Freeform Fabrication of Ionomeric Polymer-Metal Composite Actuators

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Reviewed, accepted August 3, 2005

Abstract

Ionomeric polymer-metal composite (IPMC) actuators are a type of soft electromechanically active material which offers large displacement, rapid motion with only ~1V stimulus. IPMC's are entering commercial applications in toys (Ashley 2003) and biomedical devices (Soltanpour 2001; Shahinpoor 2002; Shahinpoor, Shahinpoor et al. 2003; Soltanpour and Shahinpoor 2003; Soltanpour and Shahinpoor 2004), but unfortunately they can only actuate by bending, limiting their utility. Freeform fabrication offers a possible means of producing IPMC with novel geometry and/or tightly integrated with mechanisms which can yield linear or more complex motion. We have developed materials and processes which allow us to freeform fabricate complete IPMC actuators and their fabrication substrate which will allow integration within other freeform fabricated devices. We have produced simple IPMC's using our multiple material freeform fabrication system, and have demonstrated operation in air for more than 40 minutes and 256 bidirectional actuation cycles. The output stress scaled to input power is two orders of magnitude inferior to that of the best reported performance for devices produced in the traditional manner, but only slightly inferior to devices produced in a more similar manner. Possible explanations and paths to improvement are presented. Freeform fabrication of complete electroactive polymer actuators in unusual geometries, with tailored actuation behavior, and integrated with other freeform fabricated active components, will enable advances in biomedical device engineering, biologically inspired robotics, and other fields. This work constitutes the first demonstration of complete, functional, IPMC actuators produced entirely by freeform fabrication.

Introduction

There is a growing awareness in the engineering research community of the potential of solid freeform fabrication to greatly expand the space of manufacturable devices by enabling greater geometric freedom in designs and controlled spatial heterogeneity in material composition (Cooper, Kang et al. 1999; Duty, Jean et al. 1999; Li, Golnas et al. 2000; Dybala, Chlebus et al. 2002; Fuller, Wilhelm et al. 2002; Noecker and DuPont 2002; Ouyang, Mei et al. 2002; Stampfl, Hao-Chin et al. 2002; Bak 2003; Colvin 2004; Liu, Lee et al. 2004; Smurov and Yakovlev 2004; Domack and Baughman 2005). In light of this potential, we are developing multiple-material freeform fabrication system, and a library of mutually compatible functional components which can be produced together to create fully integrated, active, functional devices. The implied requirement for mutual compatibility of materials and processes, and the goal of spanning the largest possible space of functionality with the smallest set of materials has motivated our selection of primarily polymeric active and passive materials and liquid-state deposition methods. It is our opinion that the majority of applications for this technology in the near term are in the biomedical device and biomimetic robotics fields, with millimeter to decimeter scale. For this reason, we have chosen performance goals for functional components that are similar to the performance of biological functional analogs and more likely to be biocompatible – namely compliant structures and mechanisms, large strain actuation, and low voltage electronics. In prior work, we have demonstrated a multiple material freeform fabrication platform (Figure 3a), and fabrication of batteries, structures, joints and wiring (Malone, Rasa et al. 2004), and more recently, living tissue implants (Cohen, Malone et al. 2004). The focus of our research has shifted to the fabrication of actuators which are compatible with the aforementioned library and suitable for biomedical devices and biomimetic robotics.

In prior work (Malone and Lipson 2004), we demonstrated that two types of soft electromechanically active materials – conducting polymer (CP) and ionomeric polymer-metal composite (IPMC) – plausibly can be freeform fabricated. We have selected IPMC materials as the most promising on the basis of electromechanical performance. To motivate this decision, a brief review of the mechanisms of CP and IPMC actuation is provided below.

Background

A typical conducting polymer actuator is a thin polymer film surrounded by a liquid electrolyte (salt solution with mobile ions); an electric potential is applied between the polymer film and an electrode immersed in the electrolyte.

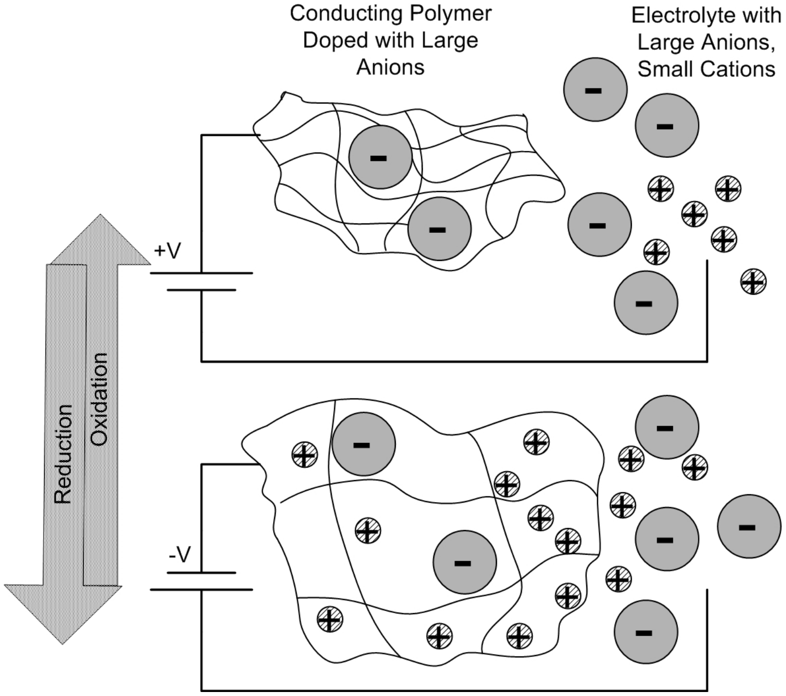
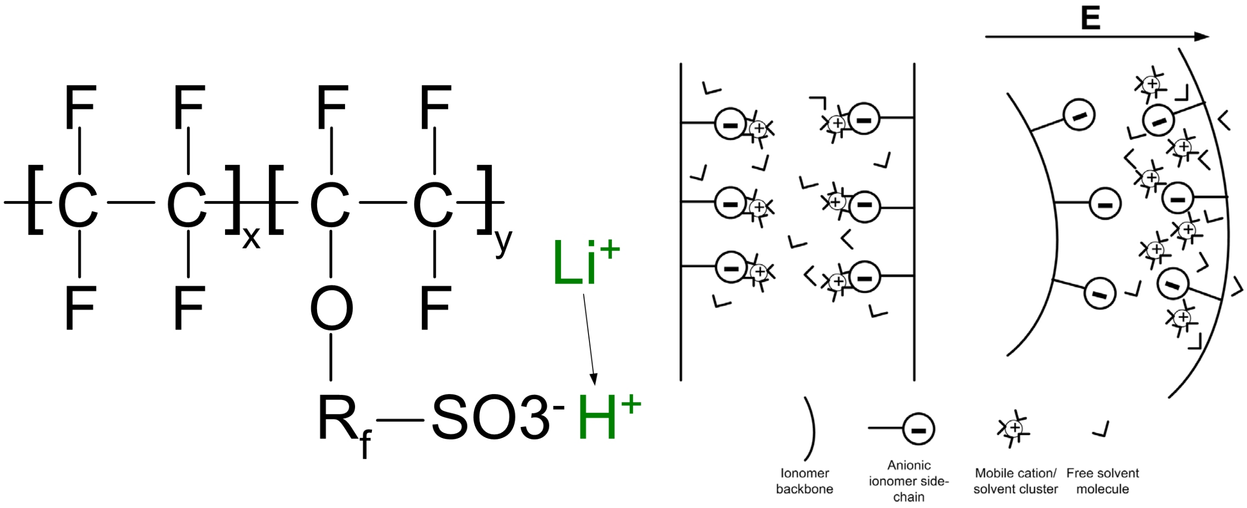


Figure 1. Illustration of the volume change of CP caused by ion diffusion. A CP film doped with large, immobile anions is immersed in electrolyte, and its electrical potential is varied with respect to the electrolyte. During oxidation, the polymer loses electrons and repels small cations in electrolyte. Large anions cannot diffuse quickly into or out of the polymer. During reduction, the polymer gains electrons; small cations can quickly diffuse into the polymer, occupying space and increasing the polymer volume.

