IONOMERIC ELECTRO-ACTIVE POLYMER ARTIFICIAL MUSCLE – OVERVIEW

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Abstract

It has been found that the most efficient, durable, and high performance actuators are those found within nature such as biological actuators including natural muscles. These 'natural' actuators operate on the basis of electrochemomechanical interactions, have no moving parts and are capable of self-reparation as well as complete force-feedback loops. These characteristics for actuators have become the benchmark to attain for current actuation technology. Unfortunately, the magnitude of performance has not been achieved by the current state-of-the-art technology. There is, however, a trend developing of actuators based upon the foundation of electromechanical actuation – ElectroActive Polymers (EAPs). The unique properties of biological muscle are large strain, moderate stress, fast response, excellent thermodynamic efficiency, and long cycle life. A new technology, EAPs, based upon polymer science and engineering, is emerging to embody certain desirable characteristics of biological muscle. An EAP is a multifunctional, smart polymer whose electronic properties can be controlled and reproducibly changed in response to the environment. Coupled with the desired mechanical properties of the base polymers, these materials are suitable for a variety of biologically inspired robotics applications including underwater propulsors. A number of EAP materials in this category recognized so far include ferroelectric polymers, conducting polymers, ionic polymeric gels, dielectric elastomers, and ionomeric electro-active polymers [Bar-Cohen, 2001].

Ferroelectric materials such as poly(vinyliedene fluoride-trifluoroethylene, PVDF-TrFE) copolymer are recently recognized as electrostrictor and relaxor and operate in dry environments. Also, dielectric elastomers are attractive for biomimetic applications, due to their large strain capability and fast-strain responses, providing low costs. Their stable operation in a wide range of temperatures and humidity, with high electromechanical coupling, is recognized. However, both materials require very high electric field for an appropriate range of actuation capabilities to attract engineering applications (~1kV/mm). Conducting polymers reported as actuators often require an aqueous ionic environment to operate. Ionic polymer gels, such as polyvinyl alcohol, polyacrylamide or polyacrylonitrile, can show electromechanical behavior. Such ionic polymer gels suffer from their weak mechanical strength and consequent structural failure under large deformations and have a short lifetime. It has been reported that ionomeric EAPs in a form of strip show a large bending capability under a small electric field (~10V/mm) with considerable force density and fast responses. Knowing that their operation is effective in wet climates, their engineering applications are perfect for underwater environments. Over the past few years the Navy has incorporated the use of an ionomeric EAP material as a biomimetic propulsor for the development of a new strategy in active noise control [Bandyopadhyay, 2002].

This paper presents the fundamental properties and characteristics of ionomeric EAPs as artificial muscles. A summary of all recent findings and its current state-of-the art manufacturing techniques, theoretical considerations, and the mechanical and electrical characteristics is presented. Also, the performance of those ionomeric EAPs manufactured by different fabrication techniques are presented and compared. In addition, a recent experimental effort to improve the properties of the base polymer carried out by a novel nanocomposite technique is presented.

1. Introduction

Some of the reasons why electroactive polymers (EAPs) are becoming an increasingly studied actuator technology is due to their large electrically induced strains (bending or extensional), low density, ease of processing, and mechanical flexibility that offer advantages over traditional electroactive materials [Bar-Cohen and Leary, 2000]. Generally, EAPs have the ability to induce strains that are as high as two orders of magnitude greater than the movements possible with rigid and fragile electroactive ceramics. EAP materials have higher response speeds, lower densities and improved resilience when compared to shape memory alloys [Bar-Cohen, 2001]. They have shown great promise towards the field of actuators with respect to soft actuation and biomimetics.

Conducting polymers are a generalized field of materials that have been increasingly studied due to their unique properties and possible applications including biomimetics and microactuation. Conducting polymers contain highly non-localized electrons in their backbones [Otero et al., 2000]. It has been observed that oxidizing (doping) or reducing (dedoping) the backbone at a level equivalent to removing or adding an electron to every four to ten monomer units, increased the conductivity of the matrix by several orders of magnitude. They were shown to exhibit nonlinear optical properties as well because in these delocalized systems, electrons are easily polarized by external electric fields such as that of the visible light. The general applications for EAPs that are currently being investigated include artificial muscles and actuators, sensors, charge accumulation devices, electrochromic materials and electron-ion transducers.

It has been noted that Kuhn (1949) and Katchalsky (1949), Kuhn, Kunzle and Katchalsky (1948), Kuhn, Hargitay, Katchalsky, and Eisenberg (1950), Kuhn and Hargitay (1951), however should be credited as the first investigators to report the ionic chemomechanical deformation of polyelectrolytes such as polyacrylic acid (PAA), polyvinyl chloride (PVA) systems. Kent, Hamlen and Shafer (1965) were also first to report the electrochemical transduction of PVA-PAA polyelectrolyte system.

One EAP characteristic, among others, that is of particular interest is its ability to produce large bending or longitudinal strain with a relatively low voltage (< 10 volts) [Sadeghipour et al., 1992; Oguro et al., 1993; Asaka et al., 1995; Mojarrad and Shahinpoor, 1997; Bar-Cohen et al., 1999a,b; De Rossi and Mazzoldi, 1999; Osada and Gong, 1999; Oguro et al., 1999; Shahinpoor, 1999; Wax and Sands, 1999; Bar-Cohen and Leary, 2000; De Gennes et al., 2000; Enikov and Nelson, 2000; Nemat-Nasser and Li, 2000; Shahinpoor and Mojarrad, 2000; Tadokoro et al., 2000a,b,c,d; 2001a,b; Nemat-Nasser and Thomas, 2001; Tadokoro et al., 2001; Newbury and Leo, 2001]. A representative ionomeric EAP, Ionic Polymer-Metal Composite (IPMC) is typically in the form of polyelectrolyte membranes that are composited with metal electrodes. IPMC exhibits the actuation capability as well as engendering a voltage from a subsequent bending of the material making them a unique material. These characteristics make this material attractive and resulted in a comprehensive investigation of the material including various theoretical and experimental models to explain the unique behavior.

2. Ionic Polymer-Metal Composites (IPMC)

Ionic polymer-metal composites have been studied rigorously over approximately the past fifteen years. Oguro originally found that a polyelectrolyte membrane-electrode composite, which was comprised of a perfluorinated sulfonate membrane (Nafion® 117) and platinum electrodes plated chemically on both sides of the membrane, quickly deformed and bent in aqueous solution by applying a low voltage (~1-5volt) between the electrodes through the membrane [Oguro et al., 1993]. Figure 1 shows the IPMC in cantilever configuration exhibiting its actuation mechanism by bending towards the anode and then cathode when subjected to an AC voltage.

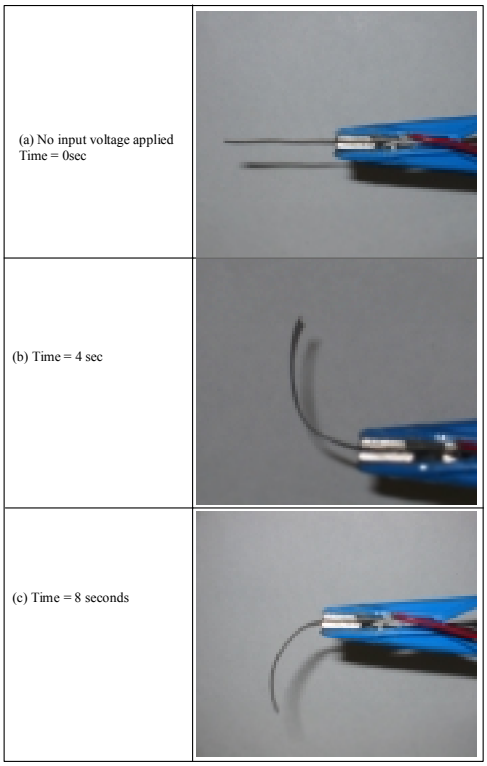


Fig. 1. Typical IPMC placed under an applied AC voltage step function input of 3.0 volts at a frequency of 0.25Hz. *(a) no voltage applied, (b) positive polarity, and (c) negative polarity.*

IPMC Fabrication

The basis for the fabrication of an IPMC typically begins with an ion exchange membrane (IEM), which provides the bulk of the material in polymer form. This is due to the unique ionic nature of the fixed perfluorinated polymer backbone of the IEM that is

permeable to cations but impermeable to anions (in case of cation exchange materials) [Eisenberg and Yeager, 1982; Mallavarapu et al., 2001; Shahinpoor and Kim, 2001a]. Different membranes can be used, the most common being Nafion™ from Dupont, USA or Flemion from Asahi, Japan. It is called ion exchange membrane because the protons, in the case of Nafion, H^+ can be exchanged with other cations [Enikov and Nelson, 2000].

If H^+ ions are exchanged with metal ions that are then reduced, a sandwich structure is produced with the top and bottom being effective electrodes composed of the metal ion that was introduced into the IEM. The two surfaces being metallic are highly conductive and can be varied and manipulated depending on the chemical process [Enikov and Nelson, 2000]. A micrograph showing the cross section of a typical IPMC sample is shown in Figure 2. This illustrates the sandwich like appearance of the material where the metal composite comprises the outside layers and the polymer matrix is the center.

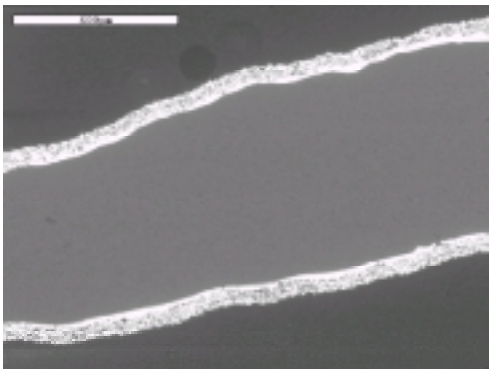


Fig. 2. A cross-section of an IPMC showing two electrodes (top and bottom) with porous expanded graphite and dense platinum. *This IPMC is manufactured by the solution-casting and further treatment with porous graphite and chemical reduction of platinum as effective compliant electrodes [from Kim and Shahinpoor, 2003].*

Actuation Principle

Upon application of an electric field upon the membrane such as shown in Figure 3, there is an observed fast bending motion towards one of the electrodes. This can be explained by examining the overall solvent flux within the complex network of the polymer.

The base polymer is an ionomer that is specifically designed and synthesized to selectively pass ions of a specific charge (cation, anion or both). When an IPMC is fully hydrated by a solvent (typically water), the morphology of the membrane structure exhibits a nanosize pore/channel structure [Nemat-Nasser, 2002]. It should be noted that the fixed ionic groups attached at the ends of the polymer sidechains interact with the distributed cations that were chemically placed within matrix as well as the solvent molecules in these cluster regions.

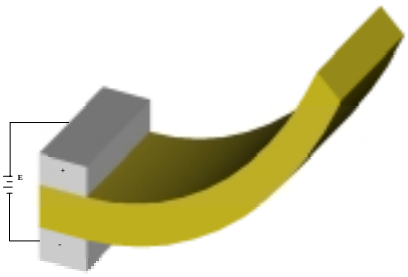


Figure 3. Bending of IPMC with an applied voltage.

