Freeform Fabrication of Electroactive Polymer Actuators and Electromechanical Devices

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Abstract
In pursuit of the goal of producing complete electromechanical systems entirely via solid freeform fabrication, we are developing a library of mutually compatible, functional, freeform elements. Several essential elements – actuation, sensing, and control electronics - still remain to be incorporated into this library. Conducting polymers (CP) are a class of materials which can be used to produce all of these functionalities. Meanwhile, research into actutable “smart” materials has produced other candidate materials for freeform fabricated actuators that are compatible with our library. We have succeeded in manually producing air-operable actuators that have processing and operating requirements that are compatible with our power source and mechanical component library elements. A survey of candidate actuator materials is presented, experiments performed with two types of actuator materials are described, and complete SFF-producible actuator devices are demonstrated.

Introduction
Imagine a compact fabrication system which could print out a complete working device, including power sources, electronics, actuators, sensors, and mechanical components, even biological materials, in almost any geometry and interconnection. The devices produced would not appear the same or operate on the same principles as devices built from mass produced components. Whole new classes of unforeseen functional devices and products would be likely to emerge from the ability of such a tool to decouple geometry and functionality to a greater extent than ever before. There are different sets of mutually compatible materials and processes which might be used to create such a library and a system. We have chosen to focus primarily on polymers, and low temperature (<300C) processes. We have also limited our system to liquid state processes, either through fused deposition, or robotic dispensing from syringe. Within these restrictions, we have been working steadily to add new freeform functionalities while continuing to improve the quality, performance, and geometry independence of the batteries, structures, joints and wiring already within the library (Malone, Rasa et al. 2004). It is the goal of the current work to add the functionality of actuation to this library. Actuator materials have been identified which are amenable to our freeform fabrication processes, and actuator designs have been successfully demonstrated which can be freeform fabricated with and can operate in concert with the other functionalities.

Actuator materials
In the interest of producing biomimetic robotics and smart structures, and for medical applications, there is significant research into electromechanically active materials – materials which change shape, volume, modulus, or some other mechanical property in response to some kind of controllable signal. The number of such actuator materials is increasing quickly and the field of research is building momentum. The majority of materials investigated still require very specialized processing which prevents them from being cofabricated with other functionalities.
Nevertheless, several types of actutable materials exist which may be compatible with our processing regime (Table 1).

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Actuation Signal</th>
<th>Actuation Strain (%)</th>
<th>Actuation Stress (MPa)</th>
<th>Actuation Bandwidth (Hz)</th>
<th>Electro-mechanical Efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>1V</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>0.1</td>
<td>(Madden, Madden et al. 2001; Smela 2003)</td>
</tr>
<tr>
<td>Pi-stacking</td>
<td>10V</td>
<td>20</td>
<td>&lt;321 (theoretical)</td>
<td>&lt; 66 (theoretical)</td>
<td></td>
<td>(Anquetil, Yu et al. 2002)</td>
</tr>
<tr>
<td>IPMC</td>
<td>2V</td>
<td>bending</td>
<td>10</td>
<td></td>
<td></td>
<td>(Shahinpoor and Kim 2001)</td>
</tr>
<tr>
<td>Dielectric elastomer</td>
<td>&gt;50V/um</td>
<td>&gt;100</td>
<td>0.1-7</td>
<td>20k</td>
<td>&gt;80 (theoretical)</td>
<td>(Pelrine, Kornbluh et al. 2000)</td>
</tr>
<tr>
<td>Ferroelectric (piezoelectric) polymer</td>
<td>&gt;10V/um</td>
<td>2</td>
<td>16</td>
<td>&gt;1k</td>
<td></td>
<td>(Zhang, Li et al. 2002)</td>
</tr>
<tr>
<td>Liquid-crystal elastomer</td>
<td>thermal (80C-100C)</td>
<td>40</td>
<td>0.2</td>
<td>10</td>
<td></td>
<td>(Thomsen, Keller et al. 2001)</td>
</tr>
<tr>
<td>Hydrogel</td>
<td>3V</td>
<td>&gt;10</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td>(Liu and Calvert 2000)</td>
</tr>
<tr>
<td>Nanotube mat</td>
<td>1.2</td>
<td>0.04</td>
<td>&gt;10</td>
<td>&gt;1k</td>
<td></td>
<td>(Baughman, Cui et al. 1999; Lewis, Kim et al. 2000; Spinks, Wallace et al. 2001)</td>
</tr>
</tbody>
</table>