The CP film actuates by changing volume as ions are forced by the potential to diffuse into or out of the bulk polymer (Figure 1). Conducting polymers are linear chain organic molecules in which successive carbon atoms along the axis of the chain are bound alternately by one shared electron pair (single, or σ-bond) and by two shared electron pairs (double, or π-bond). By adding or removing electrons from the CP chains, and embedding large positive or negative ions (known as “doping”), respectively, into the chains to maintain electrical neutrality, it is possible to make the locations of the π-bonds less well defined and to vary the electrical conductivity of the polymer (MacDiarmid 2001). With an electric potential between the CP and the electrolyte, free ions (and attached solvent molecules) from the electrolyte diffuse into or out from between the tangled polymer chains to compensate for the changed charge of the polymer, thereby causing the overall volume of the polymer to change (Figure 1) (Bar-Cohen 2001).

An Ionomeric Polymer-Metal Composite (IPMC) actuator consists of a polymer film whose surfaces are partially penetrated by conductive (typically metal) particles. The surfaces are also typically chemically plated or electroplated with metal to increase the surface conductivity. IPMC's actuate by bending in response to an electric field applied via these conductive surface electrodes. The electromechanically active polymer is what is known as an "ionomer" - a polymer which has ionic termination, typically on a side branch. Several commercially produced ionomers are available (e.g. Nafion from DuPont Inc., Flemion from Asahi Glass). Nafion is a modified PTFE (Teflon) with perfluorinated sulfonate anion side branches, and is typically produced in what is called "acid form," meaning that a proton is associated counter-ion to the sulfonate anions in the polymer side chains (Figure 2a). The standard approach to IPMC fabrication (Kim and Shahinpoor 2003) involves purchasing a solid membrane, and replacing the proton by another cation (e.g. Li^+) to improve actuation properties (Figure 2a).



(a)

(b)

Figure 2. (a) Structure of DuPont Nafion polymer; schematic exchange of cation (from H+ to Li+) to improve actuation; Rf is proprietary fluorinated group, (b) possible IPMC actuation mechanism: pressure differential from electric field driven ion and solvent motion (adapted from (Shahinpoor and Kim 2001), Figure 8).

The surfaces of the membrane are given metallic electrodes, typically by soaking in a platinum salt solution, then chemical reduction of the platinum salt to yield platinum nanoparticles in the outer few micrometers of the membrane. Platinum is the preferred metal because it is immune to corrosion over a larger range of electrochemical potential than other metals, and hence allows the use of higher driving voltages without damage. The isolated nanoparticles It appears to be essential to the actuation of the IPMC that these conductive particles be dispersed through a finite depth of the membrane in order to increase the depth of the electrostatic double-layers, and hence the fraction of the material which experiences the electric field (Nemat-Nasser and Li 2002). The platinum reduction is then often followed by a surface chemical- or electro-plating, typically with gold, to reduce the surface resistance of the electrodes. The bending of an IPMC in response to an applied electric field seems to result from a combination of mechanisms. These include the field-driven diffusion of cations and associated solvent (the anionic side groups on the polymer being immobile) causing an internal pressure gradient (Figure 2b), a change in electrostatic forces between the anionic side groups, and reorientation of the (polar) solvent molecules (Shahinpoor and Kim 2001; Nemat-Nasser and Li 2002). If the actuation signal is rapidly applied (e.g. a step), there is a rapid bending toward the negative electrode, followed by a slower relaxation back toward the positive electrode, resulting in a net motion toward the positive electrode. The fast processes are probably cation and solvent motion, electrostatic stiffness changes, polymer conformation, and solvent orientation related, while the slow process is probably solvent diffusing backward to equalize pressure through the material (Nemat-Nasser and Li 2002).

The differences in actuation mechanism for the two types of material have significant practical implications. One of the primary drawbacks of the mechanism of CP actuation for macroscopic actuation is the fact that the polymer changes volume only in proportion the actual volume of ions diffused into or out of the material (Baughman 1996; Benslimane, Gravesen et al. 2000; Bar-Cohen 2001; MacDiarmid 2001; Madden, Madden et al. 2001; Smela and Gadegaard 2001). Thus a very large current is required to actuate the material quickly, and the resistance of the materials to diffusive ionic flow makes rapid actuation inefficient. Ionomeric polymer-metal composite (IPMC) actuators are superior to CP actuators in this regard, actuating by non-diffusive as well as diffusive mechanisms (Nemat-Nasser and Li 2002; Nemat-Nasser and Wu 2003; Shahinpoor 2003). The charge density required to fully actuate a conducting polymer actuator is $>10^7$ C/m^3 (Madden, Madden et al. 2001; Madden, Vandesteeg et al. 2004), vs. $\sim10^6$ C/m^3 for IPMC actuators (Madden, Vandesteeg et al. 2004). Thus, at 1Hz operation, a 5cm by 2cm by 100μm CP actuator (10^{-7} m^3) requires >1A current to actuate, vs. 100mA or for an IPMC of same size. In mobile robotics and other power constrained applications this results in a very significant difference in the scale of the power storage or generation required, and the large thermal dissipation is undesirable in biomedical applications. Because a CP actuator is a capacitive structure, the electromechanical efficiency of CP actuators can be improved by recovering energy stored, but this requires much effort to reduce resistive losses in CP and associated electronics, and/or very slow actuator operation to be useful at the macroscopic scale. In any case, the electromechanical efficiency of CP actuators is in the vicinity of 0.1% without energy recovery, at least for polypyrrole, and could conceivably reach ~10% with perfect recovery and a restricted regime of actuation (Madden, Madden et al. 2001). By comparison, IPMC actuators are routinely achieving 1.5% efficiency (Shahinpoor and Kim 2001; Kim and Shahinpoor 2003), with significant gains possible through more careful control (Jung, Nam et al. 2003). IPMC devices are also capacitive, and subject to similar efficiency improvements via stored energy recovery. Given also that the achievable strains and stresses are roughly comparable for the two types (Madden, Vandesteeg et al. 2004), and that IPMC actuators can generate large scale motion at up to 100Hz (Nemat-Nasser and Wu 2003; Paquette and Kim 2004) in air, IPMC actuators are superior for rapid, power constrained, macroscopic actuation.

