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Considerations for Contractile Electroactive Materials and Actuators

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ABSTRACT

Ras Labs produces contractile electroactive polymer (EAP) based materials and actuators that bend, swell, ripple, and contract (new development) with low electric input. In addition, Ras Labs produces EAP materials that quickly contract and expand, repeatedly, by reversing the polarity of the electric input, which can be cycled. This phenomenon was explored using molecular modeling, followed by experimentation. Applied voltage step functions were also investigated. High voltage steps followed by low voltage steps produced a larger contraction followed by a smaller contraction. Actuator control by simply adjusting the electric input is extremely useful for biomimetic applications. Muscles are able to partially contract. If muscles could only completely contract, nobody could hold an egg, for example, without breaking it. A combination of high and low voltage step functions could produce gross motor function and fine manipulation within the same actuator unit. Plasma treated electrodes with various geometries were investigated as a means of providing for more durable actuation.

Keywords: electroactive polymer, EAP, contraction, expansion, voltage step function, artificial muscle, plasma treated electrode, spiral electrode, actuator

1. INTRODUCTION

There has been a great deal of interest in the search for materials that can efficiently transfer electrical energy directly into mechanical energy, analogous to our muscles converting electrical and chemical energy into mechanical energy to produce movement.   Advances in these endeavors have been achieved around the world, using materials such as poly(vinyl alcohol), ionized poly(acrylamide), poly(acrylic acid), poly(acrylic acid)-co-(poly(acrylamide), poly(2-acrylamide-2-methyl-1-propane sulfonic acid), poly(acrylic acid), poly(methacrylic acid), poly(styrene sulfonic acid), quarternized poly(4-vinyl pyridinium chloride), and poly(vinylbenzyltrimethyl ammonium chloride), and numerous other materials. SRI International holds many patents (US Patents 7,064,472,[1] 7,049,732,[2] 6,940,211,[3] 6,891,317,[4] 6,882,086,[5] 6,812,624,[6] 6,781,284,[7] 6,768,246,[8] 6,707,236,[9] 6,583,533,[10] 6,545,384,[11] 6,376,971,[12] 6,543,110[13]) and publications[14,15,16,17,18] in this area. Patents are additionally held by the Nippon Zeon Corporation (JP Patents 03234770,[19] 2001258275[20]) the Nitta Corporation (US Patent 5,977,685,[21] JP Patents 2001258275,[22] 07216244[23]), and many others. Piezoelectric materials have also been investigated for use as electrically responsive materials; however, most piezoelectric materials undergo length changes of only a fraction of one percent.

Cross-linked, ion-containing electroactive polymeric (EAP) materials developed by Ras Labs have shown good results in terms of strength and electroactivity,[24,25] with the ability of some of these EAP materials to contract more than 80 % within 1 minute at 50 V, and then return to their original size and shape when the

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electric input is stopped, repeatedly.[26,27] Recently, stronger EAP materials were produced that quickly contract and then expand, repeatedly, by reversing the polarity of the electric input. The contraction-expansion cycles can be cycled repeatedly, lending these EAPs to applications where life-like motion is desired.

Voltage step functions – high voltage followed by low voltage – were applied to these contractile EAPs. Using a variety of voltages produced varying amounts of contraction. This has enormous potential. A combination of high and low voltages could produce gross and fine motor skills, respectively, providing both large motor control and fine motor control (fine manipulation) within the same actuator unit.

One of the challenges of EAPs is that when they undergo motion, the electrodes, even if embedded, can become detached, which causes actuator failure. Plasma treatment and other metal treatments were explored to improve the interface between the electroactive material and the embedded electrodes. Plasma treated electrodes with various geometries, particularly spiral shaped geometries, were investigated as a means of providing for more durable actuation. Conceivably, a spiral shaped electrode, which in essence is a spring, can move when the dynamic EAP is activated and relax when the EAP returns to its original conformation. Straight shaped electrodes are prone to linear shearing of the polymer from the metal surface when the EAP is quickly activated. By improving the metal-polymer interface with both plasma surface treatment and electrode geometry, the EAP material and the electrode(s) can work as a unit, where the electrode(s) delivers the electric input much like a nerve and can also serve as a tendon between the EAP material and a lever.

The mechanism of movement in EAP materials is somewhat understood, particularly for bending;[28,29] however, the mechanism of contraction in EAP materials is not as well understood. Tanaka,[30] Osada,[31] Smela,[32,33,34] and others have investigated the contraction behavior of smart materials from change in pH, change in solvent, ionic concentration, and electric input. In our previous research, radionuclide-labeled electrolyte and tritium labeled water experiments were performed concurrently to definitively determine the chain of events that occur when the EAP materials developed by Ras Labs contract.[27,35] Molecular modeling further explored this phenomenon, followed by experimentation using different electrolyte solutions, pH considerations at the electrodes, and different ionic concentrations to determine exactly how and why contraction and expansion occur in these ion-containing EAPs.

