voltage range. In the Aquivion membrane swelled with EMI-Tf, the ionic conductivity and mobility show strong uptake dependent behaviors and undergo abrupt enhancement transitions close to the critical uptake, which suggests that the minimum uptake for the IEAP application is above its critical uptake. It was found that the ionic conduction of ILs is coupled with the segmental motion of the ionic phase of the Aquivion membrane implying that the enhancement of the ionic conduction is mainly due to the reduction of the glass transition temperature of the ionomer matrix with an increased uptake of EMI-Tf. The activation energies for ions to dissociate do not show substantial uptake dependence. With the same uptake of EMI-Tf, both Aquivion and Nafion show almost the same charge dynamics, while the short side chain Aquivion shows a better electromechanical coupling per charge than that of the longer side chain Nafion.

In the P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA ionic chains blended with 40 wt% uptake of EMI-Tf systems, a rapid drop of the conductivity, mobility and mobile ion dissociation ratio with increasing ionic chain density is observed. The conductivity follows Debye-Stokes-Einstein relation closely implying that the ionic conduction is coupled with the copolymer's segmental motion in this system. The electrostatic interactions among charges and ionic chains may slow down the chain mobility and increase the energy barrier for ion dissociation. These results suggest that the suppression of ionic conductivity, mobility and mobile ion dissociation ratio may be mainly caused by the increase in the ionic charged density of the local environment where the ions transport.

This dissertation shows that at voltages <1 V the charge dynamics in these IEAPs in a short time are dominated by the electric double layer (EDL), in which the charging time τ_{DL} follows the classic model $\tau_{DL} = \lambda_D d/(2D)$ (<< 0.1 seconds at room temperature for the IEAPs studied here) very closely where λ_D is the Debye length, d the membrane thickness, and D the diffusion constant. However, my study reveals that the EDL charges do not make much of a contribution to IEAP device responses, which are instead dominated by a much longer time charging process (> 0.1 seconds). Several recent theoretical models suggest that the charge dynamics at the later stage should follow the random diffusion time $\tau_{diff} = d^2/(4D)$, indicating that

by reducing the membrane thickness d the IEAP device response speed can be increased significantly. After examining the charge dynamics in the Aquivion membrane with 40 wt% uptake of EMI-Tf and pure BMI-PF₆ over a broad thickness range, my results show that in the longer time regimes ($t \gg \tau_{DL}$) the charge dynamics become dependent on the applied voltage. At a low applied voltage (0.1 V) the charge response seems to follow the d² dependence, whereas at a high applied voltage (> 0.5 V) where substantial actuation occurs, the charging responses do not show significant thickness dependence. These results imply that the movement of charges is mainly from the near electrode region, which might be due to the very high mobile ion concentration of the ionomer/IL systems studied here. The finding that actuation is mainly driven by the slow nonlinear charges instead of the double layer charges explains why the substantial actuation only occurs with voltage > 1 V and longer times.

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| 40 wt% uptake of EMI-Tf | 130 |
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Chapter 1

Introduction

This dissertation investigates nanosystems of electroactive polymers with the objectives of advancing understanding of these nanosystems and developing structure-property-functionality relationship; developing fabrication processes of these systems with tailored nanostructures; and, based on these processes, improving the electroactive properties of these nanosystems. The beauty of materials science is that by understanding the fundamentals of the material properties we can design and tailor the properties through physical or chemical approaches. In this dissertation, I investigated two nanostructured electroactive polymer (EAP) systems, i.e. Field Activated Electroactive Polymer (FEAP) and Ionic Electroactive Polymer (IEAP) systems, and aim to gain a fundamental understanding of the actuation of these materials related to their material properties in the nanoscale range.

1-1 Field Activated Electroactive Polymer (FEAP)

During the past decade, the nanoelectromechanical systems (NEMS), nanoacuators (such as molecular motors), and nanosensors have drawn great attention due to their potential impact on bioengineering, energy devices, and communications. For example, the feasibility of the direct electric nanogenerator based on the piezoelectric ZnO nanorod arrays has been demonstrated by several groups [1, 2]. As schematically illustrated in Figure 1-1, bending these ZnO nanorods array can generate a high electrical power output which presents an adaptable and mobile technology for harvesting energy from the environment to power nanodevices and nanosystems. Also as illustrated in Figure 1-2, the use of nanorods to estimate the cellular force sensing and control techniques has been demonstrated by Tan J. et al. From the deformation of these elastic posts, the force exerted on the cell can be evaluated [3].



Figure 1-1 The schematic of the current generation of ZnO nanorods array and its working mechanism of the nanorods current generator [1, 2].



Figure 1-2 Microposts array detector for the mapping of cell traction forces. Deviations of the pillars are monitored in real-time via dedicated image analysis algorithms. Local forces are then estimated via standard beam theory reported by Tan J. et al.[3].

One critical component in the NEMS is the actuators. The ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer based actuator exhibits a large electrostrictive strain (~4 %) with an ultra-fast response (< 10^{-3} seconds), high elastic modulus (~0.5 GPa), and high electromechanical

conversion efficiency (>10 %) [4, 5]. These attributes make it very attractive for nanoactuators and NEMS. In this dissertation, I have developed a fabrication process for producing the relaxor ferroelectric polymer nanorod arrays in diameters down to 25 nm and investigated the evolution of ferroelectric properties with decreasing the diameter of terpolymer nanorods.

Ferroelectric polymer is a kind of polymer that possesses spontaneous polarization which can be reoriented among possible equilibrium directions by an electric field. In most cases, ferroelectric polymers are in a semicrystalline form where the ferroelectric crystallites are embedded in an amorphous matrix. PVDF is polymorphic and has at least four major crystalline phases. The most important forms related to their extraordinary ferroelectric and electrostrictive responses are the form I (β -phase) and form II (α -phase) [4, 6, 7].

In the β phase, as illustrated in Figure 1-3, two chains in an all-trans planar zigzag conformation are packed into a orthorhombic unit cell whose lattice dimensions are a = 8.58 Å and b = 4.90 Å with a chain direction or fiber axis of c = 2.56 Å. Because of the all-trans conformation, the fluorine atoms are positioned on one side of the unit cell, resulting in a net dipole moment. The non-centrosymmetric crystal structure of the β -phase makes it a piezoelectric material. The conformation of form II (α -phase) is quite different from form I, as illustrated in Figure 1-4. The conformation of form II consists of alternating trans and gauche sequences, or TGTG. Therefore, the dipoles cancel each other out, resulting in a nonpolar material. Each unit cell contains two chains forming an orthorhombic lattice structure with lattice parameters a = 4.96 Å, b = 9.64 Å, and c = 4.62 Å.

Ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer is the polymer modified by introducing bulky CFE third monomer as random defects into the P(VDF-TrFE) copolymer. These defects convert the coherent polarization domain (all T chains) in normal ferroelectric P(VDF-TrFE) copolymer into nanopolar regions, in which a domain with nanometer size, all trains interrupted by trans and gauche bonds. In short, different frequency components of the polarization response will freeze at different temperatures [8, 9]. As a result, the normal ferroelectric P(VDF-TrFE) copolymer is transformed into a ferroelectric relaxor polymer. The dielectric peak temperature (T_m) shifts progressively toward higher temperatures with the frequency shown in Figure 1-5. It resembles a polar-glassy system which is driven by the thermally activated polarization fluctuation above a freezing temperature T_f . [4, 6-10]. This broad dispersive dielectric peak temperature with frequency can be described by Vogel-Fulcher-Tammann (VFT) relation.



Figure 1-3 The lattice structure and chain conformation of β phase PVDF [7].



Figure 1-4 The lattice structure and chain conformation of α phase PVDF [7].



Figure 1-5 The typical dielectric spectra of the normal ferroelectric P(VDF-TrFE) and ferroelectric relaxor P(VDF-TrFE-CFE) [9].

An electrostrictive phenomenon is one of the common electroactive responses to an applied voltage for most insulating polymers [4, 6]. The electrostrictive response can be described by the following equation as a quadratic dependence of strain on the polarization P.

$$S_{ij} = Q_{ijkl} P_k P_l , \qquad (1.1)$$

where Q_{ijkl} is the charge related electrostrictive coefficient. For an isotropic polymer,

$$S_3 = Q_{33} P^2$$
 and $S_1 = Q_{13} P^2$, (1.2)

where S_3 and S_1 are the strains along and perpendicular to the polarization direction. For an isotropic polymer, both experiment and theory indicates that

$$Q_{33} < 0$$
 and $Q_{13} > 0$

Hence, for a polymer, an increase in polarization will result in a contraction along the polarization direction. For a linear dielectric polymer, the polarization is related to the dielectric permittivity ε

$$P = (\varepsilon \varepsilon_0) E, \qquad (1.3)$$

where ϵ_0 is the vacuum dielectric permittivity (= 8.85 × 10⁻¹² F/m). Hence, Eq. 1.2 can be converted into

$$S = Q (\varepsilon - \varepsilon_0)^2 E^2$$
$$= M E^2, \qquad (1.4)$$

where M is the electric-field-related electrostriction coefficient. For an isotropic solid, the transverse strain $S_1 = M_{13} E_2$ and the longitudinal strain is $S_3 = M_{33} E_2$. Therefore, for an isotropic polymer, the coefficient shows different signs $M_{13} > 0$ and $M_{33} < 0$. In other words, it will expand along the film direction and contract along the thickness direction when an electric field is applied across the thickness.

P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer was purchased from Piezotech (France) and was prepared with a free radical polymerization using a suspension process [7]. The composition of the terpolymer determines its mechanical and dielectric properties. The current composition is optimized for better electromechanical performance. Introducing the bulky third

monomer CFE units as defects in the macroscopic polar domain converts the all-trans polar conformation to a phase with a mixture of trans-gauche (TGTG), all-trans and T_3GT_3G conformations that are macroscopically non-polar and exhibit ferroelectric relaxor behavior. Both the local polar-region reorientation and the induced local conformation change in coupled with the large lattice strain between the nonpolar phase and the polar phase contribute to large macroscopic electrostriction under an applied field. Earlier results from our group shows that for the P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer, its strain response along the thickness direction (S₃) under a field of 150 MV/m can be up to – 3.9 %, as shown in Figure 1-6. Its high elastic modulus (Y~ 147 MPa) also leads to a high elastic energy density (YS²/2, ~ 0.113 J/cm³) [5].



Figure 1-6 The longitudinal strain (S_3) as a function of the applied field of P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer.

Besides the nanoelectroactive devices, it is also interesting to study how the ferroelectric properties evolve if we further tailor the nanostructure of P(VDF-TrFE-CFE) terpolymer. In this study I developed a fabrication process for producing a nanorod array of P(VDF-TrFE-CFE) terpolymers via a melting-wetting process on an anodic aluminum oxide (AAO) template and

investigated the dielectric response and ferroelectric evolution in the nanorod array of P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer. The terpolymer nanorods were fabricated and investigated in diameters of 25 nm, 70 nm, and 200 nm. It was observed that all of the terpolymer nanorods exhibit the typical ferroelectric relaxor dielectric behavior. That is, the dielectric constant peak (T_m) shifts progressively toward higher temperatures with increasing frequency and this shift of dielectric constant peak temperature with frequency can be well described with the empirical VFT relation. The freezing temperature T_f in the VFT equation, deduced from the shift of the dielectric constant peak with frequency, is lowered as the terpolymer nanorod diameter is reduced. The existence of the ferroelectric properties shows the possibility of the terpolymer for the nano-meter scaled polymer actuator.

1-2 Ionic Electroactive Polymer (IEAP)

The IEAP actuators have the advantages of achieving large strain (> 5 %) and relatively low driving voltage (< 4 V), which make them attractive for integrating into microdevices where a direct integration with low voltage microelectronics can be readily made. However, IEAP actuators suffer a slow strain response (~ a few seconds) and low strain energy density due to low elastic modules. Besides IEAP actuators, the ion transport and storage in ionomers also have a great impact on many energy devices such as supercapacitors and batteries [11, 12].

The two critical materials in ionic devices are electrolytes and polymer membranes. The replacement of water-based electrolytes with room-temperature ionic liquids (ILs) led to breakthroughs in the durability and performance of the IEAP actuators. Ionic liquids , which are a class of salt in liquid form that contains both ions and neutral molecules, can generally provide a high concentration of mobile ions [13, 14]. The vapor pressure of ILs is negligibly low and as a result they will not evaporate out of the IEAP devices when operated in ambient conditions. It has

been demonstrated that, compared with water, the use of ILs as solvent for IEAP actuators can dramatically increase the lifetime of the transducer. Their wide electro-chemical window (~ 4 V) allows the IEAP for higher applied voltages [13, 15-17].

Ionic liquid of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) was selected in this study as the electrolyte in the IEAPs due to its high conductivity (8.6 mS/cm), low viscosity (45 cP at 25°C), and large electrochemical window (~ 4.1 V). Though Nafion is the most commonly reported ionomer for IEAP actuator applications, the short side chain Aquivion may have a better electromechanical coupling efficiency. Aquivion consists of a polytetrafluoroethylene (PTFE) backbone and double ether perfluoro side chains terminating in a sulfonic acid group and is known in the literature as a short-side-chain ionomer (in comparison to Nafion®, which is indicated as a long-side-chain ionomer) and was originally developed by Dow Chemical Company. The short-side-chain Aquivion purchased from Solvay Solexis allows us to study the side chain length effect on the charge dynamics of EMI-Tf when compared to long-side-chain Nafion. On the other hand, the P(DMAEMA-co-DiglymeMA) copolymers with differently charged DMAEMA chain densities synthesized in Professor Tim Long's group provide platforms from which to investigate the positively charged amino chain density effects on the charge dynamics of EMI-Tf.

It was found that when Aquivion ionomer is swelled with EMI-Tf above its critical uptake the formation of ionic percolation channels may occur. On the other hand, when EMI-Tf was blended with P(DMAEMA-co-DiglymeMA) copolymers, the formation of micelles was observed. Therefore, it is of great interest to investigate the charge dynamics evolution of EMI-Tf in these two distinctive ionic nanostructured materials: (i) the percolation nanostructured ionic channels of Aquivion and (ii) the nanostructured micelles of P(DMAEMA-co-DiglymeMA). We aim to correlate the charge dynamics of IL with the following critical parameters for a better design of IEAP actuators: (1) the uptake effect on the charge dynamics of ILs; (2) the influence of

the ionomer side chain length on the charge dynamics of ILs and actuation; (3) the correlation between the charge dynamics of ILs and the nanomorphology of ionomers; (4) the correlation between charge dynamics of ILs and the segmental motion of the polymer matrix; (5) the polymer membrane thickness effect on the charge dynamic of ILs; and (6) the non-linear charging effect on actuation at high applied voltages and longer times.

Though many attempts have been made to improve the performances of the actuator, such as using a conductive network composite (CNC) to increase the surface area of electrodes, these complicated electrodes prohibit analysis and understanding of the charge dynamics in these devices [18-20]. Therefore, in this study, I investigate the charge dynamics of IL in an actuator which consists of an ionomer membrane swelled with IL and two gold leaf electrodes as illustrated in Figure 1-7. This simple structure provides a well-defined geometry for charge dynamic investigation. Further, I found that using this simple structure without CNC layers, Aquivion, which possesses a better electromechanical coupling effect than Nafion, can still generate substantial strain as reported in chapter 4. In fact, several subsequent experiments with Prof. Zhang's group have shown that this actuator configuration provides a very convenient way to create microactuators, with a potential for many applications such as microactuator arrays for optical applications.



Figure 1-7 The structure of the bending actuator which consists of an ionomer membrane swelled with ILs and two gold leaf electrodes.

In the classic picture of the charge transport mechanism of the IEAP actuator, under an external field, the cations and anions move through the nanostructured ionic region to the opposite polarity of electrodes and polarize the electrodes. The charge imbalance and the size difference between the cation and anion result in the strain of the bending actuator [21]. Except the direct measured stain response, the charge dynamics, i.e., the ion transport process, and the intrinsic material parameters such as the conductivity σ and mobility μ , are fundamental material processes and properties critically influencing the actuator performance such as the strain speed, the strain level, and the electromechanical coupling efficiency.

Electrode polarization in ionic conduction systems has been studied for many decades and it has been shown that it takes less than < ms to polarize the electrodes. These earlier studies were mostly limited to low applied voltage (<1 V) [22]. On the other hand, in practical ionic devices such as ionic actuators and supercapacitors, major actuation and stored charges occur in a few seconds at voltages above 1 V [12, 18, 21, 23]. This dissertation investigates the charge dynamics of ILs in ionomer membrane over a broad time and voltage range, using a unique time domain characterization method developed during my dissertation study.

1.3. Thesis Organization

In Chapter 2, the fabrication process for AAO templates with diameters from 200 nm down to 25 nm is presented. Though the fabrication of the anodic aluminum oxide (AAO) template has been developed for decades, to systematically grow the long range highly ordered AAO template with pore sizes over a wide diameter range is still a challenge. In this dissertation, I successfully grow AAO templates with diameters from 200 nm down to 25 nm in our home-built setup through a two-step anodization process. These AAO templates provide solid nanochannel structures for further tailoring the geometry of the terpolymer relaxor by wetting the nanopore walls with terpolymer melts. The wetting kinetics of the polymer melt was investigated.

In a short time frame, a thin layer of polymer melt will spread on the pore wall, forming polymer nanotubes, while in a longer time period the polymer melt will infiltrate the polymer nanotubes again, forming the solid nanorods. These nanowire structures are confirmed by both SEM and TEM.

In Chapter 3, the ferroelectric properties of the terpolymer nanorod arrays are characterized by impedance spectroscopy. It was found that the ferroelectric properties persist down to 25 nm diameter implying the possibility of terpolymer nanorods for the nanoactuator applications. The crystallite size and orientation of these nanorods are examined by wide-angle x-ray scattering. The low crystallinity of these nanorods is also confirmed by the DSC in which no clear (crystallization) melting peak is observed. With the reduction of the diameter of terpolymer nanorods, the long range coupling among spontaneous dipoles in the relaxor was reduced, leading to the instability of the spontaneous polarization and hence lowering the relaxor's freezing temperature T_f . Also, the β relaxation process corresponding with the segmental motion of the terpolymer chain shifts to a higher frequency as the diameter of the nanorods embedded within the AAO template decreases, implying the size and/or interface effects on the glass transition temperature.

In Chapter 4 the charge dynamics of ILs in Aquivion bending actuators were investigated. For practical IEAP devices, the actuation and charge responses occur at times > 0.1 seconds, and much beyond that for charging the electric double layer (EDL) (electrode polarization). Several recent theoretical models have been developed to characterize the charge dynamics over a broad time scale, beyond the traditional EDL model. In order to characterize experimentally the charge dynamics over a broad voltage range which is often non-linear, a time domain characterization method was developed in this dissertation.

In the Aquivion membranes swelled with EMI-Tf, the ionic conductivity and mobility show strong uptake-dependent behaviors and undergo abrupt enhancement transitions close to the critical uptake, which suggests that the minimum uptake for the IEAP application should be above its critical uptake. The side chain length effect of ionomers on the electromechanical coupling efficiency is examined by comparing the electromechanical responses and charge dynamics of Aquivion and Nafion membranes in which Aquivion has shorter side chains than that of Nafion. With the same 40 wt% uptake of EMI-Tf, both Aquivion and Nafion membranes show nearly identical conductivity, mobility, and mobile ion concentration. In longer time frames, the results show that the short side chain Aquivion imparts a better electromechanical coupling efficiency than that of long side chain Nafion

In a short time frame, the charge dynamics are dominated by the double layer charging behavior and the double layer charge shows a linear relation with applied voltage up to 4 V. In a longer time frame the experiment's result shows a substantial nonlinear effect of charge accumulation at high voltages, which is several orders of magnitude larger than that due to the double layer charge, indicating that it is the later nonlinear charge accumulation that contributes to the ionic actuation for actuator as well as the huge capacitance for the supercapacitors. Hence, it is critical to understand the later stage charging process. As observed the conductivity does not change with applied voltage at least up to 4 V while the mobility and mobile ion concentration do not change with applied voltage at least up to 1 V, both of which are the experimental upper limits.

We examine the temperature dependence of charge dynamics of Aquivion membranes with different uptakes of EMI-Tf. It was found that the conductivity and mobility follow the VFT relation while the mobile ion concentration follows the Arrhenius relation. By normalizing the temperature dependence of the ionic conductivity with its ionic phase T_g , we found that samples with different uptakes of EMI-Tf have approximately the same conductivity at the same T-T_g, implying that the ionic conduction is coupled with the segmental motion of the ionic phase of Aquivion membrane. The abrupt enhancement of the ionic conduction may be mainly attributable to the rapid decrease of the glass transition temperature of the ionic phase of Aquivion matrix near the critical uptake of EMI-Tf. The temperature dependence of mobile ion concentrations of Aquivion membranes with different uptakes of EMI-Tf is also examined. The experiment results show that, within the experimental errors, the activation energy for ions to dissociate is almost independent of the uptake of EMI-Tf.

Developing advanced ionic polymer membrane actuators requires an understanding of the influence of sample geometry on the charge transport and storage, especially the thickness of the membrane sandwiched between two electrodes. In Chapter 5, the influence of the thickness of the ionomer membrane on the charge dynamics is discussed. Especially, the charge dynamics of Aquivion membrane with 40 wt% uptake of EMI-Tf and pure BMI-PF₆ liquid cell are investigated over a broad membrane thickness (d) range. It was found that the double layer charging time τ_{DL} follows the classic model $\tau_{DL} = \lambda_D d/(2D)$ very well for both systems, where D is the diffusion coefficient and λ_D is the Debye length. In the longer time frames (t >> τ_{DL}), the charge dynamics become dependent on the applied voltage. For low applied voltage (~ 0.1 V), the later stage charging process seems to follow the d² thickness dependence. However, at high voltages (> 0.5 V) in which significant ionic membrane actuation occurs, the charging process does not show d² thickness dependence and $\tau_{diff} = d^2/(4D)$, corresponding to the ion diffusion from the bulk region, was not observed in both systems, implying that the movement of diffusion charges is mainly from the near electrode region rather than from the bulk of the membranes.

Without abnormal leakage current, an apparent deviation of τ_{DL} from the proportional trend of thickness (d) relation was observed on 1.9 µm thick Aquivion membrane while it was not observed on the pure IL BMI-PF₆ system. We extrapolated the bulk resistant R_b to the thickness approaching zero for both systems and found that the swelled Aquivion membrane has a residual resistance around 10.2 ohm/cm² while the pure IL BMI-PF₆ sample has a residual resistance

approaching zero. Considering the measurement error of the setup, which is less than 0.1 ohm/cm², we suggest that there an interface resistance exists in the polymer and gold electrode interface.

In Chapter 6, the ionic chain density effect of the poly(dimethylaminoethyl methacrylateco-diethylene glycol methylether methacrylate) P(DMAEMA-co-DiglymeMA) ionomer on the charge dynamics of EMI- Tf is discussed. Different from the perfluorosulfonate ionomers with negative charged sulfonic end groups, Poly(dimethylaminoethyl methacrylate), PDMAEMA consists of a polymethacrylate backbone with positively charged dimethyl amino groups.