The main drawbacks to IPMC actuators, by comparison to CP, are a lack of a “no power catch-state” (Madden, Vandesteeg et al. 2004), in which the device maintains a given actuated strain with essentially no power input, and the fact that IPMC’s actuate strictly by bending, without volume change (Shahinpoor and Kim 2001; Nemat-Nasser and Li 2002). This last issue implies that adapting IPMC to linear actuation requires complex geometry or a mechanism of some sort. Certainly many applications exist for bending mode actuation (Jung, Tak et al. 2003; Kim, Ryu et al. 2003; Paquette and Kim 2004), and some commercialization of IPMC is underway, with biomedical devices such as heart-contraction assistance devices (Shahinpoor 2002), vision correction devices (Shahinpoor, Shahinpoor et al. 2003), intraocular pressure management devices for glaucoma management (Soltanpour 2001), a variety of biomedical micropumps (Soltanpour and Shahinpoor 2003; Soltanpour and Shahinpoor 2004), and toys (Ashley 2003) currently the target markets. The utility of linear actuation is difficult to argue against for most applications however, and the problem of manufacturing linearly actuating IPMC devices is starting to be addressed in the research literature (Kaneda, Kamamichi et al. 2003; Yamakita, Kamamichi et al. 2004). We believe that the geometric freedom and spatial control over material placement provided by freeform fabrication will enable the production of linear IPMC actuators that exceed the performance of the state of the art.

Experimental

The traditional approach to manufacturing IPMC described above is not readily adapted to freeform fabrication in that a prefabricated solid ionomer membrane must be chemically treated and metallized in several separate baths. Kim and Shahinpoor (Kim and Shahinpoor 2001) present a method of producing IPMC devices which involves Nafion ionomer membranes made by casting a liquid dispersion ("Liquid Nafion"). The authors note that the cast dispersion is very prone to cracking unless an additive (typically a low vapor pressure solvent) is added to the dispersion and solvent evaporation is gently performed. In addition, the resulting membrane must be annealed at elevated temperature in order to develop some crystallinity. Without annealing, the ionomer would remain soluble, and actuation (which requires the membrane to be saturated with solvent) would not be possible. This "solution recasting" method permits the thickness of the membrane to be customized to the actuator application, and the authors present a 2mm thick IPMC which demonstrates the significant output force increase which is possible. Note that this device is still given surface electrodes via metal reduction and plating methods. The authors suggest (but do not report results from) a method of producing the electrodes and the membrane entirely by casting stacked layers, where the electrode layers would be cast from an ionomer dispersion with suspended metal particles. This method would permit freeform fabrication of complete IPMC devices, and was taken as the starting point for the present efforts.

Initial Formulation and Hand-Made IPMC

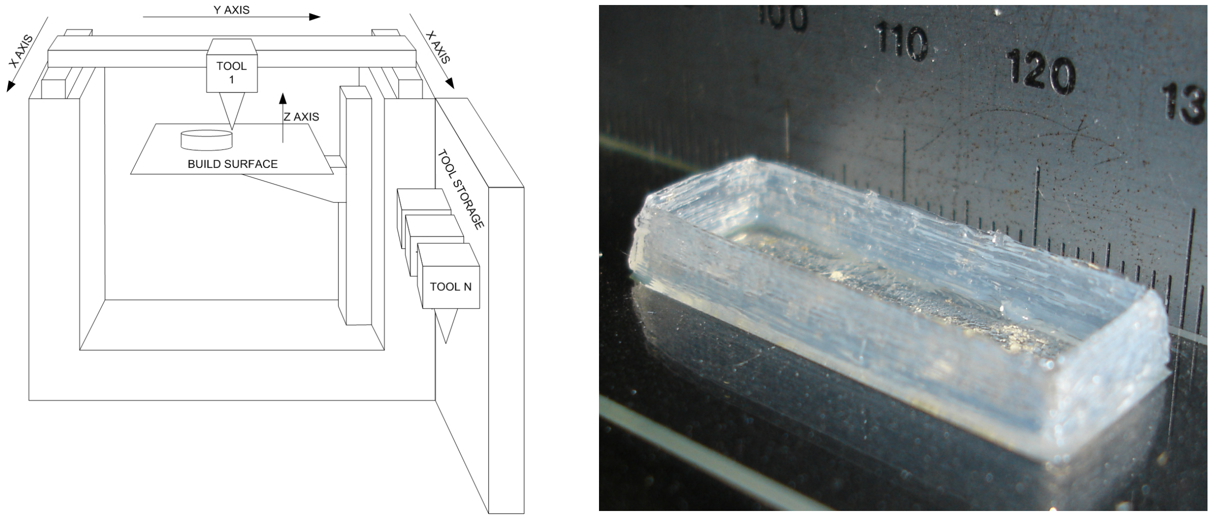
We performed an initial set of experiments which was intended to culminate in the production of a working IPMC by hand via the stacked casting method described above. 5wt% H^+ Nafion dispersion in mixed alcohol and water (Sigma Aldrich prod. # 527084) was used as the ionomer, and an initial electrode material consisted of silver powder (99.9%, 1-3μm particles) mixed in the ionomer dispersion. Silver is used in these experiments as a lower cost alternative to platinum. An annealing schedule of 45 minutes at 70C in air was found to eliminate solubility of the ionomer without causing brittleness from too high a degree of crystallinity. Casting the neat ionomer alone atop a PTFE substrate revealed that good films of at least 250um can be formed without cracking and without the addition of any additives. When cast atop a dried film of the electrode material, however, two problems occurred: firstly, the dried ionomer in the electrode layer is highly hydrophobic, and causes subsequently deposited ionomer to migrate, bead up, and crack upon drying, and secondly, the dried electrode layer (whether annealed or not) absorbs solvent from the newly applied ionomer, causing swelling, buckling and cracking of both materials. It was found that the addition of a non-ionic surfactant (DuPont Zonyl FSO-100) in a low concentration (~ 2 wt%) to the electrode material increased the affinity of the electrode material sufficiently to remove the first problem. The second problem can be minimized by deposition of subsequent layers atop prior layers that have not completely dried. This complicates the deposition of the upper electrode layer in that the suspended silver particles tend to settle during drying, and can penetrate the neat Nafion layer, causing internal electrical shorting of the finished IPMC. Careful timing and control of the deposited quantity of electrode material reduces but does not eliminate this problem.

We made several 1cm by 3cm by ~0.250um IPMC actuators by manual deposition onto a PTFE substrate and annealing as mentioned above. The devices were soaked in deionized water, for 30 minutes, and then peeled from the substrate with tweezers. The actuation of these in air was verified qualitatively under 1.5V stimulus by videography, confirming that the deposited electrode concept suggested by Kim and Shahinpoor (Kim and Shahinpoor 2001), is at least feasible.

Unfortunately, the devices are limited to only a few actuation cycles in air because of solvent loss through the surfaces and progressive development of internal electrical shorting – perhaps through migration of silver particles, or because the internal ionomer layer is too thin or flawed. In addition, the materials as formulated above, and the process described are not completely satisfactory for automated freeform fabrication. The silver particles in the electrode material settle out of suspension very quickly making the material difficult to dispense. Some means of confining the deposited liquids is required to allow freeform fabrication of an IPMC in an arbitrary two dimensional shape, and ideally this confinement should allow the actuator to be fabricated as an embedded component of a larger freeform fabricated device.