2. EXPERIMENTAL

Electroactive polymeric materials: The EAP materials were synthesized using the monomer methacrylic acid (Aldich Chemical Co., Inc., 99 %), the initiator 1-hydroxycyclohexyl phenyl ketone (Aldrich, 98 %, or Irgacure 184® from Ciba Geigy, Inc.), and the cross-linking agents ethylene glycol dimethacrylate (Aldrich, 98 %), poly(ethylene glycol) dimethacrylate (Aldrich,), or 1,1,1-trimethylolpropane trimethacrylate (Aldrich, technical grade). Inhibitors were removed using a column of inhibitor removal beads (Aldrich). Typically, 1 weight percent 1-hydroxycyclohexyl phenyl ketone was used. The amount of cross-linking agents varied between 0.5 and 10 weight percent depending upon the physical properties desired. Glycerol or distilled, oxygen-free water was used as a diluent. Different formulations were used to produce EAPs that bend, EAPs that swell, and EAPs that contract. Multi-phasic gels, with different zones having different physical properties, were also synthesized. A custom built, mercury bulb, ultraviolet oven (λ = 300 – 450 nm) was used to photopolymerize the cross-linked networks for typically 3 to 10 minutes. The reaction mixtures were polymerized in glass vials or test tubes. Molds were used for more complex shapes. For EAP materials with embedded electrodes, the electrodes were positioned in the monomer/initiator/cross-linking agent(s) mixture prior to the photopolymerization. Once the material had polymerized, electrolyte solution(s) was added to the material, which typically swelled over a finite amount of time, varying from overnight to a few days to reach final volume. LiBr was acquired from Aldrich Chemical Company while NaCl and KCl were from generic sources.

Metal electrodes: Stainless steel aircraft grade (McMaster-Carr, ASTM-A580, 302/304, 8860K11) lockwire (0.015 gauge) and foil (0.002 inch thick) was used because this is a non-hardening stainless steel with good corrosion resistance and high temperature service. Titanium (ESPI, Knd1222, G2) wire (0.001, 0.003, and 0.005 inch diameters) and foil (0.002 inch thick) were used because of the high strength and good corrosion resistance of titanium. For the shaped geometry experiments, 316L marine grade stainless steel (0.020 in diameter, 1/8 Hard) was used because of its good corrosion resistance. Control samples

were not plasma treated. Straight shaped electrode geometries were also used as comparisons using both plasma treated and untreated electrode samples.

Plasma treatment: Nitrogen, synthetic air, hydrogen, helium, and oxygen plasmas were used on stainless steel and titanium foils. Nitrogen and oxygen plasma were used on stainless steel and titanium wires. The plasma was generated using a 25 MHz RF power source at 10 to 25 W in a near vacuum (typically 1 to 2 mTorr). The metal samples were attached to an I-shaped current probe that inserted into the plasma chamber source with -35 V (0.5 to 5 mA) electric potential, which attracted the bombardment of the positive ions towards the metal samples. All metals, including controls, were degreased.

Force Displacement: A Tinius Olsen 1000 force displacement machine was used to mechanically test the strength to failure of the polymer-metal interfaces between the EAP and the electrode, at a speed of 0.50 in.min and a maximum load of 100 lbs force.

Testing for electroactivity: A 50 V Edvotek modified mini-electrophoresis apparatus was used for preliminary testing for electroactivity. Weight was determined before and after electric impulse. Physical movement of these EAP materials was visible to the naked eye and could also be measured using video-capture over a grid. A HP Power® adjustable DC-regulated power supply, 0-15V/2A, was used for testing at lower voltages. For applied voltage step functions, a power supply and power-modulating device were designed and constructed at PPPL, with the power supply consisted of three identical 15 V bipolar power supply units connected in series to provide a range of voltages: -45V, -30V, -15V, 5V, 15V, 30V, and 45V. A power-modulating device was created with flip-flop integrated circuits and relays to simultaneously allow one voltage to be turned off while a different voltage is turned on. A grounded jumper was added to provide for the emission of a wider range of voltages to increase the voltage emission range of the power generator from -90 to +90 V.

Software: ChemdrawPro v.2, Gaussian98, and GaussView v.2 were used for molecular modeling. Gimp v.2 was used to analyze area changes from videoclips of EAPS.

3. RESULTS AND DISCUSSION

Cross-linked EAP materials produced from predominantly ion-containing monomers have shown good results in terms of strength and electroactivity, particularly contraction. Recent synthetic breakthroughs have produced an electroactive material that contracts 80 % within 1 minute at 50 V (Figure 1). When the electricity is stopped, the EAP returns to its original size and conformation. In addition, stronger EAPs were developed that contract to about 50 % from their original weight within 1 minute at 50 V, and when the polarity was reversed, expand back to their original weight (sometimes exceeding original weight) within 1 minute at 50 V (Figure 2). The contraction-expansion cycles can be cycled repeatedly. Robust EAPs capable of contraction and contraction-expansion are important breakthroughs in the field of electroactivity because of the ability of these innovative materials, valves, and actuators to produce sustained biomimetic life-like motion.
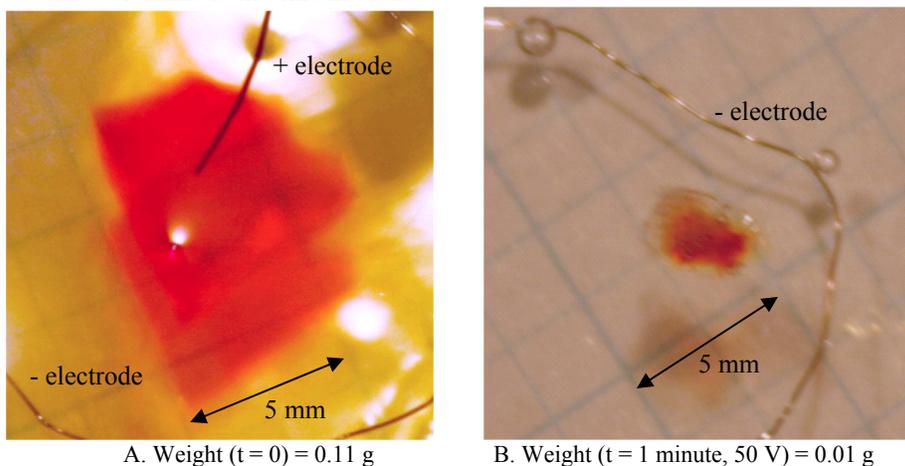

