Macromolecules

Volume 41, Number 21 November 11, 2008

Review

Beyond Nafion: Charged Macromolecules Tailored for Performance as Ionic Polymer Transducers

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Received April 28, 2008; Revised Manuscript Received August 26, 2008

ABSTRACT: Ionic polymer transducers (IPT) based on electroactive polymers (EAP) display electromechanical coupling that enables breakthroughs in the design of high-performance actuators and sensors. The ion-exchange membrane Nafion remains as the benchmark for a majority of research and development in IPT technology. Advances in IPT performance, elemental understanding of transduction mechanisms, and the development of future technologies (e.g., artificial muscles) are largely due to significant efforts to tailor complementary transducer compositions relative to commercially available Nafion. Current fundamental advances in the synthesis, characterization, and application of tailored ion-containing polymers are reviewed for increased performance, decreased cost, and improved processing of IPTs. Recent attention to the correlation of morphological structure to ion conduction mechanisms has led to new paradigms for performance. Tailoring of ionomeric membranes to isolate material interactions within the composite IPT that contribute to performance is also highlighted. Novel compositions such as ion-containing polysulfones, poly(ethylene-*co*-vinyl alcohol), polystyrene, and fluorinated acrylic copolymers have broadened the range of electromechanical performance. This perspective discusses recent research efforts and rapidly emerging fundamental understanding of the tailored synthesis of ionomers for IPTs. However, further studies are necessary to confirm the mechanisms that drive these devices under an array of compositions and geometries in emerging applications.

Introduction: The Design Space

Many functional macromolecules offer promise in electromechanical transducers that exhibit coupling between stimuli in the electrical and mechanical domains. For example, it is well-established that several natural and synthetic materials exhibit the piezoelectric effect, which is the phenomenon that provides coupling between electrical and mechanical stimuli.[1−3] Application of a voltage to a piezoelectric material will produce strain, and likewise, the application of a mechanical strain will produce an electrical signal. The existence of the piezoelectric effect in inorganic and polymeric materials such as lead−zirconate−titanate (PZT) and poly(vinylidene fluoride) (PVDF), respectively, has enabled the development of numerous devices in sensing and motion control.[4]

Recently, significant attention has been directed to the field of *electroactive polymers (EAP)*.[5−8] Electroactive polymers exhibit behavior that is functionally similar to piezoelectric materials; however, EAPs potentially enable larger strains (>1%) at lower applied voltages (<10 V). The inherent mechanism in piezoelectric ceramics is also present in piezoelectric/electrostrictive polymers, a specific class of EAP, where coupling occurs due to the rotation of electronic dipoles that exist in the crystalline lattice or polymer backbone. Other classes of EAPs include dielectric elastomers, liquid crystal elastomers, ionic polymer transducers, conducting polymers, carbon nanotube actuators, and molecular actuators.[9,10] EAP operation involves necessary physical processes such as electrostatic

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10.1021/ma800956v CCC: $40.75

attraction between charged electrodes, Maxwell stress that is generated upon the application of an electric field, and ion transport to facilitate electromechanical coupling.[11,12] An emerging class of EAP materials, which is the focus of our research efforts, involves structures that are fabricated from ion-containing polymeric membranes. We term this class of devices *ionic polymer transducers*. The field of ionic polymer transducers (IPT) evolved from the discovery that many electroactive polymers exhibit coupling properties that enable a variety of engineering devices. Despite relatively high cost, tailored ionic polymer transducers offer numerous advantages over other classes of electroactive polymers. IPTs are easily fabricated, flexible, and lightweight, and the final structures are considered as low-voltage, low-power devices that are silent to operate. A primary engineering application for IPTs is the replacement of motion-control devices where small electrical stepper motors or piezoelectric ceramics were previously the only option. In applications that do not require large actuation force or high-frequency operation, imposing a constant current or constant voltage allows for precision positioning without the need for multiple moving parts such as gears, pistons, or shafts. The device functions both as a motion-control device and simultaneously as a motion sensor. Several representative applications under development include a fluid-flow wall shear sensor,[13] an active surgical catheter,[14,15] robotic prosthetic grippers, and a cell-phone camera aperture.[16]

The majority of commercial IPT development employed the most directly accessible aspect of electromechanical coupling, i.e. actuation, where an applied voltage results in movement of the device. Quantification of displacement in bending is relative to the radius of curvature of the actuated IPT, which experimentally is nearly constant[17] and is depicted in Figure 1. If the device's displacement is restricted to zero, the result of actuation is development of force under the applied voltage. The overall concept of electromechanical coupling is reversible such that an imposed deflection of the IPT device produces a detectable output current. This active conversion typically allows for sensing or power harvesting.

IPTs are designed as composite devices that display electromechanical transduction within a hydrated ion-exchange membrane that has an electrically conducting electrode on both faces. The ionomeric membrane contains a certain molar percentage of negatively or positively charged sites covalently bound to the polymer backbone. Macromolecular composition determines both polarity and the concentration of charged versus noncharged monomeric segments, and a microphase-separated morphology, referred to as a cluster network, often results.[18] The network of hydrophilic clusters and/or channels[19] facilitates charge transport when swollen in the presence of an added diluent. Typically, the cationic counterions move toward the cathode under the application of an actuation voltage ($<$10 V) while the bound anionic species remain immobile. Earlier studies suggest that the accumulation of excess counterions in a boundary layer at the cathode increases electro-osmotic pressure in the clusters. Flow of the diluent into the clusters causes internal strain in the polymer matrix that manifests as swelling.[20−24] Simultaneous depletion of solvated counterions at the anode boundary layer results in contraction that pushes the diluent out of the clusters. In a cantilever configuration, the IPT experiences bending actuation toward the anode. Recent results also demonstrated that when one face of the IPT is fixed to a surface, electromechanical coupling produces extensional actuation in the thickness direction.[25] Figure 2 represents the process of electromechanical transduction in an IPT for the purpose of bending or extensional actuation.