Given that it is our goal to produce a library of mutually compatible functionalities, there are some further constraints on the choice of materials and actuator implementations.

1. We desire that the actuator provide useful output using only power provided by Zn-air batteries which we can produce. The baseline performance of our 5g (active materials) cells is about 10mW at 1V continuous output for >50 hours. Although we currently lack the ability to fabricate electronics to perform voltage level conversion, we can conceive of placing a few cells in series and/or in parallel to meet power requirements. Dissipation within the cells will likely limit series multi-cell battery output to < 10V – mass may limit the number of cells in parallel, depending on the desired end product (e.g. a mobile robot). Hence we require that useful actuation can be achieved at 10V or below.

2. The mechanical components that we can currently produce are of relatively low stiffness, so for efficiency of mechanical coupling, we prefer actuator materials which have large strain output to those that high stress output, but low strain.

3. We require that the actuator operate in air, under ambient conditions.

Referring to Table 1 above, these requirements allow us to eliminate several of the candidate material types.

- Pi-stacking material films are currently only produced electrochemically, so no obvious route to freeform fabrication yet exists.
- Dielectric elastomers are very attractive electromechanically, but the high actuation field would require producing and electrically and mechanically coupling to elastomer films as thin as 200nm, which seems extremely daunting given our fabrication processes.
- Piezoelectric polymers require high fields (very thin films), and typically require some solid-state processing (poling) to become electromechanically active.
• Liquid crystal elastomers are thermally actuated, and although this could be achieved through resistive heating, the additional complication and likely low efficiency make them less appealing.

• Hydrogels have been produced via ink-jet (Yoshioka and Calvert 2001), but are delicate materials, slow to actuate, and suffer limited active life because of dehydration and leakage during actuation.

• Nanotube mats have very high stress output and efficiency, operate at low voltage, but have low strain output.

We have explored the remaining two material types, CP and IPMC in greater detail.

**Conducting Polymer Actuators**

Conducting polymers are long chain organic molecules in which successive carbon atoms along the axis of the chain are bound alternately by one shared electron pair (single, or $\sigma$-bond) and by two shared electron pairs (double, or $\pi$-bond). Like most organic polymers, CP’s are normally poor electrical conductors. By adding or removing electrons from the CP chains, and embedding positive or negative ions, respectively, into the chains to maintain electrical neutrality, it is possible to make the locations of the $\pi$-bonds less well defined (MacDiarmid 2001).

Classically speaking, this allows some of the electrons more freedom to move from atom to atom, increasing electrical conductivity. Through this process known as redox doping, the conductivity of CP’s can be varied continuously from insulating to semi-conducting to metallic. This allows the fabrication in CP of many of the electronic devices currently made with doped silicon. Conducting polymers change their volume when redox doping occurs. If the CP is placed in contact with an electrolyte (salt solution with free ions) and an electrical potential is applied between the polymer and another electrode immersed in 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). The amount, rate, and polarity of the volume change depend on specific sizes and charges of the dopant ions and the electrolyte solvent used. Actuator applications of conducting polymers to date have been restricted primarily to planar (Sansiñena, Olazábal et al. 1997; Madden, Cush et al. 1999; Madden, Madden et al. 2001) and tubular (Hutchison, Lewis et al. 2000; Ding, Liu et al. 2003) thin-film devices made from polypyrrole (PPy) and polyaniline (PA), which seem to demonstrate the best combinations of mechanical strength, actuation stress, and actuation strain. Thin films minimize the time required for ions to diffuse into/out of the actuator, yielding more rapid actuation. State of the art performance for polypyrrole is 30-50MPa strength, 4MPa actuation stress, and 2.4% strain for