We investigate the charge dynamics of P(DMAEMA-co-DiglymeMA) copolymers in Cl form with 10, 30, 50 and 70 mole % of DMAEMA blended with 40 wt% uptake of EMI-Tf. As observed the conductivity, mobility, and mobile ion dissociation ratio drop rapidly with increasing the ionic chain density. It is found that the ionic conduction is coupled with the segmental relaxation frequency of copolymer following Debye-Stokes-Einstein relation very closely. No apparent conductivity deviation among all samples at a fixed relaxation frequency of copolymers is observed implying that the drop of the conductivity at room temperature may be mainly caused by the slowdown of the segmental motion of copolymers with increasing the ionic chain density. The electrostatic interactions among charges and ionic chains may slow down the chain mobility and increase the energy barrier for ion dissociation. These results suggest that the reduction in the ionic conductivity, mobility and mobile ion dissociation ratio may be mainly caused by the increase in the ionic charged density of the local environment where the charges transport.

Chapter 2

Nanorods and Nanotubes of P(VDF-TrFE-CFE) Electroactive Terpolymer

2-1 Introduction

P(VDF-TrFE-CFE) terpolymer exhibits extraordinary field activated strain (~4%) and high energy density ($YS^2/2$, ~ 0.113 J /cm³) [5]. Therefore it can potentially be applied to nanoactuators when its size is reduced. The wetting of polymer melts on the porous anodic aluminum oxide template (AAO) provides an efficient approach to fabricating the nanostructured terpolymer nanorods. In this chapter the growth conditions for a long range highly ordered porous AAO template are discussed. Only under certain specific voltages with proper electrolytes can the oxidation and dissolution processes reach the same rate, thus forming the straight alumina nanopores. To improve the long range ordered AAO template, a two-step anodization approach is employed. The creation of pre-texture from the first anodization provides the ordered initial sites for the second anodization, leading to a high quality long range ordered porous AAO template.

The polymer nanotubes can be formed by wetting the polymer melt on the pore surface in a short time. With time, the instability of the polymer melt induces its infiltration into nanotubes, forming polymer nanorods. Nanorods or tubes with diameters of 25 nm, 70 nm, and 200 nm are fabricated and their microstructures of nanotubes and nanorods are confirmed by TEM and SEM. Moreover, the preferred crystal orientation of the polymer nanowires is also reviewed.

Since the ferroelectric properties mainly originate from the ferroelectric crystallite region in the polymers, it is important to review the crystal properties in the ferroelectric terpolymer nanorod system, including its crystallinity, crystal structure, and crystallite size. Polymers usually crystallize in a lamellar crystal form in which the chains are folded and orientated as illustrated in Figure 2-1(a). Usually the thickness of the lamella is in the nanometer range and the sizes in the lateral direction are in the micrometer range. The lamellae are organized in spherulites, isotropic polycrystalline superstructures [24]. Therefore, it can be expected that not all the dimensions of the lamellae can grow into the nanopores when a two-dimensional (2D) confinement is imposed on the growth of the crystallite. The pore wall stops the growth of lamella. As suggested by Steinhart M. et al, illustrated in Figure 2-1 (b), on the top of the bulk polymer, the growth of the lamellae initiates from randomly oriented nuclei. The formation of homogeneous nucleation results in equal probability growth for all directions. When the growing of lamellae reach the pores, the growth orientation is determined by the growth direction of lamellae at the bulk polymer and template interface resulting in the observed selective growth of the crystallite orientation in the nanopores [25]. Thus it is observed that the growth of lamellae is stopped by the pore wall. Only the lamellae with a < h, k, 0 > directions that are parallel to the pore axes can grow along the pores wall. It implies that the polymer chains of PVDF are perpendicular to the pore wall, as illustrated in Figure 2-1 (b).

Steinhart M. et al. demonstrated the selective growth orientation of PVDF crystallite in 35 nm and 400 nm diameters AAO template pores by XRD. The XRD contains four reflections of α -PVDF (100) : $2\theta = 17.9^{\circ}$; (020) : $2\theta = 18.3^{\circ}$; (110) : $2\theta = 20.0^{\circ}$; and (021) : $2\theta = 26.6^{\circ}$. Their XRD scatter patterns of PVDF embedded in the AAO template show that only crystal lattice planes oriented parallel to the surface of the template contribute to the intensity of a Bragg reflection as reported in Figure 2-2. This finding implies the preferred polymer lamellae orientation in the nanopores [24, 26, 27].



Figure 2-1 (a) The schematic of lamellae (b) the schematic diagram of the growth mechanism of preferred orientation lamellae [24].



Figure 2-2 XRD reflection peaks of PVDF (a) 35 nm nanorods (b) 400 nm nanotubes (c) bulk reported by Steinhart M. et al. [25].
Anodic Aluminum Oxide (AAO) Template

Nanomaterials synthesized by template-assisted approaches have the advantages of a low cost, a high pore density, and wide choices of pore sizes. Anodic porous alumina has been applied in a wide variety of fields for many years because of its unique geometrical nanostructures. In this chapter, the synthesis of long range highly ordered porous AAO template and its application to the preparation of polymer nanotubes and nanorods will be discussed.

The porous AAO template has been studied for decades. As reported in literatures, the process's recipe window for long range ordered anodic porous alumina is very narrow. It only occurs under some specific voltages, electrolyte concentrations, and temperatures. The major factor to control the pore diameter and interpore distance is the anodization voltage, i.e., the interpore distance increases linearly with applied voltage in proper acid solutions as reported by Li A. P. et al. in Figure 2-3 [28].

The general idea for the growth of porous anodic aluminum oxide is, essentially, a result of the competition between field-assisted growth and the dissolution of aluminum oxide [29]. Initially, the oxide growth starts with the ionic conduction and reaction of AI^+ and OH^- under an applied field.

$$2Al^{+} + 3OH^{-} -> Al_2O_3 + 3H^{+} + 6e^{-}$$

Pores then start to initiate at random positions through field-assisted dissolution of the alumina.

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$

When both reactions approach the same rate, the growth of porous alumina reaches a steady state. At the bottom of the cell (the barrier layer), the oxide layer grows through the migration of Al^{3+} and O^{2-} ions under a strong electric field. The interpore distance, which is equivalent to the cell size, has a strong linear relationship with the applied voltage. For long range highly ordered hexagon packed porous structures the growth conditions are rigorously specific. Jessensky O. et al. attribute this self-organized pore structure to the stress field effect during the anodization. In

other words, the repulsive forces between neighboring cells are the source of stress at the metal– oxide interface, thus facilitating the growth of hexagonal ordered arrays as illustrated in Figure 2-4 [30].



Figure 2-3 The relation between interpore distance and applied voltage with different anodization electrolytes [28].



Figure 2-4 The schematic of the growth steps of porous anodic aluminum oxide template [30].

Methods and optimal recipes for the long range ordered anodic porous alumina have been intensively investigated with the assistance of lithography patterns [31], pre-textured approaches [32] and two-step anodization processes [33, 34]. Among these approaches, the two-step process is used in this dissertation due to its easy nature and high-quality results. The long range ordered pore structure of anodic porous alumina template with pore diameter from 25-200 nm was fabricated. The pore density can be as high as 10^9 pores per cm² [30].

The pore arrangement of anodic porous alumina in the initial stage of anodization is random and the degree of ordering is very low. The ordering of the pore arrangement showed improvement over time under the appropriate anodizing conditions. Therefore, the pore arrangement at the top of the cell is not as ordered as that at the bottom. To get a long range highly ordered pore structure of anodic porous alumina with identical pore arrangement from top to bottom, a two-step anodization process was reported by Masuda H. and Fukuda K.. As illustrated in Figure 2-5, the disordered porous layer is removed in a mixed solution of chromium oxide and phosphoric acid after a long period of anodization. The ordered array of residual textures obtained after removing the oxide layer formed in the first anodization can act as initiation sites for the second anodization which can assist the growth of straight long range highly ordered pores [33]. This approach provides a high quality result without any additional setup. In my study, I found the best recipe for fabricating long range highly ordered pore structure of 25 ± 2 nm, 70 ± 5 nm and 200 ± 10 nm is 0.3 M, H_2SO_4 at 27 V, 0.3 M, Oxalic at 60 V, and 0.1 M, H_3PO_4 at 158 V, respectively.



Figure 2-5 The schematic of the two-step anodization process for long range highly ordered porous AAO template [33].

Synthesis of P(VDF-TrFE-CFE) terpolymer nanotubes and nanorods

One of the most popular ways to fabricate one dimensional polymer nanotubes and nanorods is by wetting high energy surface substrates such as aluminum oxide, or porous silicon templates, with low energy polymer solution or melt [26, 35]. Wetting is a phenomenon that occurs when a low energy solution, or melt, is put on a high energy solid surface: the polymer melt or solution will attempt to spread on the surface due to the force imbalance among interface tensions as illustrated in Figure 2-6. After complete wetting, the high energy surface will be covered by a low surface energy precursor polymer film. The Eq.(2.1) describes the wetting process [36].

$$S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \tag{2.1}$$

where S is spreading parameter, γ_{SV} the solid-vapor, γ_{SL} the solid-liquid and γ_{LV} the liquid-vapor interfacial tension. If S<0, the droplet will stop deformation at the shape with specific contact angle θ due to the force balance where $\gamma_{SV} = \gamma_{LV} + \gamma_{SL}\cos\theta$ as illustrated in Figure 2-6. That is called partial wetting. On the other hand, if S > 0, it means that the force γ_{SL} is larger than the force summation of γ_{LV} and γ_{SL} therefore, the net force will draw the droplet to cover the hole substrate surface and approach the contact angle $\theta = 0$, which is called complete wetting.



Figure 2-6 The interface forces of a droplet on a solid substrate [36].

The formation of polymer nanotubes or nanorods depends mainly on the processing time. As mentioned in Martin's work [25, 26], the wetting process of the polymer film is a kinetic stable process and not a thermal dynamic stable process. In other words, the probability to break the kinetic stable state increases with time, which leads the system to a lower energy state. The polymer melt wets on the pore surface and spreads out to form a thin layer of polymer film on the pore wall in a short time scale. The thickness of the pore wall is usually in a few tens of nm. The probability for the thin polymer melt layer to form menisci increases with time. These menisci initiate the infiltration of polymer melt into the polymer tubes leading to the formation of polymer nanorods as illustrated in Figure 2-7 [36, 37].



Figure 2-7 A schematic of the formation of polymer nanorods in AAO template [36, 37].

2-2 Experimental

P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer was purchased from Piezotech (France) which was prepared with a free radical polymerization using a suspension process [5]. The terpolymer nanorods were fabricated using AAO templates with nanopore sizes of 25 nm, 70 nm, and 200 nm diameters. AAO templates with these nanopore diameters were prepared following the two-step fabrication process as described in the previous section. The 99.999 % high purity aluminum foil purchased from Aldrich was cleaned with acetone to remove greasy dirt. The sample was then annealed at 400 °C for at least 6 hours to enlarge the grain size of the aluminum. After polishing the aluminum foil by 4 µm silicon oxide power, the size of the aluminum grain can be observed by the naked eye. This large-sized grain of aluminum can improve the long range order of pores, since the disorder of the pores occurs near the grain boundary region. Polishing the foil with 4 µm silicon oxide powder is not enough to obtain a mirror-like surface on the aluminum foil. Therefore, electrochemical polish was employed. The powder-polished sample was then dried and anodic electrochemical polished in an acid solution mixed with H_2SO_4 : $H_3PO_4 = 1:1$. By controlling the current to keep the reaction mild for around 20 minutes, a mirror-like surface sample can be obtained. The polished sample was dried and put into the proper electrolyte for anodization. The best recipe in this study for pore diameter of $25 \pm$ 2 nm, 70 ± 5 nm and 200 ± 10 nm is 0.3 M H₂SO₄ at 27 V, 0.3 M Oxalic at 60 V, and 0.1 M H₃PO₄ at 158 V, respectively. Using the 70 nm template as an example, oxalic acid is the suitable electrolyte for applied voltage around 60 V. The sample was put in a stirred electrolyte with a temperature controlled chiller to stabilize the anodization process at 0 °C as illustrated in Figure 2-8. It takes eight hours to make the long range ordered porous structure at the bottom of oxide film. After removing the disordered pores on the top, the long range ordered concave pre-textures are left as the initial sites for the second anodization leading to the formation of high quality long range ordered porous anodic aluminum oxide template. These AAO templates formed were cleaned with deionized water thoroughly, and then were heated at 400 °C for 4 hrs to remove the moisture and other impurities. It was found that this procedure of removing impurities in the nanopore templates is crucial in order to measure the dielectric properties of the terpolymer nanorods. Residual impurities in nanopore templates can cause severe conduction loss, which can dominate the dielectric properties.

In order for the terpolymer to infiltrate the nanopores of the templates, a two-step infiltration process was developed. First, the solution of 3 wt% P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer dissolved in dimethyl formamide (DMF) was poured in/onto the top surface of the AAO nanopore template and the solvent was evaporated at room temperature. After that, the terpolymer with templates was heated at 260 °C for 4 hrs in a temperature-controlled vacuum oven (VWR), and then chilled to room temperature at a rate of 1 °C/min. The excess terpolymer at the top of the AAO templates was removed by mechanical polishing with 1 μ m sized alumina powders. The bottom AAO template was opened by first removing the aluminum layer with 1.7 wt% CuCl₂ solution with HCl:H₂O = 1:1 followed by etching with 5 wt% H₃PO₄ at 30 °C to remove alumina buffer layer. The typical thickness of the terpolymer nanorods in AAO templates in this study is in the 65 μ m to 100 μ m range.



Figure 2-8 The setup for AAO template fabrication which consists of a chiller, a DC power supply, and a stirrer.

2-3 Results and Discussion

As shown in Figure 2-9, the long range ordered porous AAO templates with pore diameter of (a) 25 ± 2 nm,(b) 70 ± 5 nm and (c) 200 ± 10 nm were fabricated by a two-step anodization process which provides solid nanochannel structures to tailor the terpolymer nanowires. The terpolymer nanotubes with a pore diameter of 200 nm were formed by wetting the ordered AAO nanopores with a layer of polymer melt at 260 °C, which is well above its melting temperature, for 30 minutes as shown in Figure 2-10(a). Because the wetting process is a kinetic

stable process and not a thermal dynamic stable process, the instability of the wetting process will induce the filling of the nanotubes in a longer time scale [4]. After heating at 260 °C for 4 hrs in vacuum, the inner pores of the polymer tubes were infiltrated again forming polymer nanorods as shown in Figure 2-10(b). From the SEM of 200 nm samples we can see a convex shape of the nanowire bottom which is evidence that the formation of polymer nanowires was driven by wetting the pore wall all the way to the bottom pore surface, as shown in Figure 2-10(c). The TEM image of Figure 2-11(a) shows that the thickness of the tube wall is around 40 nm which is also confirmed by the SEM image in Figure 2-10(a). Additionally, the TEM image of the 200 nm nanorod sample, clearly shows that the nanotube is filled with terpolymer within the inner pore of the nanotube in Figure 2-11(b). Figure 2-12(a) shows the 70 nm nanorod clusters after removing part of the AAO template and the TEM image of Figure 2-12(b) confirms its nanorod structure. The 25 nm nanorod clusters were also characterized by SEM as shown in Figure 2-12(c).



(b)



(c)



Figure 2-9 The long range ordered porous AAO templates with pore diameter of (a) 25 ± 2 nm,(b) 70 ± 5 nm and (c) 200 ± 10 nm.



Figure 2-10 The SEM images of 200 nm diameter (a) terpolymer nanotubes, (b) top view of terpolymer nanorods, and (c) bottom view of terpolymer nanorods.



Figure 2-11 The TEM images of a 200 nm diameter (a) terpolymer nanotube and (b) terpolymer nanorod. The nanotube and nanorod structure are confirmed by TEM images. The tube wall thickness is around 40 nm.



Figure 2-12 (a) The SEM image of 70 nm diameter nanorod forests, (b) the TEM image of 70 nm diameter nanorod, and (c) SEM image of 25 nm diameter nanorod forests.



Figure 2-13 The SEM image of the polished 70 nm terpolymer nanorods/AAO template composite. From this image the nanopore area can be deduced as 31.6 %.

Presented in Figure 2-13 is the SEM image of the AAO template with 70 nm diameter pores. From the SEM image, the deduced nanopore area is 31.6 % of the total surface area (or 31.6 % of the total volume is occupied by the nanopores). The volume percentage of nanopores in the template is 37.4 %, 31.6 % and 36.8 % for the nanopore sizes of 25 nm, 70 nm, and 200 nm, respectively. This volume estimation is for calculating the dielectric behavior of terpolymer nanorods from the embedded AAO template later.

2-4 Summary

A process was successfully developed to tailor the terpolymer nanorods by wetting the terpolymer melt on the pore walls of AAO template. The long range ordered pore structure of porous AAO template with pore diameter of 25 ± 2 nm, 70 ± 5 nm and 200 ± 10 nm was fabricated via a two-step anodization process. The best recipe in this study for pore diameter of 25 ± 2 nm, 70 ± 5 nm and 200 ± 10 nm is 0.3M H₂SO₄ at 27 V, 0.3M oxalic at 60 V, and 0.1M H₃PO₄ at 158 V, respectively. Different from the reported cleaning process which only uses deionized water, we anneal the AAO templates at elevated temperature to further remove the residual impurities inside the AAO nanopores and it was found that this is a crucial process step to reduce the conduction loss of terpolymer-AAO template composites for the dielectric characterization.

By wetting the terpolymer melt on these nanopore walls, the terpolymer nanowires are fabricated. The kinetic of the terpolymer melt infiltration process was investigated. It was found that in a short time frame the wetting of terpolymer melt on the nanopore walls forming terpolymer nanotubes. While in a longer time frame the instability of the thin terpolymer melt layer increases which causes the infiltration of terpolymer melt into the terpolymer nanotubes leading to the formation of terpolymer nanorods. These nanotube and nanorod structure were confirmed by both SEM and TEM.

Chapter 3

Relaxor Ferroelectric Behavior of P(VDF-TrFE-CFE) Terpolymer Nanorods

3-1 Introduction

Ferroelectric materials are strongly coupled materials in which dipoles display long range interaction. Consequently their properties and responses can be sensitive to system sizes as they approach nanometer scale. Relaxor ferroelectrics are a special class of ferroelectrics whose responses are dominated by the polar-glass freezing process [8, 10, 38-40]; it is of great interest to investigate how the ferroelectric relaxor behavior evolves as the system size diminishes. In this chapter, we study the ferroelectric relaxor polymer nanorods P(VDF-TrFE-CFE) 59.2/23.5/7.2 mol% terpolymer, which have been prepared via a melting-wetting process on an anodic aluminum oxide (AAO) template. Terpolymer nanorods in diameters of 25 nm, 70 nm, and 200 nm were prepared and investigated. It is observed that all of the terpolymer nanorods exhibit the typical ferroelectric relaxor dielectric behavior. The freezing temperature T_f in the Vogel-Fulcher-Tammann (VFT) relation, deduced from the shift of the dielectric constant peak with frequency, is lowered as the terpolymer nanorod diameter is reduced. The existence of the ferroelectric properties implies the possibility of a nanometer scale polymer actuator.

Although PVDF nanowires have been fabricated no electrical characterization result has been reported [24-26]. We found that the high ionic conduction loss due to impurities in the nanopore walls may be the main reason for prohibiting the characterization of the electrical properties of polymer nanorods. We annealed the AAO template at elevated temperature to remove impurities in the AAO template and found that this step can effectively reduce the conduction loss of the AAO template-terpolymer nanorods composites. In fact to the best of our knowledge, this is the first reported dielectric result in polymer nanorods [41].

The terpolymer nanorods were embedded in AAO template support. Therefore the segmental motion of terpolymer chain may be affected by the nanopore confinement. Kremer and co-workers studied dynamics of H-bonded liquids confined to nanopores using broadband dielectric spectroscopy. The materials (propylene glycol (PG), butylene glycol (BG) and pentylene glycol (PeG)) are in confined porous sol-gel glasses with pore sizes of 7.5, 5.0 and 2.2 nm [42]. Their results showed no confinement effect on the relaxation rates of PG and BG in 7.5 and 5 nm pores whereas for the PeG the α relaxation in 7.5 and 5 nm pores became slightly faster compared to the bulk. On the other hand, for all the materials tested in 2.5 nm pores, the peak relaxation rate is slower than that for the bulk. The authors suggested that the increase in T_g for the confined liquids in small pores was due to the existence of strong H bonding to the surface of the pore wall. Therefore, the interaction between the wall and the molecules can affect the relaxation process in nanopores; strong interactions cause T_g to increase whereas weak interactions result in a reduced T_g [42].

Petychakis et al. [43] studied the dielectric properties of polyisoprene (PI) with different molecular weights, between 2000 and 108 000 g mol⁻¹, in a treated controlled porous glass (CPG) with diameter of 10.2 nm. It was found a pronounced confinement effect on the dynamics, which also depend on the molecular weight. For the PI with molecular weight of 2000 confined in native CPG, its α relaxation time was found longer than that with molecular weight of 5000 [43]. For the higher molecular weight polyisoprene confined in the untreated CPG, it was found that the higher the molecular weight the shorter the relaxation time. In the case where the highest molecular weight PI was confined in the treated CPG, a shift in the relaxation times to lower frequencies

were observed [43]. Hence, as suggested by the authors, T_g could increase or decrease depending on molecular weight, pore size and pore surface treatment.

There are also many reports of the glass transition in thin polymer films. Keddie et al. [44] performed the measurement of T_g for thin polystyrene films constrained to substrates using ellipsometry and a reduced T_g , compared to the bulk one, was observed. Keddie et al. [44] suggested that the decrease in T_g for thickness < 40 nm was caused by the existence of a liquid-like layer at the polymer-air interface accompanied by the effects of the interaction with the substrate. No molecular weight dependence of the depression of T_g in supported PS films was observed. Keddie et al. [45] also reported results for supported thin PMMA films where an increase and decrease in the glass transition were observed. For PMMA on silicon wafers with the native oxide layer, the measured T_g increases with decreasing film thickness whereas a decrease in T_g was observed for PMMA on a gold-coated silicon surface. Keddie et al. [45] suggested that not only can the interaction between the polymer and the substrate affect the T_g measurements but also the treatment of the substrate can play an important role in the T_g behavior of the supported thin polymer films.

Russell et al. performed small-angle neutron scattering to characterize the chain structure and conformation in ultrathin (less than 100 nm) polymer films. The conformation can be deduced directly from the scattering from mixtures of protonated and perdeuterated polystyrenes. They found that the Gaussian conformation is retained parallel to the surfaces in all cases. The chain conformation in the bulk material is different from that in 2D thin films where the chains retain unperturbed Gaussian conformations in the direction parallel to the surfaces. Hence, the relaxation dynamics in 2D thin films is different from that observed in 3D bulk materials [46].

Most results reported in literature show that the glass transition at the nanometer scale is different from that of the bulk material. The change of T_g may be due to an intrinsic size effect, a confinement effect, the sample preparation effect or a combination of these effects.

3-2 Experimental

The terpolymer nanorods in diameters of 25 nm, 70 nm, and 200 nm were prepared and characterized by the following process flow as illustrated in Figure 3-1. The details of this process are reported in Chapter 2. The thickness of AAO-polymer composite is in 65-100 μ m thick range. To characterize the ferroelectric properties of the polymer nanorods embedded in the AAO template, we mechanically remove the residual polymers on top of the template with 1 μ m silicon oxide powder, which is followed by removing the aluminum substrate with HCl/H₂O 1:1mixture + 1.7 wt% CuCl₂. The bottom barrier layer was opened by floating the sample on 5 % H₃PO₄ solution. Finally a 25 nm thick layer of gold was deposited as electrodes on both sides of the sample. Dielectric characterization was carried out by an LCR meter (HP4284A) equipped with a computer-controlled temperature chamber (Delta 9023).