Containment, and Reformulation for Freeform Fabrication

Our second series of experiments focused on developing a means of freeform fabricating a container into which the IPMC materials can be cast, and on modifying the electrode material formulation to improve dispensability. One of the materials that we have successfully employed for freeform fabrication is poly(dimethylsiloxane) or PDMS, also known as silicone. This material is very chemically inert, thermally stable to over 200C, we can routinely achieve 500μm resolution when fabricating structures with it, and can deposit it with good control on most of the other materials that our system employs. Rectangular silicone wells (Figure 3b), with 1cm by 3cm by 2-5mm internal dimensions were deposited onto glass microscope slides for use as containers for IPMC fabrication. We cast several actuators into these by hand to verify their compatibility with the existing materials and process. We observed that the neat ionomer dispersion has a higher affinity for the silicone than for the electrode material, and there is a tendency for the ionomer to seep under the lower electrode, and also to be drawn toward the boundaries of the well. This apparently produces stresses in the film as it dries, leading to cracking. Adding more surfactant to the electrode material exacerbates the seepage problem such that the electrode becomes surrounded by ionomer, and electrically insulated. We added a low-vapor pressure solvent (N-N-dimethylformamide, DMF) to the ionomer dispersion to help control cracking. At 33wt% of DMF and above, the cracking problem was eliminated, at the cost of greatly increased drying time. We modified the electrode material to be more readily dispensed by mixing in a quantity of carbon black powder along with the surfactant and silver powder in the ionomer dispersion.



(a) (b)

Figure 3. (a) Schematic of multiple material freeform fabrication system with Cartesian gantry positioning system and multiple changeable deposition tools, (b) a freeform fabricated silicone well.

This results in a stable slurry, referred to as Electrode Material 6 (EM6), which can be dispensed from a 0.5mm ID syringe needle without clogging. A four-probe measurement technique was used to obtain the resistivity of this material; the values for pure silver, carbon, and platinum are provided for reference.

Table I. Formulation and Resistivity of Electrode Material 6

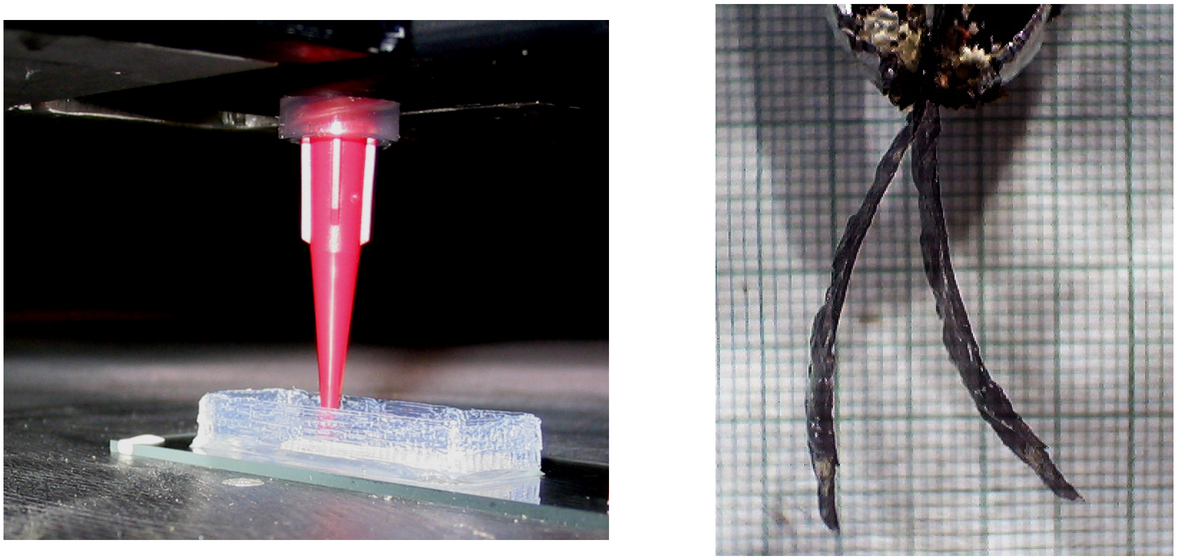
Material	**Value**	**Units**
Ag Powder, 99.9%, 1-3um	20	wt%
H^+ 5wt% Nafion Dispersion	70	wt%
DuPont Zonyl FSO-100 Surfactant	2	wt%
Carbon black	8	wt%
Resistivity	**Value**	**Units**
EM6 (3 samples, 4-probe method)	3.85(± 3.76) E-03	Ω cm
Silver, pure solid (Matweb 2005)	1.77E-06	Ω cm
Carbon, graphite (Matweb 2005)	6E-03	Ω cm
Platinum, pure solid (Matweb 2005)	1.06E-05	Ω cm

In order to be able to deposit liquid materials precisely into the silicone well, we extended the manufacturing planning software of our fabrication system to allow structurally constrained prioritization of deposition, which we term “backfill deposition”. As parts of a multiple material assembly are imported into the software, they can be assigned a sequential priority for fabrication. This priority will be obeyed by the system except where doing so would violate the relationship of one part supporting another. Thus the silicone well can be given a higher priority than the materials to be deposited into it, and it will be completely fabricated to its full height before the deposition of the first electrode layer begins (Figure 4a). This greatly improves the quality of cast materials by allowing the deposition nozzle to be at its optimal height above the layer beneath.

We deposited the reformulated materials with the freeform fabrication system to produce working IPMC devices in the following sequence:

1. A silicone well is deposited onto a glass slide
2. A layer of electrode material is backfilled into the well and allowed to dry until the surface begins to appear matte.
3. The well is backfilled with ionomer dispersion (with DMF additive) and allowed to dry until the surface does not flow.
4. The upper electrode material is deposited and allowed to air dry
5. The glass slide is placed in an oven and annealed at 70C for 45minutes
6. The silicone well is filled with deionized water for 30 minutes to saturate the IPMC
7. The device is lifted from the well with tweezers and tested

The actuation of these devices was verified qualitatively by videography as before (Figure 4). Once again, the devices suffer from internal shorting, and have a very short service life in air– typically only 2 or 3 actuation cycles. Nevertheless, these are the first completely freeform fabricated IPMC actuators.



(a) (b)

Figure 4. (a) "Backfill deposition" of electrode layer into silicone well. (b) Two superposed frames from video of actuation test of freeform fabricated IPMC. In air, 1.5V step, elapsed time 5s.

Reformulation for Improved Lifetime and Efficiency

In a third sequence of experiments, we have focused on improving the service life and reducing the input power requirements (internal shorting) of freeform fabricated IPMC actuators. It is our experience that the primary limitations on the service life of IPMC in air are the loss of solvent, corrosion of the electrodes, and progressive electrical shorting. As described above, the IPMC actuation mechanism involves, in part, the generation of an internal pressure gradient by the electrophoretic transport of ions and solvent. This pressure gradient drives solvent out through the porous electrodes. Given time it can be reabsorbed into the actuator (Nemat-Nasser and Li 2002), but while on the surface it is likely to be lost to evaporation, dripping, or contact transfer. Internal shorting causes resistive Joule heating which increases solvent evaporation. It has also been noted (Kim and Shahinpoor 2003) that solvent leakage probably also reduces the maximum achievable force output from the actuator by limiting the internal pressure gradient that can be maintained.

In order to reduce the rate of solvent loss, we have explored the use of impermeable electrode materials which can trap the solvent inside of the IPMC. There are several essential requirements that such a material must meet:

- Low modulus of elasticity
- Low electrical resistivity
- Solvent (water) impermeability
- Chemically inert to other IPMC materials
- Good adhesion to other IPMC materials
- Easily deposited

The impermeable material is intended to serve as a surface coating to the silver-filled ionomer electrode layers. As mentioned above, some conductive particle penetration into the membrane is essential to the actuation of IPMC.