![Figure 1. Illustration of the conformational change in a CP caused by ion diffusion. Conformational change results in volume change and mechanical actuation.](image-url)
long life, in-plane linear actuation of a thin (~10µm) polypyrrole film immersed in a liquid electrolyte (Madden, Madden et al. 2001). Small strain responses are observable at frequencies > 30Hz. There is some indication that out of plane actuation strains of 30% or more are achievable (Smela and Gadegaard 2001), and there is some preliminary work on novel actuator device geometries which might exploit this large strain (Della Santa, De Rossi et al. 1997). Unfortunately, practical electromechanical efficiency is currently < 1%, although Madden (Madden, Madden et al. 2001) suggests some routes to improvement. The sensitivity of CP actuator performance to the choice of electrolyte, because of ion size and mobility and electrolyte stability, means that electrolytes and CP materials must be explored in combination. The majority of CP research has involved liquid electrolytes, because liquids allow high ion mobility, but a few air-operable CP actuator designs have been investigated (Vidal, Plesse et al.; Madden, Cush et al. 1999; Hutchison, Lewis et al. 2000), and provide a good starting point for the selection or development of non-liquid electrolytes or encapsulation methods.

Conducting polymers are very appealing as actuator materials from the standpoint that electronics and sensors made with conducting polymers are already being produced using printing techniques, and are rapidly being commercialized, suggesting that facility with freeform fabrication of CP materials might accelerate the completion of our library of functionalities. The vast majority of work on CP actuation uses materials and processes that are not readily adaptable to SFF. The most common CP actuator material is polypyrrole, and the best published actuation results (Madden, Madden et al. 2001) involve polypyrrole produced via low-temperature (-30C) electrochemical synthesis (Figure 2a), which involves using electric fields in a solution of pyrrole monomer and electrolyte to cause oxidative polymerization.

Very high molecular weight films of polypyrrole, already doped and with good mechanical properties can be produced this way. As a baseline experiment, and to build experience with these materials, we produced some polypyrrole electrochemically following the method of (Yamaura, Hagiwara et al. 1988), and demonstrated its actuation in liquid electrolyte (Figure 2b).

Despite the low efficiency mentioned in Table 1, air operable CP actuator designs have been published with performance sufficient to warrant some exploration. The key challenge is to
find an SFF-amenable means of producing conducting polymer films with high molecular weight (good mechanical properties), and high conductivity. As a rule of thumb, conducting polymers are not melt processable or soluble in their conducting (doped) state, although they may be so in the insulating state. Polypyrrole and other conducting polymers are available in the doped form as dispersions (small particles suspended in liquid medium) in water or other solvents. We investigated the mechanical properties of films produced from these materials by casting films of polypyrrole dispersion (Sigma-Aldrich), and of PEDOT/PSS (Sigma-Aldrich). The results were unsatisfactory with polypyrrole (Figure 2c), while PEDOT/PSS can produce fairly robust and flexible films. To achieve air-operable actuators, some kind of electrolyte must be used – either a “solid polymer electrolyte” (SPE) which contains some liquid to allow ion migration, or a liquid electrolyte surrounded by some kind of encapsulation. Unfortunately, films cast from dispersions of these two materials remain very sensitive to the liquid components of the electrolyte, and no successful CP/electrolyte combinations were found.