A. Weight (t = 0) = 0.11 g   B. Weight (t = 1 minute, 50 V) = 0.01 g

Fig. 1. Highly contractile EAP. Note: Red dye added to (uncoated) EAP to improve visualization. EAP surrounded by electrolyte solution. Electrode removed after experiment for weight determination.
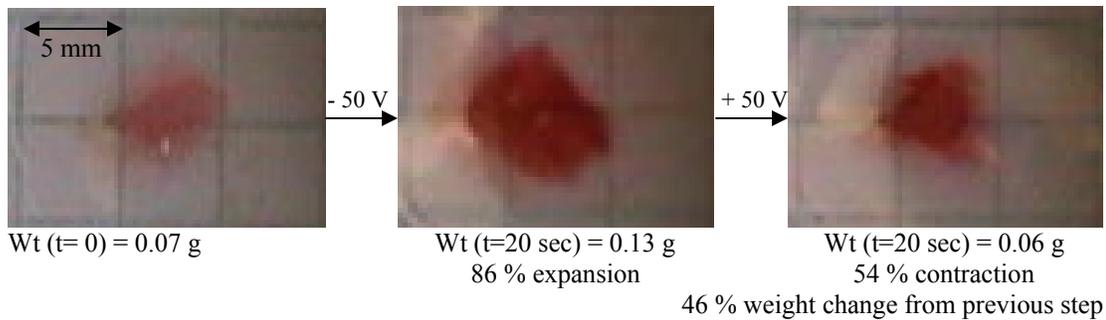
5 mm

− 50 V → + 50 V →

Wt (t= 0) = 0.07 g

Wt (t=20 sec) = 0.13 g
86 % expansion

Wt (t=20 sec) = 0.06 g
54 % contraction
46 % weight change from previous step

Fig. 2. Expansion-contraction cycle.
Note: Red dye added to (uncoated) EAP to improve visualization. EAP surrounded by electrolyte solution.

1 cm
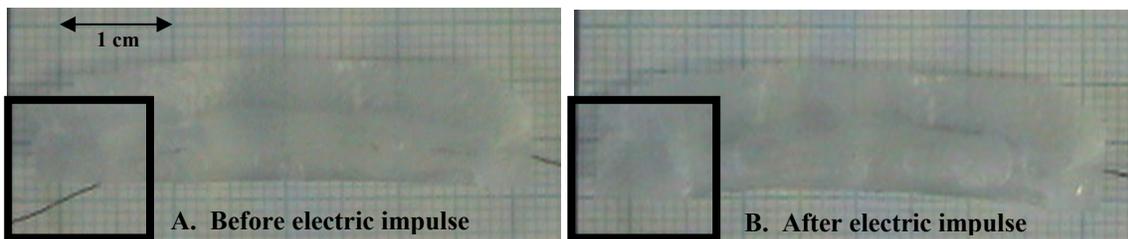
A. Before electric impulse

B. After electric impulse

Fig.3. Coated EAP material with embedded electrodes.

After electric impulse
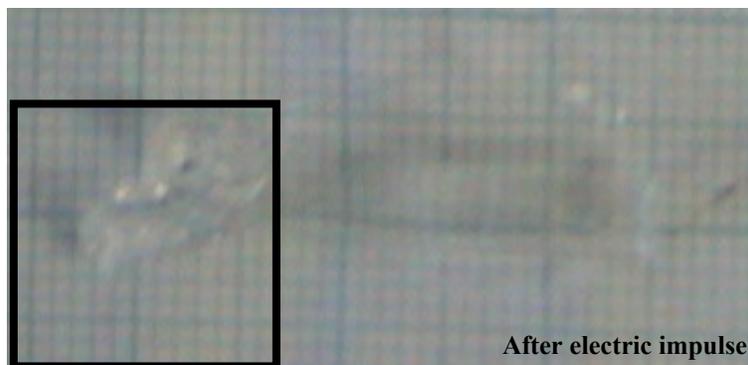
Fig. 4. Damage to EAP material in boxed area.

Using EAP materials in an actuator presents some interesting challenges. For actuators designed to act like an artificial muscle, the EAPs were synthesized with at least one embedded electrode. If the material was particularly electroactive, the material would move so quickly that the embedded wire would disengage, causing the actuator to lose its electric impulse (Figures 3 and 4).