The microstructures of the nanorods were evaluated by x-ray diffraction (XRD) using an x-ray diffractometer (Philips X'Pert Pro) with a Cu target with wavelength radiation of 0.15406 nm, as schematically shown in Figure 3-2. SEM images were observed using a field emission scanning electron microscope (FE-SEM) (LEO 1530), and TEM using a transmission electron microscope (TEM) (JEOL JEM 1200 EXII). A differential scanning calorimeter (DSC) study was performed with a TA Instrument (TA Q100) at a heating/cooling rate of 10 °C/min.



Figure 3-1 The fabrication and characterization processes for the terpolymer nanorod arrays.



Figure 3-2 The schematic of the XRD diffraction setup.

3-3 Results and Discussion

The XRD data at angles near the (110, 200) reflection for the nanorods in templates as well as the bulk films are presented in Figure 3-3. Earlier studies have shown that the crystal growth for PVDF and its copolymers in nanopores of 200 nm shows orientation with the polymer chains oriented perpendicularly to the pore walls [24, 26]. Therefore, even with 36.8 vol% of terpolymers in the AAO templates, the 200 nm diameter terpolymer nanorods display nearly the same sharp diffraction peak (see Figure 3-2 for x-ray diffraction geometry). On the other hand, the x-ray data from the nanorods of 70 nm diameter show quite different features. Although the total volume fraction of terpolymer nanorods in the 200 nm and the 70 nm diameter pore size templates is almost the same, the x-ray peak intensity of 70 nm nanorods is significantly reduced. Moreover, the crystallite size along the (110, 200) reflection direction (perpendicular to the

polymer chains) as deduced from the x-ray peak width is also reduced ($L_{(110,200)} = 34.8 \pm 5.3$ nm) in the 70 nm diameter terpolymer nanorods. $L_{(110,200)}$ is derived from Scherrer's formula [47]:

$$L_{(100,200)} = \frac{0.94\lambda}{B\cos\theta}$$
(3.1)

where λ is the x-ray wavelength (= 0.15406 nm), B is the full width at half maximum (FWHM) of the x-ray peak and θ the diffraction angle at the peak. The instrumental resolution (0.1 degree, calibrated by quartz) has been taken into account in deducing B from the data. The x-ray scattering peak was fitted by a pseudo-voigt algorithm with the fitting residual error value (Rvalue) as small as possible. In comparison, L_(110,200) for the bulk films and for 200 nm diameter nanorods are 67.9 ± 1.2 nm and 67.0 ± 2.4 nm, respectively. For nanorod samples with a 25 nm diameter, the x-ray data shows a weak diffraction peak with an even broader peak width, indicating very small L_(110,200) (= 13.7 ± 2.7 nm) in the 25 nm diameter nanorod terpolymers. The very weak x-ray peaks for the 25 nm and 70 nm terpolymer rod samples indicate very low crystallinity in these terpolymer nanorod systems. Low crystallinity in the terpolymer nanorods was also confirmed by a DSC study, which can barely detect any melting and crystallization signals in the 25 nm and 70 nm terpolymer samples as shown in Figure 3-4.



Figure 3-3 XRD profiles at diffraction angles near (110, 200) for 25 nm, 70 nm, and 200 nm diameter P(VDF-TrFE-CFE) terpolymer nanorods and bulk film.



Figure 3-4 The DSC thermalgrams of 25 nm, 70 nm, and 200 nm diamter P(VDF-TrFE-CFE) terpolymer nanorods and bulk film at a scan rate of 10 K/min.

The dielectric properties of the bulk terpolymer films are presented in Figure 3-5(a). The terpolymer exhibits typical ferroelectric relaxor dielectric behavior. That is, the dielectric constant peak shifts progressively towards higher temperatures with frequency, a shift that is well described with the empirical Vogel-Fulcher-Tammann (VFT) relation, i.e. [8, 48, 49]:

$$f_m = f_0 \exp\left(-\frac{U}{k(T_m - T_f)}\right) \tag{3.2}$$

where f_m is the frequency of the dielectric constant peak at the temperature T_m , f_0 is the preexponential factor, U is the activation energy, and T_f is the freezing temperature. The fitting to the bulk films is presented in Figure 3-6 and yields a $T_f = 21.24 \pm 0.25^{\circ}$ C. The parameters from the fitting are summarized in Table 3-1.

For the 200 nm diameter nanorods, the dielectric properties of nanorods deduced from the AAO template-terpolymer composite are shown in Figure 3-5(b). Since the two components (AAO template and terpolymer nanorods) are dielectrically parallel, the total dielectric constant ε is the summation of the two dielectric constants ε_{Terp} , the dielectric constant of the terpolymer rods, and ε_{AI} (~10) times their respective volume fraction α_{Terp} and α_{AI} ,

$$\varepsilon = \alpha_{\text{Terp}} \varepsilon_{\text{Terp}} + \alpha_{\text{Al}} \varepsilon_{\text{Al}}$$
(3.3)

We do not expect that there are anomalous dielectric behaviors of ε_{Al} in the temperature range investigated except those from the relaxor ferroelectric terpolymer. The broad dielectric peak in Figure 3-5(b) is from the terpolymer nanorods due to the relaxor behavior. In fact, the data in Figure 3-5(b) is consistent with Eq.(3.3), for a 31.6% terpolymer volume percentage in the alumina template. Fitting the shift of the dielectric constant peak with frequency for the 200 nm diameter nanorods with the VFT relation yields a $T_f = 20.83 \pm 0.41^{\circ}$ C. This T_f value, although slightly lower than that of the bulk, is still nearly the same as it when taking the error bar into consideration. Besides T_f , all the other VFT fitting parameters for the 200 nm diameter nanorods are nearly the same as those of the bulk within the error bar (see Table 3-1).

| Nanorod diameter (nm) | U (eV) | f ₀ (Hz) | $T_f(^{o}C)$ |
|-----------------------|-----------------------|---------------------|--------------|
| 25±2 | 1.03×10^{-2} | 16.32×10^6 | 14.49 |
| 70±5 | $8.29 	imes 10^{-3}$ | $7.27 	imes 10^6$ | 16.71 |
| 200±10 | $7.08 	imes 10^{-3}$ | $5.43 	imes 10^6$ | 20.83 |
| Bulk | 7.33×10^{-3} | $5.87 	imes 10^6$ | 21.24 |

Table 3-1 Summary of the VFT fitting parameters.



Figure 3-5 Dielectric constant at different frequencies versus temperature for P(VDF-TrFE-CFE) terpolymer (a) bulk film; (b) nanorods of 200 nm diameter; (c) nanorods of 70 nm diameter without the subtraction of conduction background; (d) nanorods of 70 nm diameter after the subtraction of conduction background; and (e) nanorods of 25 nm diameter.



Figure 3-6. Logarithmic frequency vs. permittivity peak temperature data for 25 nm, 70 nm, and 200 nm diameter terpolymer nanorods and bulk film. The solid lines are fitted according to the VFT relation.

The dielectric constant for the 70 nm and 25 nm diameter nanorods deduced using Eq. (3.3) is presented in Figures 3-5(c) and 3-5(e), respectively. As can be seen, due to much lowered crystallinity in the terpolymer nanorods, the relaxor dielectric peak becomes much weaker compared with that of the 200 nm diameter nanorods. Due to the increased contribution from the conduction loss (which increases with temperature), some of the dielectric curves do not show clear dielectric peaks, especially for the data of the 70 nm diameter nanorods in AAO templates. To extract the peak position from the experimental data, we assume that the overall peak shape of the 70 nm nanorods after the subtraction of conduction background, as well as that from the AAO template, is similar to that of the 200 nm nanorods. Based on this assumption, the background

dielectric constant in the temperature range investigated is taken as $\varepsilon_b = a + bT$, where T is the temperature and a and b are constants from the fitting to the dielectric data of 70 nm nanorods and 200 nm nanorods. In this procedure, the background dielectric data at the two temperature ends (-10 and 80°C) of the dielectric constant curve of the 70 nm diameter nanorods is fitted as a_1+b_1T and at the two temperature ends of the 200 nm diameter nanorods data as a_2+b_2T from which $a = a_1-a_2$ and $b = b_1-b_2$ are obtained. Dielectric data after the subtraction for the 70 nm diameter nanorods are presented in Figure 3-5(d), from which the shift of the dielectric peak with frequency can be determined and the fitting with VFT law yields a $T_f = 16.71 \pm 0.45^{\circ}C$, lower than that of the bulk films and the 200 nm nanorods. Both the pre-exponential factor f_0 and activation energy are larger than those of the bulk (see Table 3-1).

The dielectric data for 25 nm diameter nanorods display broad dielectric constanttemperature peaks. The fitting of the data with VFT law, as presented in Figure 3-6, yields a $T_f =$ 14.49±0.37°C, which is further lowered compared with the 70 nm nanorods. The activation energy U = 1.03×10⁻² eV for 25 nm nanorod terpolymers is higher than other nanorods and bulk films, suggesting increased energy barriers for the nanopolar domain reorientation for the terpolymer in confined nanorod systems.

The decrease of the freezing temperature deduced from the VFT relation could be due to the size or interface effect. Since ferroelectricity is a class of cooperative phenomena, a different degree of ordering is expected at the near surface of interface, leading to the intrinsic dependence on sample size [40, 50-53]. It is known that the ferroelectric properties of low-dimensional ferroelectric crystal significantly differ from those of the bulk. The reduction of long range coupling interaction with decreasing size of the relaxor will decrease structural stability and reduce its spontaneous polarization, hence depressing the freezing temperature [51-53].

Finite size effects on the segmental motion of P(VDF-TrFE-CFE) terpolymer nanorod systems

Figure 3-7 shows the dielectric response versus frequency of P(VDF-TrFE-CFE) terpolymer nanorods deduced from the (AAO template-terpolymer) composite. Terpolymers have two main relaxation processes: β relaxation, which is related to the dynamic glass transition of segments in the amorphous portion, and the local γ process, which originates from the fast rotation of the C-F bonds [9]. The β relaxation of terpolymer nanorods was analyzed by the Cole-Cole plot using the following equation.

$$\varepsilon^{*}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_{U} + \frac{(\varepsilon_{R} + \varepsilon_{U})}{1 + (i\omega\tau_{o})^{D_{f}}}$$
$$\left[\varepsilon' - \frac{(\varepsilon_{R} + \varepsilon_{U})}{2}\varepsilon\right]^{2} + \left[\varepsilon'' + \frac{(\varepsilon_{R} - \varepsilon_{U})}{2}\cot an\frac{D_{f}\pi}{2}\right]^{2} = \left[\frac{(\varepsilon_{R} + \varepsilon_{U})}{2}\cos ec\frac{D_{f}\pi}{2}\right]^{2}$$
(3.4)

where \mathcal{E}_R and \mathcal{E}_u are relaxed and unrelaxed dielectric constants and D_f is the distribution factor. The Cole-Cole plot fitting curve of each diameter of terpolymer nanorod deduced from the alumina template-terpolymer composite is shown in Figure 3-8.

From the summarized data in Table 3-2, we found that the average relaxation frequency of terpolymer nanorods shifted to a higher frequency with decreasing diameters at 25° C. The ferroelectric terpolymer nanorod systems are particularly prone to processing-induced defects, which include microstructural heterogeneities, variations in crystalline quality, and mechanical stresses imposed on the materials within the nanopores. Most results reported in literature show that the glass transition at the nanometer scale is different from that of the bulk material. The change of T_g may be due to an intrinsic size effect, a confinement effect, the sample preparation or a combination of these effects as discussed in the previous section [42-46].



Figure 3-7 Color red(R), green(G), blue (B), and magenta (M) represents the β relaxation of the terpolymer bulk film and nanorods of 200 nm, 70 nm, and 25nm deduced from AAO template-terpolymer composite, respectively.

| 25°C | $D_{f}\left(\beta ight)$ | AVG Relax Freq. (kHz) |
|-----------|----------------------------|--------------------------|
| Bulk | 0.566 | 162 |
| 200±10 nm | 0.549 | 325 |
| 70±5 nm | 0.436 | 450 |
| 25±2 nm | 0.409 | 480 |

Table 3-2 The Cole –Cole plot fitting parameters for 25 nm, 70 nm, and 200 nm diameter terpolymer nanorods and bulk film.





Figure 3-8 The Cole-Cole plot fitting of (a) bulk film and (b) 200 nm, (c) 70 nm, and (d) 25 nm terpolymer nanorods deduced from AAO template-terpolymer nanorods composite.

3-4 Summary

Terpolymer nanorods in diameters of 25 nm, 70 nm, and 200 nm were prepared and investigated. In fact to the best of our knowledge, this is the first reported dielectric result in polymer nanorods [41]. It is observed that all of the terpolymer nanorods exhibit typical ferroelectric relaxor dielectric behavior that is the dielectric peak shifts to higher temperature with frequency. The freezing temperature T_f in the Vogel-Fulcher-Tammann (VFT) relation, deduced from the shift of the dielectric constant peak with frequency, moves to a lower temperature, the activation energy (U) becomes higher, and the glass transition behavior shifts to a lower temperature as the nanorod diameter is reduced. The existence of the ferroelectric properties of terpolymer nanorods down to 25 nm diameter implies the possibility of a nanometer scale terpolymer actuator.

Chapter 4

Charge Dynamics of Ionic Liquids in Ionomer Membrane Actuators

4-1 Introduction

In this chapter I investigated the charge dynamics of ILs in ionomer membranes. In order to analyze the charge dynamics to high applied voltage (>1V), I have developed a time domain characterization method. In contrast to the frequency domain approach, the time domain method measures the transient current in response to a step voltage. This approach is relatively new. Therefore, we would like to emphasize our efforts in developing the measurement setup and procedures for this time domain approach.

The actuation of the IEAP actuator is a result of the charge transport and the storage of mobile ions coupled with the substantial evolution of ionic polymer matrix properties after being swelled with ILs. Many efforts have been made to improve the actuation performance, such as enlarging the surface area of an electrode with a conductive network composite (CNC) [13, 14, 18-20]. Due to the complicated structure of composite electrodes, the charge dynamics of ILs in these systems are still unclear. In this study, we investigate a simple structured actuator system, which consists of an ionomer membrane swelled with IL and two gold leaf electrodes, and aim to gain a fundamental understanding of the charge dynamics of ILs in the ionomer systems. This simple structure provides a clear and well-defined geometry for characterizing the charge dynamics of IL in an ionomer. With this simple structure we found that an ionomer like Aquivion, which possesses a high electromechanical coupling effect, can generate substantial strain.

Perfluorosulfonate ionomers, which are the most commonly used polymer matrices for

IEAP applications, consist of a polytetrafluoroethylene (PTFE) backbone and double ether perfluoro side chains terminating in a sulfonic acid group. The flexible side chains facilitate the aggregation of hydrophilic clusters. When swelled with IL, the clusters expand. Above a certain IL uptake (critical uptake), these clusters will be connected with nano-sized channels forming percolation pathways for easy ion conduction, resulting in a high conductivity in the ionomer membrane [14, 54]. Though the long side chain Nafion is the most commonly used ionomer in IEAPs, the short side chain Aquivion might have a better electromechanical coupling effect.

From the traditional charge transport mechanism of IEAP actuators, under an external field, the cations and anions move to the opposite polarity of electrodes and polarize the electrodes. The charge imbalance and the size difference between the cation and the anion result in the strain of the membrane actuator. Electrode polarization in ionic conduction systems has been studied for many decades and it has been shown that it takes less than < ms to polarize the electrodes. These earlier studies were mostly limited to low applied voltage (<1 V) [21, 22]. On the other hand, in practical ionic devices such as ionic actuators and supercapacitors, major actuation and charges stored occur in a few seconds at voltages >1 V [11, 12]. This requires developing understandings of the basic charge dynamics in these voltages and time ranges.

The frequency domain method is a well-established approach and it is widely used in characterizing the conduction in polymers or solutions at high frequency regimes and low applied voltages (< 1 V). In general frequency domain method is not suitable for nonlinear charging behavior characterization because it could cause the heating of the sample due to the loss of the sample under high voltage and high frequency stimulus. Figure 4-1 shows the typical I-V response of an Aquivion membrane swelled with 40 wt% uptake of EMI-Tf. With the increase in applied voltage, the nonlinear effect occurs, which causes the current response to rise in high applied voltage regions where the linear relation of Q = CV is not valid anymore.



Figure 4-1 The I-V curve of Aquivion membrane swelled with 40 wt% uptake of EMI-Tf at 150 mV/sec.

To investigate the charge dynamics of an IEAP actuator at high applied voltage and broad response time up to several seconds, a newly developed charge dynamic model including both drifting and diffusion charges over a broad time domain was employed. The time domain measurement reveals the continuing current in response to a step voltage for both the fast drift charge in a very short time scale and the later slow diffusion charge response to a longer time scale. By fitting the exponential decay of transient current with the time domain model, the conductivity can be separated into the contributions of mobility and mobile ion concentration, and as a result the quantitative values of charge dynamics can be obtained. These quantitative values of charge dynamics provide the basis for further analysis of the correlation between the charge motion and the electromechanical response of the polymer matrix. Besides the quantified charge dynamics, the time domain approach can provide additional information about the accumulated charge response over time under the applied step voltage. As will be shown later, this charge response with time reveals that the actuation of the IEAP actuator is driven by the slow charges in the non-linear region rather than the double layer charge.


Figure 4-2 The charge distribution of bending actuators (a) in the initial state (b) in the charged state, and (c) the strain response at a different time scale of 50 μ m Aquivion film swelled with 40 wt% EMI-Tf , t₀ = 0 represent the initial state. When a (4 V) step voltage is applied, the membrane bends toward the anode at t₂ = 25 seconds and then gradually relaxes back to the cathode at t₃ = 150 seconds.

Ionic liquids (ILs), which are a class of salt in liquid form that contain both ions and neutral molecules, possess many interesting properties that make them very attractive to be employed as electrolytes in electroactive polymer devices [15-17, 55]. For example, the vapor pressure of ILs is negligibly low, and as a result they will not evaporate out of the IEAP devices when operated in ambient conditions. It has been demonstrated that compared to water the use of

ILs as solvents for IEAP actuators can dramatically increase the lifetime of transducer [13, 14]. Their high mobility has the potential to lead to faster response of the IEAP devices, while the wide electro-chemical window (~ 4 V) allows for higher applied voltages [15-21, 56]. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) served in this study due to its high conductivity (8.6 mS/cm), low viscosity (45 cP at 25°C), and large electrochemical window (4.1 V) [19, 20]. The molecule structure and material properties of the EMI-Tf are shown in Figure 4-3 and Table 4-1.



Figure 4-3 The molecular structure of EMI-Tf [19, 20].

Table 4-1 The material properties of EMI-Tf [19].

| | MW | Viscosity | Conductivity | Density |
|--------|----------|----------------|-------------------------|----------------------|
| | (g/mole) | (Cp at 298° K) | (10 ⁻² S/cm) | (g/cm ³) |
| EMI-Tf | 260.24 | 45 | 0.86 | 1.39 |

Hyflon® is known in the literature as a short-side-chain ionomer (in comparison to Nafion® which is referred to as a long-side-chain ionomer) and was originally developed by the Dow Chemical Company at the beginning of the 80s but now is named Aquivion® by Solvay Solexis [54, 57-59]. As illustrated in Figure 4-4(a), these perfluorosulfonate ionomers consist of a

polytetrafluoroethylene (PTFE) backbone and double ether perfluoro side-chains terminating in a sulfonic acid group. The flexible side chains facilitate the aggregation of hydrophilic clusters (Figure 4-4(b)). When swelled with ILs the clusters expand. Above a certain IL uptake (critical uptake), these clusters will be connected with narrow channels forming percolation. While in the literature most ionic EAPs employ Nafion as the polymer matrix [14, 18, 20, 21], the short flexible side chains in Aquivion may provide a better mechanical coupling between the ions and the membrane backbones, and, consequently, act as a more efficient electromechanical transducer.



Figure 4-4 (a) The molecular structure of the short side chain Aquivion and the long side chain Nafion (b) the cluster network morphology model by Gierke et al [54, 57, 60].

4-2 Time domain method

Different from the frequency domain approach, the time domain method, employed in this dissertation to characterize the charge dynamics of IEAP, measures the transient current in response to a step voltage. Consider a one-dimensional liquid cell which consists of two planar parallel electrodes with a separated distance d at two ends, as illustrated in Figure 4-5. We set the reference position x = 0 in the middle of the cell, so the position of left and right electrodes are at x = -d/2 and x = d/2 respectively.



Figure 4-5 The schematic of the structure of the time domain model. The charges move between two planar electrodes separated by a distance d [61, 62].

In general, charge transport is a result of charge drift and diffusion, which can be described by the Poisson -Nernst -Planck equation:

$$\varepsilon \varepsilon_o \frac{\partial E}{\partial x} = \rho \tag{4.1}$$

$$\psi_{\pm} = \pm \mu n_{\pm} E - D \frac{\partial n_{\pm}}{\partial x}$$
(4.2)

In this equation, ρ is the charge concentration, \mathcal{E} the dielectric constant of the medium, ε_0 the vacuum permittivity, ψ is the ion flux density (current density $J = q \psi$), μ 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. For the ILs studied here, we assume $n_+ = n_ \mu$ and D are related by the Einstein equation, $D = \mu KT / q$ [61-65].

For the setup in Figure 4-5 under a step voltage (from 0 at t < 0 to V volts at t > 0), the

initial current density before the screening of electric field occurs is

$$I_0 = \sigma V S/d, \tag{4.3}$$

where σ (= qnµ) is the conductivity, d is the membrane thickness, and S is the electrode area. When the applied voltage is not high (in the order of 10 kT, where k is the Boltzmann's constant), the initial transient current follows the charging of an electric double layer capacitor C_D in series with a bulk resistor R,[64, 66],

$$\mathbf{I}(\mathbf{t}) = \mathbf{I}_0 \exp\left(-\mathbf{t}/\tau_{\mathrm{DL}}\right) \tag{4.4}$$

where $\tau_{DL} = d \lambda_D/2D = RC_D$, describes the typical charging time for the electric double layer which has a thickness λ_D , the Debye length,

$$\lambda_{D} = \left(\varepsilon\varepsilon_{0}kT / Z^{2}q^{2}n\right)^{1/2} \tag{4.5}$$

where Z is the mobile ion valence and q = e, electron charge.

It was further shown that, during longer periods of time, the charge diffusion from the bulk to the double layer region leads to power law decay of the diffusion current. Figure 4-6, shows that the initial current fits well by Eq.(4.4), followed by a power law decay of the diffusion current, having a typical random walk diffusion time constant $\tau_{diff} \sim d^2/(4D)$. Therefore, by fitting the experimental transient current I(t) with Eq. (4.4), as illustrated in Figure 4-6, σ , n, and μ can be obtained if ε of the ionomer membrane (with ILs) is known [61, 62, 65, 67],

$$\sigma = \frac{I_0 d}{VS} \qquad \qquad \mu = \frac{qVS\varepsilon\varepsilon_0 d}{4kT\tau_{DL}^2 I_0} \qquad \qquad n = \frac{4kTI_0^2 \tau_{DL}^2}{\varepsilon\varepsilon_0 q^2 V^2 S^2}$$

The impedance approach in the frequency domain is the most commonly used method to measure the charge dynamic behaviors in polymers at low applied voltage (~0.1V). Fully automatic, high-precision commercial setups for impedance measurement are available, while the setups for the time domain approach to measure the continuous charge dynamics in response to a step voltage are still under development. Based on Dr. Sheng Liu and Yang Liu's efforts on the

electromechanical researches [18-20], I have successfully built an electrical measurement system for transient current measurement in our lab and developed a procedure for reliable measurement of charge dynamics over a broad voltage range up to 4 V and time period up to several seconds .