![Figure 3. Actuation of solution-cast P3OT in liquid electrolyte; 5V step, elapsed time 5s](image)

In (Dahman 1999) a method is described which allows a compromise on the solubility/conductivity tradeoff with two conducting polymers, P3OT (poly(3-octylthiophene-2,5-diyl) and PANI (polyaniline). In the processing method described, undoped P3OT or PANI powder is dissolved/dispersed in a solvent, then doped in solution with two separate dopants, one which improves the conductivity of the material, and one which improves the processability of the material. We produced a sample of P3OT, doped only with DBSA (dodecylbenzenesulfonic acid) as processing dopant, in toluene to explore the mechanical properties of the film. Films were cast from this solution onto a Teflon substrate, and allowed to air dry. When peeled off of the Teflon, the films were found to be flexible and elastic. The actuation of this material in a liquid electrolyte was verified clearly – the motion of the film is fast enough and large enough to observe with ease in video. Figure 3 shows the change in curvature with a 5V step over 5 seconds.

Subsequently, an attempt was made to test actuation in air. A solid polymer electrolyte was produced using a modification of the methods in (Sansiñena, Olazábal et al. 1997). A low vapor pressure solvent, propylene carbonate was used to dissolve Hydrin (poly(epichlorohydrin-co-ethylene oxide, Zeon Chemical) rubber to act as a matrix for in order slow down the drying out of the electrolyte. A three-layer sandwich (P3OT-Hydrin SPE-P3OT) was made by spreading SPE on the surfaces of two 10mm X 40mm strips of P3OT film, then laying these face to face, SPE facing inward (Figure 4). Electrical contact was made via aluminum foil strips mounted on adhesive tape, which was then attached to the P3OT strips. A 1.5V DC signal at about 10mA was supplied. A very slow movement was observed to take place over about 4 minutes (Figure
5). The very slow actuation may be in part due to the low conductivity of the P3OT, which was prepared without the conductivity enhancing dopant recommended by Dahman. It is possible that the material is not actuating by ion diffusion, but instead by solvent electrolysis. A subsequent experiment will explore these possibilities.

Figure 4. Schematic of three-layer, air operable CP actuator

Figure 5. Actuation of P3OT with SPE in air (curling of tip); 1.5V step, 4 minutes total

No attempt was made to optimize the formulation of the SPE for this preliminary experiment. Significantly improved actuation can be expected from improvement in the P3OT doping and SPE formulation. Although (Chen and Inganas 1995) reports actuation of P3OT in liquid electrolyte, the present work is the first reporting of an air-operable CP actuator produced entirely by casting films from solutions. The materials are all syringe-dispensible, and hence suitable for use in our freeform fabrication system.

**Ionomeric Polymer-metal Composite Actuators**

Ionomeric Polymer-Metal Composites (IPMC’s) are actuators constructed from an anionic perfluorinated polymer membrane (e.g. a modified PTFE (Teflon) with perfluorinated sulfonate anion side groups, Figure 6) with surface electrodes. These materials are the key component in proton exchange membrane (PEM) fuel cells, and are commercially available (e.g. as DuPont Nafion). The materials are typically produced in what is called “acid form,” meaning that a proton is ionically bound to the sulfonate anions in the polymer side chains. 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 6). The surfaces of the membrane are given metallic electrodes, typically by soaking in a metal salt solution, then chemical reduction of the metal salt.

A voltage applied across the electroded surfaces of the composite causes the material to bend (Figure 7). This probably results from the migration of cations and solvent (the anionic side groups on the polymer being immobile) within the material, as well as from several associated effects: a stiffness change in the polymer, a change in electrostatic forces between the anionic side groups in the polymer, reorientation of the solvent molecules (Shahinpoor and Kim 2001). If the actuation signal is rapidly applied (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 motion, stiffness, polymer conformation, and solvent orientation related, while the slow process is probably solvent diffusing to equalize pressure through the material (Nernat-Nasser and Li 2002). A gradually ramped stimulus may result in only the slow processes occurring (Bar-Cohen 2001). IPMC actuators are superior to CP actuators in terms of their actuation speed and probably their
efficiency (difficult to find reported values in literature). Unfortunately, because their motion is not the result of net volume change, but only of bending, they are somewhat difficult to couple mechanically.