We performed a set of experiments involving 13 candidate materials in order to arrive at a material which satisfactorily meets all of these requirements. The concept we employed in developing these materials was to form a composite of metal particles embedded in a hydrophobic and/or impermeable elastomer matrix. The matrix provides the solvent barrier and low modulus, while the metal particles reduce electrical resistivity of the polymer. If the elastomer is a thermoplastic, then dispensability is achieved by dissolving the material in an organic solvent which is compatible with the other IPMC materials, or the material could be melted and extruded. If it is thermosetting, then one-part, room-temperature vulcanizing (RTV) materials are preferred so that elevated temperature curing and crosslinking agents are not required.

The 13 materials explored employed one of two elastomers - silicone and “Hydrin”. The majority of metal-filled silicone formulations that we explored failed to achieve reasonable electrical resistivity, and were rejected. A silver-filled RTV silicone (SS-26, Silicone Solutions Inc.) has acceptable resistivity. Unfortunately, it is stiff from the high concentration of metal particles, and does not adhere well to the other IPMC materials - IPMC’s produced with it delaminate immediately.

We found Hydrin C thermoplastic (poly(epichlorohydrin-co-ethylene oxide), Zeon Chemicals L.P.) to be a reasonably good elastomer for this application. Low resistivity is achieved without dramatic increase in stiffness, it is hydrophobic but soluble in several common solvents including toluene, acetone, and DMF, and it adheres well to the IPMC materials. The main drawback to the material is a somewhat higher permeability to water vapor than some alternatives (Table II).

Table II. Properties of some candidate elastomer materials

Elastomer	Water Vapor Transmission Rate at 38C (g/(m^2 * 24h))	Tensile Modulus, 25C, 100% Strain (MPa)	Tensile Strength (MPa)	Shore A Hardness
Hydrin C ("Epichlorohydrin Elastomers: Hydrin ECO" 2005)	85.87	3.1	13.2	85
Butyl Rubber (Gauthier 1995)	0.217	0.3-3.4	13.8	30-100
EPDM Rubber (Gauthier 1995)	6.045	0.7-20.7	3.4-24.1	30-90

Suspending 1-3μm silver particles in dissolved Hydrin is difficult. A commercial "flexible silver ink" (EP403920-50, SRA Inc.), which uses specialty polymers to suspend the particles without adversely affecting the conductivity was found to form a good alloy with Hydrin. Both materials are soluble in toluene, which evaporates quickly and does not attack the ionomer. The addition of surfactant was again necessary to preventing migration and cracking of subsequent layers cast atop this material. Table III presents our best formulation, referred to as Electrode Material 19 (EM19), its resistivity and that of some reference materials.

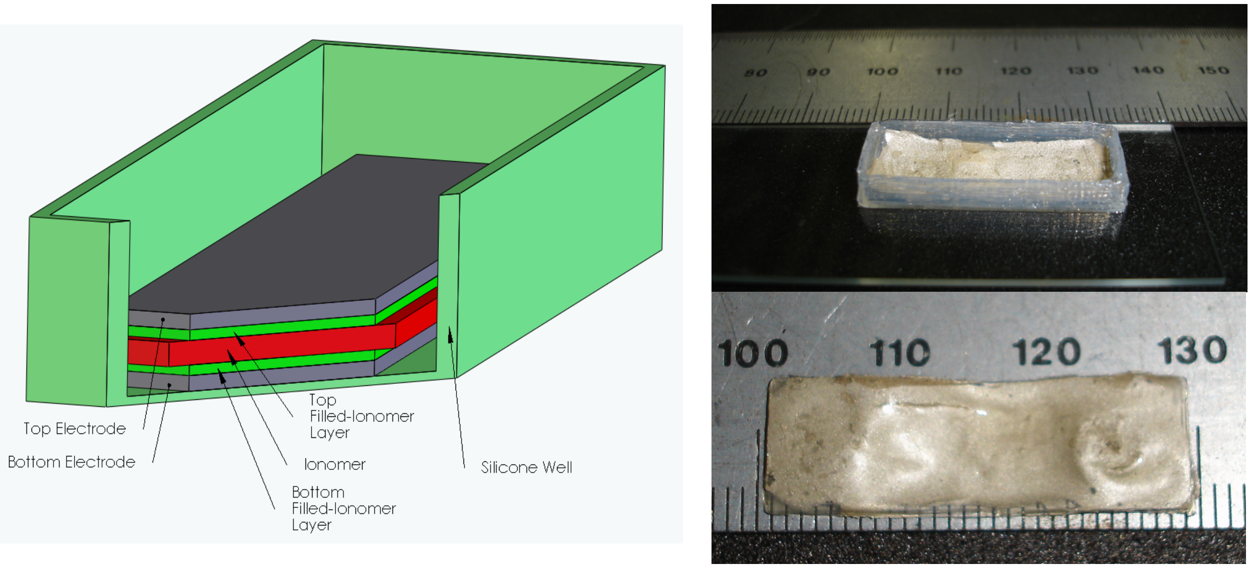
Table III. Formulation and Resistivity of Electrode Material 19

Material	Value	Units
Zeon Chemicals L.P. Hydrin C Elastomer	6	wt%
Toluene	72	wt%
SRA Inc. EP403920-50 Flexible Silver Ink	20	wt%
DuPont Zonyl FSO-100 Surfactant	2	wt%
Resistivity	**Value**	**Units**
EM19 (3 samples, 4-probe method)	6.96(± 0.96) E-03	Ω cm
Silver, pure solid (Matweb 2005)	1.77E-06	Ω cm
SRA Inc. EP403920-50 Flexible Silver Ink (Stan-Rubenstein-Associates 2005)	1E-04	Ω cm
Silicone Solutions Inc. SS-26 Silver-filled RTV (Silicone-Solutions-Inc. 2005)	5E-03	Ω cm

We have dealt with the internal shorting problems by increasing the thickness of the neat ionomer layer. Thus a larger volume of liquid Nafion must be deposited and the drying time (especially given the low vapor pressure of the DMF additive) is very long. We employ a more concentrated ionomer dispersion to mitigate this. Switching to 20wt% H$^+$ Nafion dispersion (Sigma-Aldrich prod. # 527122) requires increasing the amount of DMF added up to 50% by weight to prevent cracking, but still results in greatly reduced time for evaporation. We modified the freeform fabrication process to employ these materials:

1. A silicone well is deposited onto a glass slide.
2. A layer of EM19 electrode material is deposited into the well and allowed to dry completely.
3. A layer of EM6 electrode material is deposited into the well and allowed to dry until matte in appearance.
4. The well is backfilled to the top with ionomer dispersion (with DMF additive) and allowed to dry until the surface does not flow.
5. Repeat step 3.
6. Repeat step 2.
7. The glass slide is placed in an oven and annealed at 70C for 45minutes.
8. The silicone well is filled with deionized water for 30 minutes to saturate the IPMC.
9. The device is lifted from the well with tweezers and tested.

Figure 5 shows the CAD model of the devices that we produced with our fabrication system, and the appearance of a finished device.



(a)

(b)

Figure 5. Freeform fabricated 5-layer IPMC, (a) cutaway of CAD model showing layer sequence, (b) IPMC in its well (top), and after hydration and removal (bottom).