Actuator performance is typically quantified through blocked force production and free displacement under an applied voltage. These tests allow for the maximum actuation response under the limits of zero displacement or zero load. Measures of blocked force and free displacement are also used to calculate the gravimetric and volumetric energy density of the transducer.[26] Initial actuation is normally rapid and is correlated with the size of the free cation associated with the polymer-bound

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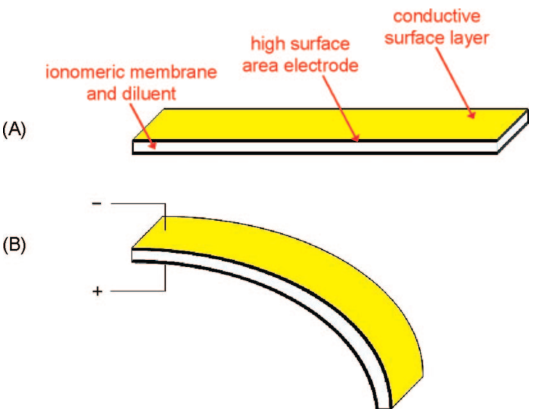

Figure 1. Schematic of typical IPT under (A) short-circuit conditions (B) applied voltage [actuator] or imposed deformation [sensor].

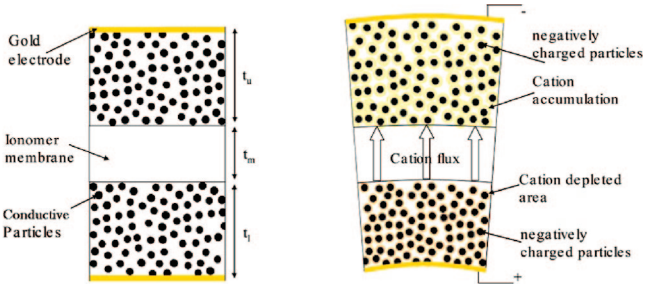

Figure 2. Schematic of the actuation process in an ionic polymer transducer, also showing a typical electrode with the particles surrounded by a charged sphere of ionomer. Reproduced with permission from ref 25. Copyright 2007 IOP Publishing Limited.

charged sites.[27] Water-swollen IPTs often suffer from back-relaxation of the transducer after the initial voltage-induced displacement. Back-relaxation occurs when the actuator motion decays back toward its original position after reaching a maximum forward displacement. The end point, which is reached under continued application of dc potential, is not typically located at the origin. Several mechanisms were proposed earlier to explain this behavior beyond the elastic nature of the polymer matrix surrounding the clusters. Because of the continued detection of current and accumulating charge at the cathode during observed back-relaxation, Nemat-Nasser et al. proposed that hydraulic pumping of diluent out of the clusters was responsible. However, these hydraulic effects were thought to originate from realignment of the sulfonate salt dipoles in the presence of an excess of free cations, causing a cation redistribution that changes the osmotic and electrostatic pressures in the cluster. Other researchers employed cyclic voltammetry and observed electrochemical reactions in platinum IPT electrodes with variation of applied potential.[22,28] Deposition of platinum oxide compounds was linked in *real time* to observation of back-relaxation. This occurrence suggested that interfacial stresses in the electrodes countered the bending motion during both cathodic and anodic scans. Overall, back-relaxation limits the frequency range and accuracy of the actuator's motion control while decreasing the ability to deliver a constant peak force to a target. The proposed mechanisms suggest back-relaxation results from the interface of all three IPT components, and optimization is required to limit its occurrence.

The main components of the IPT include an ionomeric membrane, a high surface area electrically conducting electrode, and an ion-conducting diluent. The selection and properties of all three components target ease of device construction, performance, and the specific application.[29] Ideal IPT membranes display specific ranges of elastic modulus and ionic conductivity that combine to enhance their electromechanical coupling once integrated into the device. These properties are crucial because the ionomeric membrane's main roles during actuation are to provide structure and ion transport while encapsulating the diluent. Dependent upon the range of desired displacement and force actuation, the ionomeric membrane should display a hydrated modulus of at least 50 MPa. This specific modulus was chosen based on the benchmark performance of Nafion as an actuator for both force and displacement.[26,27] As expected, the intended application for actuation leads to variation in this estimated value. In order to allow for practical and useful lifetimes in a variety of environments, film stability is critical in all forms, preferably under actuation conditions for several million cycles. Operating environments presently include open air, varied relative humidity, submersion in liquids, temperature changes, and applied potentials. Stability is not defined solely for the neat membrane but must also apply during manufacture and performance when the membrane is in intimate contact with the diluent and electrodes.[30] A critical example is the reproducible microphase-separated morphology after IPT construction that provides a sufficiently polar interface with the diluent that resists dissolution or loss of definition.[31,32] This type of morphological structure in Nafion typically produces a high ionic conductivity on the order of 100 mS/cm when swollen with a diluent (e.g., H_2O). The final ionic conductivity of the IPT is also directly dependent on the magnitude of the diluent uptake during processing. Tensile modulus typically scales inversely with increased ionic conductivity as the diluent uptake is increased. However, high ionic conductivity is necessary to produce both high free deflection and blocked force. Solution and/or melt processability are also essential to ease of manufacture, customization of IPT geometry, and production of high surface area electrodes with certain methods and materials. Overall, the ionomeric membrane must demonstrate thermal, electrical, oxidative, morphological, and mechanical stability[33,34] to maximize actuation.

The high surface area electrode is composed of either conducting particles dispersed in a matrix of the ionomer[35,36] or metal particles that are impregnated into the film as salts and reduced on or near its surface.[37,38] The former case also requires attachment of a thin metal surface layer with low electrical resistance, usually gold leaf. The latter case is specifically referred to as an ionic polymer−metal composite (IPMC) due to the electroless deposition of metals (e.g., Pt, Au, Pd, Cu) on the ionomeric membrane surface. The high interfacial surface area between the electrode and the ionomeric membrane is important for the development of charge accumulation since capacitance is directly related to the total strain performance of the resulting IPT.[39] IPT design uses metal surface layers with low electrical resistance to permit the common assumption that a constant potential difference is applied through the thickness of the device along its entire length. Several studies demonstrated that fatigue and cracking in this layer cause significant performance losses in IPTs, regardless of the electroding technique.[30,40] Ionomer design to compositionally increase compatibility and adhesion with the electrodes is one possible future strategy to address this potential limitation.