When an electric field is applied across the membrane, there is a fast bending motion towards one of the electrodes followed by a slow relaxation towards the other electrode in most cases. It is commonly believed that this bending motion is the result of an electro-osmotic pressure induced by the migration of hydrated cations and free water from these cluster regions through the nanochannels towards the electrode side (in the case of a positive polarity, the cathode side). This results in a pressure differential causing a bending stress that translates into bending towards the electrode (in the case of a positive polarity, the anode side) as is illustrated in Figure 3 where shows the bending motion of an IPMC placed in cantilevered configuration placed under a positive electric field. It should be noted that the relaxation behavior associated with a DC application of electric field will be explained later. Also, when operating at voltages above 1.23 volts result in electrolysis causing blistering and subsequent damage of the electrodes thereby degrading the performance of the material.

There are many characteristics and variables that can affect the operation and performance of an IPMC as it is a very process dependent material. The material was shown to be clearly a function of frequency in AC voltage operation [Bar-Cohen et al. 1998; 1999a,b]. When a DC voltage is applied, the IPMC initially will bend to the anode side, but after some time the material 'relaxes' to the cathode side [Asaka et al., 1995; Mallavarapu et al., 2001; Nemat-Nasser and Thomas 2001; Tadokoro et al., 2001a,b]. The IPMC material exhibits a slow time constant that limits the actuation bandwidth [Mallavarapu et al., 2001]. This limits the IPMC from such applications that require a faster

response time for a given actuation signal. The AC/DC response and the relaxation behavior will be explored further in a later section. As previously mentioned, the counter ion species, IEM, temperature and ionic clusters all have an effect on the behavior of an IPMC. One of the more important characteristics of the material is its hydration. The degree of hydration within the IPMC plays an important role in the material's overall behavior and performance.

Transduction Principle

Part of what makes an IPMC so unique is its inherent transductive properties in addition to its actuation capabilities. Similar to piezo materials, IPMCs can not only show displacements under an applied electric field, but can also engender a current from an imposed bending moment of the material. By imposing a bending moment, a bending stress is placed on the backbone of the polymer, an electric potential is generated across the composite due to the differential displacement of the effective centers of the anions and cations within each cluster, producing an effective dipole [Nemat-Nasser, 2002]. This voltage is typically in the 10's of milivolts range, which is still an order of magnitude smaller than the voltage required producing the same bending moment. Data representing this transduction principle for an IPMC is shown in Figure 4. This makes IPMCs effective for large motion sensor or damper applications [Shahinpoor, 1999].

Although this shows great promise for the material, the physics are still under investigation and the ongoing research and modeling is primarily focused on the actuation principle.

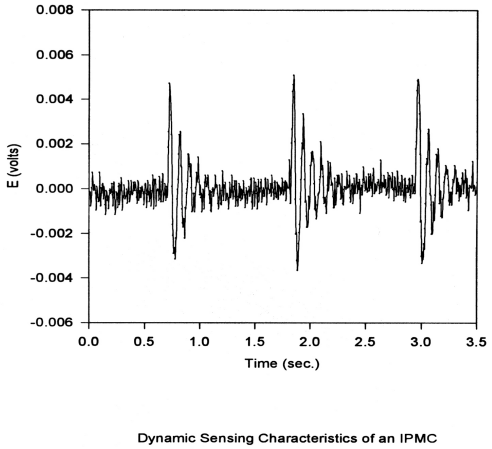


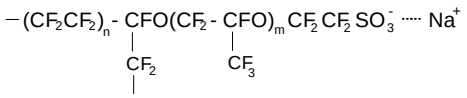
Fig. 4. Data taken from using IPMC in transduction mode from applying a small bending moment to sample. *[from Shahinpoor and Kim, 2001c]*

Ionic Exchange Membranes

Ion Exchange Membranes (IEMs, often called ionomers) are the base material for the fabricated IPMC. They are designed and synthesized to selectively pass ions of single or multiple charges such as cations, anions or both. This unique characteristic of these polymeric materials allows for selective passage of desirable cations, anions or both within the polymeric network that is the primary reason for actuation capabilities for an IPMC.

The research on IEM over the past thirty years has focused on their chemical properties and their application in separation columns, water hydrolyses, and fuel cells. It is only very recently that researchers proposed their use as actuators [Shahinpoor, 1993; Bar-Cohen et al., 1999a,b]. The most common ion exchange materials used in industry are based upon a copolymer of styrene and divinylbenzene where the fixed ionic groups are formed after polymerization [Davis et al., 1997]. The overall ratio of styrene to divinylbenzene is the determining factor in the ion exchange membrane's water uptake capabilities and ion exchange capabilities. There are several IEMs that can be used to fabricate an IPMC, with differing characteristics for each one. The most popular of these IEMs is perfluorinated alkenes with short side-chains terminated by ionic groups. These fluorocarbon polymers have linear backbones with no crosslinking and relatively few fixed ionic groups attached. It is these backbones that determine their mechanical strength. The short side chains provide ionic groups that interact with water and the passage of appropriate ions [Eisenberg and Bailey, 1986; Eisenberg, 1980]. Nafion™ of DuPont is the most common ion exchange membrane used for fabrication of IPMCs.

Nafion™: Nafion™ is a perfluorinated polymer with sulfonate groups randomly dispersed within its volume. It is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether, having the following formula [Nemat-Nasser and Li, 2000]:



Where n ~ 6.5, 100 < m < 1000, and M^+ is the counter ion [Bar-Cohen et al., 1999b]. Nafion has such advantageous features as high ionic conductivity, excellent permselectivity, outstanding chemical and thermal stability and good mechanical strength [Liu et al., 1992]. In its processed form, Nafion has a thickness of approximately 200 μm. This linear fluorocarbon polymer, having about 10 mole percent

pending acid groups is strongly affected by water content and cations, because it combines two incompatible components, the hydrophobic (fluorocarbon backbone, semi-crystalline) regions and hydrophilic ($-SO_3^-H^+$) regions [Nemat-Nasser and Li, 2000]. When exposed to water, there is a homogeneous swelling of the membrane. Nafion has the ability to absorb a considerable amount of water, which increases the cation's mobility and therefore electrical conductivity. These cations appear to migrate through the hydrophilic channels on the order of 5nm in diameter [Bar-Cohen et al., 1999a]. The ionic groups that tend to aggregate in tightly packed regions referred to as clusters [Nemat-Nasser, 2002]. Some important properties of the Nafion™ IEM can be varied due to various functional groups, i.e. SO_{3-} (sulfonate) and COO^- (carboxylate). Various properties of the two functional groups are shown in Table 1.

Table 1. Properties of the sulfonate and carboxylate ion exchange material used in the industry.

	Water Content	Current Density	Electric Conductivity	Chemical Stability
SO_{3-}	High	High	High	Good
COO^-	Low	Low	Low	Good

Table 2. Comparison of two popular perfluorinated IEM's material properties.

	IEMs	
	Nafion™	Aciplex-S™
Equivalent Weight	$1100 \frac{g}{gmole\ SO_{3-}}$	$950 \frac{g}{gmole\ SO_{3-}}$
Thickness	200μm	100μm
Conductivity	$0.1 - 0.12 \frac{S}{cm}$	$0.1 - 0.12 \frac{S}{cm}$
Area Resistance	5 Ωcm^2	0.09-0.66 Ωcm^2
Water Uptake Capacity	Up to 30% at room temperature	Up to 20% at room temperature
Volume Expansion on Hydration	12-15%	~15%

Flemion™: Perfluorinated carboxylic acid from Asahi Glass of Japan [Davis et al., 1997] can be used as a polymer electrolyte instead of sulfonic acid. Carboxylic acid membranes with higher ion exchange capacity include Flemion which is another IEM that has been used for creation of IPMCs [Bar-Cohen et al., 1999b; Leary and Bar-Cohen, 1999]. Flemion, when used in conjunction with a larger, bulky cation such as tetrabuthylammonium (TBA) helps reduce the relaxation process that happens when an applied DC voltage is sustained and the force response of the IPMC is weakened. The reason for this is the fact that these TBA cations are large that when they migrate through the nanosize pores and channels within the polymer matrix, they may not allow for a back diffusion of water that is commonly attributed to the relaxation effect.

Aciplex-S™: Aciplex-S™, from Asahi Chemical Industry Co., Ltd, of Japan is similar to Nafion™, in that they are both perfluorinated cation exchange membranes with a sulfuric acid functional group. Table 2 shows a comparison between Nafion™ and Aciplex-S™ and their material properties [Kolde et al., 1995; Asahi Chemical Industry Co., 1995].

Hydration

Water is an important factor in the resulting performance of an IPMC. If the polymer is dry, there are strong interactions between the counter ions and the fixed ionic groups of the polymer that dominate the behavior exhibiting low conductivity. However, once the IEM is hydrated, it solvates both the counter ions and the fixed ionic groups such that it lowers the interactions between cations [James et al., 2000]. This causes a very large increase in material conductivity. Each hydrated cation is essentially a tightly held sheath of water molecules bound under the electric field from the cations/anions. By looking at the absorption isotherm of Nafion™, the water structure within the IEM can be understood. During the absorption of the first 4 - 5 molecules of water per an active site such as SO_3^-, the absorption enthalpy seems constant. However, by increasing the water content further, the absorption enthalpy decreases and reaches the saturated limit. This could be due to the initial interaction of the water with the cations followed by the expansion of the polymer network due to aforementioned hydration causing an expansion of the porous channels within the polymer matrix. The enthalpy reaches approximately -13 kJ/mole of water (H^+ form), which is much less than that of condensation (approximately -53 kJ/mole of water). This is proof of an endothermic contribution as a result of the expanding polymer structure from hydration. Studies of Nafion™ and its capabilities have revealed that it can have three different types of water [Escoubes and Pineri, 1982; Davis et al., 1997]. The first being water that is closely bounded to the

ions; the second being water weakly bounded to the ions and the third type is free water.

Dry Operation

The IPMC, due to its affinity to water, is ideally suited for operation within an aqueous environment. However, many applications pertain to a dry environment. IPMCs can operate at low voltages (<1.23 volts) before electrolysis sets in, however dehydration does still happen. Bar-Cohen et al. (1998) developed a protective coating for the Nafion membranes to allow for operation within a dry environment for extended periods of time and is made note of in later publications [Bar-Cohen et al., 1999a,b; Leary and Bar-Cohen, 1999; Bar-Cohen et al., 2000]. The effective coating technique utilized a sprayed polymer which extended the effective operation time from a few minutes to about four months. The coating effectively forms a skin over the surface of the IPMC to protect the moisture content within the sample. The results indicate a promising conclusion that IPMCs could operate within dry environments for more potential actuator applications than initially assessed.

Shahinpoor and Kim (2001b) developed a fully dry solid-state IPMC capable of dry operation. They accomplished by creating a composite of poly(ethylene oxide), PEO, and poly(ethylene glycol), PEG, suitably surface-electroded and cation doped. They found effective electromechanical sensing and actuation effects with these materials and elaborate on their potential as dry soft actuators and sensors for many biomimetic/medical, industrial and scientific applications as the dry operation removes binding restrictions associated with typical IPMCs.