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![Figure 6. Structure of DuPont Nafion polymer; exchange of cation (from H⁺ to Li⁺) to improve actuation; Rₖ is proprietary fluorinated group](image)

![Figure 7. Possible IPMC actuation mechanism: pressure differential from electric field driven ion and solvent motion](image)

Production of IPMC via SFF will enable the exploration of the effect of complex device geometry on actuator properties, as well as allowing the embedding of actuators within other devices, but the standard method of producing IPMC described above is incompatible with freeform fabrication. (Kim and Shahinpoor 2002) describes a method for producing IPMC actuators from “liquid Nafion,” which is a dispersion of Nafion particles in solvent, but note that the authors have not demonstrated freeform fabricated actuators. The described process has six steps, but, as noted below, one step is incompatible with freeform fabrication, and several others are problematic from the perspective of co-fabrication with other functionalities.

1. **Obtaining liquid Nafion:** Nafion dispersions are commercially available in several loading (5% - 20%) and medium combinations (generally water and/or alcohols). The dispersions are typically used to repair Nafion membranes which are being used e.g. in fuel cells. (Kim and Shahinpoor 2002) also refers to methods for production of Nafion dispersion from commercially available Nafion membranes, and a means of producing melt-processable Nafion.

2. **Converting from Nafion from H⁺ to Li⁺ cation:** Typically, this step is carried out by soaking a solid Nafion membrane in aqueous salt solution (e.g. LiCl) at elevated temperature for several days. This step is incompatible with freeform fabrication since it is performed on a solid membrane.

3. **Casting of film:** (Kim and Shahinpoor 2002) observes that films cast directly from purchased Nafion dispersions have poor mechanical properties. Improved films are achieved by adding DMF (dimethylformamide), a low vapor pressure solvent, to their dispersions. The amount of DMF added is not reported. Thicker films can be achieved through repeated drying and readdition of liquid. The authors cast material into a Petri dish. This step is problematic for freeform fabrication in that the dispersions need to be confined during drying to control film geometry and to prevent contamination of other fabricated components by the somewhat hazardous solvents involved.

4. **Annealing of film:** The air dried films thus produced are still easily resuspended in solvent. We have verified this – within moments of immersing the film in deionized water, it disintegrates. This is undesirable because the film must be hydrated in order to actuate.
Annealing of the film is suggested in (Kim and Shahinpoor 2002), as well as by DuPont technical support, as a means of causing some degree of crystalization and a reduction of solvent susceptibility. The latter source recommends 15 minutes at 135C, while the former fail to suggest a duration, but mention 70C followed by 150C. The annealing process is incompatible with the goal of cofabricating actuators with other functionalities; batteries in particular would suffer some degradation as a result of this process.

5. **Electroding of film:** The surfaces of the film are typically made electrically conducting by the metal salt reduction technique mentioned above, which is not SFF amenable. Although not clearly demonstrated, (Kim and Shahinpoor 2002) does suggest a method of electroding that is. A metal (Ag, Pt, etc.) powder is suspended in a quantity of Nafion dispersion, then this material is cast as the first (bottom) layer, and the last (top) layer of a Nafion film.

6. **Hydration of film:** The electroded film is soaked in deionized water for a few minutes to saturate it. Water leaks and evaporates from the devices during use, limiting operational life; some means of encapsulation is desirable to prolong in-air operation.

We performed a series of experiments in order to modify or eliminate the problematic steps (steps 2, 3, 4, 6) in order to improve the compatibility of IPMC fabrication processes with our processing regime and requirements of other library functionalities. For these experiments we purchased 10 wt. % aqueous Nafion dispersion from Sigma Aldrich. The dispersion is in H⁺ (acid) form, as purchased. Additional experiments were performed to verify published experiments and to explore other avenues.