Apparatus

To provide more quantitative testing of the performance of the IPMC devices being produced, we developed a test apparatus (Figure 6) which interfaces with a PC-based data acquisition system (IOTech DAQBoard 2000, running DASYLab DAQ software). This apparatus allows the application of a controlled voltage waveform to the actuator, while simultaneously collecting applied voltage, current, and force output by the actuator. The actuator is clamped on one end to a 12g counterweight which rests atop a laboratory scale with a 5mg resolution (ADAM ACB Plus-150). The other end of the actuator is held in a spring clamp, the tips of which form isolated electrical contacts. The spring clamp is held in a laboratory ring stand. A power operational amplifier receives a voltage command from the DAQ system, and attempts to maintain this voltage across the actuator electrodes by applying a current to the actuator via the spring clamp contacts. The applied current is sensed by the data acquisition system by analog to digital (A/D) conversion of the voltage drop across a current sensing resistor in the current path. The actual voltage achieved by the amplifier is also measured by A/D at the output of the amplifier. The force output is sensed by the scale, which streams readings via serial communications at about 40Hz to the DAQ system.

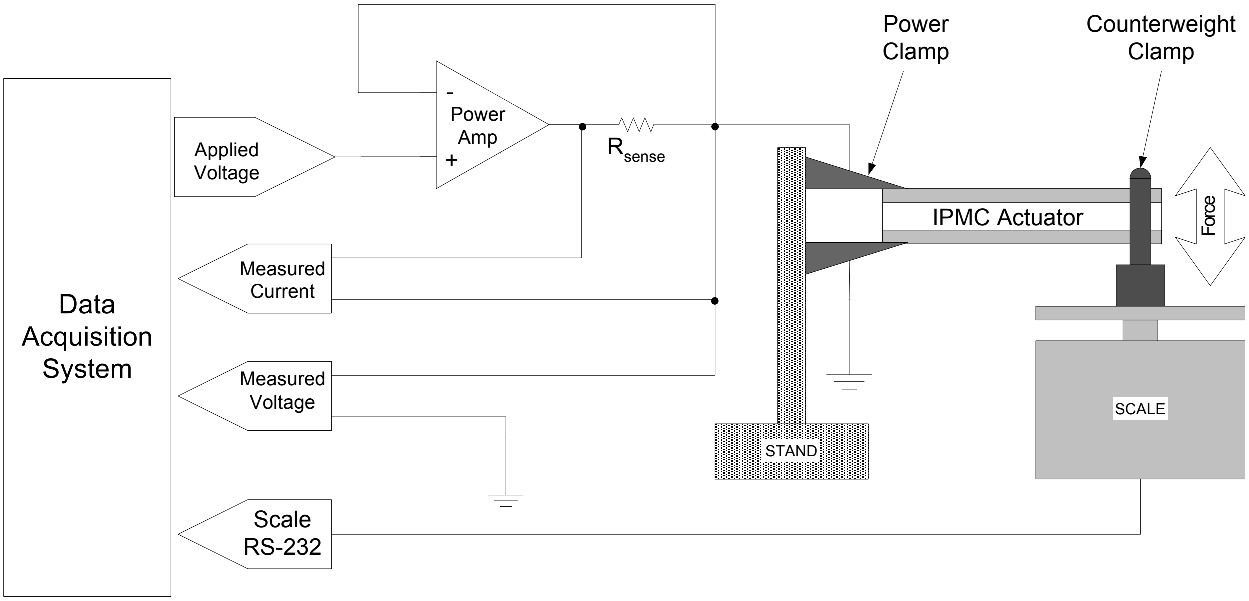


Figure 6. Schematic of test apparatus for acquiring force output, voltage, and current versus time.

The simultaneous collection of these data allows us to calculate applied power, measure cycle life, and correlate applied signals with force output.

Results

We have tested several 5-layer freeform fabricated devices using the above apparatus. There is a large variation in the output force from cycle to cycle, and the power delivered to the devices is very noisy (see Figure 7). This latter effect is probably a result of the particulate nature of the conductive phases of the electrode materials making and breaking conductive paths as the device bends and solvent migrates. A discrete Fourier transform of the input and output signals clearly demonstrates correlation. At this time, all testing takes place with a 0.1Hz, 1.5V square wave applied signal, and the output dynamic force can be seen to peak strongly at this frequency and its harmonics (Figure 8). In order to extract the maximum blocked force for each cycle in the large datasets, peaks in the force data are automatically identified using the zeros of the first difference of the force data. Figure 9 provides a detail of the results of this algorithm. Our highest performance device achieved more than 250 (bi-directional actuation, 513 total peaks) cycles in air, operating continuously without rehydration for about 40 minutes.

Its maximum blocked force was 0.678mN, and average of peak blocking force over the entire testing period was 0.150 (+/-0.130)mN. The RMS power delivered to the actuator was 9.4mW. Table IV presents these results in comparison to some of the best results published for IPMC actuators produced by any means.

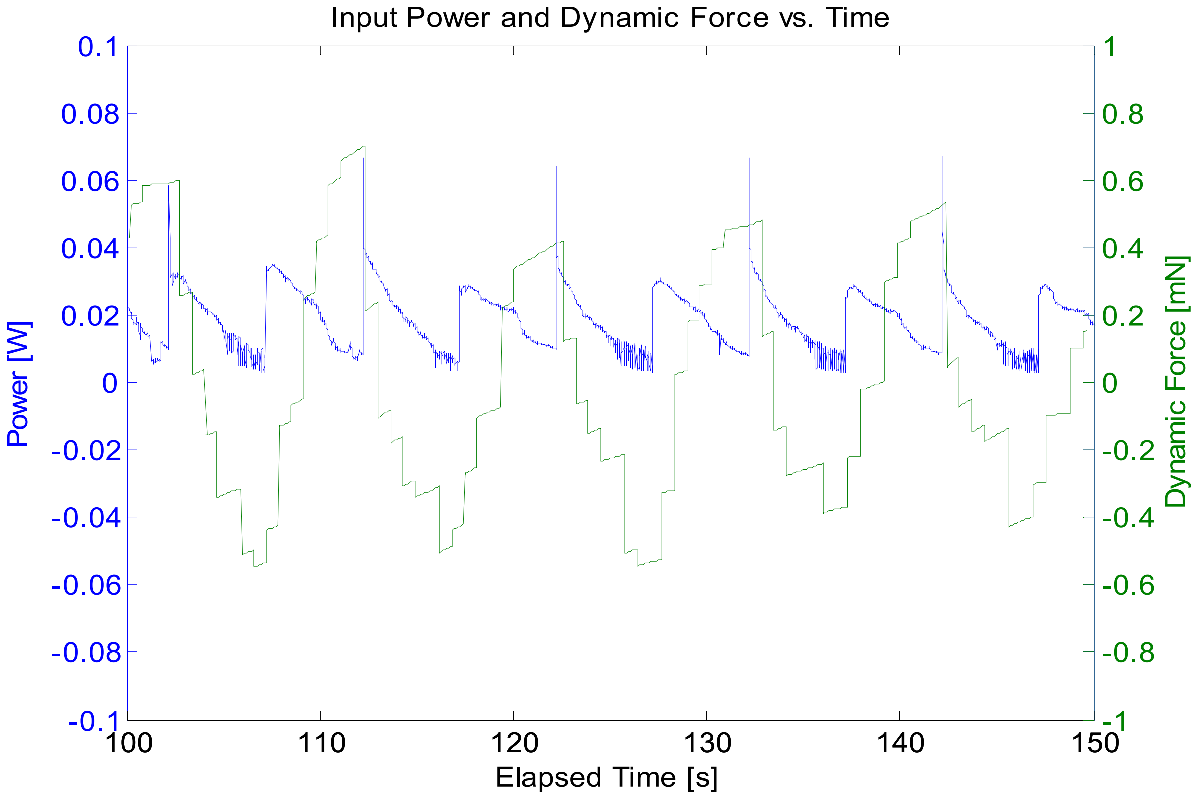


Figure 7. Detail of force and consumed power vs. time for best freeform fabricated IPMC