Plasma treatment was used to improve the interface between the electrode metal and the electroactive material. Plasma is partially or wholly ionized gas with about an equal number of positively and negatively charged particles. Some scientists have named plasma the "fourth state of matter."[36] While plasma is neither gas nor liquid, the properties of plasma are similar to those of both gases and liquids. Sterilization and improving the adhesion between two surfaces are common applications. Good adhesion requires strong interfacial forces by chemical compatibility and/or chemical bonding. Plasma surface treatment can create chemically active functional groups such as amine, carbonyl, hydroxyl and carboxyl groups, which can greatly improve interfacial adhesion. Plasma is used to improve bonding on substrates such as glass, polymers, ceramics, and metals. Plasma treatment can also substantially enhance performance.

Preliminary experiments explored the bonding between these EAP materials with plasma treated metals provided by the US Department of Energy's Princeton Plasma Physics Laboratory at Princeton University (PPPL). The results were encouraging, with much better bond strengths in the plasma treated metals compared to the untreated control. For both stainless steel and titanium, oxygen plasma treatment provided the best metal-polymer interfaces for the embedded electrodes.

The electrode geometry also plays a key role in producing a viable actuator using these EAPS. The shape of the electrode, which is embedded in the EAP, was studied to compare the strengths of polymer-metal interfaces with various electrode shapes. Different spirals were constructed using 316L stainless steel wire

(Figure 5). The cylindrical spirals were the primary electrode shape tested. The polymer-metal interfacial strength of the spirals was compared to that of the straight electrode. Half of the samples were oxygen plasma treated for 4 hours while the other half of the samples (controls) were not plasma treated to compare the combined effect of both plasma treatment and electrode geometry.   Straight shaped electrode geometries were also used as comparisons using both plasma treated and untreated electrode samples. All of the electrode samples were degreased prior to plasma treatment (no plasma treatment for controls), followed by *in situ* polymerization of the EAP around the electrode samples. Force displacement was used to determine the strengths of the polymer-metal interfaces.
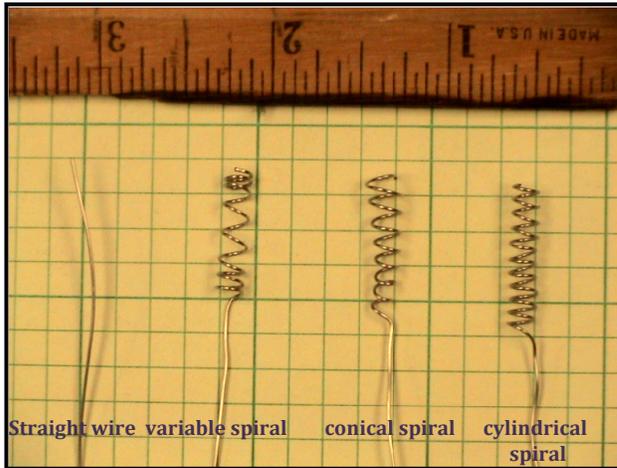
The spiral shaped electrodes had a slightly smaller threshold force compared to the straight wires, but required the force to be applied for a much longer period of time for the wire to be totally pulled out   (Table 1). This makes sense considering that the spiral electrode has roughly 5 times the length of wire embedded in the EAP as the straight wire. While the straight wire has to overcome one threshold before it comes out fairly easily, the spiral was pulled out loop by loop with a relatively constant force being applied the entire time (Figure 6). The greater impact in terms of durability was the shape of the embedded electrode for 316L stainless steel.

Fig. 5. Electrode geometries.
Table 1. Strength and durability for experimental electrodes.

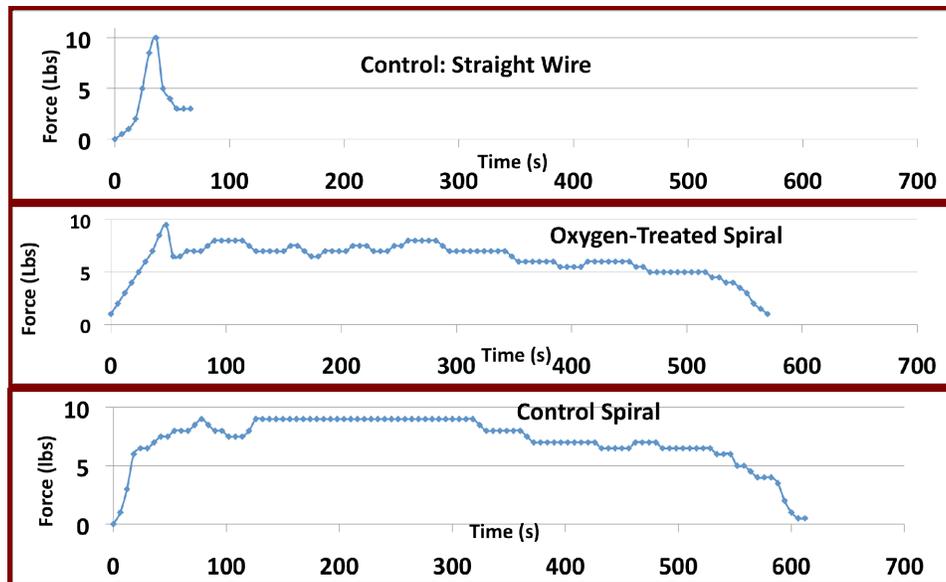| Electrode	Avg. Max Force (Lbs)	Avg. Time (Minutes)
Oxygen-Treated Spiral	8.8	10.5
Control Spiral	9.2	9.8
Oxygen-Treated Straight	10.5	1.5
Control Straight	12.1	1.3