Cation Species

In an IPMC, the mechanism for actuation is believed to be electro-osmotic pressure [Zawodzinski et al., 1993; Helfferich, 1995]. When an electric field is applied across a typical electrolyte, cations and anions migrate in opposite directions with there being no net momentum transferred to the solvent [Fedkiw and Her, 1990]. In the case of an IPMC, the anions (i.e. $-SO_3^-$ group in the case of Nafion™) are fixed to the polymer matrix while the counter-ion is free to move within the polymer nanochannels. When an electric field is imposed across the effective electrodes of a hydrated IPMC, the cation that is hydrated (carrying water molecules) will then migrate to the cathode resulting in a bending to the anion side. There is also free water that is essentially 'pumped' as well due to the cations pushing the water through these channels on their way to the electrode. Several cation species have been used in IPMCs and studied with varying results for each pertaining to overall deflection, force generated and transduction by the IPMC.

Shahinpoor and Kim (2000) studied the effects of various cations in an IPMC in terms of blocking force (maximum force) for actuator applications. Blocking force is found by measuring the force generated at zero displacement. The cations that were used were Na^+, Li^+, K^+, H^+, Ca^{++}, Mg^{++}, Ba^{++}, and $R_nNH_4^{+}{}_{4-n}$ (tetramethylammonium-TMA and tetrabuthylammonicum-TBA). The samples were all from the same batch of fabricated IPMC to be consistent in the comparison. Figure 5 shows the results of the experiment in terms of relative blocking force using the Na^+ cation as the baseline. They found that Li^+ showed the best response (in terms of force generation) when the input to the IPMC is a sinusoidal wave input of 1.2 volts with ½ Hz. The results suggested that the underlying principle of IPMC actuation is related to the presence of water movement due to electrophoretic migration of hydrated counter-ions [Shahinpoor and Kim, 2000].

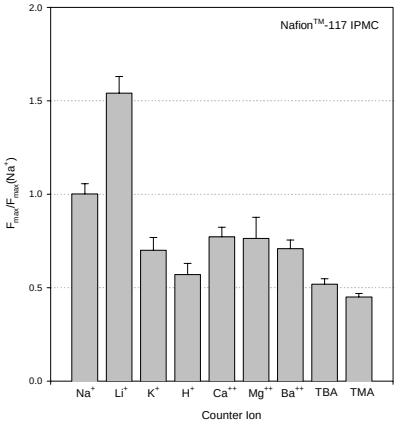


Fig. 5. Effects of various cations on the actuation of the IPMC muscle. *Comparisons were made against Na^+ in terms of maximum force generated at zero displacement. A sinusoidal input voltage of 1.2 V_{rms} and a frequency of ½ Hz were set for all experiments. Na^+ was chosen as a reference since it is coordinated with four water molecules [from Shahinpoor and Kim, 2000].*

The trend exhibited by the Li^+ ion showing the largest force generation is primarily due to hydration processes with respect to mobile cations that have an important impact on actuation behavior of the IPMC. The maximum force generated at the tip of the cantilever under a given voltage of 1.2 V_{rms} is close in order of magnitude to the ones generated with counterions; Li^+

>> Na^+ > (K^+, Ca^{++}, Mg^{++}, and Ba^{++}) > (H^+, TBA, and TMA). This phenomena occurred in both Nafion™ based IPMC and Flemion™ based IPMC [Onishi et al., 2000; Tokuyama Co., 2000; Abe et al., 1998]. In the set of Li^+, Na^+, and K^+, it should be noted that Li^+ is the smallest bare ion in the set by far (its radius, r[Li^+] < r[Na^+] < r[K^+]), however it has the lowest mobility (the drag to its motion through the solution, u[Li^+] < u[Na^+] < u[K^+]) [Moor, 1972; Atkins, 1982; Moor et al., 1992; Gebel et al., 1987; Komoroski and Mauritz, 1982; Bhattacharya et al., 2001]. All these observations could be related to the hydration phenomena associated with cations in the polymer matrix of an IPMC. This is the reason why large organic hydrophobic ions such as TBA and TMA generate less force than Li^+ and Na^+ based IPMC's. An important aspect regarding the use of such alkylammonim ions could be attributed to their large and bulky size relative to the small cations that were investigated. Overall, the hydration process within the membrane in connection with the electrophoretic effect is fairly complex in the sense that the mobile cations experience a large viscous drag and, at the same time, exert force due to the generated strain, while they are moving through the water containing polymer network. This could be interpreted as the cations within these nanosized clusters and channels actually rub against each other creating a shear resistance in the form of an overall drag in the solvent flux [Komoroski and Mauritz, 1982]. This could possibly increase the viscous drag and lower the overall conductivity. Bar-Cohen and Leary (2000) also mentioned that using the cation tetrabuthylammonium with Flemion IEM could reduce the relaxation resulting from a constant DC voltage input to the IPMC over time.

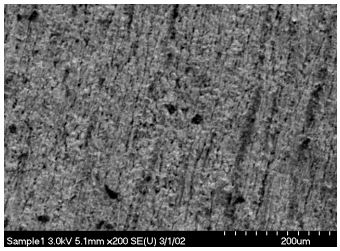
Electrode Compositing

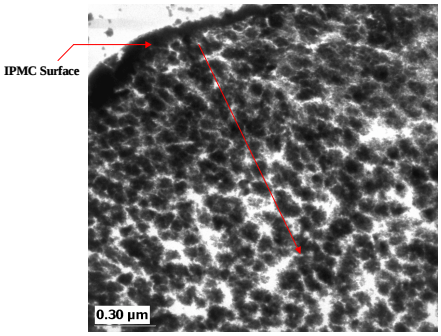
There are various chemical reduction processes that can be used to produce the desired deposition of noble metal particles into the surface of the membrane. The reason why noble metals are used is because of the acidic and corrosive environment in the IEM (Nafion™). Other metals (or conducting mediums) that can be used include palladium, silver, gold, carbon, graphite, and nanotubes. The most popular method is by chemical platinization of a Nafion™ IEM [Liu et al., 1992]. For an IEM to function as an IPMC, Nafion™ can be metallized on both of its surfaces. There are several ways for depositing electrodes of the membrane surface. The electrodes may be: (a) mechanically pressed onto the IEM [Niedrach, 1964; Lawrence and Wood, 1981; White 1982], (b) electrochemically deposited [Nagel and Stucki, 1982; Banziger et al., 1983], or (c) chemically deposited [Takenaka et al., 1982]. In the case of Takenaka [1982], an anionic metal ion in a solution in contact with one face of the IEM is reduced by a reducing agent that diffuses through the membrane from a solution in contact with the opposite face. Liu et al. (1992) used a variation of Takenaka and Torikai's procedure by using a two-step, impregnation-reduction procedure in which a cationic metal ion is first impregnated into the Nafion and is subsequently reduced *in situ* in a following operation [Fedkiw and Her, 1990]. Metal ions are dispersed throughout the hydrophilic regions of the polymer, and are subsequently reduced to the corresponding zero valent metal atoms [Bar-Cohen et al., 1999b]. Liu (1992) also reported that for an ideal electrode, it should have the following characteristics, (a) good interparticle contact for low electronic resistance, (b) porous structure so that mass transfer through the deposit will not be a limiting factor, (c) large electrode-IEM contact area to provide electrochemically active surface area, and (d) metal-film deposition predominantly within the Nafion in a thin layer adjacent to the membrane surface. The chemical reducing agent used in the electroding process does not penetrate the IEM; therefore the surface is typically pretreated by methods such as surface roughening. This allows the metal salt that diffuses out of the membrane to react with the reducing agent while within the membrane surface. Depending on the chemical process, the metal can be deposited into the membrane in the range of 1 μm to 20 μm deep. It can be seen that the importance of the electroding process determines the effective capacitance, resistance and current density of the IPMC, and the resulting responsive behavior of the material. An SEM of a typical IPMC that has been platinized through a chemical impregnation/reduction process as described above is shown in Figure 6.

As would be anticipated by the chemical impregnation/reduction process, the surface appears nonuniform, where the black particles and clusters represent platinum particles. A TEM of another IPMC sample is shown in Figure 6. By examining Figure 6, it can clearly be seen that the density of the Platinum particles (black clusters) is much greater at the surface of the membrane. This is due to the reducing agent's inability to penetrate deep into the membrane. The density decreases at the dispersion distance is increased.

The IPMC can also be electroplated with the metal to include an outer layer of metal on the surface as well as the previous embedded metal particle layer. This is another method that is used to modify the material's properties and response. The overall surface conductivity is increased by using this method. The benefits of this is that the electric field placed at the

electrodes is capable of reaching the entire length of the IPMC sample with little degeneration of overall voltage magnitude. Typical surface electroplating metals include gold, platinum and graphite.





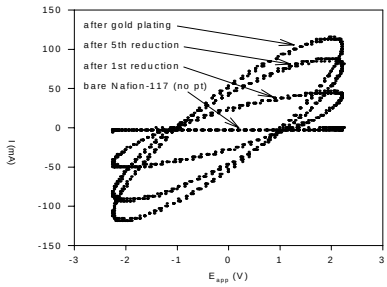
Arrow through TEM indicates increasing penetration depth

Fig. 6. (top) An SEM micrograph of a typical IPMC (surface); (bottom) A TEM micrograph of typical IPMC that has been electroded with Platinum particles. *The top left region of micrograph indicates the surface of the IPMC (particle density is greater) [from Kim and Shahinpoor, 2003].*

Particle Manipulation

In electroding an IPMC, there are three possible tasks or methods in altering the overall performance of the material in a positive way [Kim and Shahinpoor, 2003]. The first being a repetitive platinum reduction process, the second being the use of dispersing agents and the third is by performing a base material stretching, i.e. uniaxial mechanical stretching.

It has been found that repetitive platinum reduction in a wet batch system leads to improve the performance of IPMCs in terms of larger force characteristics. This phenomenon is most likely due to the increased charge capacity on the surface of the IPMC as well as an increase in the electric field as the electrode spacing gets closer on the surface of the IPMC. The resulting power consumption of an IPMC under a sinusoidal wave input is shown in Figure 7 illustrating the change brought on by altering the fabrication processes. It can be seen that in general, power consumption is increased as the repetitive platinum reduction process is repeated. There is a distinct phase change in the power consumption as the reduction process is repeated as well. This indicates a possible increase in charge capacity as mentioned before resulting in an alteration in the material's time constant and therefore response time. Also, Figure 7 shows the current/voltage characteristics of the IPMC under the same sinusoidal input for various fabrication stages in terms of hysteresis. By examining the figure, it can be seen that the plain IEM (Nafion™) has almost no current response under the applied input signal. Also, the additive reduction processes as well as the surface electroplating by gold progresses the current responses as the reductions are repeated.