Figure 4-6 The transient current of the Aquivion membrane with 40 wt% uptake of EMI-Tf when a voltage step from 0 V to 25 mV is applied.

I summarize my experience on the time domain approach measurement. Figure 4-7 shows the developed time domain electrical measurement setup in our lab. To enhance the measurement precision the following issues must be addressed. The transient current in response to a step voltage consists of a fast drift current and a slow diffusion current. The fast drift current occurs at a very short time, usually << 1 ms. To improve the resolution of the initial part of the transient current for data fitting, the signal output of the potentiostat Princeton 2237 was connected to a high sampling rate oscilloscope to collect data during the fast charging process ($< 1 \ \mu$ s). During the sample preparation, the ILs may not distribute uniformly causing concentration gradient in the membranes, especially for the samples with low uptake of ILs. The charge redistribution needs time to reach the equilibrium state, and as reported in literature the water

content can affect the charge dynamics of the IL and the chemical window of the IL system [68]. Therefore, samples should be put in the vacuum oven at an elevated temperature for long enough to remove the moisture and to help the ILs reach their equilibrium state before measurement. The electrical measurement was carried out in a sealed metal box with desiccant inside to help prevent the absorption of moisture. The sealed metal box was equipped with a thermal couple to monitor the temperature during the measurement.

During the measurement, the accumulation of blocked charges on the sample electrode interface and the charge imbalance in the membrane may affect the electrical measurement. Therefore, several cycles of Cyclic Voltammetry (CV) scan with a low voltage and with a high scan rate were performed to help clean the electrode surface. Then the samples were shorted for at least 30 minutes to assist the charges to redistribute to the equilibrium state [68]. Each measurement should be done at least three times to make sure that the result is repeatable before moving on to the next measurement conditions. We set the measurement time within 10 seconds to keep the system in a reversible state; this time scale is also long enough to provide sufficient information for most data analysis. We performed the measurement from 10 mV to 4 V (step voltages). At a low applied voltage, the signal/noise ratio is poor due to the very low current signal. In particular, the measured signal of the diffusion part of the current is not able to be processed for times longer than 10 seconds. At high applied voltages (> 0.5 V), the applied voltage is large enough to change the state of the sample substantially and to drive the sample to an irreversible state if the charging time is long enough. As a result the system cannot be recovered to the same reference state and the measured results are not repeatable or comparable. Therefore, the charging time at high applied voltages should be as short as possible.



Figure 4-7 The time domain electrical characterization setup

4-3 Experimental

Aquivion (EW790) membrane and EMI-Tf were purchased from Solvay Solexis and Aldrich, respectively. All of the materials were dried in a vacuum at 80 °C to remove moisture before processing. Aquivion membranes swollen with various EMI-Tf uptakes were prepared by varying the soaking time for the Aquivion membrane in EMI-Tf at 80 °C to approach the target values. 50 nm thick gold foils (L.A.Gold Leaf) were hot-pressed on both sides of the membrane to serve as the electrodes. The uptake of IL within the Aquivion membrane was calculated by measuring the weight gain after swelling. In this study, membranes with 9, 17, 29 and 40 wt% uptake of EMI-Tf were prepared and their thicknesses are 55, 57, 59, 62 µm after the swelling with ILs, respectively. Nation with 40 wt% uptake of EMI-Tf was prepared following the same procedure and its thickness is 63 μ m. Samples were held at an elevated temperature (~80 °C) for more than 12 hours to enhance the uniform dispersion of ILs inside the membranes. This is especially important for films with a low uptake of ILs. The electrical measurement was carried out in a sealed metal box with desiccant inside to prevent the absorption of moisture. The sealed metal box was equipped with a thermal couple to monitor the temperature during the measurement. The impedance spectroscopy was measured by a potentiostat Princeton 2237. To obtain the dielectric constant ε of the membranes, the samples were cooled down in an environmental chamber (Versa Tenn III) to shift the dielectric spectrum to the measureable frequency window of the set-up, which is below 1 MHz (so that the dielectric constant before the screening of the applied field occurs can be measured at frequencies >> $1/\tau_{DL}$). As shown in Figure 4-8 (a), the measured dielectric constant of Aquivion with 0, 9, 17, 29, and 40 wt% uptake of EMI-Tf is 7.6, 8.2, 9.3, 10.4 and 11.1 respectively. The dc conductivity was calculated by $\sigma = d/RS$, where R is the impedance curve intersection on the Z' axis of the Nyquist plot as shown in Figure 4-8(b).



Figure 4-8 (a) the Cole-Cole plot of Aquivion (AQ) membrane with various EMI-Tf uptakes under various temperatures (b) the Nyquist plot of Aquivion membrane with 17 wt% uptake of EMI-Tf

The transient current vs. time was collected by a potentiostat Princeton 2237, and the output was connected to a high sampling rate oscilloscope to collect data during the fast charging process (< 1 μ s). The accumulation of blocked charges on sample electrode interface and the charge imbalance in the membrane may affect the electrical measurement. Therefore, several cycles of a Cyclic Voltammetry (CV) scan with a low voltage and a high scan rate were performed to help clean the electrode surface. Then the samples were shorted for at least 30 minutes to ensure that the charges redistributed to the equilibrium state [68].

The time-dependent bending actuations of the actuators under applied voltage were

recorded using a probe station (Cascade Microtech M150) equipped with a Leica microscope. A DC step voltage was applied to the actuator and images of bending actuation as a function of time were recorded using a CCD camera (Pulnix 6740CL). The radii of the curvatures of the bending actuators were determined using image-processing software. The Aquivion (EW 790) swelled with 9, 17, 29 and 40 wt% of EMI-Tf was prepared by soaking the 50 µm commercial membrane in the pure EMI-Tf under different period of time at 80 °C. We repeated the soaking process to gradually reach the target value of each sample. The 50 µm Nafion (EW1100) swelled with 40 wt% uptake of EMI-Tf follows the same procedure. Each sample was cut into a 5 mm by 5 mm square and fixed on a 3M paper frame with a 3 mm diameter hole.

The small-angle x-ray scattering (SAXS) measurements were carried out using the PSU MCL SAXS instrument equipped with a Cu K α radiation source at 45 kV, 65 mA, and the wave length of the resulting x-ray is $\lambda = 1.542$ Å as shown in Figure 4-9. A two-dimensional area proportional detector was used to collect the scattering signal, and the sample to detector distance was 1.5 m. The detector is sampled at 512 × 512 pixels. The active area and the direct beam position are centered in the pixel grid and the 512 pixel length corresponds to the 120 mm active area diameter. An x-ray photo diode is centered in front of the detector to act as a beam stop and measures the direct or transmitted beam intensity. Forward current in the diode is measured with a Kiethley picoammeter. Scattering data were collected for 180 minutes. A silver behenate secondary standard was used to calibrate the scattering vector. The optical and the chamber are under vacuum to minimize air scattering. The data are calculated by: 1. Calculating the center of an Ag-behenate scattering image and then inputting the calculated center coordinates (in pixels) as the center of data images. 2. Calibrating for q with the known q value (0.1076 A⁻¹) of the first order Ag-behenate reflection and the determined pixel value of the center of that reflection. 3. Azimuthally integrating an isotropic scattering pattern to obtain a 1D intensity vs. q plot.



Figure 4-9 The SAXS scattering setup

For the dynamic mechanical analysis, samples of 50 µm Aquivion 790 swelled with 9, 17, 29 and 40 wt% uptake of EMI-Tf were prepared and cut into a rectangular sample of 5 mm in width by 15 mm in length. Measurements were carried out using a TA- DMA 2980 Dynamic mechanical analyzer. The sample is subjected to a mechanical oscillation of constant amplitude with 1Hz frequency. The test is operated from -60 to 200 °C at a heating rate of 2 °C/min.

4-4 Results and Discussion

Charge transport behavior of Aquivion membranes swelled with EMI-Tf at room temperature

The current responses for Aquivion with 40 wt% of EMI-Tf under various step voltages are presented in Figure 4-10. From these curves, conductivity σ under different applied voltages can be determined from I₀ (up to 4 volts in the experiment). On the other hand, the data shows that fitting to Eq.(4.4) can be performed only for I(t) at V \leq 1 volts. Beyond that, there is no distinctive crossover region in the I(t) curve between the exponential decay of the drifting current and the power law decay of the diffusion current.



Figure 4-10 The transient current and numerical fit for Aquivion membrane with 40 wt% uptake of EMI-Tf under different applied step voltages.

In Figure 4-11(a), σ determined from the ac impedance curve (Nyquist plot, Figure 4-8 (b)) under 0.1 V is also shown. The two methods yield nearly identical values of σ , indicating that

both methods can be used to determine σ at low voltage. On the other hand, at high voltage, the ac electric impedance method to determine σ may become difficult due to the non-linear electric response and even possible heating in the samples.

Results for the conductivity σ , free charge concentration n and mobility μ as a function of IL uptake are presented in Figure 4-11. The data reveals that the mobile ion concentration increases almost linearly with the IL uptake. In contrast, the conductivity and mobility display abrupt changes with the increase of IL uptake, revealing a critical uptake of EMI-Tf in the Aquivion (EW790) membrane ~ 29 wt% (0.88 mol EMI-Tf/ mol of SO_3^{-}) above which the conductivity and mobility dramatically increase. In the study of IL uptake in Nafion membranes, Leo et al. found that the critical uptake is closely related to the minimum amount of IL required to displace the counter ions away from the exchange sites [14]. Above the critical uptake, the ionomers form percolation pathways for charges to transport and also there are more mobile ions that do not strongly interact with the exchange sites. Therefore, with the increase of IL content the mobile charge concentration increases and the mobility and conductivity are enhanced. It is noted that the critical uptake of EMI-Tf in Aquivion is higher than that of EMI-Tf in the Nafion membrane (23 wt%, ~ 1 mol of EMI-Tf/mol of SO₃), which may be due to the fact that Aquivion (EW790) has a higher side chain density than Nafion (EW1100). With 40 wt% of EMI-Tf uptake, at which a substantial actuation is observed in both Aquivion and Nafion membranes, the conductivities of Aquivion and Nafion membranes are close to each other (Aquivion = 1.1×10^{-4} S/cm. Naifon = 2.1×10^{-4} S/cm).



Figure 4-11 (a) conductivity, (b) mobility, and (c) free charge concentration as a function of EMI-Tf uptake in the Aquivion membrane when a voltage step from 0 V to 0.1V is applied.



Figure 4-12 (a) conductivity, (b) mobility, and (c) free charge concentration of the Aquivion membranes with different uptakes of EMI-Tf and Nafon with 40 wt% uptake of EMI-Tf under different applied voltage steps.

Figure 4-12(a) presents the conductivity σ of the Aquivion membrane with different EMI-Tf uptakes as a function of voltage, up to 4 volts. The data shows that within the

experimental error (± 10 %), σ does not change with applied voltage for all EMI-Tf uptakes. Figures 4-12(b) and (c) are the mobility and mobile ion concentration vs. the applied voltage, measured up to 1 V, and within the experimental error no systematical variation with applied voltage was observed. As shown in the same Figure, Nafion membrane swelled with 40 wt% EMI-Tf shows similar charge dynamics behavior to Aquivion membrane, i.e., the voltage independent charge dynamics. These results indicate that the double layer charging time τ_{DL} as well as the overall charge dynamics do not change much with a voltage below 1 volt. At voltages higher than 1 volt, the data shown in Figure 4-10 reveal that the overall charging process becomes slower. This might be caused by the increased dissociation of ion clusters in EMI-Tf at high voltages [27].

In Table 4-2, we summarize the mobile ion concentration in Figure 4-12(c) and compare them with the total ion concentration from the EMI-Tf. As can be seen, only about 0.5 % to 0.55 % of EMI-Tf is dissociated for all the ILs uptakes below 1 volt. This low dissociation ratio of IL may be due to the fact that the Bjerrum length of EMI-Tf is larger than its ion pair distance and hence the Coulomb force dominates [22].

| Uptake (wt%) | Estimated charges $(1/cm^3)$ | Total charges (1/cm ³) | Dissociation ratio |
|--------------|------------------------------|------------------------------------|-----------------------|
| 40 | 1.37×10 ¹⁹ | 2.48×10^{21} | 5.55×10 ⁻³ |
| 29 | 1.03×10 ¹⁹ | 2.04×10^{21} | 5.04×10 ⁻³ |
| 17 | 7.82×10^{18} | 1.43×10 ²¹ | 5.47×10 ⁻³ |
| 9 | 4.35×10 ¹⁸ | 8.58×10^{20} | 5.08×10 ⁻³ |

Table 4-2 The estimated mobile charge concentrations, the calculated total charges, and the dissociation ratios of membranes with different uptakes of EMI-Tf.

Figure 4-13 presents τ_{DL} (Figure 4-13(a)), λ_D (Figure 4-13(b)), and $\tau = d^2/(4D)$ (Figure 4-13(c)) vs. ILs uptakes. The high conductivity in the membrane above the critical uptake results in

a very fast charging time of the double layer, $\tau_{DL} < 0.5$ ms. The Debye length λ_D is ~ 1 nm due to the high free ion concentration and becomes small with decreasing EMI-Tf uptake. On the other hand, the bulk diffusion time constant $\tau_{diff} = d^2/(4D)$, which is the time needed for charges to diffuse from bulk to electrodes, is still around ~ 10 s even above the critical uptake. As will be shown later, for the membrane bending actuators, the actuation is mainly determined by the diffusion and dissociation charges that are stored near the electrodes.



Figure 4-13 Double layer (a) time constant, (b) thickness, and (c) diffusion time constant as a function of EMI-Tf uptake when a voltage step from 0V to 0.1V is applied.

Charge responses at longer time scales

Under an applied field, and in a very short time (< ms) the charges drift towards electrodes to form electric double layers, which leads to the depletion regions near the two electrodes. The induced charge concentration gradient drives the charges from the bulk to the near electrode regions. This diffusion transient current is negligible during the initial double layer charging, but it becomes dominant at longer times because it decreases much more slowly than the exponential decay [61, 66]. Figure 4-14 shows the transient current of Aquivion samples swelled with 9, 17, 29 and 40 wt% of EMI-Tf in response to a 25 mV step voltage. We found that the diffusion current follows the power law decay at the low applied voltage region.

$$I_{diff} = At^{-n} \tag{4.6}$$

The relation between μ and D follows the Einstein relation $D = \mu kT$ where k is the Boltzmann constant. By fitting Eq. (4.6) to the measured transient current, the decay exponent of the diffusion current can be estimated. From Table 4-3, we can see that the decay exponent of the diffusion current seems to depend on the uptake of EMI-Tf.

| Uptake (wt%) | Exponent n | Diffusion coefficient D (cm ² s ⁻¹) | |
|--------------|-----------------------|---|--|
| 40 | 1.16 | 1.21×10^{-6} | |
| 29 | 7.85×10 ⁻¹ | 8.31×10 ⁻⁷ | |
| 17 | 3.70×10 ⁻¹ | 1.31×10 ⁻⁷ | |
| 9 | 3.73×10 ⁻¹ | 3.91×10 ⁻⁸ | |

Table 4-3 The fitting exponent of the power law decay diffusion current for samples swelled with 9, 17, 29 and 40 wt% of EMI-Tf and the diffusion coefficient



Figure 4-14 The transient current of Aquivion samples swelled with 9, 17, 29 and 40 wt% uptake of EMI-Tf in response to a 25 mV step voltage.

Figure 4-15 are the results reported from Strubbe's study of charge dynamics of nonaqueous liquids in response to a step voltage [27]. It shows that under low applied voltages, the transient current approaches zero over time while under high applied voltages (>1 V), a high non-zero residual current persists to longer times. The actual mechanism for this residual current is not clear. Strubbe F. et al. proposed a possible mechanism for the residual current and partly attributed it to the generation of charges due to the ion pair or cluster dissociation [27].

$$AB \rightleftharpoons A^+ + B^-$$

The authors suggest that the probability of generating mobile charges by ion pair dissociation increases with applied voltage, leading to the measured residual current. Figures 4-16 and 4-17 show the transient current of Aquivion membranes swelled with 40 wt% and 9 wt% of EMI-Tf respectively. At a low applied voltage, the initial part of the current follows the

exponential decay as described by the time domain model, while at longer times the current follows the power law decay. As shown in Figures 4-16 and 4-17, when the applied voltage reaches a certain level (> 1V), a high residual current is observed implying that the charge dissociation occurs [27]. For example, in the Aquivion membrane swelled with 40 wt% uptake of EMI-Tf, the measured total charge accumulated on the two electrodes, at the time equal to its diffusion time $\tau_{diff} = 7.8$ seconds under 4 V, is 175.1 % of the measured mobile charges. This result implies that there are 75.1 % of extra charges generated. The charge dissociation may contribute to part of the accumulated charges on two electrodes at longer time scales, which is responsible for the observed substantial stain. Additionally, the crossover between the double layer charging current and the diffusion current becomes unclear, which also interferes with the time domain model fitting.



Figure 4-15 Transient current for 0.5 cm² sample of 1 % OLOA in dodecane with $d = 7 \mu m$ for applied voltage V= 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 V reported by Strubbe F. et al. [27].



Figure 4-16 The transient current of Aquivion membrane swelled with 40 wt% uptake of EMI-Tf in response to different step voltages.



Figure 4-17 The transient current of the Aquivion membrane swelled with 9 wt% uptake of EMI-Tf in response to different step voltages.

In Figure 4-18(a), we present the charge stored vs. time in the Aquivion membrane which has 40 wt% of EMI-Tf uptake under different step voltages and shows a substantial bending actuation at > 3 volts (see Figure 4-2(c). From the data and using the τ_{DL} and τ_{diff} determined at voltages below 1 V, we plot in Figure 4-18(b) the charge stored at the time τ_{DL} and τ_{diff} as a function of applied voltage. The data shows that the charge stored at τ_{DL} increases linearly with applied voltage. In other words, the ratio between the charge stored and the voltage, which is the overall capacitance, does not change with the applied step voltage, and the differential capacitance for the electric double layer, which is defined as $\Delta Q/\Delta V$, does not change with applied voltage up to the highest voltage measured (4 volts). On the other hand, the charge stored at t = τ_{diff} increases linearly with voltage up to 1 V. Beyond that, a much faster (non-linear) increase with applied voltage is observed, which seemingly causes a slowdown of the charge process in Figure 4-18(a). This may be due to the nonlinear effect of the current response at a high applied voltage. Comparing the stored charges with the response of the substantial strain, it was found that the strain is dominated by the slow nonlinear charges. This explains why the substantial strain occurs only under a high applied voltage and during longer times.



Figure 4-18 (a) charge storage with time (40 wt% uptake) under different applied voltage step (10 mV to 4 V). (b) storage of double layer charge and diffusion with dissociation charges under different applied voltage step. The inset graph is the charge ratio (Q_{DL}/Q_{diff}) as a function of the applied voltage step.

Figure 4-19 is the charge stored in the Aquivion membrane with different EMI-Tf uptake vs. time after the application of a 4 V step voltage (at t = 0). The data shows that the stored charge increases with IL uptake up to the critical uptake (29 wt%). Above that, the rate of increase of the stored charge with the IL uptake becomes much smaller. This is also true for the diffusion time τ_{diff} , which does not show much change with the IL uptake above the critical uptake. Hence, above the critical uptake, further increase in the uptake of IL will not cause a marked increase in the charging speed, the charge storage, or, consequently, the bending actuation of the Aquivion membranes. Therefore, we suggest that the minimum amount of ILs for IEAP is at least above its critical uptake.



Figure 4-19 Charge storage as a function of time for Aquivion membranes with four different uptakes when a voltage step from 0 to 4 V is applied. The inset shows the charge storage at 7.8 s (diffusion time for 40 wt% uptake) for different uptakes

The side chain length effect on the electromechanical coupling

The electromechanical response of the Aquivion membrane was measured (see Figure 4-2(c)) and compared to that of the Nafion membrane with the same 40 wt% of EMI-Tf uptake, far above the critical uptake in both ionomers. The measured conductivity of these two membranes are similar (Aquivion $(1.1 \times 10^{-4} \text{ S/cm})$, Naifon $2.1 \times 10^{-4} \text{ S/cm}$). The slightly larger σ in the Nafion membrane indicates an easier ion transport path resulting from less coupling between the ions and the polymer matrix. Presented in Figure 4-20(a) is the curvature (1/R where R is the radius) of the bending membrane actuators vs. time after the application of a step voltage of 4 volts. The strain near the two electrodes (anode and cathode) is proportional to the curvature (1/R). The data reveals several interesting features: (i) the initial slope of the curvatures of the two ionomers is nearly the same, indicating similar actuation speed of the two membranes; (ii) the maximum positive curvature of the Aquivion membrane is higher than that of the Nafion, indicating a higher strain generated by the positive charges; (iii) the maximum negative curvature of the Aquivion is also much larger than that of Nafion (higher negative strain generated by negative charges in Aquivion). As shown in earlier publications, the presence of both cations and anions in the membrane may cause cancellation in bending actuation [21]. For example, in Figure 4-2(b), if positive charges at the cathode and negative charges at the anode generate same value of strain at the same time, there will be no bending actuation. Due to different effective sizes of the positive charges and negative charges (cations and anions may form clusters rather than bare ions in the processes of ion transport and storage), the strains generated by the positive and negative charges are different, causing bending actuation as we observed here. The results in Figure 4-20(a) indicate that the ions in Aquivion can generate much more bending strain, compared with that of Nafion membrane. Moreover, the transient strain response data also reveals that the transport time for positive charges and negative charges in the Aquivion is different (negative charges are slower), causing observed time dependent bending actuation [21].

Figure 4-20(b) shows the charge stored in the two membranes under the same electric conditions as in Figure 4-20(a). Combining the data in the two figures indicates that the bending strain generated per charge is much larger in Aquivion than that in Nafion. The difference in the strain generation is likely caused by the weaker elastic coupling of the excess ions to the membrane backbones in Nafion, due to longer flexible side chains, compared with that of Aquivion. As shown in Kreuer's study, from the SAXS, the average width of the hydrophilic channels of Aquivion is smaller and did not increase as much as that of Nafion with increasing water uptake [59]. This implies that by reducing these soft side chain lengths, the excess ions in the ionomers may couple more effectively with the backbones to generate strain on the membranes.



Figure 4-20 (a) the curvature change with time (b) the accumulated charge/area of a 62 μ m thick of Aquivion and Nafion membrane when a voltage step from 0 V to 4 V is applied.

Since the ions mainly transport across the ionomer matrix, the microstructure of the ionomer would play an important role on the charge dynamics of IL. Therefore we are interested in the correlation between the charge dynamics of IL and the morphology of the ionomer. One of the most commonly used approaches to characterize the microstructure of ionomer is the small angle x-ray. Several models have been proposed to interpret the data from SAXS [54]. Though the explanation and the real structure of Nafion are still debated, the Gierke model provides a simple explanation of the morphology of the ionomer. In the Gierke model, the charged ionic side chains gather together, forming spherical ionic rich phases with an inverted micelle structure surrounded by the inert perfluorocarbon backbones. The size of the clusters is estimated to be around 3-5 nm depending on the water uptake. When swelled, the clusters are connected with nano-sized ionic channels, forming percolation ionic networks for the ions to transport. From this model the distance evaluated is the center to center cluster distance not the size of a single cluster [57, 60].