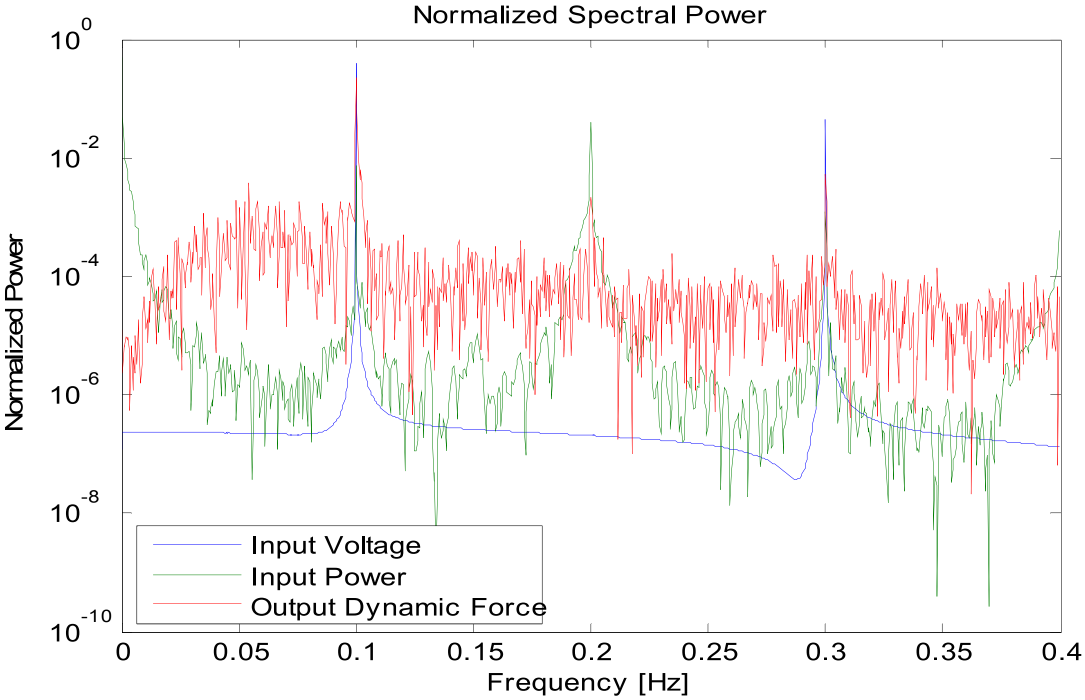


Figure 8. Normalized DFT power spectrum of inputs and output for best freeform fabricated IPMC

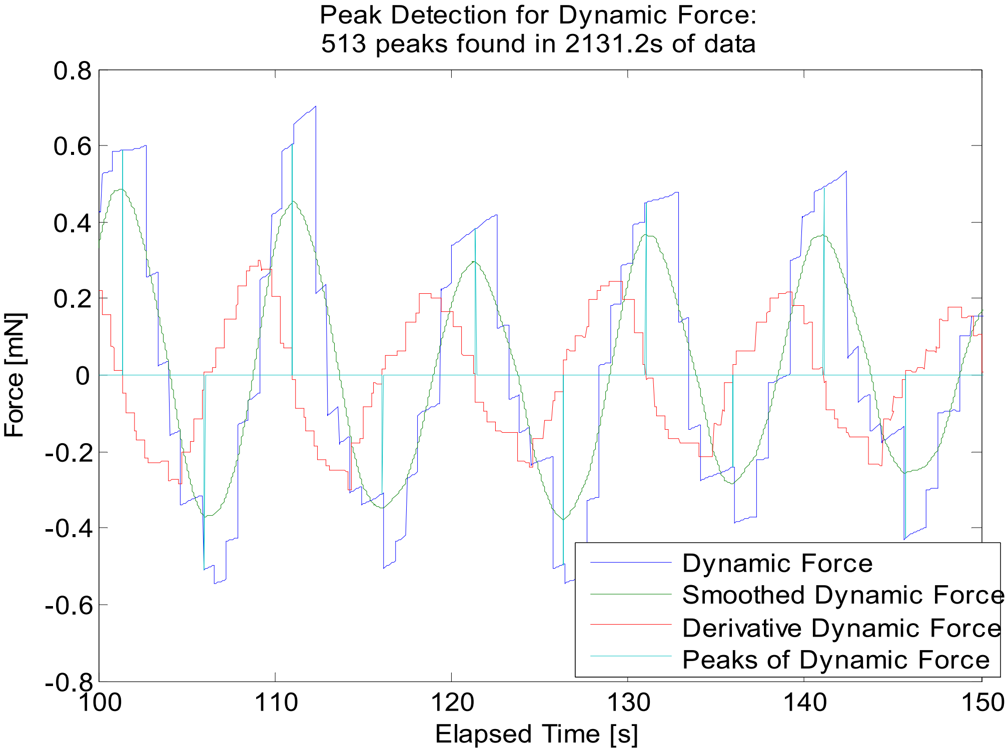


Figure 9. Detail of automatic peak detection data for peak force statistics of best freeform fabricated IPMC

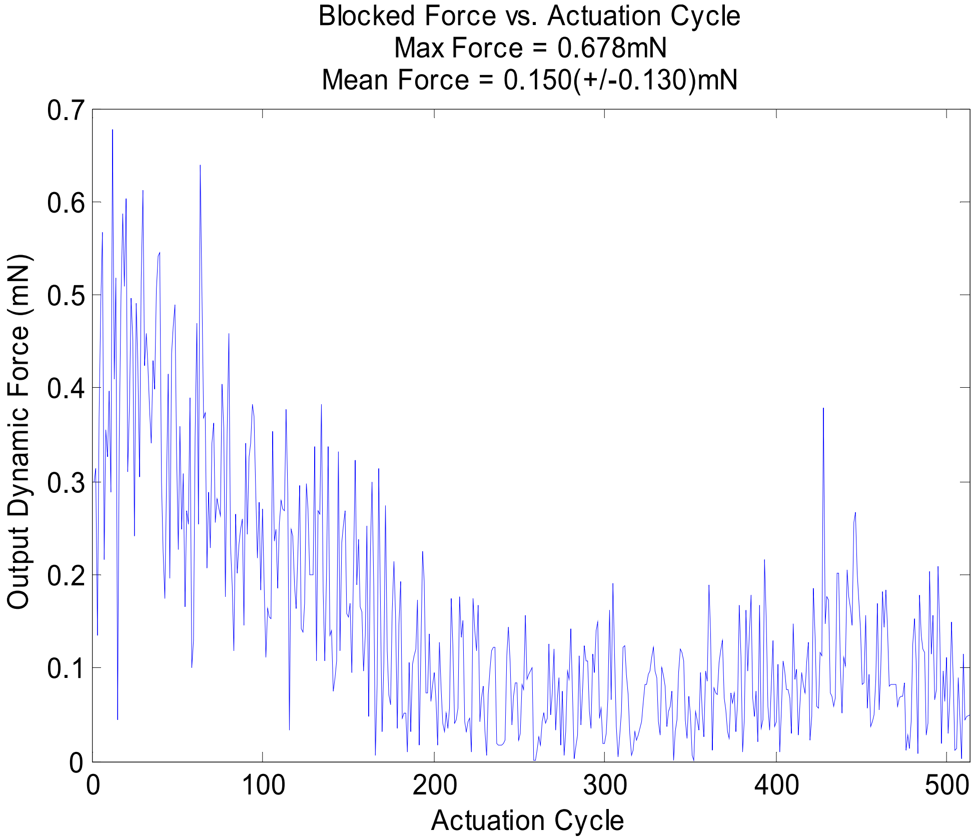


Figure 10. Variation in blocked force versus actuation cycle for best freeform fabricated IPMC