A range of diluents are available for either submerged or open-air IPT operation including water, ethylene glycol, glycerol, formamide, and various ionic liquids.[41−45] Important factors in the choice of an IPT diluent are viscosity, vapor pressure, electrolytic stability, dielectric constant, and hydrophilicity. The diluent viscosity was directly related to IPT strain rate due to an influence on both the mobility of free ions as well as resistance to flow in and out of the clusters. Thus, within certain time scales of applied dc and ac potential, higher diluent viscosity can minimize back-relaxation. Vapor pressure is extremely important to open air operation where evaporation during actuation significantly decreases performance. Enhanced electrolytic stability prevents degradation of the diluent under actuation voltages and larger ranges typically lead to increased performance. Increases in the dielectric constant of the diluent regularly lead to higher ionic conductivity of the final device. These properties contribute to the performance magnitude, limits, and lifetime of IPTs, especially considering the influence of the diluent's solvation power within the ionomeric morphology.[46] Optimization of the stability of charge transport and charge accumulation within the IPT are critical to performance. Tailored IPT membranes will expand the Nafion-based understanding of IPTs to improve processing, morphology, and electrical and mechanical properties for augmented charge transport, higher modulus, larger strains, larger applied force, and increased energy density. This perspective focuses on recent efforts in ionomer design that attempt to improve IPT performance with novel polymers and hybrid compositions.

Nafion as the Benchmark

Since IPMCs were first proposed 15 years ago,[47−49] the area of ionic polymer transducers experienced enormous growth as shown in Figure 3. Despite the large increase in recent publications, the number of studies involving noncommercial synthetic ionomeric membranes remains relatively small. The interactions between the ionomeric membrane, diluent, and electrodes are better understood on the basis of Nafion and its analogues; however, many opportunities for tailoring new ionomers exist to enhance IPT performance. Bar-Cohen's recent review highlighted the performance of commercial ionomer-based IPTs in various actuator applications from robotic fish to miniature grippers.[50] Cumulative modeling efforts combined with empirical data from experiments provided a design loop for better understanding of the electromechanical transduction mechanism in actuator and sensor applications.[51,52]

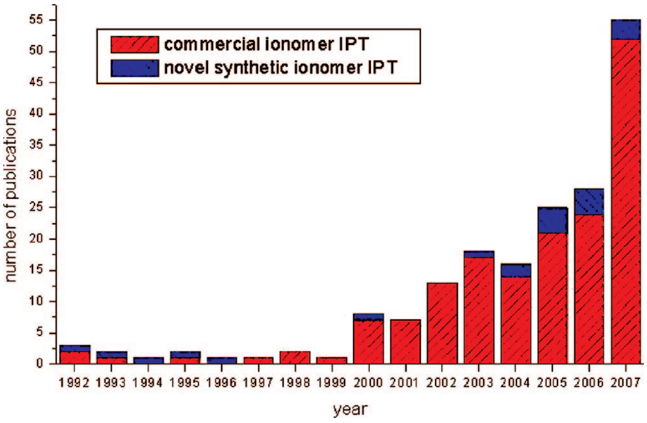

Figure 3. Peer reviewed IPT publications in the past 15 years employing commercial or synthetic ionomers.

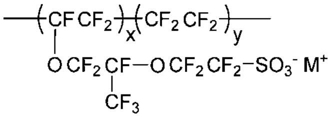

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Figure 4. Chemical structure of Nafion in the sulfonate salt form.

DuPont reportedly synthesizes Nafion through the radical copolymerization of a sulfonyl fluoride-terminated perfluoroether monomer and tetrafluoroethylene. The final polymer is semicrystalline with a polytetrafluoroethylene (PTFE) backbone and short perfluoroether branches that are terminated with sulfonyl fluoride groups. The precursor form is processable using both solvent and melt fabrication techniques. Reaction of the precursor membranes with potassium hydroxide in dimethyl sulfoxide and water converts the sulfonyl fluoride functionalities to potassium sulfonate salts that are freely converted to other cations through soaking in specific salt solutions or strong acids. Similar perfluorinated membranes such as Flemion from Asahi Glass and Aciplex from Asahi Chemical differ from Nafion in length, composition, and ionic functionality of the side chain.[53] The chemical structure of Nafion is shown in Figure 4.

Prior to a discussion of next generations of ionomers beyond Nafion, it is important to note the structure−property relationships that make Nafion desirable for constructing IPTs. Mauritz and Moore recently reviewed Nafion and its fundamental structure−property relationships.[54] Since the introduction of Nafion in 1962, primary uses involved chlor-alkali separations and proton-exchange membranes in fuel cell development. The two main characteristics that set Nafion apart for these applications, as well as in IPTs, are an extremely hydrophobic, semicrystalline PTFE matrix and microphase separation of the hydrophilic sulfonate functionalities. The semicrystalline PTFE matrix provides modulus greater than or equal to 100 MPa in the dry state and resistance to dissolution while swelling with hydrophilic diluents.[55] Although the nature of Nafion's morphology still remains under debate, most empirical models suggest the formation of multiplets and/or aggregates of the sulfonate groups.[56−58] These ionic aggregates provide a physical network in the dry state[59] and a pathway for ion-associated transport to achieve ionic conductivities on the order of 100 mS/cm when swollen with hydrophilic diluents.[32,60]

Perfluorinated membranes such as Nafion established the basis of IPT technology and continue to drive research and development toward applications, especially in medical devices and

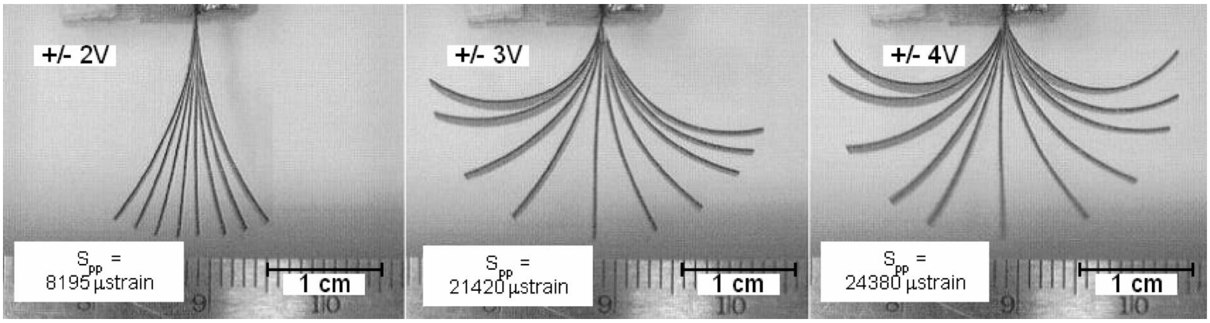

Figure 5. Deflected shapes for an ionic liquid-swollen Nafion-IPT as a function of voltage amplitude for a square wave potential input. Reproduced with permission from ref 17. Copyright 2006 Elsevier.