Fig. 6. A comparison of the oxygen-treated spiral response to applied force and the response of a straight electrode.
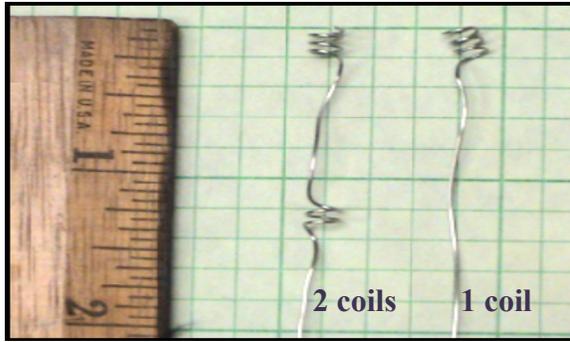
Fig. 7. Combinations of spiral and straight electrodes.

More electrode geometries were designed in response to the results from the spiral electrode experiment. The spiral and straight electrode geometries were combined and two new designs were tested (Figure 7). Combining the spiral and straight electrode geometries produced results that were a hybrid of the results from the straight and spiral wires. As seen in Figure 8, the larger peaks over a short amount of time were the result of straight sections of wire while the more constant, lower force sections were the result of the spiral. The force applied to the spirals sometimes has a periodic function while the loops of the spiral are pulled out one by one. The differing characteristics of the straight and spiral electrodes can be compared to the differences between shear strength and endurance. The straight electrode is able to withstand a comparatively large force for a short period of time with an abrupt failure. The spiral electrode, meanwhile, is able to withstand a reduced force for a much longer period.
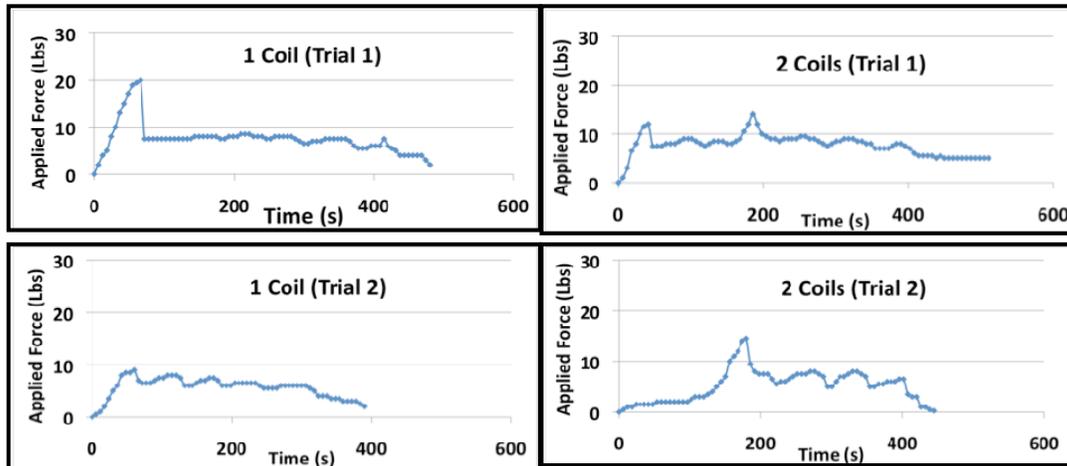

Fig. 8. Trials of each electrode shape.

An ionic EAP based actuator (3.16 g), with an embedded spiral stainless steel wire as the positive electrode and an external platinum negative electrode, was mechanically tested isometrically with a 587.7 mg counterweight. The experimental design used a Mettlar® analytical balance and a pulley system (Figure 9). The isometric mechanical testing of an activation-relaxation cycle is shown in Figure 10. This was a fairly large actuator. We have observed that the smaller the actuator, the faster and more pronounced the contraction. Moving forward, we are prototyping actuators using small, thin (exploring even fiber-like) contractile EAPs, that can then be bundled together in units to form larger, fast responding contractile actuators capable of life-like biomimetic movement.

Voltage step functions (high voltage followed by low voltage) and reversed polarity were applied to these contractile EAPs. The power supply consisted of three identical power supply units connected to provide a range of voltages: -45V, -30V, -15V, 5V, 15V, 30V, and 45V. A power-modulating device was created with flip-flop integrated circuits and relays to simultaneously allow one voltage to be turned off while a different voltage is turned on. The voltage could either be maintained (control) or reduced in a step function manner. The change in size of the EAP was used to determine how much the EAP contracted, with the mass of the EAP determined before and after contraction.