Table IV. Comparison of performance of freeform fabricated IPMC to other published IMPC results

Type	Dimensions	Test Conditions	Force (mN)	Est. Shear Stress (MPa)	Est. Shear Stress/Power (MPa/W)[1]
Freeform fabricated H^+ Nafion IPMC	20mm by 9mm by 1mm	1.5V, 0.1Hz square	0.678	1.5E-03	1.6E-01
Recast Li^+ Nafion IPMC, standard Pt/Au(Kim and Shahinpoor 2002)	15mm by 5mm by 2mm	2V, 0.5 Hz square	60	4.5E-02	9.0E-01
Standard Li^+ Nafion IPMC, standard Pt/Au (Shahinpoor and Kim 2001)	20mm by 5mm by 0.2mm	1V, 0.5Hz square	16	1.6	6.4E+01
Stretched Li^+ Nafion IPMC, standard Pt/Au (Kim and Shahinpoor 2003)	10mm by 5mm by 0.2mm	1.5V, 0.5Hz square	60	3.0	8.0E+01

Discussion

As presented in Table IV, the best reported blocked forces (fourth row) are nearly 100 times higher than those of our freeform fabricated device. Scaling to shear stress per unit power increases this gap to a humbling 500 times, but interestingly, the "recast" IPMC (second row) is merely 5.62 times better than our freeform fabricated IPMC in this measurement. The recast IPMC was made by casting the ionomer membrane from liquid dispersion, followed by traditional platinum and gold electroding (Kim and Shahinpoor 2002). The similarly poor performance of the devices made with liquid ionomer dispersions suggests that some microstructural traits of a cast membrane make it inferior (for actuation) to the commercially produced ones. Kim and Shahinpoor (Kim and Shahinpoor 2002) report that passive tensile stress/strain behavior is different for cast and commercial membranes. DuPont produces Nafion membranes both by casting and by extrusion – unfortunately the type used is never mentioned in the literature. It should also be noted that the freeform fabricated devices are using H^+ as the counter-ion in the ionomer for simplicity; it is well documented (Kim and Shahinpoor 2003) that use of other counter-ions can improve blocked force by 2-3 times, suggesting that the remaining deficit may be accounted thusly.

Future Work

As mentioned above, all of the above experiments have, for simplicity, made use of Nafion ionomer dispersion as purchased, in what is referred to as the "acid form" - that is with a proton as the counter ion which is associated with the anionic side chains of the ionomer (Figure 2a). As has been observed in the literature (Nemat-Nasser and Li 2002; Kim and Shahinpoor 2003), the force output of IPMC actuators is dramatically affected by the choice of counter ion, with Li^+ offering perhaps more than 2.5-fold increase in force over H^+. We have already tested a convenient method of converting the counter ion to Li^+ by the simple addition of LiOH to the ionomer dispersion, and are in the process of investigating the effects of this change on the other

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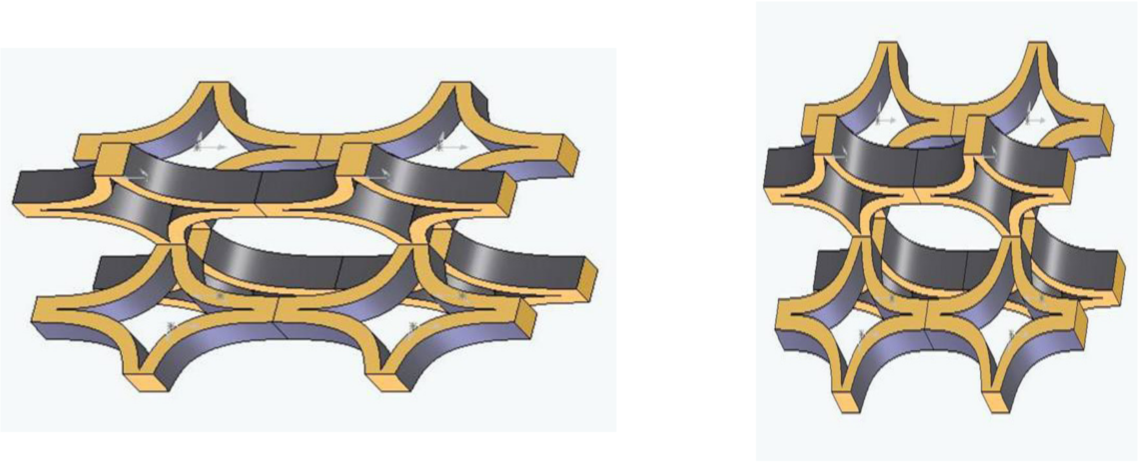
[1] The referenced literature does not contain simultaneous data for force and power, nor for force, voltage and current. We have used selected 25mA as a reasonable average current based on Kim and Shahinpoor 2003, Figures 11-13.

materials and the manufacturing process. Several other modifications may also yield large improvements in performance, including reducing the size of conductive particles used in Electrode Material 6 to the nanometer level (Kim and Shahinpoor 2001), forming a nanocomposite of the ionomer with Montmorillionite clay particles (Paquette, Kim et al. 2003), and using a lower modulus, more vapor impermeable elastomer in Electrode Material 19. Achieving truly three dimensional actuators will require modifying the materials to achieve very rapid drying and thin layers out of the horizontal plane. Figure 11 presents a concept for a three dimensional actuator geometry which would produce linear actuation.



(a) (b)

Figure 11. Concept of 3-dimensional IPMC geometry which converts bending motion to linear motion, (a) relaxed, (b) contracted.

It is our aim to approach the performance of conventionally produced IPMC's, and then to exploit the geometric control afforded by freeform fabrication to develop IPMC designs which are customized for applications and integrated with devices to a degree not otherwise possible.

Conclusion

In the quest to develop a complete library of functional electromechanical elements which can be freeform fabricated and are mutually compatible, we have been investigating electromechanically active materials. Ionomeric Polymer-Metal Composite materials have been selected as the most compatible with our fabrication system, with the freeform fabricated functional elements that we already produce, and with the goal of producing actuation suitable for biomedical devices and bio-inspired robotics. We have developed new material formulations and manufacturing processes which have allowed us to produce the first ever completely freeform fabricated IPMC actuators. The performance of these devices has been quantitatively measured. We have presented the first cycle life measurements for in-air operation of an IPMC. The output blocked force measured is inferior to that produced by IPMC devices produced in the standard manner, but we are in the process of incorporating materials modifications (e.g. conversion of the ionomer to Li^+ form) which are well-known to produce multifold increases in force output. The freeform fabrication process developed includes the fabrication of wells to contain the liquid active materials during their casting. In that these wells can be deposited at an arbitrary location, atop almost any other material, this represents a major step toward fabricating actuators as integral components of complete, freeform fabricated electromechanical devices.

Acknowledgments

This work was supported in parts by the U.S. Department of Energy, grant DE-FG02-01ER45902.

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