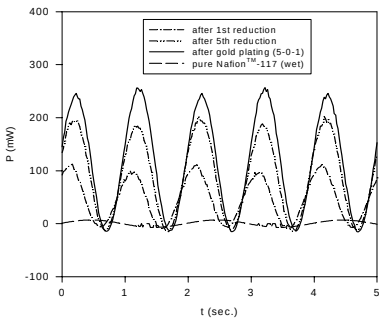


Fig. 7. Power consumption for various platinum reductions for an IPMC. *The phase shifts as the number of plating increases and Current/Voltage response of IPMC under a sinusoidal voltage input [from Kim and Shahinpoor, 2003].*

The second method that was mentioned, the use of dispersing agents, is favorable due to the problem of leakage of an IPMC. During actuation, the cations that migrate with the free water towards one of the electrodes results in an increased concentration of water at the electrode and sometimes, subsequent leakage of solvent. An IPMC that is porous allows for

effective water transport resulting in increased strains [Shahinpoor and Kim, 2001a,b]. This also can result in leakage of water causing a decreased performance of the material caused by decrease in hydration. The average size of primary platinum particles of the IPMC are found to be typically 40-60 nm which is much larger that that of the developing particles associated with ion-clusters that are approximately 5 nm [Shahinpoor and Kim, 2001a]. This proves that the initial particles coagulate during the chemical reduction and eventually grow larger. By introducing a dispersing agent during the reduction process it is possible to reduce the particle coagulation. This will result in an increased particle penetration into the IEM as well as an even distribution of particles due to their decreased size and separation [Kim and Shahinpoor, 2003]. Figure 8 shows the effect of adding a dispersing agent during the reduction process to the surface of an IPMC. It is clear to see that the surface becomes smoother and what would seem more evenly distributed after the dispersing agent treatment. The dispersing agents used by Kim and Shahinpoor were found to dramatically improve the force characteristics of the IPMC showing much smaller time constants that means faster response times.

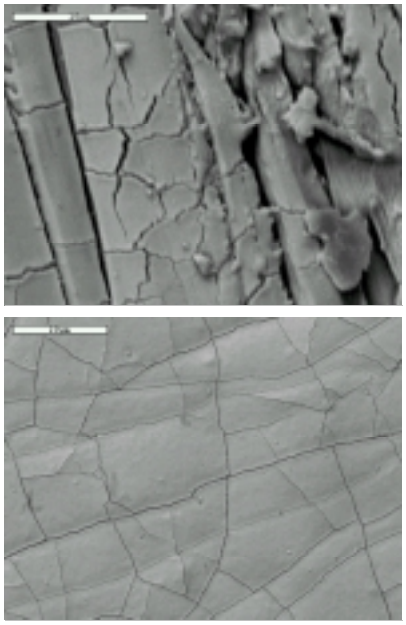


Fig. 8. SEM micrographs illustrating surface morphologies of an IPMC sample: (top) without the use of (bottom) with the use of dispersing agent *[from Kim and Shahinpoor, 2003]*

The third method mentioned, base material stretching, relates to the penetration depth of the platinum particles during the reduction process. If the penetration depth of the particles could be increased, the performance of the IPMC would be improved due to the increased density of platinum particles and subsequent improved electrical characteristics of surface electrodes. By effectively stretching the base material before the chemical impregnation process, the permeability of the IPMC will increase due to the stretched pores. This allows for an increased platinum particle density and a larger distribution. As can be seen from this section, the effective electrodes play a crucial role in the performance of an IPMC. This makes this component of IPMC fabrication one important parameter to alter in order to obtain desired or improved actuation/sensing characteristics. By improving the overall conductance of the material, the response is faster as well as larger force generation. The overall capacitance of the material is also increased.

Clusters

IPMCs have a unique structure within the polymeric network. Ionic groups within an IPMC tend to aggregate to form tightly packed regions that are referred to as clusters [Tadokoro et al., 2000a; Li and Nemat-Nasser, 2000]. The hydrophobic region in a water saturated IEM (such as Nafion) is composed of the area around the fluorocarbon polymer backbone, and the hydrophilic regions which contain these ionic groups and counter ions that interact with water and allow the passage of ions. These clusters are fully interconnected and are readily saturated by water. Nemat-Nasser (2002) studied the cluster morphology in a water-swollen Nafion perfluorinated membrane using a micromechanics approach. They assume that the ionic groups are permanently attached to the fluorocarbon backbone, while the counter ions are free to move through the interstitial regions that are saturated with water for their modeling of the material. The cluster size is observed to be on the nanoscale range (typically 4-5 nm). The negative ions indicate the functional groups of the particular IEM, (i.e. SO_3^- and COO^-). The cluster size is assumed to be determined by the electrostatic dipole interaction of the ions, the elastic energy of the polymeric chain reorganization, and the surface energy of the cluster. So, the degree of hydration of the IPMC as well as the cation species plays an important role in determining the size of the clusters within the material.

Temperature

The capability for the IPMC to be capable of functioning within an extremely large temperature range would be ideal. This would allow for various intriguing applications including planetary applications [Bar-Cohen et al. 1999a,b, 2000] as well as other typical actuator applications. The mechanics of the

IPMC within these extreme temperature ranges (whether high or low), however, are quite complicated due to the material's reliance upon hydration by water. There have been investigations using solvents other than water such as glycols, but the research is still in its infancy. Bar-Cohen et al. (2000) observed that the IPMC's deflection response did decrease with low temperatures; there was still a deflection of approximately 2 mm for a Nafion and Flemion membrane that has been platinized at environmental temperatures of as low as -150 °C. It should be noted that the IPMC samples used had a protective polymer coating on them to help protect them. The research in this field is still limited although it does show promising results in its early stages.

Figure 9 depicts one of the sample runs by Paquette et al. (2003) at a temperature of approximately -30°C in the chamber. The surface temperature of the IPMC during experiment is shown to fluctuate around -33°C. The blocking force for this run is about 0.35 gm_f, which is about one third of typical values under room temperature conditions (~1gm_f with 1 volt input voltage). This suggests that there is a definite influence of the operating temperature on the material behavior of the sample IPMC. It is also interesting to note that once the external step voltage was removed (was still connected with resistor) that the voltage displayed a capacitor discharging behavior.

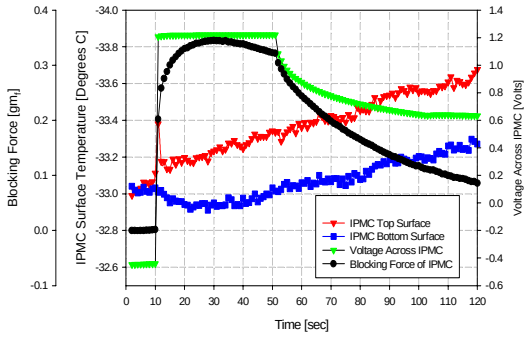


Fig. 9. Force response of a prepared IPMC sample at the step input voltage of 1.22 volts in a subzero environment (-33 °C). *[from Paquette et al., 2003]*

Electric Properties

The electrical behavior of the IPMC is also highly dependent upon several variables including hydration, IEM, cation type, electrode composite, etc. For instance, the value for the material's resistivity is directly related to the electroding process where the resistivity decreases with a more dense dispersion of metal particles within the polymer matrix as previously discussed. Figure 10 shows how the surface resistivity decreases with an increase of penetration depth of the implanted metal particles (in this case platinum). This is of course due to the material's increased conductivity as the penetration depth is increased and further explains the importance of the effective electrodes as a means of manipulating overall electrical properties. As mentioned previously, this allows for a faster force response time via a smaller time constant. Figure 11 shows capacity data as a function of the number of plating. As can be seen, the capacity is increased as the number of plating increases. A good way to study the behavior of the material and to analyze its electrical responses is to subject the IPMC to either an AC or DC voltage input.

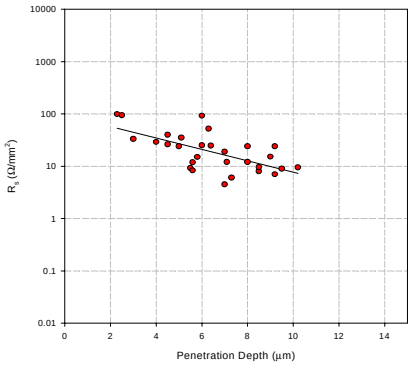


Fig. 10. Four-point probe surface resistivity measurement of samples with various penetration *depths* *[from Kim and Shahinpoor, 2003]*

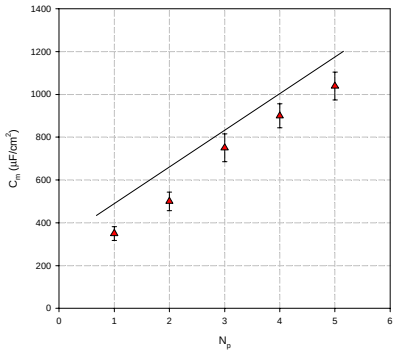


Fig. 11. Capacity data. N_p is the number of plating in a batch solution containing metals ions and conditioned reducing solutions. *The plating was performed up to 5 times. The solid line represents the previously published data from Onishi et al., 2000. [from Paquette et al., 2002]*

AC/DC Operation

An IPMC behaves differently for differing types of applied electric fields, as one would expect due to the nature of IPMC actuation. The typical voltage applications that have been researched are (a) constant DC voltage, (b) AC voltage with a step input, sinusoidal input or triangle wave input.

A constant DC voltage input (positive polarity) to an IPMC results in the anticipated bending to the anode side. The material will then begin to relax back towards the cathode side after sufficient time. This is perhaps because the water molecules that hydrate the mobile cations along with the free water that is pumped to the cathode side begin to return to a state of lesser resistance. This relaxation behavior will be explained further in the next section. By increasing the input voltage across the IPMC to above 1.22 volts, the hydrated sample will show signs of electrolysis characterized by Equation (1).

$$H_2O_{(l)} \rightarrow H_{2(g)} + O_{2(g)} \qquad (1)$$

This formation of hydrogen and oxygen results in a bubbling on the surfaces of the IPMC often results in degradation of the electrodes and of course, dehydration of the material itself resulting in a degradation of the performance. Possible dry operation of the IPMC was through the use of a protective polymer coating.

The IPMC will bend to either the anode or cathode side depending on the voltage polarity, so under an AC voltage input, the IPMC undergoes a swinging movement and the displacement and force generation depends not only on the voltage magnitude, but the frequency as well. By lowering the frequency of the IPMC, the resulting force is increased. This is due to the fact that the method of motion is through an electro-osmotic pressure differential in the two sides of the IPMC as was discussed previously. The ions can not migrate to the other side instantaneously since they have to migrate (along with water) through the nanoscale channels and pores which is why when the material is subjected to increasing frequencies the material does not achieve its full force potential before the polarity switches and the IPMC begins to deflect to the opposing side. That is why DC operation is the ideal situation to measure maximum force (blocking force) for the IPMC.

By studying the current response of a typical IPMC, it can be shown that the material is initially charging due to the initial current spike via ionic diffusion [Leary and Bar-Cohen, 1999]. Figure 12 illustrates the capacitive nature of the IPMC in the form of consumption of charge (current vs. time). This further reveals the effect that the effective electrodes of the IPMC have upon the performance. By studying Figure 12, it is interesting to note that for larger input voltages, the charge consumption is greatly increased. This is because the IPMC uses the charge but also stores it within the material resulting in the behavior of a capacitor as well as showing traits of a battery by storing charge that is not completely released. This phenomenon is yet to be completely described with regards to the physics of the situation.