Figure 11 compares a control voltage experiment of 45 V for 40 seconds, for an overall contraction of 60 %, to a step voltage experiment of 45 V for 10 seconds followed by 5 V for 30 seconds, for an overall contraction of 21 %. The normalized results indicate that the amount of contraction is dependent on the

amount of voltage applied. Voltage reduction could be very useful for creating motor function. It is very important for muscles to be able to partially contract, exemplified by the act of holding an egg with one's fingers. If muscles could only completely contract, nobody could hold an egg without breaking it. A combination of high and low voltages could produce gross and fine motor skills, respectively, providing both large motor control and fine motor control (fine manipulation) within the same actuator unit.
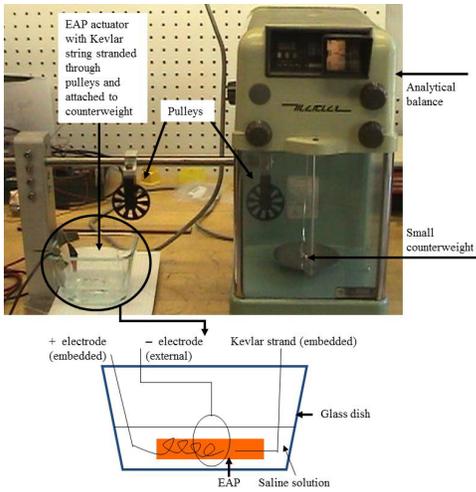

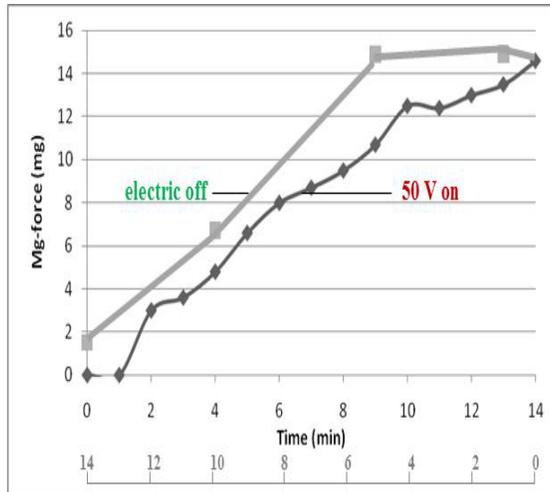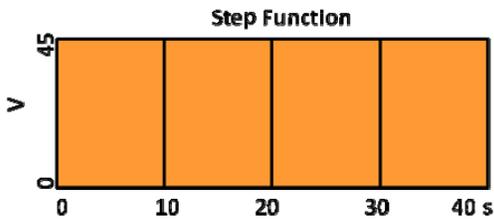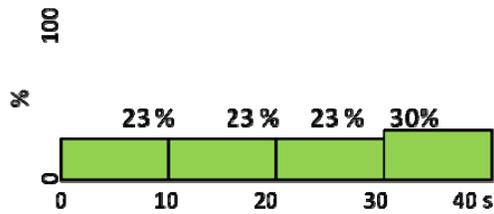**Fig. 9.** Isometric mechanical testing set-up.
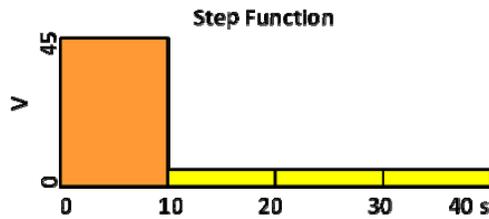

Fig. 10. Activation-relaxation cycle

45 V 40 seconds
Wt (0) = 0.2344 g
Wt (40 s) = 0.0936   40 % of original weight
60 % overall contraction by weight

45 V 10 seconds, 5 V 30 seconds
Wt (0) = 0..3049 g
Wt (40 s) = 0.2413 g   79 % of original wt.
21 % overall contraction by weight

Normalized EAP contraction at the end of each quarter
(contribution to overall contraction of each step function)

Normalized EAP contraction at the end of each quarter
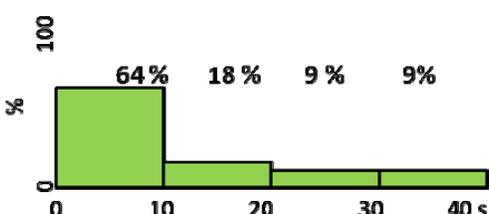(contribution to overall contraction of each step function)

Fig. 11. Applied voltage step function experiments.

By applying 50 V for 1 minute and then reversing the polarity and applying the voltage for another minute, the EAP can contract and then expand back to and beyond its original size. This EAP contraction-expansion can be cycled (Figures 2 and 12).
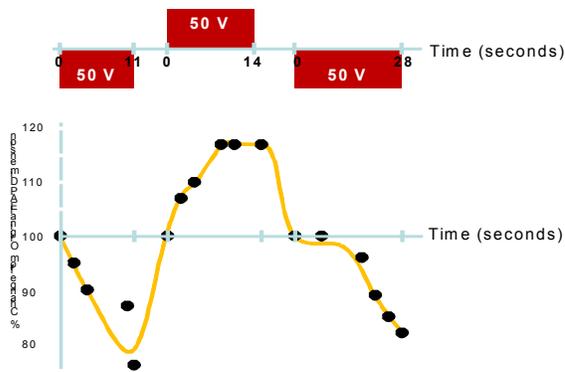
Fig. 12. Reverse polarity experiment.

Based on previous research following radionuclides,[27,35] contraction is due the net outflux of sodium ions to the externally placed negative electrode, which also causes a huge outflux of water molecules, virtually simultaneously, causing a rapid and profound contraction of the EAP. In selected formulations, when the polarity is reversed, rapid expansion of the EAP occurs, and the contraction-expansion can be cycled repeatedly. An important finding is that he sodium ions do not move at all unless electrically stimulated.