The comparison of SAXS data between Nafion and Aquivion under different hydration states has been reported by Kreaur and Mystry et al. as illustrated in Figure 4-21. λ represents the number of water molecules per ionic side chain. For $\lambda = 2$ the scattering peak of Nafion at the high q ~0.2A⁻¹ position is attributed to the ionic cluster. The peak at position q~0.04A⁻¹ is believed to be related to the crystalline region within the polymer, and the observed upturn is attributed to the long range disorder distribution of ionic domain [59]. Both Kreaur and Mystry suggest that, with a similar hydration state, short side chain Aquivion (Dow 858) ($\lambda = 3.9$) shows an ionomer peak at a higher position than that of long side chain Nafion ($\lambda = 2$), implying a smaller inter cluster size due to the short side chain nature of the Aquivion as illustrated in Figure 4-21 [59, 70, 71].



Figure 4-21 The SAXS results of Nafion and Aquivion (Dow 858) under different hydration states reported by Kreaur and coworkers [59].



Figure 4-22 The SAXS data of Aquivion (EW 790) membranes swelled with 0, 9, 17, 29 and 40 wt% uptakes of EMI-Tf and Nafion with 40 wt% uptake of EMI-Tf.

In this investigation, we aim to focus on the study of short side chain ionomers which have been demonstrated having a better electromechanical coupling performance than that of Nafion in the previous chapter. Since Nafion has been studied, we would just include the Nafion swelled with 40 wt% uptake of EMI-Tf as a reference. Figure 4-22 shows the SAXS scattering pattern of Aquivion (EW790) swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf and Nafion swelled with 40 wt% uptake of EMI-Tf. The ionic cluster peak feature is not observed until it surpasses the critical uptake which implies the larger aggregation of the ionic cluster region of Aquivion membrane with increasing uptake of EMI-Tf. This may be the reason for why the charge dynamics and the mechanical responses undergo abrupt transitions near the critical uptake.

For Aqiuvion and Nafion swelled with same 40 wt% uptake of EMI-Tf, as shown in Figure 4-22, the Nafion membrane shows an ionic cluster peak at $q \sim 0.14$ A, while for the Aquivion membrane only part of the ionic cluster peak was observed. These findings imply that there is an ionomer peak at a higher q position. The smaller inter ionic cluster size may be the reason for its better electromechanical coupling than that of Nafion. When ions are driven into the ionic cluster region of short size chain Aquivion, the ions may interact with the backbone to generate strain rather than to interact with the ionic side chains to enlarge the size of the ionic cluster, leading to a better electromechanical coupling effect than that of long side chain Nafion.

The temperature dependence of the ionic conductions and the segmental motions of Aquivion

membranes swelled with EMI-Tf

The actuation of IEAP is a result of the charge transport within the polymer matrix and storage near the electrodes. A critical uptake of EMI-Tf of Aquivion membrane was found, above which the ionic conduction and actuation undergo enhancement transitions. Understanding how ionic conduction behaviors correlate to the status of a polymer membrane swelled with different uptakes of IL would be critical for a better design of IEAP. Segmental motion is a cooperative process in polymers and generally corresponds to the glass transition behavior of the polymer matrix. At temperatures below the glass transition temperature, the polymer behaves like a rigid glass; it exhibits rubber-like prosperities above T_g at longer time scales where the long range polymer chain can move. Consequently, the segmental dynamics strongly affect the movement of ions in a polymer matrix, which raises the macroscopic ionic conduction [72, 73]. In Zhang S.H. et al's study on the segmental dynamics and ionic conduction in poly(vinyl methyl ether) - Lithium perchlorate complexes, they found that the temperature dependence of ionic conduction of different samples shows almost the same ionic conductivity at the same T-T_g and suggest that the ionic conduction behavior is coupled with the segmental dynamics of the polymer matrix [72, 73]. In this chapter, further investigations into the correlation between the charge transport and the segmental motion of the polymer were carried out.

It is expected that below the critical uptake the movement of ions should be coupled with the segmental motion of the polymer matrix, since the ions are embedded in the polymer matrix. As observed near the critical uptake, the ionic conduction and the strain response of the IEAP actuator undergo abrupt enhancement transitions which may be due to the percolation of the ionomer that facilitates the charge transport behavior [14, 23]. Therefore, it is of great interest to investigate the correlation between the ionic conduction and the segmental motion of the ionomer over a broad uptake range. Previous investigations on the mobile ion dissociation ratio of Aquivion membranes with different uptakes of EMI-Tf show that the dissociation ratio of the mobile ion concentration at room temperature is only about 0.5 % of the total charges. This means that only a very small part of the ions are dissociated as free ions. Hence the correlation between the ion dissociation energy and the uptake of EMI-Tf would be of interest.

Figure 4-23 shows the DMA results of in phase modulus and the ratio of the loss to the storage which is the tan δ . The glass transition (T_g) is seen as a large drop in the storage modulus when viewed on a log scale against a linear temperature scale, as shown in Figure 4-23. The value reported as the T_g here is the peak of the tan δ which is usually (10-20 K) above the DSC T_g of

the polymer. The results are summarized in Table 4-4. Aquivion consists of a ploytetrafluoroethylene backbone and double ether perfluoro side chains terminating in a sulfonic acid group. From the literature, two thermal transitions were observed in DMA as well as a rubbery plateau due to physical ionic domains [58]. The first transition at -100 °C corresponds to the poly-tetrafluoroethylene, and the second transition at ~125 °C is commonly considered to be the glass transition of the ionic phase of Aquivion [58]. As shown in Figure 4-23, the rubbery plateau region and the ionic phase T_g revealed substantial decrease (from 1 GPa to 50 MPa) with an increase in the EMI-Tf uptake and the rubbery plateau region persists up to 40 wt% uptake. The peak position at 398, 324, 289.9, 264.3, and 256.9 K represents the glass transition temperature of the ionic phase of the Aquivion membrane swelled with 0, 9, 17, 29, 40 wt% uptakes of EMI-Tf respectively.



Figure 4-23 The DMA data of the Aquivion membranes with different uptakes of EMI-Tf at 1Hz and 2 °C/min heating rate.

| wt% | 40 | 29 | 17 | 9 | 0 |
|---------------------------|------|------|-------|-------|--------|
| $tan\delta$ (T_g) (K) | 256 | 264 | 289 | 324 | 398 |
| Modulus (Mpa) | 51.2 | 58.9 | 127.4 | 823.6 | 1231.2 |

Table 4-4 Summary of the glass transition temperature of ionic phase and modulus of Aquivion membranes with different uptakes of EMI-Tf

The modulus of the Aquivion membranes swelled with 0, 9, 17, 29, and 40 wt% uptakes of EMI-Tf is 1231, 823.6, 127.4, 58.9 and 51.2, (Mpa) respectively. It was observed that above the critical uptake the modulus did not change much with an increase in the uptake of EMI-Tf. Figure 4-24 shows the temperature dependence of the ionic conductivities of Aquivion membranes with different uptakes of EMI-Tf. As observed, the conductivity decreases rapidly with temperature which can be described by the Vogel-Fulcher –Tammann (VFT) relation [72, 73],

$$\sigma = \sigma_0 \exp[\frac{-B}{T - T_0}]$$

where σ_0 is the intrinsic conductivity at a very high temperature, B is the activation parameter for conduction with unit (K) and T₀ is the temperature where the σ approaches 0. The fitting results are summarized in Table 4-5. The Vogel temperature T₀ deduced from the VFT relation does not only shift to lower temperature with increasing uptake of EMI-Tf but also shows an abrupt change near the critical uptake. The intrinsic conductivity σ_0 at a very high temperature increases with an uptake of EMI-Tf which may be due to the increase of ion content.



Figure 4-24 The temperature dependence of the ionic conductivities of Aquivion membranes swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.

| Table 4-5 The VFT | fitting parameters | of the temperature | dependence | of the | conductivities | of |
|--------------------|----------------------|---------------------|---------------|--------|----------------|----|
| Aquivion membranes | s swelled with 9, 17 | 7, 29 and 40 wt% up | takes of EMI- | Tf. | | |

| wt% | 40 | 29 | 17 | 9 |
|--------------------------------|--------|--------|--------|--------|
| Conductivity σ_0 (S/cm) | 0.876 | 0.689 | 0.301 | 0.241 |
| B (K) | 1092.1 | 1143.8 | 1161.1 | 1308.2 |
| T ₀ (K) | 175.2 | 179.8 | 196.1 | 205.5 |

It is known that the ionic conduction is correlated to the segmental motion of the polymer matrix. The polymer segmental motion facilitates the transportation of ions through the membrane [72-76]. Figure 4-25 shows the temperature dependence of the ionic conductivities results after being normalized by the glass transition temperatures of Aquivion membranes with

different uptakes of EMI-Tf. It was found that Aquivion membranes with different uptakes of EMI-Tf have approximately the same conductivity at the same T-Tg. These results imply that the ionic conduction of charges is coupled with the segmental motion of the Aquivion matrix over a broad uptake range. This correlation may explain why above the critical uptake the increase rate on the ionic conductivity decreases, since above the critical uptake, as shown in Figure 4-23, the glass transition temperature (T_g) of the Aquivion membrane did not change as much as that below the critical uptake. The abrupt increase in the ionic conductivity near the critical uptake region may be attributable to the decrease in the glass transition temperature of the Aquivion matrices.



Figure 4-25 T_g normalized temperature dependence of the ionic conductivities of Aquivion membranes with different uptakes of EMI-Tf.

Another important parameter is the Vogel temperature T_0 , which is the temperature obtained by extrapolating the VFT relation to the temperature where the conductivity approaches zero. The difference of (T_g - T_0) for 9, 17, 29 and 40 wt% uptake samples is 118.5, 89.3, 83.3, 80.9, K respectively. As shown in Figure 4-26, by normalizing the temperature dependence of the conductivities using their Vogel temperatures, a trend similar to that normalized by the glass transition temperatures was obtained. Aquivion membranes with 17, 29 and 40 wt% uptakes of EMI-Tf have similar conductivities at the same T- T_0 , while the conductivity of the 9 wt% uptake sample shows a deviation from the others. This result implies that the Vogel temperature T_0 may not be suitable for analyzing the correlation between the ionic conduction and the segmental motion of the polymer matrix.



Figure 4-26 T_0 normalized temperature dependence of the ionic conductivities of Aquivion membranes swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.
By applying the time domain model to the transient current, the ion mobility and the mobile ion concentration can be obtained as described by Eq. (4.4). Figure 4-27 presents the temperature dependence of the ion mobilities of Aquivion membranes swelled with different uptakes of EMI-Tf. As observed, the mobility decreases rapidly with temperature, and this nonlinear relation of mobility versus temperature can be described by the Vogel –Fulcher – Tammann (VFT) equation [72, 76, 77],

$$\mu = \mu_0 exp[\frac{-B}{T - T_0}]$$

where T_0 is the Vogel temperature in which the ion mobility goes to zero, B is a fitting constant with unit (K), and μ_0 is the ion mobility at a very high temperature. The fitting results are listed in Table 4-6. As observed, the Aquivion sample with higher mobility freezes at a lower temperature. As shown in Figure 4-28, after being normalized by the ionic phase of T_g , Aquivion membranes with different uptakes of EMI-Tf have approximately the same ion mobility at the same T-Tg. These results imply that the ion mobility is coupled with the segmental motion of the Aquivion matrix. In summary, the normalized temperature dependence of the ionic conductivity and the ion mobility results suggest that the fundamental mechanism for ion transportation is coupled with the segmental motion of the ionic phase of the polymer matrix. Therefore, both the uptake of EMI-Tf and the percolation of the Aquivion membrane may be reasons for the decrease in T_g of the polymer matrix and hence facilitate the segmental motion of the polymer matrix.



Figure 4-27 The temperature dependence of the ion mobilities of Aquivion membranes with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.

| Uptake (wt%) | 40 | 29 | 17 | 9 |
|--|--------------|--------------|---------------|---------------|
| $\mu_0 (\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1})$ | 0.0265±0.002 | 0.0147±0.001 | 0.0038±0.0003 | 0.0022±0.0002 |
| B (K) | 735.2±50 | 649.1±50 | 539.9±50 | 581.7±50 |
| T ₀ (K) | 183.2±2 | 195.4±2 | 218.9±2 | 231.2±2 |

Table 4-6 The VFT fitting parameters of temperature dependence of the ion mobilities of Aquivion membranes swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.



Figure 4-28 T_g normalized temperature dependence of the ion mobilities of Aquivion membranes with different uptakes of EMI-Tf.

Figure 4-29 shows that the temperature dependence of mobile ion concentration follows Arrhenius relation [76, 77],

$$n = n_0 exp[\frac{-E_a}{RT}]$$

where n_0 is the total charge concentration at a very high temperature, which represents that virtually all the ions are separated. Therefore, n_0 can be regarded as equivalent to the stoichiometric ion concentration. The fitting parameters of Arrhenius relation are summarized in Table 4-7.



Figure 4-29 The temperature dependence of the mobile ion concentrations of Aquivion membranes swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.

| wt% | 40 | 29 | 17 | 9 |
|------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Concentration $n_o (1/cm^3)$ | 4.33×10 ²² | 2.19×10 ²² | 9.56×10 ²¹ | 3.82×10 ²¹ |
| E _a (kJ/mole) | 19.3±0.5 | 19.1±0.5 | 18.4±0.5 | 17.3±0.5 |
| Stoichiometric | 2.48×10^{21} | 2.04×10^{21} | 1.43×10 ²¹ | 8.58×10^{20} |

Table 4-7 The Arrhenius fitting parameters of Aquivion membranes swelled with 9, 17, 29 and 40 wt% uptakes of EMI-Tf.

The previous investigation results reveal that the ion dissociation ratio of Aquivion membranes with different uptakes of EM-Tf at room temperature remains ~0.5% of the total charge. This implies that only a small part of the ions are dissociated as free ions. The activation energy for ion to dissociate for the 40, 29, 17 and 9 wt% uptake sample is 19.3, 19.1, 18.4 and17.3 kJ/mole respectively. Within the experimental errors, the activation energy for ions to dissociate does not show a significant change caused by the uptake of EMI-Tf.

4-5 Summary

In conclusion, a time domain approach was successfully developed and was applied to investigate the charge dynamics of ILs in a short side chain ionomer membrane (Aquivion) swelled with EMI-Tf. By applying the time domain model to the exponential decay of the transient current, the ionic conductivity can be separated into the contributions of mobility and mobile ion concentration, and these quantitative values of charge dynamics can be used for further systematic analysis. A critical uptake near 29 wt% of EMI-Tf in the Aquivion membrane is observed, above which the ionic conductivity and mobility increase markedly. It is also observed that the dissociation ratio of the swollen EMI-Tf remains ~ 0.5 % and seems to be independent of the EMI-Tf uptake at room temperature. Also the experimental results reveal that the conductivity does not change with applied voltage up to 4 V, and the mobility and the mobile ion concentration of the ionic polymer membrane actuator is dominated by the nonlinear current at high applied voltages, may explain why the substantial strain occurs only above 1 V at longer times. A comparison of the actuation strain of the ionomers with different side chain lengths

shows that the short side chain Aquivion exhibits a better electromechanical coupling with ions than that of the long side chain Nafion, while the actuation speeds of the two membranes under the same electrical stimulus are almost the same. Therefore, the short side chain ionomer is preferred for ionic polymer actuator applications.

The morphologies of Aquivion membranes with different uptakes of EMI-Tf are presented. The result shows that the ionic cluster scattering of the Aquivion membrane swelled with EMI-Tf remains unclear until it has exceeded the critical uptake which is consistent with the abrupt change in the ionic conduction. We examine the correlation between ionic conduction and the segmental motion of the Aquivion membrane swelled with EMI-Tf. It is found that the conductivity and mobility follow the VFT relation while the mobile ion concentration follows the Arrhenius relation. By normalizing the temperature dependence of the ionic conductivity with its ionic phase T_g , it was discovered that Aquivion membranes with different uptakes of EMI-Tf have approximately the same ionic conduction behavior at the same T-Tg implying that the change of the ionic conduction is mainly attributable to the change of Tg of ionic phase of Aquivion membranes under different uptake conditions. These results suggest that the ion transport is coupled with the segmental motion of the ionic phase of Aquivion matrix. The activation energy for charge to dissociate deduced from the Arrhenius relation does not show much change with the EMI-Tf uptake implying that the uptake of EMI-Tf does not significantly influence the charge dissociation behavior.

Chapter 5

Influence of the Ionic Polymer Membrane Thickness on Charge Dynamics of Ionic Liquids in Ionic Polymer Actuators

5-1 Introduction

Developing advanced ionic polymer membrane actuators requires the understanding of the influence of sample geometry, especially the thickness of the membrane sandwiched between two electrodes, on the charge transport and storage. In these devices, both the diffusion and drift processes depend on the distances over which the ions travel. In this paper the charge dynamics of the Aquivion membrane with 40 wt% uptake of EMI-Tf and pure BMI-PF₆ liquid cell are investigated over a broad membrane thickness (d) range. It was found that the double layer charging time τ_{DL} follows the classic model $\tau_{DL} = \lambda_D d/(2D)$ very well for both systems, where D is the diffusion coefficient and λ_D is the Debye length. In the longer time regimes (t >> τ_{DL}), the charge dynamics become dependent on the applied voltage. For low applied voltage (~ 0.1 V), the later stage charging process seems to follow the d² thickness dependence. However, at high voltage (> 0.5 V) in which significant ionic membrane actuation occurs, the charging process does not show d² thickness dependence and $\tau_{diff} = d^2/(4D)$, corresponding to the ion diffusion from the bulk region, was not observed in both systems, implying the movement of diffusion charges is mainly from the near electrode region rather than from the bulk of the membranes.

Ion transport and storage in ionomer membranes are of great interest for electroactive polymer (EAP) devices, such as actuators, sensors, energy harvesting devices, and supercapacitors [11, 12, 19-21, 78]. In general, charge transport is a result of drift and diffusion, described by the ion mobility μ , diffusion coefficient D, and mobile ion concentration n. μ and D

are related through the Einstein equation, $D = \mu KT / q$ [61, 66]. During charging, ions in the electrolyte move towards electrodes of opposite polarity due to an electric field between charged electrodes created by applied potential which is equivalent to potential drop at the two electrodes as illustrated in Figure 5-1(a). For the metal-ionic conductor-metal (MIM) system of Figure 5-1 (a) under a step voltage (from 0 at t < 0 to V volts at t > 0), the initial current before the screening of the electric field in the films occurring is $I_0 == \sigma V S/d$, where σ (= qn μ) is the conductivity, d is the membrane thickness, and S is the electrode area. When the applied voltage is not high (eV is not too high compared with kT, where k is the Boltzmann's constant), the initial transient current follows the charging of the electric double layer capacitors C_D in series with a bulk resistor R_{bulk} (see Figure 5-1(b)) [55, 61, 79],

$$I(t) = I_0 \exp(-t/\tau_{DL})$$
(5.1)

where $\tau_{DL} = \lambda_D d/(2D) = RC_D$, describes the typical charging time for the electric double layer which has a thickness λ_D , the Debye length,

$$\lambda_D = \left(\varepsilon\varepsilon_0 kT / Z^2 q^2 n\right)^{1/2} \tag{5.2}$$

where Z is the mobile ion valence (= 1 for the ionic liquids investigated in this paper), and q = e, electron charge. It is also noted that our recent study shows that for the ionic systems investigated here, this model is still valid for applied voltage at least up to 1 volt [23].

From the classical picture of the ionic system, in the initial charging process, the mobile charges in a region of thickness $\sqrt{\lambda_D d/2}$ near the electrode will migrate to near the electrodes (Debye layer thickness λ_D which is ~ 1 nm for the ionic systems investigated in this paper) with diffusion constant D. Hence, this diffusion time is equal to $\tau_{DL} = RC = \lambda_D d/(2D)$ [65-67, 79]. As a result, there is a charge deficient region near the interface which will be filled by ion diffusion from the bulk. Several theoretical models have predicted that this later diffusion process has a time constant $\tau_{diff} = d^2/(4D)$ which is much larger than τ_{DL} since d >> λ_D [11, 61, 62, 64, 65]. For most ionic electroactive devices, the response time is much longer than τ_{DL} , which is $<< 10^{-2}$ seconds for the films studied here, and substantial actuation and device functions occur during the later stage of the charging process near the electrode on time scale τ_{diff} . Hence, one critical question is whether by reducing the ionic conductor thickness d, a much fast device response speed can be achieved if $\tau_{diff} = d^2/(4D)$. A fast device response is highly desired for almost all the electroactive devices.



Figure 5-1 (a) Schematics of an ionic membrane sandwiched between metal electrodes under an applied voltage. Schematic of the voltage drop across the membrane after the membrane is charged, illustrating that most voltage drop occurs near the blocking electrodes where the mobile ions screen the charges in the metal electrodes (b) The equivalent circuit of ionic membrane metal system where R_{bulk} is the bulk resistance of the membrane and C_D is from the electrical double layer. (c) A modified equivalent circuit of ionic membrane metal system which has an interface resistor R_{in} at the polymer/electrode interface. R_{in} might be caused by the change of the ionomer morphology near the electrodes.

This paper investigates the influence of the ionomer membrane thickness d (in thickness ranging from 0.8 μ m to 20 μ m) on the ion transport and storage processes for the ionomer of Aquivion with 40 wt% uptake of EMI-Tf (1-ethyl-3-methylimidazolium

trifluoromethanesulfonate). Ionic liquids (ILs), which are a class of salt in liquid form that contain both ions and neutral molecules, are used here as electrolytes because of many interesting properties that make them very attractive for ionic electroactive polymer (EAP) devices [11, 12, 23, 56, 67, 69, 80-84]. For example, the vapor pressure of ILs is negligibly low and as a result they will not evaporate out of the EAP devices when operated in ambient condition. It has been demonstrated that comparing to water the use of ILs as solvent for EAP actuators can dramatically increase the lifetime of transducer [23]. Their high mobility leads to potentially fast response of EAP devices while the wide electro-chemical window (~4V) allows for higher applied voltages [11, 12, 23, 56, 67, 69, 80-84]. Both cations and anions are present in ILs and for the study here, it is assumed n⁺ = n⁻ (the superscripts + and – indicate positive and negative charges).

Our earlier study has shown that 40 wt% uptake of EMI-Tf is above the critical IL uptake where the conductivity of the ionomer/IL membrane exhibits much higher conductivity than that of the pure ionomer [23]. Besides the ionomers with ILs, the charge dynamics of a pure IL, 1butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆), at different thicknesses sandwiched between the electrodes is also studied. Pure ILs provide an attractive ionic system for study the charge dynamics with different electrode gaps without the complication of ionomer membranes which may have surface layers with properties different from that of bulk. BMI-PF₆ is chosen for the pure IL study because its conductivity is suitable for the experiment setup. A very high conductivity will cause high current in thin MIM cells which is beyond the range of the experimental setup.

The experimental results reveal that over a broad thickness range, the initial charge dynamics can be described well by the RC circuit model where the resistance R is determined by the bulk conductivity of the ionic conductors and C is determined by the Debye length, which does not change with the membrane thickness d. Consequently, τ_{DL} increases linearly with the

ionomer thickness or the gap width between the anode and cathode d. On the other hand, experimental results reveal that for the MIM systems studied, the later stage charge responses display voltage dependence. Under 0.1 V applied step voltage, the charging process seems to follow d² thickness dependence, while for data acquired at 0.5 V and higher, the charge diffusion time becomes progressively shorter with increased voltage than that predicted from $\tau_{diff} = d^2/(4D)$, suggesting that the mobile charges diffusing to the interface at a later stage is mainly from a region at a distance much shorter than d/2 for membranes of d = 11 µm and 20 µm thick.