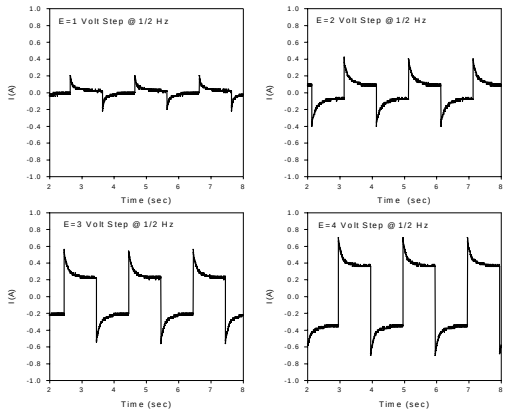


Fig. 12. Current responses to step voltages of 1, 2, 3 and 4 volts *[from Kim and Shahinpoor, 2003]*.

Of course, all of the other factors such as cation species, IEM, electroding and hydration play a key role in the overall response for dc and ac operation of IPMCs. Figure 12 once again illustrates the importance of the electroding procedure previously mentioned in terms of the capacity of the IMPC. It can be clearly seen that as the number of platings is increased, the capacity of the IPMC is increased. This may be due to the double layers adjacent to platinum particles or nearby metallic layers. There are a couple of models that will be discussed later with respect to modeling the behavior of an IPMC based upon an equivalent circuit model. An equivalent circuit model was recently proposed by Paquette et al. (2002; 2003) attempting to explain the initial nonlinear capacitive behavior of the IPMC.

Relaxation

As mentioned previously, under dc voltage application across an IPMC, a relaxation of the material is observed. This has been documented by several research groups [Bar-Cohen et al., 1999a; Bar-Cohen

and Leary, 2000; Enikov and Nelson, 2000], and has yet to be agreed upon as to the physics behind the phenomena. It is primarily believed to be due to the water bound to the cations as well as the free water that was pumped to the electrode side beginning to back diffuse towards the other electrode in an attempt to obtain its least energy state. Enikov and Nelson (2000) are one of the few researchers to include a back diffusion (relaxation) term within their model.

Experimental Approach to Tailor Base Polymer Properties

As observed previously, the capacitive and resistive behavior of the base polymer truly governs the generative force responses. Such a finding is the motivation to perform experimental study on the optimization of the base polymer so as to obtain desirable performance the IPMC. An experimental approach by the authors to improve the base polymer properties was attempted by the new clay-based nanocompositing technique (Alexandre and Dubois, 2000; Theng, 1974; Nam et al., 2003).

The performance of the IPMC manufactured by this newly developed nanocompositing technique was gauged by measuring the blocking force, F_T, in a cantilever configuration under a certain voltage across the IPMC strip by changing frequencies. In Figure 13 representative data are provided for the case of step voltage of 2 V in the frequency range of 0.1-50 Hz for both a conventional IPMC and a nanocomposite IPMC (~3% loading), respectively. In general, the performance of the nanocomposite IPMC shows a significantly larger force generation than the conventional IPMC. The relative importance of blocking forces generated by the nanocomposite IPMC against ones of the conventional IPMC is constituted as:

$$E_{ff} = \frac{F_{T,NC-IPMC}}{F_{T,C-IPMC}} \qquad (2)$$

Where $F_{T,NC\text{-}IPMC}$ and $F_{F,C\text{-}IPMC}$ represent the blocking forces generated by nanocomposite IPMCs and conventional IPMCs, respectively. Noticeably, the performance of the nanocomposite IPMC is of significance in a certain frequency range (5-20 Hz) exhibiting more than a 100% increase in the blocking force. Such a non-linear behavior may attribute to water transport within the polymer matrix or material's electrostatic nature. Currently, this issue is being investigated.

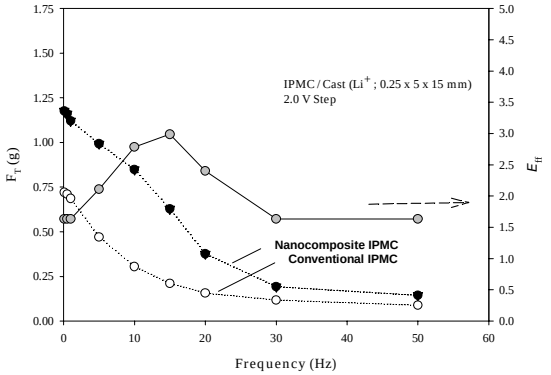


Fig. 13. The measured blocking forces of a nanocomposite IPMC and a conventional IPMC *[from Nam et al., 2003]*.

3. IPMC Modeling

Ionic Polymer-Metal Composites are a very process dependent material as was elaborated upon in the previous sections. This makes the material's predictability and modeling increasingly difficult. The overall behavior of the material is still not fully agreed upon by researchers. Consequently, there have been many models that have been proposed to model the behavior of the material based on the many parameters involved with IPMCs. Several of these models will be discussed in the following discussions. The models are separated by the following categories: (1) based upon actuation principle, (2) based upon transduction principle, and (3) based upon an electro-mechanical coupling. As is evident in the larger number of models based upon actuation, that is the primary mode that is studied, resulting in few models for transduction and even fewer for the coupling effect.

3.1 Theoretical Models for Actuation

There are several models proposed by researchers that try to explain the various intricacies of the behavior of an IPMC while in actuation. They range from equivalent circuit models, beam theory to micromechanics among others. The models shown here try to quantify either the force produced by the material, the resulting deflection or curvature, or both.

Shahinpoor Model

Shahinpoor (1999) proposed a mechanical model based upon an Euler-Bernoulli beam that also employs an electrostatic solution. The electric field affects the entire charge distribution in the material and creates a distributed moment along the arc length of the beam. He relates the finite curvature, K_E, as a function of arc

length and time using Hookes' law related to the equivalent moment M_E that is also a function of arc length and time to get:

$$K_E = \frac{1}{\rho_E} = \frac{M_E}{EI} \tag{3}$$

where ρ_E is the local radius of curvature, E is the IPMC Young's modulus of elasticity and I is the local moment of inertia of the cross section of the beam (as a function of arc length and time). Since the electric field is spread across the effective electrodes of the IPMC which are dendritic in appearance, the assumption of an assembly of point charges is made with a subsequent stress field, σ_E, shown in Eq. (4).

$$\sigma_E = 4\pi\varepsilon_o D E^{*2} \tag{4}$$

where the stress field is a function of arc length, time, electric field and η (cross section variable) and ε_o is the permittivity of free space and D is the dielectric constant of the IPMC polymeric part. The final equation for the resulting curvature is shown in Equation (5) and (6).

$$K_E = a^* E^*_{av}{}^2 \tag{5}$$

$$a^* = 8\pi\varepsilon_o D_{av} \Big/ EH \tag{6}$$

where E^*_{av} is the average electric field, a^* is the material parameter and D_{av} is an average dielectric constant across the section of the beam.

Shahinpoor also looked at the electrostatic solution. A linear approximation is made for the static deflection of the iono-elastic beam and the assumption of a constant electric field results in Equation (7) for deflection.

$$y(S) = \frac{1}{2} a^* E^*_{av} S^2 + b^* S + c^* \tag{7}$$

The solution that he found for the electro-dynamic solution also uses a linear approximation and is shown in Equation (8).

$$\rho bH\left(\frac{\partial^2 y}{\partial t^2}\right) + EI\left(\frac{\partial^4 y}{\partial S^4}\right) = 2a^* EI\left[E^*_{av}\left(\frac{\partial^2 E^*_{av}}{\partial S^2}\right) + \left(\frac{\partial E^*_{av}}{\partial S}\right)^2\right] \tag{8}$$

E^*_{av} is then found by formulating an equivalent circuit with appropriate initial conditions to solve for the deflection.

Bar-Cohen and Leary Model

Bar-Cohen and Leary (2000) developed a model based solely upon beam theory. When a cantilevered beam subjected to pure bending is bent into an arc of a circle, the curvature ($1/R=\rho$) of the neutral surface is expressed in Equation (9).

$$\frac{1}{R} = \frac{PL}{EI} \tag{9}$$

where P is a concentrated load located at the free end of the cantilever of length L and the E and I are the elastic modulus and flexural rigidity, respectively. This equation uses appropriate values for E and I and neglecting viscous forces of the surrounding water it can estimate the induced tip force generated by a given voltage. This is after the curvature of an IPMC induced by a specific voltage is measured so it is empirically based. This is a simple model that is good for approximations of generative tip force in the experimental phase of studying an IPMC.

This is a straightforward model that helps with experimental investigations for general material behavior. One detractor might be that it requires an experimental measurement of the curvature for input values.

Nemat-Nasser Model

Nemat-Nasser (2002) developed a micromechanical model which accounts for the coupled ion transport, electric field and elastic deformation to predict the response of the IPMC. The theory is developed by studying the structure of the clusters within the polymer matrix that were previously mentioned. The transduction part of the theory will be discussed later. The basis of their theory is that the interaction between an imbalanced charge density and the backbone polymer can be presented by an eigenstress (Nemat-Nasser and Hori, 1999). He examines the internal stresses induced by interaction between ion pairs inside a cluster and the dipole induced by imposing a bending. He then solves the basic field equations for this case and show good agreement with experimental results.

By studying a thin strip of IPMC with an applied potential, ϕ_o, the resulting bending moment was found and is expressed in Equation (10).

$$M = \int_{-w/2}^{w/2}\int_{-h}^{h} x\sigma_{zz}\,dxdy = k_o\kappa_e\phi_o a\left[h\cosh(ah) - \frac{\sinh(ah)}{a}\right]\frac{w}{\sinh(ah)} \approx k_o\kappa_e\phi_o aw \tag{10}$$

where k_o is the constitutive parameter of the eigenstress due to the imbalanced charge density and κ_e is the dielectric constant of the material, w is the width of the membrane and ϕ_o is the initial potential. The resulting curvature equation is shown in Equation (11).

$$R_c = \frac{\bar{Y}I}{M} = \frac{2\bar{Y}h^2}{3k_o\kappa_e\phi_o a} \tag{11}$$

where h is half of the membrane thickness and $\bar{Y}$ is the effective Young modulus of the composite. The constitutive parameters are estimated based on the microstructure and composition of the membrane.