artificial muscle research.[61−63] The continued importance of this commercial ionomer is evident in multiple recent advances concerning IPTs. The most common electrode geometry results from an electroless deposition method where the ionomer membrane is repeatedly impregnated with a metal salt followed by addition of a reducing agent to deposit a dendritic high surface area metallic layer near the surface.[64,65] Recent advances revealed that reversing this technique distributed controlled electrode gradients across the thickness of the membrane instead of high concentrations at the outside surface.[66] This new method allowed for greater actuation lifetimes for submersed IPTs under large applied potential (5 V). Akle, Leo, and co-workers separately demonstrated that a method termed the direct application process (DAP) aided in tuning the electrode composition for optimal performance with RuO_2 or single walled carbon nanotube (SWCNT) conducting powders, regardless of the composition of the central ionomer membrane.[67] Similar to the previously established capacitive relationship to peak strain, a percolation threshold existed in through-thickness electrical conductivity when related to strain rate. Further investigation revealed that increased surface area-to-volume ratio of conducting powders in IPT electrodes increased strain in a direct correlation with increased capacitance.[17,39] Figure 5 depicts the cantilever bending response of an ionic liquid-swollen Nafion-IPT, constructed with the DAP method, with varied magnitude of the input voltage. Asaka and Onishi et al. separately demonstrated the correlation between high electrode interfacial area with the ionomeric membrane and increased strain with Flemion-IPTs.[64]

Performance augmentation and fundamental understanding of the diluent's role in IPT operation were recently highlighted. Bennett, Leo, and co-workers observed that cation size and ionic liquid interactions with Nafion influenced morphological stability, charge transport, ionic conductivity, and actuation speed.[46] Nafion-IPT construction with a hydrophobic ionic liquid led to a swelling of the PTFE matrix and disruption of the cluster network. The lack of morphological stability for this combination of membrane and diluent decreased ionic conductivity of the IPT and resulted in slower transducers. Flemion-IPTs were also investigated with glycerol and various ionic liquids as environmentally stable diluents.[44,68] Overall, employment of encapsulation methods or nonvolatile diluents in IPT design enabled long-term actuation in air with minimal loss of performance and a significant decrease in back-relaxation.[43,69,70] Akle and Leo et al. also demonstrated within an electrode study that increased uptake and decreased viscosity of the IPT diluent led to higher response speeds in Nafion-IPTs, likely due to increased ion mobility.[67] In water-based Flemion-IPTs, similar trends were observed where actuation speed and charge-specific displacement depended on cation size and the related amount of freezable water in the IPT.[60] These actuation tests were performed under a constantly varied peak-to-peak voltage (triangle wave) to impose a constant current. Neither Flemion nor Nafion-IPTs demonstrated back-relaxation under these conditions and with identical electrode materials. Earlier studies demonstrated that Flemion differed from Nafion through the absence of back-relaxation during actuation under application of a step in dc potential.[15] The different actuation character was attributed to the effect of different pK_a values of the anions bound to the otherwise similar polymer backbones.[71] The pK_a of Nafion's sulfonate salt, similar to trifluoromethane−sulfonic acid, is approximately −6 while the pK_a of the carboxylate salt, analogous to trifluoromethane−acetic acid, in Flemion is nearly 0.5. During dc step actuation, a large excess of cations enter the clusters in the cathode boundary layer. Stronger acidity of the bound anion was hypothesized to impose a larger dipole and increase the driving force for rearrangement of the excess charges. This rearrangement led to a decrease in electro-osmotic pressure and expulsion of excess diluent at the cathode to manifest back-relaxation. Triangle wave excitation of the IPT likely avoids back-relaxation, regardless of the ionomer, through a gradient accumulation of charge similar to a series of infinitely small steps.

Customized Nafion-IPT geometry and response were recently made possible through development of solution and melt processing methods to modify Nafion membranes for increased IPT actuation in bending.[72] Recent studies from Moore et al. demonstrated methods for orientation of the membrane, which resulted in varied morphological structures and distinctly anisotropic actuation that manifested as twisting.[73,74] Nafion-IPT performance improvements were also possible through a distinctly different route. Combinations of field-activated or other ionic EAPs with IPTs are termed hybrid electromechanical transducers. For example, the formation of conducting polypyrrole on the surface of Nafion before IPT construction led to increased blocked force, free displacement, and actuation bandwidth.[75] A similar study bonded a ferroelectric EAP membrane, poly(vinylidene fluoride) (PVDF), to a Nafion-IPMC, which resulted in concurrent actuation and sensing capabilities.[76] The research trends and performance enhancements developed through optimization of IPT components with Nafion will likely influence the tailored design and synthesis of novel IPT ionomers.

Emerging Ionomeric Membranes from Step-Growth Polymerization: Inspiration from Alternative Energy

Ionic transport, elastic modulus, processability, and chemical and thermal stability are critical to both IPT and proton-exchange membrane fuel cell (PEMFC) performance. Perfluorinated ionomers including Nafion set the benchmark in PEMFCs before

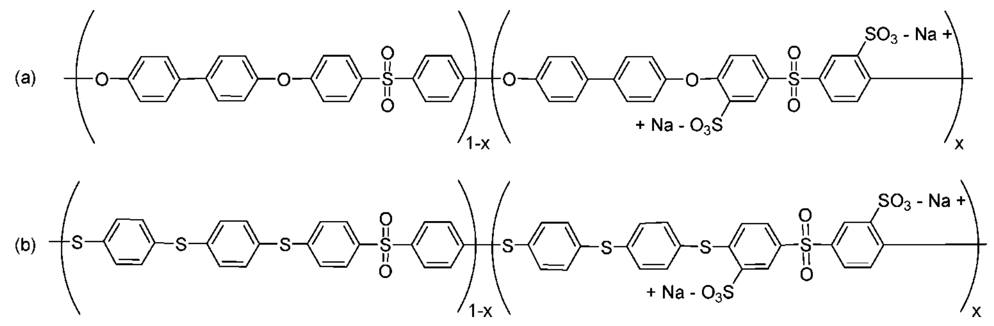

Figure 6. Chemical structures for (a) SPAES and (b) SPATS.