5-2 Experimental

Aquivion (EW830) solution as illustrated in figure 5-2, 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) are purchased from Solvay Solexis and Aldrich, respectively. EMI-Tf is chosen for IL in Aquivion membrane because of its high conductivity (8.6×10^{-3} S/cm), low viscosity (45 cP at 298 K) and larger electrochemical window (4.1 V). It is one of the commonly used ILs in ionic polymer actuators [69, 85, 86]. BMI-PF₆ is chosen for the study of pure IL cell (without ionomer membrane) due to its relatively low conductivity and proper viscosity (1.4×10^{-3} S/cm and 450 cP) at room temperature, which make it easier for the sample preparation and for carrying out electrical characterization. In fact, in order to employ the time domain method for BMI-BF₆ cell, the temperature was further lowered to -20 °C to reduce the conductivity. All the materials were dried in vacuum at 80 °C to remove moisture before processing and characterization.

Aquivion solution blends with 40 wt% uptake of EMI-Tf are prepared and then diluted by an *N*-Methyl-2-pyrrolidone (NMP) solvent with a ratio of 1:3 for thicker films (11 μ m and 20 μ m thick) and 1:8 for thinner films (0.8 μ m and 1.9 μ m thick). Films are solution cast on metalized Si substrates. In this study, the Si/Ti/Au substrate is prepared by an e-beam evaporator with the electrode area of 1mm². Film thickness is controlled by the amount of mixture casted on the substrate. After drying at 96 °C for 10 hrs, the film is annealed under vacuum at 150 °C for 2hrs followed. To form the metal-ionic conductor-metal (MIM) sample system, 30 nm thick gold film is deposited as the top electrode.

Pure IL was sandwiched between two Si/Ti/Au electrodes with the 1 mm² electrode surface area to form the MIM sample system. 3 μ m Mylar and 20 μ m, 60 μ m thick kapton films are employed as the spacers for different thicknesses of the ionic conductors. The distance between electrodes was calibrated by measuring the capacitance C = ε_{0*} S/d where S is the surface area of electrode and vacuum permittivity $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm⁻¹.The measured thickness of the gap is 4 μ m, 23 μ m and 64 μ m respectively for the MIM systems with these spacers. To infiltrate the IL into the gap between the two electrodes, BMI-PF₆ was dropped on the gap and heated at 90 °C at vacuum overnight. The capillary force drives the BMI-PF₆ from one end to the other to fill the whole gap between the electrodes.

The electrical measurement was carried out in a sealed metal box with desiccant inside to prevent the absorption of moisture. The box is equipped with a thermocouple to monitor the temperature during the measurement. The impedance spectroscopy was measured by a potentiostat Princeton 2237. The dc conductivity was calculated by $\sigma = d/RS$, where R is determined from the Nyquist plot (see Figure 5-3(a)) [14, 23, 68]. To obtain the dielectric constant of the membranes, the samples were cooled down in an environment chamber (Versa Tenn III) to reduce the conductivity of the MIM system so that the dielectric constant before the screening of the applied field occurs, at frequencies $>> 1/\tau_{DL}$, can be measured within the frequency window of the set-up which is below 1 MHz. In contrast to the conductivity which decreases with temperature, the dielectric constant of the ionomers shows only very weakly temperature dependent and the value thus acquired can be used for room temperature [71, 86].

The transient current vs. time was acquired by a potentiostat (Princeton 2237) which output was connected to a high sampling rate oscilloscope to collect data during the fast charging process (< 1 μ s). The applied voltage is from 0.1 V to 4 V. The accumulation of blocked charges on membrane electrodes and the charge imbalance in the membrane may affect the electrical measurement. Therefore, several cycles of Cyclic Voltammetry (CV) scan with a low voltage (< 1 V) and high scan rate were performed to help cleaning the electrode surface then the samples were shorted for at least 30 min to ensure that the charges redistribute to the equilibrium state as possible [62, 68, 87].



Figure 5-2 The molecule structure of the short side chain Aquivion ionomer (EW830)



Figure 5-3 (a) The Nyquist plot used to determine the membrane resistance R and (b) the current density (dots) and fitting (solid curve) to Eq. (5.1) of the 20 μ m thick Aquivion membrane with 40 wt% uptake of EMI-Tf under 0.1 V step voltage.

By fitting experimental transient current I(t) under a step voltage with Eq.(5.1), as illustrated in Figure 5-3(b), and using the ε of the ionomer membrane (with ILs) acquired from the impedance measurement, σ , μ , and n can be obtained [61, 65, 87]. Besides the time domain study, impedance spectroscopy is also employed.

5-3 Results and Discussion

The current responses of Aquivion with 40 wt% uptake of EMI-Tf under various step voltages (from 0.1 V to 4 V) were characterized for membranes of 0.8 μ m, 1.9 μ m, 11 μ m, and 20 μ m thick to investigate the influence of the membrane thickness d on the charge dynamics of this MIM system. Figure 5-4 presents the charge response data acquired under 0.1 V and 2 V step voltages for membranes of different thicknesses. The deduced σ , μ , τ_{DL} , λ_D , and n from Eq. (5.1) under 0.1 V for this MIM system are summarized in Table 5-1.



Figure 5-4 Charge density as a function of time for the Aquivion film with 40 wt% uptake of EMI-Tf under 0.1 V and 2 V at the membrane thickness of $d = 0.8 \mu m$, 1.9 μm , 11 μm , and 20 μm . The charge response time τ_{DL} (= RC_D, see Eq. (5.1)) for films of 1.9 μm , 11 μm , and 20 μm thick is also indicated in the figure labeled as τ_1 (2.49×10⁻⁴ s), τ_2 (7.25×10⁻⁴ s), and τ_3 (1.29×10⁻³ s) respectively. The data show that the charge dynamics at short time scale is controlled by the charging of electrical double layer. The abnormal high charge response of 0.8 μm sample may be a result of the high leakage current due to the reduction of the bulk thickness. The error bar is indicated by the size of the symbols in the figure.

| Membrane thickness (d) | 20 µm | 11 µm | 1.9 µm |
|---|-----------------------|-----------------------|-----------------------|
| Conductivity σ (S/cm) | 9.1×10 ⁻⁶ | 9.0×10 ⁻⁶ | 4.9×10 -6 |
| Mobility μ (cm ² V ⁻¹ s ⁻¹) | 2.45×10 ⁻⁶ | 2.37×10 ⁻⁶ | 1.22×10 -6 |
| Concentration n (1/cm ³) | 2.31×10 ¹⁹ | 2.36×10 ¹⁹ | 2.53×10 ¹⁹ |
| Double layer $\tau_{DL}(s)$ | 1.29×10 ⁻³ | 7.25×10 ⁻⁴ | 2.49×10 ⁻⁴ |
| Diffusion $\tau_{diff}(s)$ | 15.60 | 4.86 | 0.31 |
| Debye length (nm) | 0.82 | 0.81 | 1.12 |

Table 5-1 Summary of charge dynamics of Aquivion membrane with 40 wt% uptake of EMI-Tf, estimated by fitting the measured transient current to Eq.(5.1) of samples with different membrane thickness (d) under 0.1 V step voltage at 25 $^{\circ}$ C.

Within the experimental uncertainty, σ , μ , λ_D , and n determined from 20 μ m and 11 μ m thick membranes are the same. On the other hand, the σ and hence μ determined for the membranes of 1.9 µm thick are smaller than that in the thicker membranes (reduced by about half from the values of 20 µm and 11 µm membranes), which are not expected for a macroscopic membrane, while n and λ_D are still nearly the same as that in the thick membranes. We postulate that such a reduction in the experimentally determined σ and μ is caused by an interface effect. That is, in the RC circuit of Figure 5-1(c), there is an additional interfacial resistor R_{in} which is not significant towards the total resistance of the MIM system when the membrane is thick. In the thin membranes (R_{bulk} is proportional to the membrane thickness), R_{in} can become significant compared with R_{bulk} , consequently causing the reduction of the observed σ and μ (see Figure 5-1(c)). Such an interfacial resistor might be caused by the change of ionomer microstructures near the electrodes. Combining the data from 1.9 μ m, 11 μ m, and 20 μ m thick membranes yields an estimated $R_{in} = 10.2 \ \Omega \ cm^{-1}$, which is comparable to R_{bulk} in 1.9 µm thick films. From $\tau_{DL} = RC$, $(R = R_{in} + R_{bulk})$, an increase in R due to R_{in} also causes an abnormal increase in τ_{DL} in 1.9 μm thick membrane. Without R_{in} , $\tau_{DL} = \lambda_D d/(2D)$ implies that τ_{DL} should decreases linearly with reduced membrane thickness d. Data in Figure 5-5 indicates that this is not the case for $d = 1.9 \,\mu m$ thick films, which is consistent with the results of σ in Table 5-1. In spite of the changes in the

measured σ from 1.9 µm thick membrane, the charge stored and hence the interfacial capacitance (C = charge/voltage) for the three membranes (d = 1.9 µm, 11 µm, and 20 µm) at their respective τ_{DL} (as indicated by τ_1 , τ_2 , and τ_3 for films of 1.9 µm, 11 µm, and 20 µm thick in Figure 5-4, respectively) do not change with the film thickness d, as measured in the whole voltage range.



Figure 5-5 The τ_{DL} as a function of membrane thickness d for Aquivion membrane with 40 wt% uptake of EMI-Tf. τ_{DL} is determined from fitting Eq.(5.1) with the measured transient current as illustrated in Figure 5-3(b). The film of 1.9 µm thick reveals a longer τ_{DL} than that predicted from Figure 5-1(b), indicating the existence of interface resistance which is significant when the film becomes thin.

The data for the membranes of 0.8 μ m thick displays very different behavior where the current becomes much larger than that in other films. It is likely that there is significant leakage current in such a thin film, which superimposes on the regular diffusion and drifting currents. As illustrated in Figure 5-1(a), due to the electric double layer, most voltage drop occurs within the Debye length near the electrodes, which is about 1 nm for the MIM systems studied here. Hence, the field level in the interface region can reach ~ 0.1 GV/m or larger, which can induce strong charge injection from the electrodes. For thick membranes, the bulk resistance limits the current

flow, resulting in low leakage current (the current flow is bulk limited). While for thin membranes, this resistance becomes small (the currents due to diffusion and drifting in the bulk region also become large) and consequently the current flow is interface limited, causing high leakage current as observed. The high leakage current in 0.8 μ m thick membranes makes it difficult to perform quantitative data analysis and to deduce τ_{DL} , n, λ_D , etc.

The impedance data, measured under 0.1 V, for the membranes with various thicknesses as a function of frequency is shown in Figure 5-6. As can be seen, the capacitances at the frequencies below that for the charging of Debye layer ($f = 1/\tau_{DL}$) are nearly the same for the membranes of 1.9 µm, 11 µm, and 20 µm, which is consistent with the transient charge data in Figure 5-4. For membranes of 0.8 µm thick, the high leakage current causes a very large apparent capacitance which increases with reduced frequency.



Figure 5-6 The capacitance as a function of frequency for the Aquivion film with 40 wt% uptake of EMI-Tf under 0.1 V step voltage The charge response frequency $f = 1/\tau_{DL}$ for films of 1.9 µm, 11 µm, and 20 µm thick is labeled as $f_1 (4.03 \times 10^3 \text{ Hz})$, $f_2 (1.37 \times 10^3 \text{ Hz})$ and $f_3 (7.75 \times 10^2 \text{ Hz})$ respectively. The data reveals that the C_D in Figure 5-1(c) does not change with film thickness d for 1.9 µm, 11 µm, and 20 µm thick films. The observed abnormal high capacitance response with frequency of 0.8 µm sample may be attributed to its high leakage current. The error bar is indicated by the size of the symbols in the figure.

We now examine the current and charge responses at longer time beyond τ_{DL} which is the time domain for most practical ionic electroactive devices [14, 18-21, 23, 41, 62]. As revealed in Figure 5-4, in contrast to the strong thickness dependence observed for τ_{DL} , the later stage charging responses seem not to exhibit significant change with the membrane thickness when the membrane thickness d is reduced from 20 μ m to 1.9 μ m. In Table 5-1, $\tau_{diff} = d^2/(4D)$ is also listed which is 0.31 seconds for 1.9 µm thick film and increases to 15.6 seconds for 20 µm thick film. In order to display data more clearly and compare them with τ_{diff} directly, the charge density of these films is plotted against t/d^2 as presented in Figure 5-7. The data show that under 0.1 V, the later stage charging process seems to follow d^2 dependence. However, for higher voltages, the data deviates from the d² dependence. At applied voltage > 0.5 V, the data show that the charging time for films of 11 μ m and 20 μ m becomes much shorter than that based on the d² dependence, compared with films of 1.9 µm thick. The results suggest that the charge diffusion to the electrodes at high voltages (> 0.5 V) for the MIM systems studied here is mainly from regions near the electrodes rather than from the whole film (which would show d² dependence). Hence at times much longer than τ_{DL} and voltages higher than 0.5 V the thickness variation does not cause significant changes or the charging process for thick membranes (11 μ m and 20 μ m thick) is much shorter than the d^2 dependence in the charge responses, compared with 1.9 µm thick membranes.



Figure 5-7 Charge density as a function of t/d^2 for the Aquivion film with 40 wt% uptake of EMI-Tf under (a) 0.1V, (b) 1 V, (c) 2 V, (d) 3V, and (e) 4V at the membrane thickness of d = 1.9 μ m, 11 μ m, and 20 μ m. The error bar is indicated by the size of the symbols in the figure.

ILs provide a convenient system to study thickness dependence of charge dynamics while avoiding the interface and surface effects caused by the morphology changes at interfaces of ionomers. For the MIM system with pure IL of BMI-PF₆, the thinnest d for which we can fabricate the MIM cell is 4 μ m. The charging responses under 0.1 V and 2 V step voltages for various gap thicknesses d are presented in Figure 5-8. The deduced σ , μ , τ_{DL} , λ_D , and n from Eq. (5.1) under 0.1 V are summarized in Table 5-2.



Figure 5-8 Charge density as a function of time for the ionic liquid BMI-PF₆ under 0.1 V and 2 V at the membrane thickness of d = 4 μ m, 23 μ m, and 64 μ m. The charge response time τ_{DL} (= RC_D, see Eq. (5.1)) for films of 4 μ m, 23 μ m, and 64 μ m thick is also indicated in the figure labeled as τ_1 (7.05×10⁻⁵ s), τ_2 (2.73×10⁻⁴ s), and, τ_3 (8.09×10⁻⁴ s), respectively. The data show that the charge dynamics at short time scale is controlled by the charging of electrical double layer. The data error is indicated by the size of the symbols at each data curve. The error bar is indicated by the size of the symbols in the figure.

| Electrodes distance (d) | 64 µm | 23 µm | 4 µm |
|---|-----------------------|-----------------------|-----------------------|
| Conductivity σ (S/cm) | 3.01×10 ⁻⁵ | 3.15×10 ⁻⁵ | 3.34×10 ⁻⁵ |
| Mobility μ (cm ² V ⁻¹ s ⁻¹) | 2.31×10 ⁻⁵ | 2.52×10 ⁻⁵ | 2.48×10 ⁻⁵ |
| Concentration n (1/cm ³) | 8.14×10 ¹⁸ | 7.88×10 ¹⁸ | 8.46×10 ¹⁸ |
| Double layer $\tau_{DL}(s)$ | 8.09×10 ⁻⁴ | 2.73×10 ⁻⁴ | 7.05×10 ⁻⁵ |
| Diffusion $\tau_{diff}(s)$ | 20.22 | 2.41 | 0.17 |
| Debye length (nm) | 1.28 | 1.32 | 0.825 |

Table 5-2 Summary of charge dynamics of ionic liquid BMI-PF₆ between two parallel plate electrodes, estimated by fitting the measured transient current to Eq.(5.1) of samples with different electrode distance (d) under 0.1 V step voltage at -20 $^{\circ}$ C.



Figure 5-9 The τ_{DL} as a function of membrane thickness d of BMI-PF₆ liquid cell. τ_{DL} is determined by fitting Eq.(5.1) with the measured transient current as illustrated in Figure 5-3(b).

For BMI-PF₆, there is no obvious change of σ and μ with thickness and within the experimental error the data obtained from 4 μ m thick IL is the same as that from 64 μ m thick IL. Also as shown in Figure 5-9 the τ_{DL} of BMI-PF₆ is linearly proportional to the cell thickness. This is different from that observed in the Aquivion/EMI-Tf membranes where an interfacial resistor R_{in} becomes significant at thin membranes. As we have suggested that R_{in} for the Aquivion/EMI-Tf membranes is caused by the change in the ionomer morphology near the metal electrodes, which does not exist for the pure ILs. The impedance data for this MIM system is presented in Figure 5-10 which shows that capacitance at $f = 1/\tau_{DL}$ does not change with the gap thickness between the electrodes, which is consistent with the data observed from the time domain responses in Figure 5-8.



Figure 5-10 The capacitance as a function of frequency for ionic liquid BMI-PF₆ at the electrodes distance of $d = 4 \ \mu m$, 23 μm , and 64 μm under 0.1 V step voltage. The charge response frequency $f = 1/\tau_{DL}$ for electrodes distance of 4 μm , 23 μm , and 64 μm thick is also indicated in the figure labeled as f_1 (1.4×10⁴ Hz), f_2 (3.66×10³ Hz), and f_3 (1.23×10³ Hz), respectively. The data shows that the C_D in Figure 5-1(b) does not change with electrodes distance d for 4 μm , 23 μm , and 64 μm thick gap distances. The error bar is indicated by the size of the symbols in the figure.

In analogous to that observed in the Aquivion/EMI-Tf membranes. The current responses at longer times beyond τ_{DL} do not show significant changes with thickness except at 0.1 V. Figure 5-11 presents the charge response data versus t/d². The charging time obtained under 0.1 V seems to follow approximately d² thickness dependence. For higher voltages (> 0.5V), the deviation of the charging time from the d² dependence becomes progressively stronger. In fact, for data under ≥ 2 V, the later stage charging process seems not to show much change with the membrane thickness, implying that at high voltages the ion diffusion is mainly from the regions near the electrodes (< 2 µm).



Figure 5-11 Charge density as a function of t/d^2 for the ionic liquid BMI-PF₆ under (a) 0.1 V, (b) 1 V, (c) 2V, (d) 3V, and (e) 4V step voltages at the membrane thicknesses $d = 4 \mu m$, 23 μm , and 64 μm . The error bar is indicated by the size of the symbols in the figure.

5-4 Summary

The influence of the ionomer membrane thickness on the ionic charge dynamics of the Aquivion/EMI-Tf with Au electrodes is investigated. It was observed that in the membrane thicknesses from 1.9 μ m to 20 μ m, there is no obvious change of λ_D and n with thickness and voltage which are expected from the classical pictures of charge dynamics at charging the interface capacitor C_D with thickness ~ λ_D , which is about 1 nm for the membranes of Aquivion with 40 wt% uptake of EMI-Tf. The experimental results reveal that in this MIM system, there is an interfacial resistor R_{in} , which is probably caused by the change of the ionomer morphology near the electrodes and becomes significant when $d = 1.9 \mu m$. As a result, there is an abnormal change of σ and τ_{DL} deduced from the experimental data for membrane of 1.9 µm thick. For charging responses at times >> τ_{DL} which is the time domain where most electrical and electromechanical actions occur for the ionic electroactive devices, experimental data reveal that charge dynamics depends on the applied voltage. For 0.1 V, the later stage charging process seems to follow d² membrane thickness dependence. With increased voltage, the charging time deviates progressively from the d^2 thickness dependence and the thick membranes (11 μ m and 20 μ m thick) can be charged much faster than that predicted from $\tau_{diff} = d^2/(4D)$, compared with 1.9 µm thick membranes.

The influence of the gap thickness d between the electrodes on the charge dynamics of a pure IL, BMI-PF₆, when d is varied from 4 μ m to 63 μ m is also investigated. The experimental results show that in analogous to the Aquivion/EMI-Tf membranes, the charge dynamics at initial time also follow the charging of interfacial capacitor C_D in series with a bulk resistor. Hence, τ_{DL} increases linearly with thickness d. For the pure IL, there is no interfacial resistor effect as observed in the Aquivion/EMI-Tf membranes. For the charge dynamics at times >> τ_{DL} , the results for the pure IL are very similar to that observed in the ionomer membranes. That is, for the

data obtained under 0.1 V, the later stage charging process which is governed by ion diffusion process seems to follow d^2 dependence and for voltages > 0.5 V, this later stage charging time does not show d^2 thickness dependence as the gap between the electrodes varies from 4 µm to 63 µm. The data seem to suggest that at these high voltages, the later stage charge responses do not show marked thickness dependent.

Chapter 6

Ionic Chain Density Effects of P(DMAEMA-co-DiglymeMA) on the Charge Dynamics of EMI-Tf

6-1 Introduction

The actuation strain and speed of ionic electroactive polymer (EAP) actuators are mainly determined by the charge transport through the actuator and excess ion storage near the electrodes. Hence how the morphology of the polymer matrix affects the charge transport is of interest [88-90]. For example, the formation of ionic percolation channels, by swelling the ionomer membrane with IL above its critical uptake, can enhance the charge transport in the perfluoro ionomers membranes such as Aquivion [14]. On the other hand, when blended the Poly(dimethylaminoethyl methacrylate)-Poly(methyl methacrylate) PDMAEMA-PMMA copolymer with salt, the formation of micelles was observed which may impede the ion transport in the membrane [63, 91-94]. A micelle structure was proposed by Wesley et al. as illustrated in Figure 6-1. It illustrates that salt might induce the formation of micelles by charge screening and packing of the copolymer chains [94]. PDMAEMA consists of a polymethacrylate backbone with positively charged dimethyl amino groups as shown in Figure 6-2. Potentially it can be used in drug delivery [82, 95-98] and biomedical applications [99-103]. The ionic conductance of PDMAEMA/PEO polymer electrolyte with Li-TFSI salt has been investigated by Cha E. H. et al. and they found the ionic conductivity decreases with increasing the PDMAEMA content [63, 91]. When it exceeds a certain content of PDMAEMA (> 13 wt %), the electrolyte mixture shows a rapid drop in conductivity [63, 91]. More recently, Klein et al. investigated the charge dynamics of doped polyphosphazene and polyphosphazene ionomers (i.e. polymer matrices with and

without ionic side chain groups), and found that with the similar chemical structures and compositions, the sample with ionic chains has an ionic mobility 10 times slower than that without ionic chains. The authors attribute this reduction of the charge mobility to the ionic charged local environment where the charges transport. The electrostatic forces among charges and the ionic chains could slow down the charge mobility [74]. Meanwhile, the low mobility and high activation energy could also partly be attributed to the observed micelles. The coronal chains that surround clusters are dynamically inhibited [104, 105]. Therefore, micelles of multiple cations and anions may decrease the local chain mobility and thus the ion mobility. The electrostatic effect of adjacent ions may increase the activation energy for ion dissociation [74].