Enikov and Nelson model

Enikov and Nelson (2000) developed a continuum mechanical model of Nafion based metal-polymer actuators. Global integral postulates are written for the conservation of mass, momentum, energy, and charge, Gauss' law, and the second law of thermodynamics. They then take the global equations and localize them in the volume and on the material surfaces bounding the polymer. Then, a finite element formulation is used to predict the evolution of the counter ion concentration, 'free' water content, electric potential, and stress/strain during actuation. As previously mentioned, this model includes stress relaxation phenomena due to water flow that is governed by Darcy's law (Enikov and Nelson, 2000). Enikov and Nelson come up with the following equations of state for the IPMC:

$$T_{ij} = 2GL'_{ij} + \frac{K}{3}L_{kk}\delta_{ij} - B\Delta\theta\delta_{ij} - \sum_s A^s\left(N^s - N_o{}^s\right)\delta_{ij} \tag{12}$$

$$P_i = \varepsilon_o X E_i \tag{13}$$

$$\underline{\mu^s} = -A^s L_{ii} + R\theta\left[\ln\left(f^s N^s\right)\right] \tag{14}$$

where G, K, X, B^s, F^s, N^s, are the shear modulus, the bulk modulus, the electric susceptibility, thermal expansion coefficient, free energies and entropies of formation summed over all components. Also, R is the universal gas constant and f^s is the activity coefficient of component s. The resulting equation defining the flux through the IPMC is:

$$J_k{}^s = -N^s W^s\left(-A^s L_{ii,k} + R\theta\frac{f^s N^s{}_{,k} + f^s{}_{,k} N^s}{f^s N^s} + \tilde{z}^s\phi_{,k}\right) \tag{15}$$

By assuming, that the ideal solution properties $f^s = 1$, Equation (15) becomes significantly simplified. Also assuming that the diffusion coefficient and the electric mobility are connected by the Einstein relation, the resulting equation has the form:

$$J_k{}^s = -D^s N_{,k}{}^s - \tilde{z}^s W^s\phi_{,k} + W^s A^s N^s L_{ii,k} \tag{16}$$

where the first two terms are the usual Nernst – Plank diffusion terms and the last term is the pressure driven diffusion (relaxation) (Enikov and Nelson, 2000). Enikov and Nelson note that from the relative signs in Equation (16), one can see that the last term is in the direction of increasing volumetric strains e.g. towards stretched and away from compressed regions of the polymer. Unlike most models, it does account for the relaxation behavior associated with IPMCs.

Asaka and Oguro Model

Asaka and Oguro (2000) propose a model for the bending of polyelectrolyte membrane platinum composites by electric stimuli. The model, in which electric fields can induce mechanical deformation in the IPMC via electrokinetically induced pressure gradients, was applied to the kinetics of the bending response. They start by defining a water flux term that includes two parts, a gradient in fluid pressure and an electro-osmotic flow. Then, by applying a linear, elastic constitutive law describing the swelling stress that is generated during deformation from equilibrium and also solving for the local compressive strain defined in terms of hydration, a solvable partial differential equation is found. The initial and boundary conditions are specified and the resulting solution is found for the hydration change in the membrane. They then follow the same technique used by Pei and Inganas (1992); they relate the curvature, $1/R$, at time, t, to the strain. They verified their theoretical correlations through experimentation and found agreement with the response dependence on the characteristic time (before relaxation), membrane thickness and the water transference coefficient of the IPMC. The model that they proposed also includes the interfacial stress between the electrode of the IPMC and the actual polymer itself.

This is a nice model relating the material to an equivalent circuit based on varying impedances that represent the material. The model, however, does not account for the back solvent flux (relaxation) associated with IPMCs in actuation under DC voltages.

Xiao and Bhattacharya Model

Xia and Bhattacharya (2001) present a multi-scale approach to modeling the electro-mechanical behavior of ionic polymers. They chose to develop a mesoscopic model because for any optimal design formulation of polymers such as IPMC, the impossibility to separate the deformation mechanism from the structure exists.

First, they assume that changes in ionic concentration leads to a local dilation of the polymer, and then model this phenomenologically. They then proceed to develop a model in the setting of finite deformations which is quasi-static and they further assume that elastic waves and electric pulses are much faster than ionic diffusion so the only time dependence involved is through the ionic diffusion. Next, they reduce their formulated equations to one dimension appropriate for a flat sheet with electrodes on the two faces (like a typical IPMC membrane). Lastly, they finish by constructing a phenomenological model of a strip of IPMC. The finished phenomenological model has three material constants E, κ_v and τ, inherent to it that is the effective elastic modulus, the saturation curvature at unit applied voltage and the time constant, respectively. The deformation solution is found by inserting an applied load and given time-dependent voltage. Once those values are applied at each time t, the characteristic equation is integrated to obtain an eigen-curvature κ. The eigen-curvature is then solved for to obtain the deformation. This is then repeated across each value of t to get a characterizing deformation.

Kanno-Tadokoro Model

The model that Kanno and Tadokoro (2001) developed consists of an electrical property, a stress generation property and a mechanical property. It is based upon a Nafion platinum composited IPMC with Na^+ as the mobile cation. The electrical property consists of three elements distributed in the whole membrane including resistance of porous surfaces platinum layers, resistance of Nafion, and RC elements approximating experimental voltage/current response. They go on to say that the applied voltage as an input is converted to distributed current through the membrane by the surface resistances and the inherent capacitance in the model to express the time response from input voltage to current. The stress generation property has the distributed current that is transformed into distributed internal stress by an equation in LaPlacian form. It includes an internal stress vector, a strain vector and a viscoeleastic dynamic property. Kanno-Tadokoro note that the surfaces of the membrane have internal stresses of distributed compression and expansion, which generate bending moment for the motion. Although the stress does originate in ionic motion, this model is a less precise prediction of motion than an ionic motion based model but is still suitable for design purposes. The equation is approximated by a second order delay to account for the phenomenon that occurs when hydrated cations (in this case, Na^+) migrate towards the cathode upon application of a voltage. There is an initial time lag of about 0.2 seconds from the ionic motion. This is accounted for in the model by the second order delay mentioned previously. Finally, the mechanical property is dynamically modeled as an elastic body or a viscoelastic body including mass and damping.

3.2 Theoretical Models for Transduction

There are not as many models for the transduction of the IPMC due to its nonlinear characteristics associated with the material that makes it difficult to model. The material has shown promise for transduction applications, but the overall value for capacitance associated with the IPMC is very process dependent and varies from sample to sample. Here, two models by Nemat-Nasser (2000) and Shahinpoor (1999) are shown.

Nemat-Nasser and Li Model

Nemat-Nasser and Li (2000) have proposed a model to explain the transduction that takes place within an IPMC. This model, like their actuation model, is based upon a micromechanical model which accounts for the coupled ion transport, electric field and elastic deformation to predict the response of the IPMC .

By imposing a bending moment upon the IPMC, the derived voltage is modeled based upon electrostatic theory to obtain Equation (17) and (18) for the resulting potential difference and the electric field, respectively.

$$\Delta\phi = 2hE \tag{17}$$

$$E = 12\sum_{n=0}^{n=\infty}\left[\frac{\mu}{(2n+1)^3 4\pi\kappa_w\left(\frac{2\kappa_p}{\kappa_w}+1\right)\left(\frac{r_d}{2}\right)^3}\right] \tag{18}$$

where κ_w is the dielectric constant of water, μ is the induced dipole, r is the magnitude of the position vector with respect to the induced dipole. This theory

is dependent upon the cluster morphology that they attributes to the IPMC.

This model, being one of only a couple to model the transduction behavior of an IPMC is dependent upon an electrostatic interaction assumption as was Nemat-Nasser model for actuation.

Shahinpoor Model

Shahinpoor (1999) refers to the transductive behavior as the ionic flexogelectric effect in polymeric gels. He proposes a theoretical model based upon Kirchhoff's law due to the capacitance and resistance that the IPMC exhibits. The expression that Shahinpoor formulated for the electric potential field per unit charge at the point (r_i, Z_i) is:

$$R(r_i, Z_i) = \sum_{n=-\infty}^{\infty} \left(\frac{r_i}{\left((Z_i - nb_i)^2 + r_i^2 \right)^{\frac{s+1}{2}}} \right) \quad (19)$$

The mean Coulomb's attraction or repulsion force associated with the mean field R (as a function of a cross section variable and Z) is then given by F, shown in Equation (20).

$$F(\eta, Z) = kq^2 l^* R(\eta, Z) \quad (20)$$

where k is a constant of proportionality, l^* is the length of the gel strip and q is the total charge between a pair of adjacent ionic surfaces in the gel strip (i.e. IPMC). Shahinpoor also notes that the average stress over the cross section of the gel strip with width w, and thickness 2*C is defined as:

$$\sigma(\eta, Z) = \left(\frac{-16\pi k l^* q^2 b^{-3}}{wC} \right) \left(K_1 \left(\frac{2\pi\eta}{b} \right) \cos\left(\frac{2\pi Z}{b} \right) \right) \quad (21)$$

The negative sign in Equation (21) ensures that the stress is negative when the gel is in a contracted state. The resulting curvature was found to be:

$$\kappa_E = \left(\frac{\lambda_+ - \lambda_-}{2C} \right) \quad (22)$$

where λ_+ and λ_- are the real values of the following set of cubic equations (23) and (24) that refer to the stretches in the most remote fibers in the gel under bending.

$$\lambda_+^3 + \left(\frac{3\sigma_+}{E_+} \right) \lambda_+^2 - 1 = 0 \quad (23)$$

$$\lambda_-^3 + \left(\frac{3\sigma_-}{E_-} \right) \lambda_-^2 - 1 = 0 \quad (24)$$

where E_+ and E_- are the elastic moduli of the local ionic concentration and temperature. So, the value of λ_+ - λ_- is related to the stresses σ_+ and σ_-, and these stresses are in turn related to the charges q and Q. The total charge Q is then related to the voltage v and the other electrical parameters (capacitance and resistance).

3.3 Theoretical Modeling for Electro-Mechanical Coupling

Ideally, it would be nice to have a set of correlating equations to describe both actuation and transduction of an IPMC. This way, the physics would be in order and certain aspects of the behavior would not be based upon experimental correlations. Presented here are two models that are both formulated on the basis of irreversible thermodynamics.

De Gennes, Okumura, Shahinpoor and Kim Model

De Gennes et al. (2000) presented a set of coupled equations based on linear irreversible thermodynamics to describe the behavior of a typical IPMC. The model is a compact description of the actuation and transduction principles inherent to the IPMCs by defining it in the linear regime, and in static conditions.

They introduce the linear irreversible thermodynamic relationship for charge transport (with a current density J normal to the membrane) and solvent transport (with a flux Q) to describe this electromechanical coupling of ionic gels (i.e. IPMCs). The standard Onsager relations for the system have the form,

$$J = \sigma E - L_{12} \nabla p \quad (25)$$

$$Q = L_{21} E - K \nabla p \quad (26)$$

Equations (25) and (26) couple the electric field, E, as well as the mechanical pressure gradient, ∇p. These equations can be elaborated upon to explain the *'direct effect'* (actuation) as well as the *'inverse effect'* (sensing or transduction) of IPMC's. It should be noted that these Onsager relations developed by De Gennes *et al.* are for a static model. Note that σ, L_{12} (=L_{21}), and K are electric conductance, cross-coefficient, and permeability, respectively.

In this paper, they state that for the *direct effect* (applying an electric field to generate a force from the material), which assumes that the electrode surface is

impermeable to water (Q = 0), the pressure gradient is found from using Equation (27), such that

$$\nabla p = \frac{L}{K} E \tag{27}$$

For this direct effect, the following equation for mechanical torque (per unit width), Γ, that is coupled with the electric field is,

$$\Gamma = \frac{1}{12} \frac{1-2\sigma_p}{1-\sigma_p} \frac{Lh^3}{K} E \tag{28}$$

Equation (28) can be used to determine the force generated by the IPMC (blocking force) with a specific electric field applied across the IPMC. It should be noted that this model does not account for relaxation.