**Conversion of cation (modification of step 2)**

To eliminate the problems with step 2, we achieve the exchange to Li⁺ form entirely in the liquid state through dialysis in two different processes. Consultation with DuPont Nafion technical support revealed that the aggregated particles in the Nafion dispersions are typically of at least 100kg/mol. For this reason we selected 25kDa pore size dialysis tubing as a compromise between Nafion retention and dialysis rate. In the first method, the Nafion dispersion is placed in the dialysis tubing, and the tubing is immersed in 1.5M LiCl solution. The solution is stirred continuously, and refreshed every 12 hours for six cycles. Excess LiCl is then removed by immersing the dialysis tubing in deionized water, and similarly stirring and refreshing for three additional 12 hour cycles. The second, faster approach involves dissolving an excess of LiCl directly in the as-purchased aqueous Nafion, then dialysing it against deionized water for three 12 hour cycles. It must be noted that the weight percent of Nafion in the dispersions following the conversion to Li⁺ form via dialysis are not necessarily the same as in the purchased material.

**Casting of films/annealing (elimination of step 4)**

We explored several alternatives for the preparation of films. In general films were cast onto a Teflon substrate, and allowed to dry at room temperature under a fume hood (constant air flow). Initially, films were cast directly from the Li⁺ aqueous dispersion, without additives. Our experience replicated (Kim and Shahinpoor 2002), in that the films cracked upon drying, and the pieces were too fragile to handle.

As a verification of published approaches, a ratio of 1:4, DMF:Nafion (post-dialysis) dispersion by volume resulted in transparent, durable films which can be peeled off of the substrate with tweezers and handled. The film was annealed (15 minutes at 135C), electroded by coating the surfaces with silver grease (CircuitWorks CW7100), hydrated in deionized water for
several minutes, and tested for actuation. The test was successful, with the device moving visibly and repeatedly within a second in response to variation of applied voltage between 0V and 2V, and current typically less than 10mA. Application of 10V caused a short circuit failure of the device before video documentation could be obtained.

To explore the effect of the DMF/water ratio, a quantity of aqueous dispersion was allowed to completely dehydrate. The resultant dry material weighed 1.4g. It was dissolved in 6 mL of DMF, resulting in a viscous, but transparent dispersion at 25wt%. Film was successfully cast from this concentrated dispersion, and was durable enough to handle. The film was prepared for testing exactly as above. This test was a complete failure, however, with no motion observed, regardless of applied voltage. Little or no current flowed, so electrical shorting was not the cause.

In all of the above cases, the material was still found to require annealing, and to be somewhat fragile, especially after hydration. To remedy this problem, a small quantity of Hydrin SPE matrix rubber dissolved in DMF (about 10 wt% Hydrin in DMF) was added to the Nafion dispersion. The idea is that the very long chain Hydrin polymer molecules might act as a reinforcing matrix for the Nafion without hindering ion and solvent transport. 0.1g of dehydrated Nafion was mixed with 2mL of DMF and this was mixed with 0.1g of Hydrin/DMF solution. The resultant material was cast, and the resultant films was found to be mechanically superior to Nafion alone. A piece of this material was hydrated without annealing, and found to maintain its integrity about as well as annealed Nafion. When tested, the material was not found to be electromechanically active.

![Figure 8. Actuation of annealed Nafion/Hydrin blend; 5V step, elapsed time 45s](image1)

![Figure 9. Actuation of unannealed Nafion/Hydrin blend; 5V step, elapsed time 60s](image2)

This failure suggested that either the Hydrin was interfering with the actuation of the Nafion, that annealing was essential to actuation, or that the lack of water during casting was at fault. In that this last issue was in common between the Hydrin/Nafion blend and the concentrated Nafion cast from straight DMF, both of which failed to actuate, the Hydrin/Nafion blend (1.5mL) was tried with the addition of aqueous Nafion dispersion (4mL). The liquid clouded immediately upon addition of the aqueous dispersion, and the cast film was opaque, but retained the good mechanical properties even upon hydration without annealing. A piece of this
film was annealed and tested for actuation as before, with silver grease electrodes. This test was successful (Figure 8), and a subsequent test also verified the actuation of unannealed material (Figure 9). With this polymer blend we have achieved an IPMC that does not require annealing, although annealing still seems to be beneficial for the mechanical properties of the material.