The poly(dimethylaminoethyl methacrylate-*co*-diethylene glycol methylether methacrylate) P(DMAEMA-*co*-DiglymeMA) copolymers were synthesized by free radical copolymerization in tetrahydrofuran (THF) by Dr. Matthew Hunley at Virginia Tech in Professor Tim Long's group. By changing the content of DMAEMA, the ionic chain density of the copolymer can be varied. It is of great interest to understand how the ionic chain density affects the charge dynamics of ILs. In this chapter, we investigate the charge dynamics of P(DMAEMA-*co*-DiglymeMA) copolymers with different ionic chain densities which are blended with 40 wt% uptake of EMI-Tf. Especially we investigate how the morphology of the polymer matrix evolves with ionic chain density, the charge dynamics evolve with ionic chain density and the correlation between the ionic conduction behavior and the segmental motion of the polymer matrix.



Figure 6-1 Schematic representation of the PDMAEMA-PMMA block copolymer/sodium dodecyl sulfate (sds) salt micelles with a core comprised of salt tail and solubilized PMMA and a shell of PDMAEMA chains wrapping themselves around the micelles [94].

6-2 Experimental

A series of P(DMAEMA-*co*-DiglymeMA) copolymers were provided by Dr. Matthew Hunley at Virginia Tech in Professor Tim Long's group. The P(DMAEMA-*co*-DiglymeMA) copolymers were synthesized by free radical copolymerization in tetrahydrofuran (THF) with DMAEMA content of 10, 30, 50 and 70 mole% and were neutralized with HCl to form the corresponding polyelectrolyte as illustrated in Figure 6-2.



Figure 6-2 Schematic representation of the synthesis of the P(DMAEMA-*co*-DiglymeMA) copolymers and neutralization with HCl.

We blended these copolymers in Cl form with 40 wt% uptake of EMI-TF following the same uptake of EMI-Tf for the general IEAP actuator application. For equivalent weight calculations, the charged PDMAEMA monomer is 193.67 g/mol and the uncharged monomer P(DiglymeMA) is 188.22 g/mol, so the equivalent weight should be 188.75, 189.85, 190.94, and 192.03 g/mole for copolymers with 10, 30, 50, and 70 mole% of DMAEMA ionic chain densities, respectively. The density of the synthesized copolymer is assumed to be around 1.3g/cm³. The molecular weight of EMI-Tf is 260.24 g/mole and the density is 2.06 g/cm³. The calculated charge densities are listed in Table 6-1. The neutralized Cl concentration is equal to the ionic chain concentration of DMAEMA.

| DMAEMA mole% | MW (g/mole) | $\frac{\text{Cl}^2}{(1/\text{cm}^3)}$ | $EMI^{+} + Tf^{-}40$ wt% uptake $(1/cm^{3})$ | Total (1/cm ³) |
|-----------------|----------------|---------------------------------------|--|-------------------------------|
| 10 | 188.76 | 3.01×10 ²⁰ | 1.74×10 ²¹ | 2.04×10 ²¹ |
| 30 | 189.85 | 8.98×10 ²⁰ | 1.74×10 ²¹ | 2.64×10 ²¹ |
| 50 | 190.94 | 1.48×10 ²¹ | 1.74×10 ²¹ | 3.23×10 ²¹ |
| 70 | 192.03 | 2.07×10^{21} | 1.74×10 ²¹ | 3.82×10 ²¹ |

Table 6-1 The material parameters of P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

DSC study was carried out and the results reveal that PDMAEMA homopolymer has a T_g at 19 °C, while P(DiglymeMA) has a much lower T_g at -37 °C. The T_g of P(DMAEMA-*co*-DiglymeMA) in Cl form with DMAEMA content of 10, 30, 50, and 70 mole% is -11.7, 30, 80, and 111°C, respectively. The increase of T_g with the positively charged component density implies the electrostatic interactions of the ionic charged components of copolymer, while the T_g s of samples blended with 40 wt% uptake of EMI-Tf are not found by DSC.

The P(DMAEMA-co-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA were blended with 40 wt% uptake of EMI-Tf. Then 10 mg of each mixture was diluted with 10 ml ethanol and stirred at room temperature for 3hrs. A Malvern Zetasizer Nano series was used to determine the dispersion of the P(DMAEMA-co-DiglymeMA)/EMI-Tf /ethanol suspensions. The particle sizes of the P(DMAEMA-co-DiglymeMA)/EMI-Tf in ethanol suspensions were measured. The nanodispersions from optical properties measurement exhibited an average particle size of < 1 nm (undetectable), 72 nm, 257 nm and 680 nm in diameter, for P(DMAEMA-co-DiglymeMA) with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf, respectively.

The Cl form of P(DMAEMA-*co*-DiglymeMA) with 10, 30, 50 and 70 mole % of DMAEMA copolymers were blended with 40 wt% uptake of EMI-Tf and dissolved in ethanol as mixtures. The solution was cast on a Si/Ti/Au substrate with a 50 µm thick kapton as a spacer. After being dried in vacuum for 48 hrs at 90 °C, the top Si/Ti/Au electrode was placed on top of the sample and was heated to 120 °C under a vacuum to further melt the mixture for 4 hrs and then the samples were left in the vacuum for another 48 hrs at 90 °C to remove the bubbles and solvent. The thickness of the samples was measured by subtracting the electrode's thickness and was in the range of 55 to 65 µm. A clamp was used to keep the electrodes in contact with the sample during temperature scan. The sample was sealed in a metal box equipped with a thermal

couple and desiccant inside. Details of the electrical measurement including the time domain and frequency domain methods are described in chapter 4.

6-3 Results and Discussion

Figure 6-3 shows the micelle diameter evaluated by Malvern Zetasizer light scattering. The average micelle diameter of P(DMAEMA-*co*-DiglymeMA) copolymer containing 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf is < 1 nm (undetectable), 72 ± 10 nm, 257 ± 20 nm and 680 ± 20 nm, respectively. These results show that the micelle size increases with DMAEMA ionic chain density.



Figure 6-3 The average micelle diameters of P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf and diluted with ethanol as mixtures.

When considering the correlation between the charge response and the strain of the actuator, two important parameters should be taken into consideration: the strain level and the response time. As observed, substantial strain occurs under applied voltage >1 V and reaches its maximum in a few seconds [20, 21, 23]. The charge dynamics estimated from the τ_{DL} can only reveal the initial part of the information about the charge transport in the actuator, while the charge response in a longer time frame which contributes to the substantial strain is not included. Therefore, collecting the charge response in a longer time frame alonger time frame is necessary to reveal more information about the correlation between the strain and the accumulated charges.

The conductivity, mobility as well as the mobile ion density can be deduced by fitting the measured transient current with a time domain model. Figure 6-4(a), (b) and (c) show that the conductivity does not show much change with applied voltage up to 4 V and the mobility and mobile ion concentration do not show systematic change with applied voltage up to 1 V. As shown in Figure 6-4(b) and (c), the deviation of the mobility and mobile ion concentration may be due to the poor quality of the transient current signal of the sample. The low conductivity of sample may result in a small current signal with high noise level leading to the fitting uncertainty in the shape of the transient current in which the mobility and mobile ion concentration are determined. Because ionic conductivity is determined by the magnitude of the initial transient current, this noise induced uncertainty is relatively low. Besides the charge response with applied voltage in a short time (double layer time constant), the charge response in a longer time frame is also important since this is where the actuation occurs. Figure 6-5 shows the charge responses of samples containing 10 to 70 mole% of DMAEMA under 0.1 V and 4 V step voltages at 30 °C. It was shown that at low voltage (0.1 V), the mobile ions migrate to the electrodes and polarize them in their double layer time constants τ_{DL} . Table 6-2 shows that the ion mobility decreases when the ionic chain density is increased. As a result the membrane with a higher ionic chain density shows a longer double layer charging time τ_{DL} . As observed at high applied voltage (4 V),

the current rises up showing a nonlinear charging behavior. The actual mechanism of the nonlinear charging behavior is not clear and would be a good topic for the future work.



Figure 6-4 (a) The conductivity, (b) mobility, and (c) mobile ion concentration of P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf in response to different applied step voltages.



Figure 6-5 Charge responses of P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole % of DMAEMA blended with 40 wt% uptake of EMI-Tf under 0.1 V and 4 V step voltages.

| DMAEMA (mole%) | 10 | 30 | 50 | 70 |
|---|-----------------------|-----------------------|-----------------------|-----------------------|
| Conductivity σ (S/cm) | 5.14×10 ⁻⁵ | 5.64×10 ⁻⁶ | 1.76×10 -7 | 1.94×10 ⁻⁸ |
| Mobility μ (cm ² V ⁻¹ s ⁻¹) | 3.11×10 ⁻⁵ | 1.56×10 -6 | 1.11×10 -7 | 1.32×10 -8 |
| Concentration n (1/cm ³) | 1.04×10 ¹⁹ | 2.26×10 ¹⁹ | 9.91×10 ¹⁸ | 9.23×10 ¹⁸ |
| Double layer $\tau_{DL}(s)$ | 7.12×10 ⁻⁴ | 7.64×10 ⁻³ | 0.201 | 1.475 |

Table 6-2 Charge dynamics of P(DMAEMA-DiglymeMA) copolymers with 10, 30, 50 and 70 mole % of DMAEMA blended with 40 wt% uptake of EMI-Tf under 0.1V step voltage at 300K.
Figures 6-6 (a) and (b) show the ionic conductivity and mobility versus the ionic chain density at room temperature. Both the conductivity and mobility of the ions decrease rapidly when the DMAEMA chain density is increased.



Figure 6-6 (a) The ionic conductivity and (b) mobility as a function of the DMAEMA content for the P(DMAEMA-*co*-DiglymeMA) copolymers blended with 40 wt% uptake of EMI-Tf.

As shown in Figure 6-7, the dissociation ratio of mobile ions at room temperature decreases rapidly with increasing ionic chain density and the data are summarized in Table 6-3. It seems that the increase of DMAEMA chain density facilitates the formation of micelles and suppresses the mobile ion dissociation ratio. This reduction of the charge conductivity, mobility and mobile ion dissociation ratio may be due to the increase in ionic charged density of local environment where the charges transport. The electrostatic forces among charges and the ionic chains may slow down the chain mobility and increase the energy barrier for ion dissociation. [74]. Meanwhile, these observed micelles may also slow down the chain mobility. The coronal chains that surround clusters are dynamically inhibited. Therefore, micelles of multiple cations and anions may decrease the local chain mobility and thus the ion mobility [75, 77]. The electrostatic effect of adjacent ions may increase the activation energy for ion dissociation [73].



Figure 6-7 The mobile ion dissociation ratio as a function of the DMAEMA content for the P(DMAEMA-*co*-DiglymeMA) copolymers blended with 40 wt% uptake of EMI-Tf at 300 K.

Table 6-3 The mobile ion concentration data of P(DMAEMA-*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf at 300 K.

| DMAEMA (mole%) | 10 | 30 | 50 | 70 |
|------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Theoretical n (1/cm ³) | 2.05×10^{21} | 2.64×10 ²¹ | 3.22×10 ²¹ | 3.81×10 ²¹ |
| Measured n @ 300K | 1.25×10 ¹⁹ | 1.45×10 ¹⁹ | 6.28×10^{18} | 5.8×10 ¹⁸ |
| Dissociation ratio % | 0.61 | 0.55 | 0.19 | 0.15 |
| $T_{g}(K), t = 100 s$ | 236 | 256 | 280 | 287 |

Figure 6-8 shows the temperature dependence of the ionic conductivities of P(DMAEMA-*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf. It was shown that the conductivity decreases rapidly with increased temperature and the temperature dependence of the ionic conductivity can be described by the Vogel-Fulcher-Tammann (VFT) relation [77],

$$\sigma = \sigma_0 \exp[\frac{-B}{T - T_0}]$$

where σ_0 is the intrinsic conductivity at a very high temperature (T >> T₀), B is the pseudoactivation parameter for conduction with unit (K), and T₀ is the temperature where the σ approaches 0. The fitting parameters are summarized in Table 6-4. It is shown that the pseudoactivation energy B increases with the ionic chain density implying the increase of the energy barrier for ionic conduction. The Vogel temperature T₀ also increases with the ionic chain density. It seems that the charges become more and more difficult to move for ionic conduction with increasing the ionic chain density. The copolymer samples with higher DMAEMA chain density possess extra Cl⁻ ions, and this might be the reason for their higher intrinsic conductivity σ_0 as shown in Table 6-4.



Figure 6-8 The temperature dependence of the ionic conductivities of P(DMAEMA-*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

| DMAEMA (mole%) | 10 | 30 | 50 | 70 |
|-----------------------------------|-----------|-----------|-----------|----------|
| Conductivity σ_0 (S/cm) | 0.17±0.01 | 0.21±0.02 | 0.52±0.05 | 2.66±0.2 |
| B (K) | 892 ±50 | 1120 ±80 | 1555±150 | 1868±150 |
| T ₀ (K) | 194±2 | 197 ±2 | 201±2 | 204±2 |

Table 6-4 The VFT fitting parameters of the conductivities of P(DMAEMA-co-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

The segmental motion of the polymer chain is a cooperative process and is generally correlated with the glass transition behavior. At temperatures below the glass transition temperature, the polymer behaves like a rigid glass, whereas above T_g , it exhibits rubber-like behavior at longer times when the long range polymer chain can move. Consequently, the segmental dynamics strongly affect the movement of ions in the polymer matrix, which could leads to the macroscopic ionic conduction [76, 77]. It is known that the correlation between the segmental motion and the ionic conductivity with the glass transition temperature of the polymer matrix [76, 77]. However, neither the DSC nor DMA can provide T_g s of P(DMAEMA-*co*-DiglymeMA) copolymers with 40 wt% uptake of EMI-Tf. The dielectric α relaxation at a frequency domain offers another approach to analyzing the relaxation of the copolymer with increasing DMAEMA chain density at 323 K.



Figure 6-9 The dielectric loss versus frequency plot at 323 K of P(DMAEMA-*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

Figure 6-10 shows that the temperature dependence of the α relaxation frequency which corresponds to the segmental motion of the copolymer chain follows the VFT relation [76, 77].

$$f_{max} = f_0 \exp[\frac{-B}{T - T_0}]$$

where f_0 is a constant, T_0 is the Vogel temperature in which the segmental relaxation frequency approaches zero, and B is the pseudo activation energy with unit K. The fitting results are summarized in Table 6-5. The pseudo-activation energy B increases with ionic chain density implying the higher energy barrier for segmental motion. It is observed that at a fixed temperature, the relaxation frequency decreases with increased ionic chain density as shown in Figure 6-10. The electrostatic force interaction of the ionic chains may be the reason for the increase of pseudo- activation energy B and the decrease of chain mobility [74, 76, 77].



Figure 6-10 The segmental relaxation frequencies as a function of temperature of P(DMAEMA*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

Table 6-5 The VFT fitting parameters of the segmental relaxation frequencies of P(DMAEMAco-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf .

| DMAEMA (mole%) | 10 | 30 | 50 | 70 |
|-----------------------|------------|-----------------|-----------|-----------|
| f_0 | 12.47 ±1.2 | 11.34 ± 1.1 | 10.95±1.1 | 11.71±1.1 |
| B (K) | 701±50 | 745 ±50 | 938±80 | 1114 ±80 |
| T ₀ (K) | 207 ±3 | 214 ±3 | 223±3 | 227 ±3 |
| $T_{g}(K), t = 100 s$ | 236 ±2 | 256±2 | 280±2 | 287±2 |

In order to correlate the charge dynamics with the segmental relaxation frequency of a polymer matrix, the Debye-Stokes-Einstein (DSE) relation is employed. The DSE model can provide insight into the charge dynamics which connect the ionic conductivity and the polymer chain dynamics. This relation predicts that $\sigma \times \tau_{\alpha} \cong$ constant or $\sigma \propto f_{\alpha}$ for the ideal conduction of a sphere through a viscous medium with a characteristic relaxation frequency f_{α} or relaxation

time τ_{α} . Therefore, the coupling between the ionic conduction and the polymer segmental relaxation frequency can be presented by a log–log plot with a slope of 1 [107].

Figure 6-11 shows that the ionic conductivity is coupled with the segmental relaxation frequency of the copolymer following the DSE relation. At a fixed segmental relaxation frequency samples with different ionic chain densities have approximately the same ionic conductivity implying that the charge transport behavior is dominated by the segmental motion of the copolymer matrix. Hence, the drop of the ionic conductivity at room temperature may be mainly caused by the slowdown of the segmental motion of the copolymer matrix with increasing the ionic chain density.



Figure 6-11. The ionic conductivities versus segmental relaxation frequencies of P(DMAEMA*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf.

6-4 Summary

We investigate the charge dynamics of P(DMAEMA-co-DiglymeMA) copolymers with 10, 30, 50, and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf. The observed voltage-independent of charge dynamics are similar to those found in chapter 4. The formation of micelles and the decrease in the ionic conductivity, mobility and mobile ion dissociation ratio with the increased ionic chain density have been observed. It is found that the conductivity is coupled with the segmental relaxation frequency of the copolymer following Debye-Stokes-Einstein relation very closely. At a fixed segmental relaxation frequency samples with different ionic chain densities have approximately the same ionic conductivity implying that the charge transport behavior is dominated by the segmental motion of the copolymer matrix. Hence, the drop of the ionic conductivity at room temperature may be mainly caused by the slowdown of the segmental motion of the copolymer matrix with increasing the ionic chain density. The electrostatic interactions among charges and ionic chains may slow down the chain mobility and increase the energy barrier for ion dissociation. These results imply that the reduction of the ionic conductivity, mobility and mobile ion dissociation ratio may be mainly caused by the increase in the ionic charged density of the local environment where the charges transport.

Chapter 7

Conclusions and Future Work

7-1 Summary of This Work

A synthesis process of P(VDF-TrFE-CFE) 59.2/23.5/7.2 mole% terpolymer nanorods by wetting an AAO template was developed, which can be used to tailor polymer nanoactuators while also provides a platform to investigate the evolution of the ferroelectric properties of terpolymer in a confined nanosystem. Terpolymer nanorods in diameters of 25 nm, 70 nm, and 200 nm were prepared and investigated. It is observed that all the terpolymer nanorods exhibit the typical ferroelectric relaxor dielectric behavior that is the dielectric constant peak (T_m) shifts progressively toward higher temperatures with frequency and this shift of dielectric constant peak temperature with frequency can be described by the empirical Vogel-Fulcher-Tammann (VFT) relation. The freezing temperature T_f deduced from the VFT equation is lowered as the terpolymer nanorod diameter is reduced. The existence of ferroelectric properties down to 25 nm diameter nanorods implies the possibility of nanometer scale terpolymer actuator applications.

In the IEAPs, charges transport through the ionic system and the subsequent accumulation and depletion of excess ions at the electrodes determine the response behavior of the electroactive devices. The formation of the ionic percolation channels can facilitate the charge transport within the membrane. On the other hand, when the P(DMAEMA-co-DiglymeMA) copolymer is blended with EMI-Tf, the formation of micelles was observed.

Instead of the frequency domain approach which is commonly used for low applied voltage (< 1V) characterization, we developed a time domain model to investigate the charge dynamics of IL in an ionomer over a broad voltage range up to 4 V and a longer time frame up to

few seconds. We aim to focus on the following critical parameters for a better design of the IEAP actuator: (1) the uptake effect on the charge dynamics of ILs; (2) the ionomer side chain length influence on the charge dynamics of ILs and actuations; (3) the correlation between the charge dynamics of IL and the morphology of the ionomer; (4) the correlation between charge dynamics of IL and the segmental motion of the polymer matrix; (5) the polymer membrane thickness effect on the charge dynamics of ILs; and (6) the non-linear effect on charge dynamics at high applied voltages and longer time frames.

Aquivion membranes swelled with uptakes of 9, 17, 29 and 40 wt% EMI-Tf are examined. A critical uptake near 29 wt% of EMI-Tf in the Aquivion membrane is observed, above which the ionic conductivity and mobility increase markedly. It is also observed that the dissociation ratio of the swollen EMI-Tf remains ~ 0.5 % and seems to be independent of EMI-Tf uptakes. The experimental results reveal that the conductivity does not change with applied voltage up to 4 V, and the mobility and mobile ion concentration do not change much with applied voltage up to 1 V. Furthermore, the finding that the actuation of the ionic polymer membrane actuator is dominated by the nonlinear current at high applied voltages, may explain why the substantial strain occurs only above 1 V at longer times. A comparison of the actuation strain of ionomers with different side chain lengths shows that the short side chain Nafion, while the actuation speeds of the two membranes under same electrical stimulus are similar. Therefore, the short side chain ionomers are preferred for ionic polymer actuator applications.

The morphologies of Aquivion membranes with different uptakes of EMI-Tf are presented. The results show that the ionic cluster scattering of the Aquivion membrane is not clear until the uptake of EMI-Tf is above its critical uptake which is consistent with the abrupt change of the ionic conduction. When compared with Nafion swelled with the same 40 wt% uptake of EMI-Tf, Aquivion seems to have an ionic cluster scattering at higher q position implying a smaller inter ionic cluster size which may be the reason of why the Aquivion has a higher electromechanical coupling than that of Nafion. We examine the correlation between the ionic conduction and the segmental dynamic of the Aquivion membrane swelled with EMI-Tf. Our systems cover a broad uptake range of EMI-Tf from far below (9 wt%) to well above (40 wt%) the critical uptake (~29 wt%). It is found that the conductivity and mobility follow the VFT relation while the mobile ion concentration follows the Arrhenius relation. By normalizing the temperature dependence of the ionic conductivity with its ionic phase T_g , samples with different uptakes of EMI-Tf have approximately the same conductivity at the same T-Tg, implying that the change of the ionic conductivity is mainly attributable to the change of T_g of the ionic phase of Aquivion membranes under different uptake conditions. These results suggest that the ionic conduction is coupled with the segmental motion of the Aquivion matrix. Also the temperature dependence of the mobile ion concentrations of Aquivion membranes with different uptakes of EMI-Tf is examined. It is found that the activation energy for charges to dissociate, deduced from the Arrhenius relation, does not change much with the uptake of EMI-Tf.

We examine the double layer time constant by systematically reducing the membrane thickness over a broad range in two systems. One is Aquivion membranes swelled with 40 wt% uptake of EMI-Tf for membrane thickness from 20 μ m to 0.8 μ m, and the other is the pure IL BMI-PF₆ with electrodes separated at a distance of 64 μ m to 4 μ m. The experiment results show that the double layer time constant $\tau_{DL} = \lambda_D d/(2D)$ is consistently proportional to the thickness d over a wide thickness range and the conductivity results from the time domain approach and frequency method (at 0.1 V) are almost the same.

From the RC circuit model, we can see that the applied voltage mainly drops on these two double layer capacitors. With such a high mobile ion concentration of 1×10^{-19} cm⁻³, the Debye length is thin to ~1 nm, and therefore the high electric field across the double layer capacitor can be very high (for 1 V, 0.5 GV/m). Without the bulk resistance, the charge injection

due to the high electric field can lead to a high leakage current. For the 0.8 μ m Aquivion sample with 40 wt% uptake of EMI-Tf, a clear abnormal charge response is observed which prohibits analysis of this sample. Therefore, we suggest that the thinnest thickness of the Aquivion membrane with 40 wt% uptake of EMI-Tf for actuator application is around 0.8 μ m.

Without an abnormal leakage current, an apparent deviation of τ_{DL} from the proportional trend of thickness (d) relation was observed on 1.9 µm thick Aquivion membrane while it was not observed on the pure IL BMI-PF₆ system. We extrapolated the bulk resistant R_b to the thickness approaching zero for both systems and found that the swelled Aquivion membrane has a residual resistance around 10.2 (ohm/cm²) while the pure IL BMI-PF₆ sample has a residual resistance approaching zero. Considering the measurement error of the setup is less than 0.1 ohm/cm², we suggest that an interface resistance exists at the polymer and gold electrode interface. We carefully examined the charge response with time for different thicknesses and found that there is a double layer charging response time delay which follows the $\tau_{DL} = \lambda_D d/(2D)$. After that no significant thickness dependence of charging behavior was observed at a time scale larger than τ_{DL} .