The distinct movement of sodium ions and water molecules that occurs during electric impulse causes EAP contraction, but why is this cation migration, and subsequent water molecule migration, occurring? Molecular modeling excluded the hypothesis of selective mobility due to pore sizes within the EAP. This is because in order to be flexible enough to be electroactive, the pore sizes in these cross-linked PMA based EAPs are huge compared to any of the electrolyte systems investigated, including ionic liquids (Figure 13).
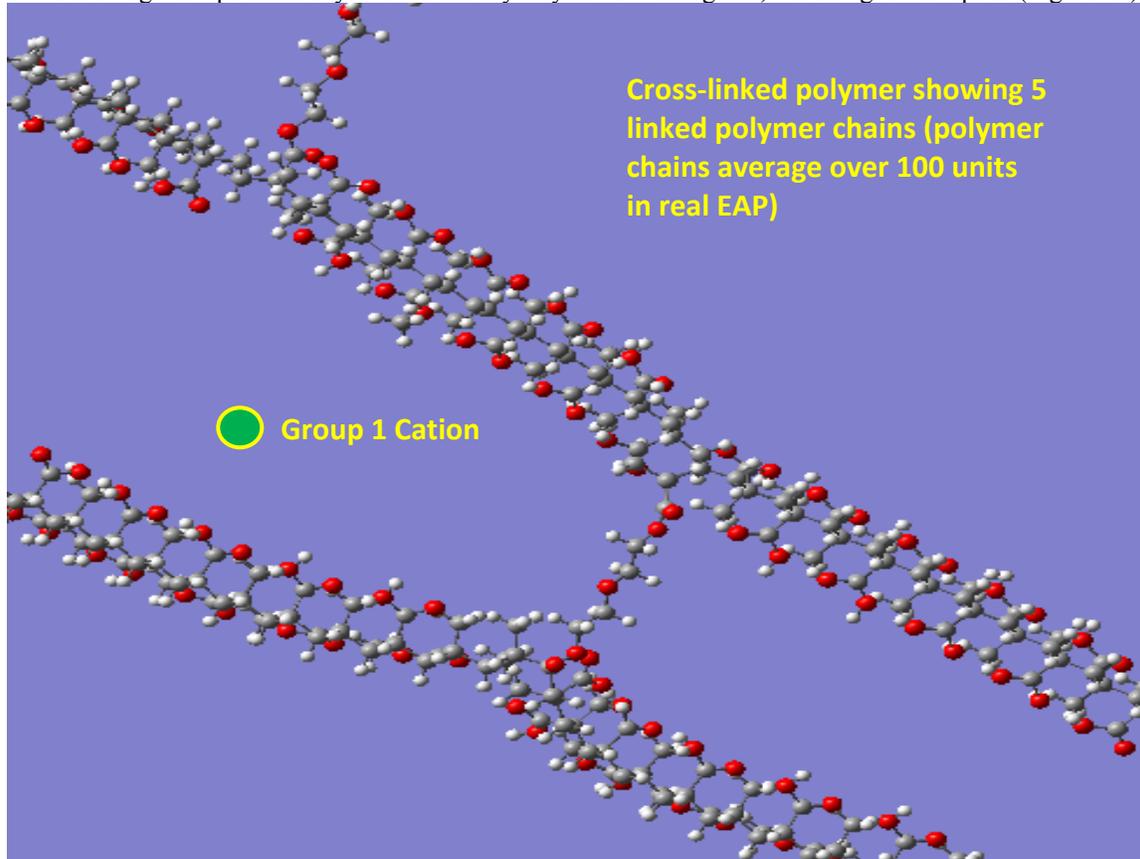

Cross-linked polymer showing 5 linked polymer chains (polymer chains average over 100 units in real EAP)

Group 1 Cation

Fig. 13. Molecular model of ion-containing EAP.

Different ions move at different rates within an aqueous environment. For simple electrolytes composed of Group 1 cation associated with a group 7 anion, such as LiCl, NaCl, KCl, LiBr, NaBr, KBr, the cation moves much faster in an electric field than its associated anion. The movement of cations and the subsequent movement of water is behind the profound levels of contraction observed in these hydrogels.

Based on the sizes of the Group 1 ions lithium, sodium, and potassium, one may predict that the lithium ion, with its tiny atomic radius of 0.69 Å, would migrate the fastest in an electric field, thus producing the highest level of contraction in an EAP. However, in an aqueous environment, lithium has the highest hydrodynamic radius (2.38 Å) compared to the other Group 1 cations, so in fact moves the slowest in an electric field (Table 2)[37] and produces the least amount of contraction (Figure 14). Conversely, the potassium ion, with its large atomic radius of 1.38 Å but small hydrodynamic radius of 1.25 Å (virtually same as atomic radius) moves very quickly in an electric field (Table 2)[37] and produces the highest amount of contraction (Figure 14).

Experimentally, three PMA based EAPs (from the same synthetic batch) were swollen in three different Group 1-Group 7 dilute electrolyte solutions: 0.2 M LiBr, 0.2 M NaCl, and 0.2 M KCl. The EAPs were then subjected to 50 V, 200 mA electric input for 3 minutes, with the positive electrode embedded in the EAP and the negative electrode external to the EAP. The EAPs swollen with potassium chloride produced the fastest and most pronounced contraction of 32 %, followed by sodium chloride at 26 % contraction, and followed by lithium bromide at 21 % contraction (Figure 14).