Table 1. Physical Properties for Commercial and Synthetic IPT Membranes

ionomer	bound/free ion form	ion exchange capacity (mequiv/g)	diluent	uptake (wt %)	hydrated modulus (MPa)	ionic conductivity (mS/cm)
Nafion-117[80]	SO_3^-/Na^+	0.91	H_2O	22	120	110
Flemion[27]	CO_2^-/Na^+	1.45	H_2O	24	169	8.5[60]
Aciplex A-172[94]	NR_4^+/Cl^-	0.185	H_2O	n/a	n/a	n/a
SPAES[80]	SO_3^-/Na^+	1.53	H_2O	40	640	80
SPATS[80]	SO_3^-/Na^+	1.17	H_2O	20	1040	60
PVA-*co*-AA[48]	CO_2^-/H^+	n/a	H_2O	31[95]	n/a	2[95]
SSEBS[96]	SO_3^-/Li^+	1.59[97]	H_2O	164[97]	n/a	382[97]
PE-*co*-VA-SSA[98]	SO_3^-/H^+	0.36 (min) 1.18 (max)	H_2O	36 82	n/a	n/a
PE-*co*-VA-*g*-SPEO[99,100]	SO_3^-/K^+	1.32 (min) 1.93 (max)	H_2O	n/a	n/a	0.304 1.65
FA-*co*-AA[101]	CO_2^-/Li^+	1.47	H_2O	50	n/a	n/a
FA-*co*-AA[102]	CO_2^-/Na^+	1.47	H_2O	15	n/a	n/a
FMA-*co*-AA[103]	CO_2^-/H^+	1.63	H_2O	15	0.63	n/a
FMA-*co*-SA[104]	SO_3^-/Li^+	0.905	H_2O	94	0.25	n/a
FMA-*co*-SA-*co*-HEMA[105]	SO_3^-/H^+	1.34	H_2O	41	0.71	n/a
FMA-*co*-AMA[106]	NR_4^+/Cl^-	1.23	H_2O	7	1.41	n/a
PVDF-*g*-SNEC[107]	SO_3^-/H^+	n/a	H_2O	25	n/a	138
(PVDF-*co*-HFP)-*g*-SPS[108]	SO_3^-/Na^+	2.89	H_2O	186	n/a	75.6
(PE-*co*-TFE)-*g*-SPS	SO_3^-/Na^+	2.83	H_2O	194	n/a	81.2
(PTFE-*co*-HFP)-*g*-SPS	SO_3^-/Na^+	1.65	H_2O	88	n/a	13.6

their consideration as IPT membranes. Examples of novel step-growth ionomers that were synthesized for PEMFC applications include sulfonated and carboxylated versions of poly(arylene ether sulfone)s, poly(ether ketone)s, polyimides, polybenzimidazoles, and polyphosphazenes.[77,78] Design of charge transport membranes has focused on modification of stable hydrophobic polymers with controlled levels of polar functionality. This contrast in chemical composition, similar to that found in Nafion, facilitates microphase separation that is advantageous for charge transport. In a similar fashion to the development of IPTs, PEMFCs are multicomponent composites that depend on the optimization of electrode−ionomer interfaces, mechanical properties, diluent, and charge transport for performance. Because of these similarities, several synthetic PEM step-growth ionomers are under investigation as possible IPT membranes.[79,80] Currently, only a few studies exist concerning novel step-growth ionomers for IPT applications and most efforts have concentrated on sulfonated polysulfones.

Poly(arylene ether sulfone)s (PAES) are engineering thermoplastics that are thermally, mechanically, hydrolytically, and oxidatively stable.[81] These properties, as well as relatively high glass transitions temperatures compared to Nafion, originate from the aromatic chemical structure and corresponding rigidity of the polymer backbone. The vast majority of polysulfones are amorphous due to the kinked nature of the sulfone linkage in the backbone.[81] Sulfonated polysulfones are ionomers that offer high ionic conductivity (~80 mS/cm) and the ability to form tough, ductile films from solution ($E_{\text{hydr}} \approx 640$ MPa). However, PAES ionomers still lack adequate melt processability. Present synthetic efforts for fuel cell membranes have catalyzed novel compositions for IPTs.[82,83] The polysulfone ionomers that have received attention as potential electromechanical transducers included both sulfonated poly(arylene ether sulfone) (SPAES or BPSH) and sulfonated poly(arylene thioether sulfone) (SPATS). The chemical structures of these random copolymers are provided in Figure 6. Ionic conductivity and elastic modulus of these ionomers are provided for comparison with relevant commercial IPT ionomers in Table 1. These sulfonated poly(arylene ether)s were synthesized through a nucleophilic aromatic substitution reaction in an aprotic solvent, in the presence of weak base, under dry conditions, at ~165 °C to attain high molecular weight.[84] As observed in the structure of both macromolecules, the flexible linkages are the ethers and thiols in SPAES and SPATS, respectively. SPAES is considered more rigid since there is one less linkage in between the aromatic rings of the backbone. Biphenol was chosen as the starting monomer for SPAES instead of the more common bisphenol A to increase chain rigidity, resulting in a higher glass transition temperature, higher elastic modulus, increased blocked force, and possibly increased energy density of the IPT dependent on preservation of free deflection. McGrath and Harrison et al. provided details on the synthesis and characterization of SPAES with different bisphenol monomers.[85] Although SPATS is less rigid than SPAES, one intended benefit of the thiol in the backbone was increased adhesion to gold at the polymer−electrode interface[86] to extend the IPT lifetime and performance limits.