The equation for determining the electric field produced by an imposed bending moment, Γ becomes Equation (29),

$$E = \frac{12(1-\sigma_p)}{1-2\sigma_p} \frac{L}{\sigma h^3} \Gamma \tag{29}$$

The relation between the actuation and transduction becomes the term $L^2/\sigma K$ which is the ratio of the two coefficients.

The presented model is a compact and robust model that generally describes the actuation/transduction behavior in a coupled format.

Newbury et al. Model

Newbury (2002) formulated a coupled, electromechanical model of a Nafion-based ionic polymer transducer used in the cantilevered bender configuration. Their model is simple, dynamic, and is able to represent the transducer as either a sensor or as an actuator. They begin by using a single input, single output linear circuit. The linear transformer model enables the development of relationships between the force, deflection, current, and voltage for any electrical or mechanical boundary condition.

Due to the lack of a concise constitutive model for an IPMC, this brings about their conception of a 'transducer' model. This model bypasses the need for a model of fundamental electromechanical mechanism of the actuator and only focuses on the variables that are important for using the polymer transducer as a bender (actuator or sensor) (2002). The two-port network that is used includes the current and voltage at the electrodes and the force and velocity at the tip of the bender transducer. These values are placed in a Laplacian domain expression. Newbury et al. then proposes four different boundary conditions: 1. short circuit (v=0), 2. open circuit (i=0), 3. blocked ($\dot{u}=0$) and 4. free (f=0). These boundary conditions are then applied to the constitutive Laplacian equation that was developed previously and then solved. They found that the short circuit current is found to be proportional to the induced actuator velocity with the constant of proportionality equal to $7.5x10^{-4}\ A/(m/s)$. A comparison of simulated and experimental responses for the IPMC in a cantilever configuration validated the form of the model as well as the empirically determined model parameters. This model is not as fundamental as a transducer model developed from first principles, but the authors believe that it will bring insight into the electromechanical mechanisms in ionic polymer materials and be useful for designing systems that incorporate these materials.

4. Naval Applications

One interesting naval application of IPMCs was attempted by Bandyopadhyay (2002) (also Krol Jr. et al., 2002). The demonstration of using IPMCs for the alteration of radiative noise in underwater propulsors was successful. By introducing IPMCs at the trailing edge of an upstream stator blade and articulating them like a fish tail fin, the tail oscillations of the blade was controlled to achieve a desired noise spectrum. Also, Mojarrad (2001) used IPMCs as a propulsion fin for robotic swimming structures as a boat or fish-like object swimming in aqueous medium.

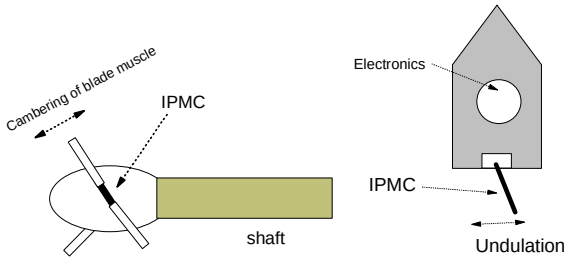


Fig. 14. Cambering of blade muscle *[left, after Bandyopadhyay, 2002]*; **Robotic swimming structure** *[right, after Mojarrad, 2001]*

5. Remarks

Ionic Polymer-Metal Composites are a unique electroactive polymer capable of actuation as well as transduction. The material's potential prompted many models to describe the phenomena in terms of its actuation, transduction as well as the coupling of the

two. The material operates at low driving voltages and is a soft actuator among other attractive attributes offering many possible applications.

It was shown that the IPMC requires a complicated fabrication process involving many parameters. These fabrication processes result in the material performance to be dependent upon many variables such as ion exchange membrane, cation species, hydration, electroding process, as well as various treatment processes described to improve material properties. The material's electrical properties were discussed and it was shown that the material has a capacitive nature to it due to its double layer electrodes.

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7. References

Abe, Y., Mochizuki, A., Kawashima, M., Yamashita, T., S., "Effect on Bending Behavior of Counter Cation Species in Perfluorinated Sulfonate Membrane-Platinum Composite," Polymers for Advanced Technologies **9**, 1998, pp 520-526.

Alexandre, M., Dubois, P., "Polymer-layered Silicate Nanocomposites: Preparation, Properties, and Uses of a New Class of Materials," Materials Science and Engineering, **28**, 2002 (1-63).

Asahi Chemical Industry Co., Ltd, Data Sheet-Aciplex, 1995.

Asaka, K., Oguro, K., Nishimura, Y., Mizuhata, M., Takenaka, H., "Bending of Polyelectrolyte Membrane-Platinum Composites by Electric Stimuli I. Response Characteristics to Various Waveforms," Polymer Journal, **27(4)**, 1995, pp 436-440.

Asaka, K., Oguro, K., "Bending of Polyelectrolyte Membrane Platinum Composites by Electric Stimuli Part II. Response Kinetics," Journal of Electroanalytical Chemistry, **480**, 2000, pp 186-198.

Atkins, P.W., Physical Chemistry, 2nd edition, Oxford University Press, 1982.

Bandyopadhyay, P. R., "Maneuvering Hydrodynamics of Fish and Small Underwater Vehicles," Integrative and Comparative Biology, **42 (1)**, 2002, pp. 102-117.

Banziger, R., Christen, H., Stucki, S., U.S. Pat., 4,396,469, 1983.

Bar-Cohen, Y., Xue, T., Shahinpoor, M., Simpson, J. O., Smith, J., "Flexible, Low-Mass Robotic Arm Actuated by Electroactive Polymers (EAP)," SPIE Proc. 1998, Paper No. 3329-07.

Bar-Cohen, Y., Shahinpoor, M., Harrison, J. O., Smith, J., "Flexible Low-Mass Devices and Mechanisms Actuated by EAPs," SPIE Proc., 1999a, pp 51-56.

Bar-Cohen, Y., Leary, S., Shahinpoor, M., Harrison, O. J., Smith, J., "Electro-Active Polymer (EAP) Actuators for Planetary Applications," SPIE Proc., 1999b, pp 57-63.

Bar-Cohen, Y., Leary, S., "Electroactive Polymers (EAP) Characterization Methods", SPIE Proc., 2000, pp 12-16.

Bar-Cohen, Y., "Electroactive Polymer (EAP) Actuators as Artificial Muscles – Reality, Potential and Challenges", ISBN 0-8194-4054-X, SPIE Press, 2001, pp. 1-671.

Bhattacharya, K., Li, J., Xiao, Y., "Electromechanical Models for Optimal Design and Effective Behavior of Electroactive Polymers," in Electroactive Polymer (EAP) Actuators as Artificial Muscles (ed. Y. Bar-Cohen), SPIE, Bellingham, Washington, 2001.

Davis, T. A., Genders, J. D., Pletcher, D., A First Course in Ion Permeable Membranes, the Electrochemical Consultancy, Hants, England, 1997.

De Gennes, P. G., Okumura, K., Shahinpoor, M., Kim, K. J., "Mechanoelectric Effects in Ionic Gels, Europhysics Letters," **50(4)**, 2000, pp 513-518.

De Rossi, D., Mazzoldi, A., "Linear Fully Dry Polymer Actuators," SPIE Proc., 1999, pp 35-43.

Eisenberg, A., Ions in Polymers, Advances in Chemistry Series, American Chemical Society, Washington D.C., 1980.

Eisenberg, A., Yeager, H. L., Perfluorinated Ionomer Membranes, ACS Symposium Series 180, ACS, Washington DC, 1982.

Eisenberg, A., Bailey, F. E., Coulombic Interactions in Macromolecular Systems, ACS Symposium Series, **302**, American Chemical Society, Washington D.C.,1986.

Enikov, E., Nelson, T., Bradley J., "Electrotransport and Deformation Model of Ion Exchange Membrane Based Actuators," SPIE Proc., 2000, pp 129-139.

Escoubes, M., Pineri, M., in Perfluorinated Ionomer Membranes (ed. A. Eisenberg and H. L. Yeager), ACS Symposium Series, **180**, Chapt. 2, 1982.

Fedkiw, P., Her, W.-H., J. Electrochem. Soc. **136**, 899, 1989; P. S. Fedkiw and W-H. Her, Abstract 16, pp 23, The Electrochemical Society Extended Abstracts, Vol. 88-1, Atlanta, GA, Meeting, May 15-20, 1988; P. S. Fedkiw, U.S. Pat., 4,959,132, 1990.

Gebel, G., Aldebert, P., Pineri, M., "Structure and Related Properties of Solution-Case

Perfluosulfonate Ionomer Films," Macromolecules, **20**, 1987, pp. 1425-1428.

Gierke, T. D., Munn, G. E., Wilson, F. C., "Morphology of Perfluorosulfonated Membrane Products (Wise-Angle and Small-Angle X-Ray Studies)," in Perfluorinated Ionomer Membranes, ACS Series 180, ACS, Washington D.C., 1982.

Gruger, A., Régis, A., Schmatko, T., Colomban, P., "Nanostructure of Nafion Membranes at Different States of Hydration," Vibrational Spectroscopy, **26**, 2001, pp 215-225.

Helfferich, F., Ion Exchange, Doverr Pub: New York, 1995.

James, P. J., Elliott, J. A., McMaster, T. J., Newton, J. M., Elliott, A. M. S., Hanna, S., Miles, M. J., "Hydration of Nafion Studied by AFM and X-ray Scattering," Journal of Materials Science, **35**, 2000, pp 5111-5119.

Katchalsky, A., "Rapid Swelling and Deswelling of Reversible Gels of Polymeric Acids by Ionization," Experientia, **V**, 1949, pp 319-320.

Kent, C. E., Hamlen, R. P., Shafer, S. N., "Electrolytically Activated Contractile Polymer," Nature, **206**, 1965, pp 1149-1150.

Kim, K. J., Shahinpoor, M., "Ionic Polymer-Metal Composites: II. Manufacturing Techniques," Smart Material Structures, **12**, 2003, pp. 65-79.

Kolde, J. A., Bahar, B., Wilson, M. S., Zawodzinski, T. A., Gottesfeld, S., Electrochemical Society Proceedings, **95-23**, 1995, pp. 193.

Komoroski, R. A., Mauritz, K. A., "Nuclear Magnetic Resonance Studies and the Theory of Ion Pairing in Perfluorinated Ionomers," in ref. Eisenberg, A. and H. L. Yeager, 1982.

Krol, W., Annaswamy, A., Bandyopadhayay, A Biomimetic Propulsor for Active Noise Control: Theory, NUWC-NPT Technical Report #11,350, 2002.

Kuhn, W., Kunzle, O., Katchalsky, A., "Verhalten Polyvalenter Fadenmolekelionen in Losung," Halvetica Chemica Acta, **31**, 1948, pp 1994-2037.

Kuhn, W., "Reversible Dehnung und Kontraktion bei Anderung der Ionisation eines Netzwerks Polyvalenter Fadenmolekulionen," Experientia, **V**, 1949, pp 113-125.

Kuhn, W., Hargitay, B., Katchalsky, A., Eisenberg, H., "Reversible Dilation and Contraction by Changing the Stat of Ionization of High-Polymer Acid Networks," Nature, **165**, 1950, pp 514-516.