**Electroding (exploration, verification of published approach)**

A variety of materials were explored for electroding, including silver grease, conducting polymers (including the PEDOT/PSS and P3OT used in CP actuator experiments), and metal powders. A series of experiments were performed in which the electrode materials were cast or laid down on a Teflon substrate, and Nafion dispersion or Nafion/Hydrin blend was cast on top of them. The majority of these experiments failed, although the reasons seemed to be one of two: chemical incompatibility (with P3OT; likely the DBSA dopant or residual toluene was the cause), or contraction and crumpling of the electrode layer during evaporation of solvent from the subsequent Nafion or Nafion/Hydrin layers. There were two successes. A thick layer of PEDOT/PSS about 0.25mm, which was fully air dried was able to survive having Nafion cast onto it, but did crack somewhat. The method suggested by (Kim and Shahinpoor 2002) seems to work best. 0.5g of 2µm Ag powder was mixed with 250µL of aqueous Nafion dispersion, and ~10µL of DuPont Zonyl FSO-100 fluorosurfactant was added to promote dispersion of the silver. This material was cast as a film, and was found to form a high conductivity material via digital multimeter.

**Encapsulation and hydration (modification of steps 3 and 6)**

Standard IPMC electroding techniques result in porous electrodes. The result is that water leaks out of the actuator, as well as evaporating from it. Not only does this reduce the operating life of the device (at least without rehydration), but it has been suggested that leakage reduces the actuation efficiency of IPMC devices by reducing the achievable internal pressure gradients in the material. For this reason an impermeable film electrode is desirable, and is why conducting polymers were explored as electrode materials. Unfortunately, PEDOT/PSS, which was marginally successful, is also water soluble. Applying an impermeable, low modulus skin to the IPMC was evaluated as a means of preventing leakage, regardless of the choice of electrode. The candidate membrane material selected is PDMS (poly(dimethylsiloxane), Dow Corning 734 Flowable Silicone RTV rubber). This material is within the suite of materials used in our SFF system; we routinely deposit 0.3mm thick films of this material. A sample of Nafion/Hydrin film was cast and air dried, and painted with PEDOT/PSS aqueous dispersion. Rather than hydrating by soaking the film, which would likely damage the PEDOT, it was assumed that the water from the PEDOT would serve to hydrate. When the PEDOT was visibly dry, electrical contact was made via wires with dots of silver grease, and the sample was mounted on Scotch tape. The entire actuator was then coated by hand in PDMS. Once dry, the device was tested for actuation. Figure 10 shows the device tip elevating about 1mm in 50s in response to 5V.

While the performance is not spectacular, actuation was definite and repeatable, validating the approach of hydration via PEDOT, and the compatibility of silicone encapsulant with actuation. Current was less than 10mA. From the perspective of producing these actuators via SFF, especially in unusual geometries and integrated with other functionalities, this successful test of silicone as an encapsulant is critical: silicone can be used to confine the liquid actuator materials during film casting, is electrically insulating, inert and chemically resistant,
but can be made thin enough, and has a sufficiently low modulus to not interfere excessively with actuation.

Figure 10. Actuation of silicone encapsulated Nafion/Hydrin; 5V step, elapsed time 50s

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. Conducting polymers and proton exchange membrane materials have been identified as most compatible with our liquid deposition/fused deposition processes and the other functional elements which we can already produce. Significant new processing methods and material modifications have been developed. Actuators of both types have been made by hand-dispensing materials from syringes, layer by layer, which is a reasonable proxy for robotic freeform fabrication, and in-air actuation has been demonstrated conclusively in at least one case. Producing an isolated actuator with our SFF system using either of these materials will not pose a significant challenge. The major tasks ahead are the optimization of materials and processes, the significant challenge of measuring the electromechanical performance of these devices, and the development of designs and methods which will allow the co-fabrication of actuators with other functionalities in an integrated, operational device.

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