Akle, Leo, and co-workers performed electromechanical characterization of SPAES and SPATS-IPTs in comparison with Nafion-IPTs while also investigating several different electrode compositions through the impregnation−reduction and DAP

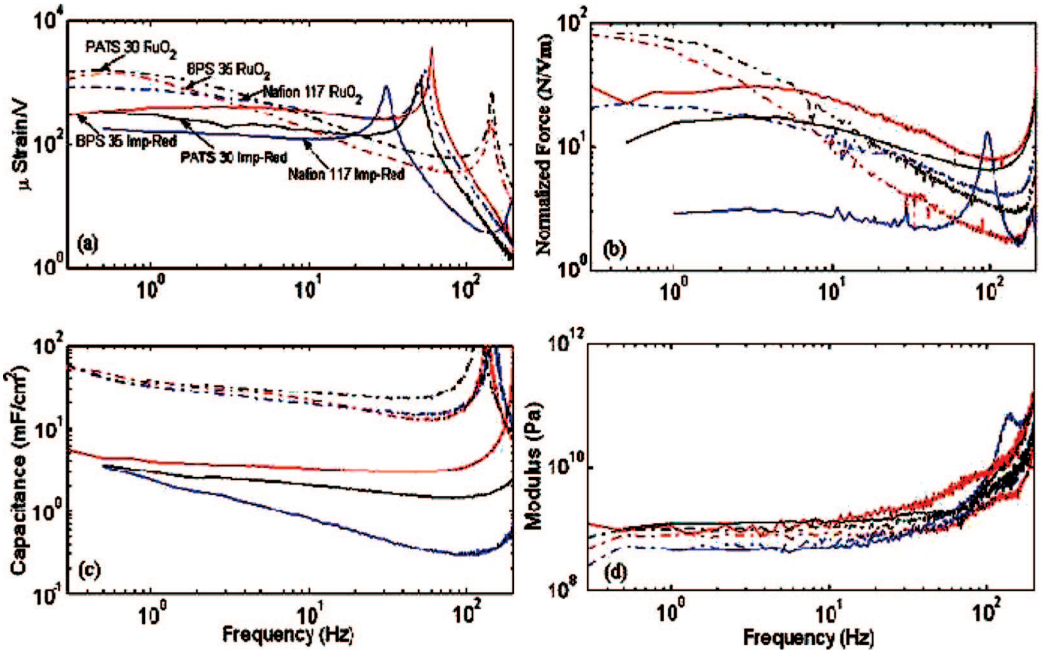

Figure 7. (a) Microstrain per volt, (b) normalized force, (c) capacitance, and (d) modulus vs frequency for BPS 35 (red), PATS 30 (black), and Nafion 117 (blue) to construct IPTs using impregnation−reduction and RuO$_2$-based direct assembly electrodes. Reproduced with permission from ref 80. Copyright 2006 the Electrochemical Society.

processes.[87,88] SPAES and SPATS were designed with a higher ion-exchange capacity, fully amorphous structure, higher glass transition temperature, and a higher modulus compared to Nafion. Transducers prepared from each ionomer were optimized for reducing agent concentration where the impregnation−reduction application of electrodes was applied. All transducers were characterized for blocked force production, free deflection, capacitance, and sensitivity. Nearly all sulfonation levels of the SPAES and SPATS-IPTs outperformed the Nafion-IPT in force and bending actuation at frequencies up to 10 Hz. Since all of the ionomers were in the sulfonate salt form and saturated with water, characteristic back-relaxation occurred where some samples passed their point of origin even under continued application of a dc potential. Similar to Nemat-Nasser's studies of back-relaxation in water-swollen sulfonate ionomers, such as Nafion-IPTs,[89] these SPAES and SPATS-IPTs show back-relaxation under dc step potential inputs[87] and would not outperform similar transducers constructed with Flemion in the realm of precision movement and motion control. Regardless, SPAES and SPATS outperformed Nafion in every IPT response to ac/dc potential inputs except for low-frequency sensing, where the values were comparable. Furthermore, the larger pK_a of the sulfonate salt (weaker acid) on SPAES and SPATS decreased the magnitude of back-relaxation in comparison to Nafion. Similar results for all IPTs shown in Figure 7 likely originated from the composition of the electrodes rather than the ionomer selection, since the DAP electrode matrix was composed of Nafion even in the novel membrane-IPTs. Similar bending performance of the three ionomers in transduction under varied electrode deposition and composition suggested that direct application of RuO$_2$ electrodes provided larger capacitance (up to 50×) than the impregnation−reduction technique with platinum for all ionomer compositions investigated.[80] Figure 7 also shows that regardless of the electroding technique employed, SPAES and SPATS-IPTs outperformed Nafion-IPTs in actuation across the majority of the frequency range investigated for microstrain per volt, modulus, and force output. Specifically, the larger force output of SPAES and SPATS than Nafion was expected based on much higher values of hydrated modulus for these ionomers. Below 10 Hz, SPAES and SPATS-IPTs achieved a combination of free deflection and blocked force resulting in a higher peak energy density than the Nafion-IPTs. This parameter is important to consider because all ionomers were in the same ionic form. SPATS performed the best through a combination of the lowest ionic conductivity and the highest hydrated modulus. The higher capacitance of the IPTs constructed with the DAP method further accentuated the importance of these parameters for maximum electromechanical performance across commercial and novel ionomers. Studies are also underway in our laboratories to introduce controlled levels of branching into SPAES to observe the effect of topology on morphological development and IPT performance.[90−93] These experiments are anticipated to display actuation without back-relaxation due to the use of ionic liquids, in a similar fashion to ionic liquid-swollen Nafion-IPTs.

Emerging Ionomeric Membranes from Chain-Growth Polymerization: Inspiration from Hydrogels

During the initial development of IPTs, perfluorosulfonated ionomers such as Nafion and sulfonated polystyrene cross-linked with divinylbenzene emerged as leading candidates. The latter group seemingly arose from the efforts of Kuhn and Katchalsky concerning chemomechanical transducers from polymeric acid networks in 1949.[109−111] Fifteen years passed before these transducers were discovered to also have electrochemomechanical properties.[112] This discovery combined with similar research on reconstituted collagen fibrils led to the development of soft ionic polymers and hydrogels for artificial muscles.[113−115] Typically these polymers were lightly cross-linked polyelectrolytes that operated while either submerged or encapsulated in an electrolyte environment. The level of cross-linking was varied to achieve balance between increased rigidity and decreased swelling. These two properties typically related to the transducer's ability to perform as force and bending actuators, respectively.[116]

In 1992, the first formal study summarizing the concept and dynamics of using ionic polymeric gels such as polyacrylamide

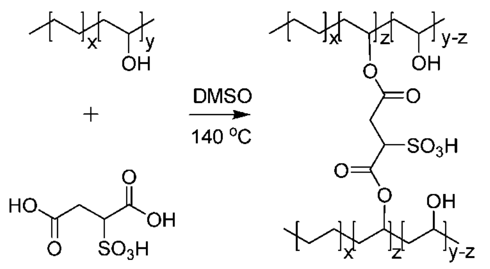

Figure 8. Synthetic scheme for cross-linking EVOH with sulfosuccinic acid.