Kuhn, W., Hargitay, B., "Muskelahnliche Kontraktion und Dehnung von Netzwerken Polyvalenter Fadenmolekulionen," Experientia, **VII**, 1951, pp 1-11.

Lawrence, R. J., Wood, L. D., U.S. Pat., 4,272,353, 1981.

Li, J., Nemat-Nasser, S., "Micromechanical Analysis of Ionic Clustering in Nafion Perfluorinated Membrane," SPIE Proc., 2000, pp 103-109.

Liu, R., Her, W., Fedkiw, P. S., "In Situ Electrode Formation on a Nafion Membrane by Chemical Platinization," Journal of Electrochemical Society, **139(1)**, 1992, pp 15-23.

Mallavarapu, K., Newbury, K., Leo, D., "Feedback Control of the Bending Response of Ionic Polymer-Metal Composite Actuators," SPIE Proc., 2001, pp 301-310.

Millet, P., Pineri, M., Durand, R., "New Solid Polymer Electrolyte Composites for Water Electrolysis," Journal of Applied Electrochemistry, **19**, 1989, pp 162-166.

Mojarrad, M., Shahinpoor, M., "Ion-Exchange-Metal Composite Artificial Muscle Actuator Load Characterization and Modeling," SPIE Proc., 1997, pp 294-301.

Mojarrad, M., Characterization and Modeling of Ionic Polymeric Smart Materials as Artificial Muscles and Robotic Swimming Structures, PhD Dissertation, University of New Mexico, 2001.

Moor, W., Physical Chemistry, 4th edition, Prentice-Hall, New Jersey, 1972.

Moor, R.B., Cable, K. M., Croley, T. L., "Barriers to Flow in Semicrystalline Ionomer. A Procedure for Preparing Melt-Processes Perfluorosulfonate Ionomer Films an Membranes," Journal of Membrane Science, **75**, 1992, pp. 7-14.

Nagel, N., Stucki, S., U.S. Pat., 4,326,930, 1982.

Nam, J.-D., Choi, H. R., Tak, Y. S., Kim, K. J., "Novel Electroactive, Silicate Nanocomposites Prepared to be Used as Actuators and Artificial Muscles," Sensors and Actuators: A. Physical, **105(1)**, 2003, pp. 82-89.

Nemat-Nasser, S., Hori, M., Micromechanics: Overall Properties of Heterogeneous Materials, Elsevier, North Holland, 2nd ed., 1999.

Nemat-Nasser, S., Li, J. Y., "Electromechanical Response of Ionic Polymer Metal Composites," SPIE Proc., 2000, pp 82-91.

Nemat-Nasser, S., Thomas, C. W., "Ionomeric Polymer-Metal Composites", in Electroactive Polymer (EAP) Actuators as Artificial Muscles, Reality, Potential, and Challenges, ed. Bar-Cohen, Y., SPIE Press, Washington, U.S.A., 2001.

Nemat-Nasser, S., "Micromechanics of Actuation of Ionic Polymer-metal Composites", Journal of Applied Physics, 92(5), 2002.

Newbury, K. M., Leo, D. J., "Mechanical Work and Electromechanical Coupling in Ionic Polymer Bender Actuators", Proceedings of the ASME International Mechanical Engineering Congress and Exposition, paper number AD-23705, 2001.

Newbury, K., "Characterization, Modeling and Control of Ionic Polymer Transducers," Ph.D. Dissertation, VPI, 2002.

Niedrach, L. W., U.S. Pat., 3,134,697, 1964.

Oguro, K., K. Asaka, and H. Takenaka, "Actuator Element," U.S. Patent #5,268,082, 1993.

Oguru, K., Fujiwara, N., Asaka, K., Onishi, K., Sewa, S., "Polymer Electrolyte Actuator with Gold Electrodes," SPIE Proc., 1999, pp 64-71.

Onishi, K., Sewa, S., Asaka, K., Fujiwara, N., Oguro, K., "Bending Response of Polymer Electrolyte Actuator," SPIE Proc., 2000, pp 121-128.

Osada, Y., Okuzaki, H., Hori, H., "A Polymer Gel with Electrically Driven Motility," Letters to Nature, **355**, 1992, pp 242-244.

Osada, Y., Gong, J. P., "Intelligent Gels -Their Dynamism and Function," SPIE Proc., 1999, pp 12-18.

Otero, T. F., Cantero, I., Villanueva, S., "EAP as Multifunctional and Biomimetic Materials," SPIE Proc., 1999a, pp 26-34.

Otero, T. F., Cantero, I., Sansiñena, D., Marco A., "Artificial Muscles Working in Both Aqueous Solutions or Air," SPIE Proc., 1999b, pp 98-105.

Otero, Toribio F., Grande, H., Cantero, I., Sarasola, A., "Muscles and Artificial Muscles. Electrochemically Stimulated Conformational Relaxation Model," SPIE Proc., 1999c, pp 122-132.

Otero, T., Fernandez, H., Francisco, J., Cheng, S., Alonso, D., Villanueva, S., "Modulation of EAP Properties through the Variables of Synthesis," SPIE Proc., 2000, pp 148-158.

Paquette, J. W., Kim, K. J., Nam, J.-D., Tak, Y. S., "An Equivalent Circuit Model for Ionic Polymer-Metal Composites and Their Performance Improvement by a Clay-Based Polymer Nano-Composite Technique," Proceedings of ASME IMECE"02, New Orleans, LA, Paper # ASMS40, 2002.

Paquette, J. W., Kim, K. J., Nam, J.-D., Tak, Y.S., "An Equivalent Circuit Model for Ionic Polymer-Metal Composites and Their Performance Improvement by a Clay-Based Polymer Nano-Composite Technique," Journal of Intelligent Materials Systems and Structures (JIMSS), (in print).

Paquette, J. W., Kim, K. J., Fuchs, A., "Low Temperature Operation of Ionic Polymer Metal Composites Actuators," Proceeding of SPIE 10th Annual International Symposium on Smart Structures and Materials, San Diego, California, # 5051-28, 2003.

Pei, Q., Inganas, O., Journal of Physical Chemistry, **96**, 1992, 10507.

Sadeghipour, K., Salomon, R., Neogi, S., "Development of a Novel Electrochemically Active Membrane and Smart Material Based Vibration Sensor/Damper", Smart Materials and Structures, **1(2)**, 1992, pp 172-179.

Shahinpoor, M., "Conceptual Design, Kinematics and Dynamics of Swimming Robotic Structures Using Ionic Polymeric Gel Muscles," Smart Structures and Materials **1**, 1992, pp 91-94.

Shahinpoor, M., "Microelectro-Mechanics of Ionic Polymeric Gels as Artificial Muscles for Robotic Applications," 1993 IEEE Robotics and Automation Conference, **2**, 1993, (New York) pp 380-385.

Shahinpoor, M., "Electro-mechanics of Iono-elastic Beams as Electrically Controllable Artificial Muscles," SPIE Proc., 1999, pp 109-120.

Shahinpoor, M., Kim, K. J., "Effects of Counter-Ions on the Performance of IPMCs," SPIE Proc., 2000, pp 110-120.

Shahinpoor, M., Mojarrad, M., "Soft Actuators and Artificial Muscles," U.S. Patent, #6,109,852, 2000.

Shahinpoor, M., Kim, K. J., "Ionic Polymer-Metal Composites: I. Fundamentals," Smart Materials and Structures, **10**, 2001a, pp 1-15.

Shahinpoor, M., Kim, K. J., "Fully Dry Solid-State Artificial Muscles Exhibiting Giant Electromechanical Effect," SPIE Proc., 2001b, pp 428-435.

Shahinpoor, M., Kim, K. J., "Novel Physically Loaded and Interlocked Electrode Developed for Ionic Polymer-Metal Composites (IPMCs)," SPIE Proc., 2001c, pp 174-181.

Shahinpoor, M., Kim, K. J. "A Novel Physically-Loaded and Interlocked Electrode Developed for Ionic Polymer-Metal Composites (IPMCs)", Actuator and Sensors-A. Physical, **96(2/3)**, 2002, pp. 125-132.

Tadokoro, S., Murakami, T., Fuji, S., Kanno, R., Hattori, M., Takamori, T., Oguro, K., "An Elliptic Friction Drive Element Using an ICPF (Ionic Conductiong Polymer Gel Film) Actuator," IEEE Control Systems, **17(3)**, 1997, pp 60-68.

Tadokoro, S. Yamagami, S., Ozawa, M., Kimura, T., Takamori, T., Oguro, K., "Multi-DOF Device for Soft Micromanipulation Consisting of Soft Gel Actuator Elements," Proc. Of IEEE Intl. Conf. on Robotics and Automation, Detroit, 1999, pp 2177-2182.

Tadokoro, S., Yamagami, S., Takamori, T., Oguro, K., "Modeling of Nafion-Pt Composite Actuators (ICPF) by Ionic Motion," SPIE Proc., 2000a, pp 92-102.

Tadokoro, S., Fukuhara, M., Bar-Cohen, Y., Oguro, K., Takamori, T., "A CAE Approach in Application of Nafion-Pt Composite (ICPF) Actuators – Analysis

for Surface Wipers of NASA MUSES-CN Nanorovers," SPIE Proc., 2000b, pp 262-272.

Tadokoro, S., Fuji, S., Takamori, T., Oguro, K., "Distributed Actuation Devices Using Soft Gel Actuators," Distributed Manipulators, Kluwer Academic Press, 2000c, pp 217-235.

Tadokoro, S., Takamori, T., Oguro, K., "Modeling IPMC for Design of Actuation Mechanisms", in Electroactive Polymer (EAP) Actuators as Artificial Muscles, Reality, Potential, and Challenges, ed. Bar-Cohen, Y., SPIE Press, Washington, U.S.A., 2001a.

Tadokoro, S., Takamori, T., Oguro, K., "Application of the Nafion-Platinum Composite Actuator," SPIE Proc., 2001b, pp. 28-42.

Takenaka, H., Torikai, E., Kawami, Y., Wakabayashi, N., Int. J. Hydrogen Energy, **7**, 397, 1982; H. Takenaka and E. Torikai, Jpn. Pat. 5,538,934, 1980.

Theng, B. K. G., The Chemistry of Clay-Organic Reactions, Wiley, New York, 1974.

Tokuyama Corp., Technical Data, 2000.

Wax, S. G., Sands, R. R., "Electroactive Polymer Actuators and Devices," SPIE Proc., 1999, pp 2-9.

White, P. S., U.S. Pat., 4,364,813, 1982.

Xiao, Y., Bhattacharya, K., "Modeling Electromechanical Properties of Ionic Polymers," SPIE Proc., 2001, pp 292-300.

Yeager, H. L., "Transport Properties of Perfluorosulfonate Polymer Membranes", in Perfluorinated Ionomer Membranes, ACS Series **180**, ACS, Washington D.C., 1982.

Yoshida, H. and Y. Miura, J. Membrane Science, **68**, 1992, pp. 1-9.

Zawodzinski, T. A., Derouin, C., Radzinski, S., "Water Uptake by and Transport Through Nafion 117 Membranes," J. Electrochem. Soc., **140(4)**, 1993, pp 1041-1047.