The influence of the ionic chain density on the charge dynamics was examined by investigating the charge dynamics of P(DMAEMA-*co*-DiglymeMA) copolymers with 10, 30, 50 and 70 mole% of DMAEMA blended with 40 wt% uptake of EMI-Tf. The formation of micelles and the decrease in the ionic conductivity, mobility and mobile ion dissociation ratio with increased ionic chain density have been observed. It is found that the ionic conductivity is coupled with the segmental relaxation frequency of the copolymer following Debye-Stokes-Einstein relation very closely. No apparent conductivity deviation among all samples at a fixed relaxation frequency is observed implying that the charge transport behavior is dominated by the segmental motion of the copolymer. Therefore, the drop of conductivity at room temperature may

be mainly caused by the slowdown of the segmental motion of the copolymer chain with increasing the ionic chain density. The electrostatic interactions among charges and ionic chains may slow down the chain mobility and increase the energy barrier for ion dissociation. These results suggest that the reduction in the ionic conductivity, mobility and mobile ion dissociation ratio may be caused by the increase of the ionic charged density of the local environment where the charges transport.

In summary, we have some suggestions for a better design of IEAP actuators. 1. The minimum amount of uptake of ILs is above its critical uptake, 2. The short side chain Aquivion membrane did show a better electromechanical coupling efficiency than that of the long side chain Nafion, 3. The thinnest membrane for actuator application should be the thickness before the large leakage current occurs. 4. The charge transport in both the Aquivion membranes and the P(DMAEMA-co- DiglymeMA) copolymers are coupled with the segmental motion of the polymer matrices.

7-2 Suggestions for Future Work

For the FEAPs, the dielectric results show that the ferroelectric properties of P(VDF-TrFE-CFE) terpolymer are affected by the size confinement and persist down to 25 nm diameter. Therefore, it would be of interest to know how the size confinement affects the electrostrictive behavior of the terpolymer nanorods. A systematic investigation on strain measurement by AFM should be carried out. Lee A. S. et al., have demonstrated the strain measurement of polymer fibers by AFM [108].

For the IEAPs, this study found that the nonlinear charging behavior occurs at higher applied voltages (>1V) and at longer times where the substantial strain appears as shown in Figure 4-1 and 4-18, but the real mechanism for this nonlinear charging behavior in response to a

step voltage is still unclear. Therefore, it would be worthwhile to further develop the understanding of nonlinear charging behavior which is crucial for IEAP's, as well as supercapacitor and battery applications.

In the ionic liquid system, water could affect charge dynamic behaviors and the electrochemical window. In this dissertation, we mainly focus on the IL EMI-Tf which is hydrophilic. Therefore, we spend a lot of effort avoiding the moisture effect. Samples are prepared at an elevated temperature under a vacuum and the electrical measurements are carried out in a sealed metal box with desiccant inside. By rigorously avoiding moisture in the sample as much as possible, we focus on investigating the fundamental understanding of charge dynamics of IL in a polymer matrix. However, from the practical point of view, the IEAP actuator works in ambient conditions where the moisture contents can be varied. Therefore, a systematic investigation of how the moisture affects the charge dynamics of IL in IEAP and the actuation of actuator would be crucial. Except the hydrophilic ILs, using hydrophobic ILs as electrolytes may be another feasible approach to avoid water effects on the IEAPs.

As an actuator, the electromechanical conversion efficiency is important. Our previous results show that the electromechanical conversion efficiency of the IEAPs is below 0.1%. The fundamental reasons for this low efficiency are not clear yet. The observed nonlinear charging behavior at high applied voltage of the IEAPs implies that the input energy may be mainly stored in the IEAP rather than converted into mechanical strain. The IEAP may actually be more like a capacitor than a transducer. Therefore, a series of experiments and theory modeling would be required to determine the root causes of this low electromechanical conversion efficiency.

In the investigation of the side chain length effect on the electromechanical coupling efficiency, the strain and stored charge results indicate that the short side chain Aquivion membranes have a better electromechanical coupling efficiency than that of long side chain Nafion. Also our recent investigation of P(VDF-HFP) based polymer swelled with EMI-Tf shows

that without ionic side chains, the polymer system can still generate strain. Therefore, more systematic studies of the side chain length effect on the electromechanical coupling efficiency should be carried out. On the other hand, in the IEAP system swelled with IL, both cations and anions can move. This implies that under applied voltage, both cations and anions contribute to strain but on the opposite polarity electrode and hence cancel each other out, reducing the electromechanical coupling efficiency. Ideally, if we can synthesize a single mobile ion ionomer with enough mobile ion concentration, the cancellation effect may be reduced. We may also choose ILs with a large effective size difference between cation and anion (cluster) as electrolytes to reduce the strain cancellation effect. The Bjerrum length $\lambda_B = \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 kT}$ relation implies that if we can provide ILs with a large dielectric constant ε_r to reduce the association interaction between cation and anion, it might be possible to improve the ion dissociation ratio and provide more mobile ions. Blended ILs with a high dielectric constant solvent or with high dielectric constant polymer matrices such as P(VDF-TrFE-CFE) (ε_r =55) may be feasible.

Appendix

Figure A-1 shows the raw data of dielectric loss tand at different frequencies versus temperature for P(VDF-TrFE-CFE) terpolymer bulk film and P(VDF-TrFE-CFE) terpolymer nanorods of 200 nm, 70 nm and 25 nm diameter embedded in AAO template.



Figure A-1 Dielectric loss tan δ at different frequencies vs. temperature for P(VDF-TrFE-CFE) terpolymer (a) bulk film (b) nanorods of 200 nm diameter; (c) nanorods of 70 nm diameter and (d) nanorods of 25 nm diameter embedded in AAO template.

Figure A-2 shows the raw data of dielectric constant at different frequencies versus temperature for P(VDF-TrFE-CFE) terpolymer nanorods of 200 nm,70 nm and 25 nm diameter embedded in AAO template.



Figure A-2 Dielectric constant at different frequencies vs. temperature for P(VDF-TrFE-CFE) terpolymer nanorods of (a) 200 nm; (b) 70 nm and (c) 25 nm diameter embedded in AAO template.



Figure A-3 The dielectric constant of pure alumina vs. frequency

Figure A-4 is the data reported by Viehland D. et al, for 10-mol % lead titanate in lead magnesium niobate [10]. An activation energy and freezing temperature of 0.0407 eV and 291.5 K were reported by analyzing the frequency dependence of the temperature at the dielectric maximum using the Vogel-Fulcher relationship as reported in Figure A-5[10].



Figure A-4 Dielectric constant as a function of temperature at measurement frequencies of 0.1, 0.2, 0.4, 1, 2, 4, 10, 20, 40, 100 kHz. The highest dielectric response is the 0.1 kHz curve, the lowest is the 100 kHz curve, and the other curves between are in order of increasing frequency.(reported by Viehland D. et al.[10])



Figure A-5 Inverse of the temperature of the dielectric maximum as a function of the measurement frequency. (reported by Viehland D. et al.[10])

Figure A-6 shows the conductivity versus segmental relaxation frequency of Aquivion membrane with 9, 17, 29, and 40 wt% uptake of EMI-Tf. The result shows that the ionic conductivity is coupled with segmental relaxation frequency f_{α} of Aquivion membrane by following the DSE relation.



Figure A-6 The conductivity versus segmental relaxation frequency of Aquivion membrane with 9, 17, 29, and 40 wt% uptakes of EMI-Tf.

Figure A-7 shows the charge density versus t/d of 1.9, 11 and 20 μ m thick Aquivion membranes with 40 wt% uptake of EMI-Tf under 0.1 and 2 V step voltages and Figure A-8 shows the charge density versus t/d of 4, 23 and 64 μ m thick BMI-PF₆ liquid cell under 0.1 and 2 V step voltages.



Figure A-7 The charge density versus t/d of 1.9, 11 and 20 μ m thick Aquivion membrane with 40 wt% uptake of EMI-Tf under 0.1 and 2 V step voltages.



Figure A-8 The charge density versus t/d of 4, 23 and 64 μ m thick BMI-PF₆ liquid cell under 0.1 and 2 V step voltages.

Bibliography

- 1. Wang XD, Song JH, Liu J, and Wang ZL. Science 2007;316(5821):102-105.
- 2. Wang ZL and Song JH. Science 2006;312(5771):242-246.
- 3. Tan JL, Tien J, Pirone DM, Gray DS, Bhadriraju K, and Chen CS. Proceedings of the National Academy of Sciences of the United States of America 2003;100(4):1484-1489.
- 4. Zhang QM, Cheng ZY, and Bharti V. Applied Physics a-Materials Science & Processing 2000;70(3):307-312.
- 5. Zhang SH, Neese B, Ren KL, Chu BJ, and Zhang QM. Journal of Applied Physics 2006;100(4).
- 6. Zhang QM, Bharti V, and Zhao X. Science 1998;280(5372):2101-2104.
- 7. Bauer F. Ieee Transactions on Dielectrics and Electrical Insulation 2010;17(4):1106-1112.
- 8. Viehland D, Jang S, Cross LE, and Wuttig M. Philosophical Magazine B-Physics of Condensed Matter Statistical Mechanics Electronic Optical and Magnetic Properties 1991;64(3):335-344.
- 9. Zhang SH, Klein RJ, Ren KL, Chu BJ, Zhang X, Runt J, and Zhang QM. Journal of Materials Science 2006;41(1):271-280.
- 10. Viehland D, Jang SJ, Cross LE, and Wuttig M. Journal of Applied Physics 1990;68(6):2916-2921.
- 11. Garcia B, Lavallee S, Perron G, Michot C, and Armand M. Electrochimica Acta 2004;49(26):4583-4588.
- 12. Balducci A, Bardi U, Caporali S, Mastragostino M, and Soavi F. Electrochemistry Communications 2004;6(6):566-570.
- 13. Bennett MD and Leo DJ. Sensors and Actuators a-Physical 2004;115(1):79-90.
- 14. Bennett MD, Leo DJ, Wilkes GL, Beyer FL, and Pechar TW. Polymer 2006;47(19):6782-6796.
- 15. Tokuda H, Hayamizu K, Ishii K, Abu Bin Hasan Susan M, and Watanabe M. Journal of Physical Chemistry B 2004;108(42):16593-16600.
- 16. Tokuda H, Ishii K, Susan M, Tsuzuki S, Hayamizu K, and Watanabe M. Journal of Physical Chemistry B 2006;110(6):2833-2839.
- 17. Tokuda H, Hayamizu K, Ishii K, Susan M, and Watanabe M. Journal of Physical Chemistry B 2005;109(13):6103-6110.
- 18. Liu S, Liu WJ, Liu Y, Lin JH, Zhou X, Janik MJ, Colby RH, and Zhang QM. Polymer International 2010;59(3):321-328.
- 19. Liu S, Liu Y, Cebeci H, de Villoria RG, Lin JH, Wardle BL, and Zhang QM. Advanced Functional Materials 2010;20(19):3266-3271.
- 20. Liu S, Montazami R, Liu Y, Jain V, Lin MR, Heflin JR, and Zhang QM. Applied Physics Letters 2009;95(2).
- 21. Liu Y, Liu S, Lin JH, Wang D, Jain V, Montazami R, Heflin JR, Li J, Madsen L, and Zhang QM. Applied Physics Letters 2010;96(22).
- 22. Klein RJ, Zhang SH, Dou S, Jones BH, Colby RH, and Runt J. Journal of Chemical Physics 2006;124(14).
- 23. Lin JH, Liu Y, and Zhang QM. Polymer 2011;52(2):540-546.
- 24. Steinhart M, Goring P, Dernaika H, Prabhukaran M, Gosele U, Hempel E, and Thurn-Albrecht T. Physical Review Letters 2006;97(2):-.

- 25. Steinhart M, Murano S, Schaper AK, Ogawa T, Tsuji M, Gosele U, Weder C, and Wendorff JH. Advanced Functional Materials 2005;15(10):1656-1664.
- 26. Steinhart M, Wendorff JH, Greiner A, Wehrspohn RB, Nielsch K, Schilling J, Choi J, and Gosele U. Science 2002;296(5575):1997-1997.
- 27. Strubbe F, Verschueren ARM, Schlangen LJM, Beunis F, and Neyts K. Journal of Colloid and Interface Science 2006;300(1):396-403.
- 28. Li AP, Muller F, Birner A, Nielsch K, and Gosele U. Journal of Applied Physics 1998;84(11):6023-6026.
- 29. Parkhutik VP and Shershulsky VI. Journal of Physics D-Applied Physics 1992;25(8):1258-1263.
- 30. Jessensky O, Muller F, and Gosele U. Applied Physics Letters 1998;72(10):1173-1175.
- 31. Huang JQ, Chiam SY, Tan HH, Wang SJ, and Chim WK. Chemistry of Materials 2010;22(13):4111-4116.
- 32. Yin A, Tzolov M, Cardimona D, Guo L, and Xu J. Iet Circuits Devices & Systems 2007;1(3):205-209.
- 33. Masuda H and Fukuda K. Science 1995;268(5216):1466-1468.
- 34. Masuda H, Yada K, and Osaka A. Japanese Journal of Applied Physics Part 2-Letters 1998;37(11A):L1340-L1342.
- 35. de Gennes PG. Physica a-Statistical Mechanics and Its Applications 1998;249(1-4):196-205.
- 36. Degennes PG. Reviews of Modern Physics 1985;57(3):827-863.
- 37. Sharma A and Reiter G. Journal of Colloid and Interface Science 1996;178(2):383-399.
- 38. Eliseev EA and Glinchuk MD. Journal of Applied Physics 2007;102(10).
- 39. Wu ZQ, Duan WH, Wu J, Gu BL, and Zhang XW. Journal of Applied Physics 2005;98(9).
- 40. Jimenez R, Amorin H, Ricote J, Carreaud J, Kiat JM, Dkhil B, Holc J, Kosec M, and Alguero M. Physical Review B 2008;78(9).
- 41. Lin JH, Lu SG, Lin M, Geuss M, and Zhang QM. Applied Physics Letters 2009;95(2).
- 42. Gorbatschow W, Arndt M, Stannarius R, and Kremer F. Europhysics Letters 1996;35(9):719-724.
- 43. Petychakis L, Floudas G, and Fleischer G. Europhysics Letters 1997;40(6):685-690.
- 44. Keddie JL, Jones RAL, and Cory RA. Europhysics Letters 1994;27(1):59-64.
- 45. Keddie JL, Jones RAL, and Cory RA. Faraday Discussions 1994;98:219-230.
- 46. Jones RL, Kumar SK, Ho DL, Briber RM, and Russell TP. Nature 1999;400(6740):146-149.
- 47. Patterson AL. Physical Review 1939;56(10):978-982.
- 48. Bharti V and Zhang QM. Physical Review B 2001;63(18).
- 49. Tyunina M and Levoska J. Physical Review B 2001;63(22).
- 50. Ishikawa K, Yoshikawa K, and Okada N. Physical Review B 1988;37(10):5852-5855.
- 51. Lang XY and Jiang Q. Journal of Nanoparticle Research 2007;9(4):595-603.
- 52. Zhong WL, Wang YG, Zhang PL, and Qu BD. Physical Review B 1994;50(2):698-703.
- 53. Fong DD, Stephenson GB, Streiffer SK, Eastman JA, Auciello O, Fuoss PH, and Thompson C. Science 2004;304(5677):1650-1653.
- 54. Mauritz KA and Moore RB. Chemical Reviews 2004;104(10):4535-4585.
- 55. Galinski M, Lewandowski A, and Stepniak I. Electrochimica Acta 2006;51(26):5567-5580.
- 56. Ueki T and Watanabe M. Macromolecules 2008;41(11):3739-3749.
- 57. Hsu WY and Gierke TD. Journal of Membrane Science 1983;13(3):307-326.

- 58. Ghielmi A, Vaccarono P, Troglia C, and Arcella V. Journal of Power Sources 2005;145(2):108-115.
- 59. Kreuer KD, Schuster M, Obliers B, Diat O, Traub U, Fuchs A, Klock U, Paddison SJ, and Maier J. Journal of Power Sources 2008;178(2):499-509.
- 60. Gierke TD, Munn GE, and Wilson FC. Journal of Polymer Science Part B-Polymer Physics 1981;19(11):1687-1704.
- 61. Beunis F, Strubbe F, Marescaux M, Beeckman J, Neyts K, and Verschueren ARM. Physical Review E 2008;78(1).
- 62. Beunis F, Strubbe F, Neyts K, and Verschueren ARM. Applied Physics Letters 2007;90(18).
- 63. Cha EH, Lim SA, Lee CW, and Macfarlane DR. Journal of Power Sources 2006;163(1):269-273.
- 64. Kilic MS, Bazant MZ, and Ajdari A. Physical Review E 2007;75(2):021502-021514.
- 65. Beunis F, Strubbe F, Marescaux M, Neyts K, and Verschueren ARM. Applied Physics Letters 2007;91(18).
- 66. Bazant MZ, Thornton K, and Ajdari A. Physical Review E 2004;70(2).
- 67. Marescaux M, Beunis F, Strubbe F, Verboven B, and Neyts K. Physical Review E 2009;79(1).
- 68. Lockett V, Sedev R, Ralston J, Horne M, and Rodopoulos T. Journal of Physical Chemistry C 2008;112(19):7486-7495.
- 69. Krause C, Sangoro JR, Iacob C, and Kremer F. Journal of Physical Chemistry B 2010;114(1):382-386.
- 70. Mistry MK, Choudhury NR, Dutta NK, and Knott R. Langmuir 2010;26(24):19073-19083.
- 71. Kreuer KD, Ise M, Fuchs A, and Maier J. Journal De Physique Iv 2000;10(P7):279-281.
- 72. Zhang SH and Runt J. Journal of Physical Chemistry B 2004;108(20):6295-6302.
- 73. Zhang SH, Dou SC, Colby RH, and Runt J. Journal of Non-Crystalline Solids 2005;351(33-36):2825-2830.
- 74. Klein RJ, Welna DT, Weikel AL, Allcock HR, and Runt J. Macromolecules 2007;40(11):3990-3995.
- 75. Atorngitjawat P and Runt J. Journal of Physical Chemistry B 2007;111(48):13483-13490.
- 76. Fragiadakis D, Dou SC, Colby RH, and Runt J. Macromolecules 2008;41(15):5723-5728.
- 77. Fragiadakis D, Dou S, Colby RH, and Runt J. Journal of Chemical Physics 2009;130(6).
- 78. Kotz R and Carlen M. Electrochimica Acta 2000;45(15-16):2483-2498.
- 79. Kilic MS, Bazant MZ, and Ajdari A. Physical Review E 2007;75(2):21503-21512.
- 80. Fukumoto K, Yoshizawa M, and Ohno H. Journal of the American Chemical Society 2005;127(8):2398-2399.
- 81. Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, and Rogers RD. Green Chemistry 2001;3(4):156-164.
- 82. Karanikolopoulos N, Pitsikalis M, Hadjichristidis N, Georgikopoulou K, Calogeropoulou T, and Dunlap JR. Langmuir 2007;23(8):4214-4224.
- Lu W, Fadeev AG, Qi BH, Smela E, Mattes BR, Ding J, Spinks GM, Mazurkiewicz J, Zhou DZ, Wallace GG, MacFarlane DR, Forsyth SA, and Forsyth M. Science 2002;297(5583):983-987.
- 84. Ue M, Takeda M, Toriumi A, Kominato A, Hagiwara R, and Ito Y. Journal of the Electrochemical Society 2003;150(4):A499-A502.
- 85. Serghei A, Tress M, Sangoro JR, and Kremer F. Physical Review B 2009;80(18).
- 86. Wakai C, Oleinikova A, Ott M, and Weingartner H. Journal of Physical Chemistry B 2005;109(36):17028-17030.

- 87. Beunis F, Strubbe F, Marescaux M, Neyts K, and Verschueren ARM. Applied Physics Letters 2010;97(18).
- Acar O, Sen U, Bozkurt A, and Ata A. International Journal of Hydrogen Energy 2009;34(6):2724-2730.
- 89. Suzuki A, Sen U, Hattori T, Miura R, Nagumo R, Tsuboi H, Hatakeyama N, Endou A, Takaba H, Williams MC, and Miyamoto A. International Journal of Hydrogen Energy 2011;36(3):2221-2229.
- 90. Komarov PV, Veselov IN, and Khalatur PG. Polymer Science Series A 2010;52(2):191-208.
- 91. Cha EH, Macfarlane DR, Forsyth M, and Lee CW. Electrochimica Acta 2004;50(2-3):335-338.
- 92. Gohy JF, Creutz S, Garcia M, Mahltig B, Stamm M, and Jerome R. Macromolecules 2000;33(17):6378-6387.
- 93. Sui XF, Yuan JY, Zhou M, Zhang J, Yang HJ, Yuan WZ, Wei Y, and Pan CY. Biomacromolecules 2008;9(10):2615-2620.
- 94. Wesley RD, Dreiss CA, Cosgrove T, Armes SP, Thompson L, Baines FL, and Billingham NC. Langmuir 2005;21(11):4856-4861.
- 95. Luo YL, Yuan JF, Liu XJ, Xie H, and Gao QY. Journal of Bioactive and Compatible Polymers 2010;25(3):292-304.
- 96. Sun XY, Zhou YF, and Yan DY. Science in China Series B-Chemistry 2009;52(10):1703-1710.
- 97. Yan Q, Yuan J, Zhang F, Sui X, Xie X, Yin Y, Wang S, and Wei Y. Biomacromolecules 2009;10(8):2033-2042.
- 98. Ravi P, Sin SL, Gan LH, Gan YY, Tam KC, Xia XL, and Hu X. Polymer 2005;46(1):137-146.
- 99. Benoit DSW, Henry SM, Shubin AD, Hoffman AS, and Stayton PS. Molecular Pharmaceutics 2010;7(2):442-455.
- 100. Varkouhi AK, Lammers T, Schiffelers RM, van Steenbergen MJ, Hennink WE, and Storm G. European Journal of Pharmaceutics and Biopharmaceutics 2011;77(3):450-457.
- 101. Yao Y, Feng DF, Wu YP, Ye QJ, Liu L, Li XX, Hou S, Yang YL, Wang C, Li L, and Feng XZ. Journal of Materials Chemistry 2011;21(12):4538-4545.
- 102. Tao L, Chou WC, Tan BH, and Davis TP. Macromolecular Bioscience 2010;10(6):632-637.
- 103. Schallon A, Jerome V, Walther A, Synatschke CV, Muller AHE, and Freitag R. Reactive & Functional Polymers 2010;70(1):1-10.
- 104. Moffitt M, Yu YS, Nguyen D, Graziano V, Schneider DK, and Eisenberg A. Macromolecules 1998;31(7):2190-2197.
- 105. Nguyen D, Williams CE, and Eisenberg A. Macromolecules 1994;27(18):5090-5093.
- 106. Bobnar V, Vodopivec B, Levstik A, Cheng ZY, and Zhang QM. Physical Review B 2003;67(9):-.
- 107. Corezzi S, Campani E, Rolla PA, Capaccioli S, and Fioretto D. Journal of Chemical Physics 1999;111(20):9343-9351.
- 108. Lee AS, Peteu SF, Ly JV, Requicha AAG, Thompson ME, and Zhou C. Nanotechnology 2008;19(16).

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