and poly(vinyl alcohol-*co*-acrylic acid) (PVA-*co*-AA) as IPTs appeared in the literature.[48] The most important aspect of this study in terms of IPT operation was the concept of encapsulating the ionomeric gel and electrolyte within an electroded compliant container.[117] Containment of the IPT membrane and diluent facilitated the creation and control of geometries where actuation force and bending were applied without submersion in the presence of large boundary electrodes.[118,119] Furthermore, encapsulation led to the first observation in IPTs of mechanoelectric sensing with ionomeric gels[120−122] and their increased development in IPT technology.[123] Recent studies employed the commercially available hydrogel sulfonated poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SSEBS) cross-linked with vinylsilanes to design low-cost transducers in comparison to Nafion-IPTs.[96] Actuation results were based on electroless deposition of the electrodes and submersion in aqueous solution. This cost-effective substitute operated in water to achieve a maximum tip displacement of ~1 mm in response to an applied dc potential of 2.0 V. Employment of para-substituted sulfonated polystyrene blocks provided a sufficiently weak acid to significantly reduce back-relaxation. Subsequent studies demonstrated that the addition of multiwalled carbon nanotubes as a filler further increased displacement and response speed in cantilever bending, especially at higher frequency.[124]

Phillips and Moore synthesized poly(ethylene-*co*-vinyl alcohol) cross-linked with sulfosuccinic acid (PE-*co*-VA-SSA), as depicted in Figure 8. The ionomeric membrane's morphology was examined on the nanometer and angstrom length scales with small-angle X-ray scattering (SAXS) and ^{23}Na nuclear magnetic resonance (NMR) spectroscopy, respectively. ^{23}Na NMR revealed isolated sodium sulfonate ion pairs and a wide distribution of ion pairs that aggregated into multiplets. SAXS results only detected a very broad ionomer peak in the 63 wt % sulfosuccinic acid-modified EVOH sample. The corresponding results for Nafion displayed a narrower distribution of multiplets and a more distinct ionomer peak. Characterization of PE-*co*-VA-SSA-IPT performance revealed slower actuation speed, smaller strains, and lower blocked force compared to Nafion. However, PE-*co*-VA-SSA-IPTs performed similarly to Nafion-IPTs without back-relaxation at identical conditions. These results coupled with NMR measurements of diffusion coefficients (i.e., Nafion > PE-*co*-VA-SSA) suggested that more diffuse morphological structure directly related to decreased actuation performance, regardless of the specific ionomer.[98] There is also a notable difference in acidity between Nafion and PE-*co*-VA-SSA due to the location of the sulfonic acid functionality. Separately, poly(ethylene-*co*-vinyl alcohol) with controlled molecular weight poly(ethylene oxide) grafts placed at the vinyl alcohol sites were designed as IPT membranes. The grafted PEO chains were then sulfonated through a ring-opening of 1−3 propane sultone in the presence of potassium *tert*-butoxide to create ionomers (PE-*co*-VA-*g*-SPEO) of varied ion exchange content (IEC) for IPT construction.[99] This study provided polymer architecture analogous to the short-chain branches on Nafion and was one of the few studies to investigate the effect of ionomer topology on actuation performance. Location of the sulfonate salt at the end of the PEO graft caused the IEC to significantly decrease with longer graft lengths. Increased graft lengths led to morphological changes detected with AFM and XRD, decreased ionic conductivity, and lower actuation performance overall.[100] However, a local maximum was detected in the conductivity and bending stress with increased graft length that possibly indicated an optimal branch length for microphase separation and charge transport.

Partially fluorinated IPT membranes were also developed as analogues to the chemical composition of Nafion. The radical copolymerization of fluoroalkyl acrylate (DuPont Zonyl TA-N, FA) and acrylic acid (AA) resulted in novel IPT membranes.[101,102] Variation of the AA content demonstrated the need to balance swelling behavior with IEC to achieve maximum actuation. Likely due to the choice of a carboxylate salt, copolymers with 35−50 mol % AA displayed significant actuation without back-relaxation in force and bending. AA levels above 50 mol % led to soft gels with water uptakes above 500 wt % and little or no actuation capabilities. Similar synthetic IPT studies included the copolymerization of fluoroalkyl methacrylate (DuPont Zonyl, FMA) with monomers such as acrylic acid (AA), 2-acrylamido-2-methyl-1-propanesulfonic acid (SA) (cross-linking of SA with varied percentages of 2-hydroxyethyl methacrylate (HEMA)), and 2-(dimethylamino)ethyl methacrylate (AMA). The objective was to provide melt processability (typically unavailable with Nafion) through variation in polymer composition for control of thickness and shape of the IPT membrane. The FMA-*co*-AA and FMA-*co*-SA were both weak acid-based ionomers swollen with water that displayed significant actuation in bending without back-relaxation. IPT performance again displayed a maximum based on ion content. At ion contents greater than those associated with the observed maximum displacement, the level of water absorption caused cracks in the electrodes likely associated with the decrease in actuation at high ion contents. Blocked force was not measured, but decreased modulus with increased ion content implied that this parameter would also have a maximum.[103,104] In a subsequent study, incorporation of up to 6 wt % HEMA effectively provided sites to cross-link the copolymers (FMA-*co*-SA-*co*-HEMA) at constant ion content; thus, swelling in water decreased. Increased cross-linking monotonically decreased current and displacement responses; however, covalent network formation increased the available actuation force. The force maximum, ~300% of the value for FMA-*co*-SA, resulted from incorporation of only 1 wt % HEMA. Furthermore, the current and strain rate only decreased 10% in comparison to a decrease of nearly 80% for the highest level of cross-linking.[105] In this case, polymer topology through covalent cross-linking reduced swelling in a high IEC polymer to achieve a significant increase in the energy density of this class of novel IPTs. The copolymerization of FMA and AMA introduced a seldom investigated parameter into IPT construction, i.e., anion transport (FMA-*co*-AMA) based on a fixed quaternary ammonium counterion. Similar to the acid−based ionomer studies, a maximum in bending and force actuation based on ion content was observed without back-relaxation.[106] Anion transport in IPTs reverses the response direction to the applied potential and was originally reported using a version of the commercial perfluorinated ionomer Aciplex A-172.[94]

IPT performance was further investigated through construction of hybrid transducers with ionic groups grafted to ferro-

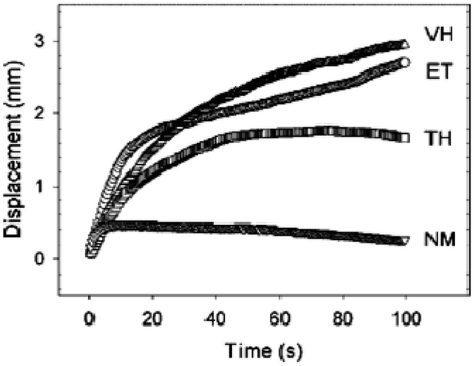

Figure 9. Displacement of PVDF-*co*-HFP (VH), PE-*co*-TFE (ET), PTFE-*co*-HFP (TH), and Nafion (NM) IPMCs recorded for 100 s with an applied dc voltage of 2 V. Reproduced with permission from ref 108. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

electric polymers. Operation of the hybrid-IPTs was still performed with voltages (~2 V dc) much too low to induce conformational changes and electromechanical transduction based on the ferroelectric polymer mechanism. Chen et al. received a patent for a hydrophobic fluorinated matrix combined with a polar ionic phase through radiation grafting of *N*-ethylenecarbazole to preformed poly(vinylidene fluoride) with subsequent sulfonation (PVDF-*g*-SNEC). Compared to a similarly constructed Nafion-IPT, the platinum-electroded hybrid-IPT achieved 25% greater free displacement and 200% larger blocked force with only a 70% increase in ionic conductivity and 25% greater swelling ratio. IEC and modulus were not reported.[107] Jho, Han, and co-workers also employed this approach through radiation grafting of polystyrene−sulfonic acid to the ferroelectric polymers poly(vinylidene fluoride-*co*-hexafluoropropylene) ((PVDF-*co*-HFP)-*g*-SPS), poly(ethylene-*co*-tetrafluoroethylene) ((PE-*co*-TFE)-*g*-SPS), and poly(tetrafluoroethylene-*co*-hexafluoropropylene) ((PTFE-*co*-HFP)-*g*-SPS). Hybrid-IPTs were constructed from these modified EAPs and were compared to performance of a Nafion-IPT. The water uptake and final ionic conductivity of the hybrid-IPTs were much greater than for the Nafion-IPT. The bending actuation results are depicted in Figure 9. Total free deflection scaled with increased IEC, while ionic conductivity and strain rate did not follow the IEC and were proportional to water uptake. All of the hybrid transducers displayed at least 10 times greater tip displacement without back-relaxation; however, the blocked force of the Nafion-IPT was greater. In contrast to typical IPTs, blocked force of the hybrid-IPTs increased with increasing water uptake.[108,125] Although hydrated moduli were not reported, dry moduli of the ferroelectric polymers is approximately equal to the elastic modulus of dry Nafion. In this case, modification of the IPT chemical composition resulted in a 5-fold increase in energy density based on charge transport without a dramatic loss of mechanical properties.

Conclusions

As highlighted herein, a foundation of Nafion-based IPT technology is well established despite the ionomer's complex morphology, cost, and processing challenges. Growth of potential and commercial applications of Nafion-IPTs motivated further exploration into the benefits of tailoring membrane properties for performance. An ionomeric membrane optimized for IPT application must exhibit mechanical integrity, a stable chemical composition, and consistent physical properties over long cycling lifetimes when swollen with an electrolyte diluent. A high-performance IPT membrane in bending and force actuation typically requires an ionic conductivity greater than 100 mS/cm and a hydrated modulus greater than 50 MPa. The emerging goal is to fundamentally understand the significance of each ionomer parameter as it relates to electromechanical transduction and performance. Synthetic polymers designed specifically to address the effects of molecular weight distribution, chemical composition, stereochemistry, topology, morphology, and the interface with varied IPT components will provide fundamental structure−property relationships. The effects on transduction performance in IPTs will direct engineering design for specific applications while operating within a balance where synthetic efforts can tailor electrical and mechanical properties of the ionomeric membrane.

Chemical composition was the most extensively investigated polymer parameter and had a significant effect upon every aspect of the membrane's properties and device performance. The largest discovery was the designation of acid strength of the bound anion as the largest contributor to the origins of back-relaxation. The importance of charge storage at the interface between the electrode and ionomer to total strain existed regardless of the chemical composition of the ionomeric membrane. However, the link between chemical composition and morphological structure to IPT performance was clarified through investigation of ionomers tailored for comparison. Results of those studies suggested that well-defined microphase separation enabled more efficient charge transport and increased nucleation of electrode particles which led to higher interfacial surface area. These investigations suggested that increases in capacitance and ionic conductivity are both achievable based on morphology and lead to greater performance. The typical tradeoff in transducer performance for electroactive polymers exists between blocked force production and free displacement. Opportunities for IPT performance gains without this tradeoff were shown through increased energy density and energy conversion efficiency of the transducer.[126] Adjustment of polymer topology through controlled cross-linking enhanced blocked force production while allowing for increased mechanical integrity at high IEC levels. Higher IEC is typically required for sufficient ionic conductivity in ionomers with less distinct microphase separation. Optimization of branched topologies while preserving the IEC could similarly lead to increased modulus, better solubility/processability than cross-linked systems, enhanced functionality for compatibility, and a tuned morphological structure. This bottom-up approach will further enable methods for attaining increased performance through geometry and optimized IPT components, as was demonstrated for piezoelectric transducers.[127] The specific polymer parameters of molecular weight and stereochemistry remain available for IPT tuning and to this point are relatively unexplored. Fundamental investigation of IPT membrane design will also contribute to extensive efforts to establish understanding of solid-state ionomer properties,[33,34] especially at the interface with ionic liquids.[128] Systematic variations in membrane properties will reveal more details of the mechanism for electromechanical transduction in these charge-transport-based composite devices. Feedback between design and performance will create a cycle where fundamental understanding of ionomer design and structure−property characterization facilitate improvement and enable further commercialization of IPTs in the future.

Acknowledgment. This material is based upon work supported by the U.S. Army Research Laboratory and U.S. Army Research Office under Contract/Grant W911NF-07-1-0452 Ionic

Liquids in Electro-Active Devices Multidisciplinary University Research Initiative (ILEAD MURI). Funding in part was also provided by the Macromolecular Science and Infrastructure Engineering Integrative Graduate Education and Research Traineeship (MS&IE IGERT), a National Science Foundation program at VPI and SU.

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MA800956V