Table 2. Ionic crystallographic radii, hydrodynamic radii, molar equivalent conductivities, and diffusion coefficients of lithium, sodium, and potassium cations at infinite dilution at 25 °C.[37,38,39,40]

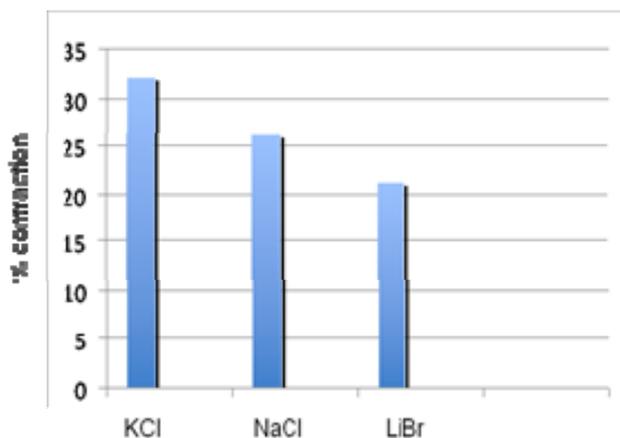| Group 1 (Alkali) Metal	Ionic radii r_c (Å)	Hydrodynamic radii r_h (Å)	Molar conductivities $\lambda^\infty \times 10^4$ (m^{2}S/mol)	Diffusion coefficients $D \times 10^9$ (m^2/s)
Li$^+$	0.69	2.38	38.66	1.029
Na$^+$	1.02	1.84	50.08	1.334
K$^+$	1.38	1.25	73.48	1.957

Fig.14. Contraction of PMA based EAPs for three different electrolyte systems.

Besides the cations being attracted to the very negative external electrode during electric impulse, there is also a local electrochemistry effect at each electrode, which causes chemical changes in these PMA based EAPs. In an aqueous environment, NaCl dissociates into sodium and chloride ions:

$$NaCl \rightarrow Na^+ + Cl^-$$

At the anode, which is the embedded positive electrode, two things are occurring. Some of the chloride anions in this dilute solution are becoming oxidized and forming a small amount of chlorine, while water is oxidized and forming oxygen and protons at the embedded positive electrode.
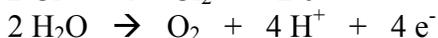
$$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$$
$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad \text{Acidic Environment at Anode}$$

The formation of protons at the positive embedded electrode within the EAP dramatically lowers the pH. This produces a very acidic environment for the EAP. Meanwhile at the cathode, which is the external

negative electrode, water undergoes reduction, releasing hydrogen at the cathode and forming hydroxide ions, which raises the pH, producing a basic environment.
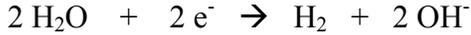
$$2\,H_2O \;+\; 2\,e^- \;\rightarrow\; H_2 \;+\; 2\,OH^- \qquad\qquad \text{Basic Environment at Cathode}$$

Recall that these polymethacrylic acid based EAPs contain weak acid groups along the main polymer chains. In an acidic environment, the acid groups are neutralized by the input of protons during the electric impulse on the anode, which is the embedded positive electrode, so the EAP becomes neutrally charged. The sodium ions leave the EAP from this two-fold effect: 1) the sodium counter ions now have no ionic affiliation with the protonated acid groups of the EAP (these groups lose their charge and become neutral during electric impulse) and 2) these sodium ions are very attracted to the cathode, which is the external negative electrode. As the sodium ions migrate rapidly out of the EAP, the water molecules in the hydration layers around the sodium ions are also dragged of the EAP, resulting in contraction. When the polarity is reversed, the strong negative charge is now at the embedded electrode and the localized electrochemistry is producing a basic environment within the EAP, thus the EAP regains its negative charges along the polymer chains. The sodium ions return to the EAP when the polarity is reversed, again from this two-fold effect of both 1) migration to the negative electrode and away from the positive electrode and 2) local electrochemistry within the EAP returning the negative charge to the weak acid groups along the polymer chains as the acidic groups are deprotonated. As the sodium ions migrate rapidly back into the EAP, the water molecules in the hydration layers around the sodium ions are simultaneously dragged back into the EAP, resulting in expansion.

The electrolyte concentration in these EAPs is very low, though, so movement purely by the ions and associated water shells does not fully explain the pronounced contraction observed in these EAPs when electrically stimulated. In fact, if the water shell migration were the only water movement occurring, lithium would be expected to have the highest contraction of the Group 1 cations due to the large amount of hydration layers (Table 2). The converse is observed, where potassium, in fact, has the highest level of contraction compared to sodium and lithium cations. The contraction observed once ion migration is underway can be explained, however, by osmosis. Once the cations migrate out of the EAP in response to the electric impulse, then an ionic concentration gradient occurs. Due to osmosis, water rapidly leaves these flexible EAPs due to the higher ion concentration outside of the EAP once the cations have migrated external to the EAP due to the placement of the cathode (the external negative electrode) and due to the local pH effects at the anode (the embedded positive electrode). The osmotic effect can be experimentally determined by placing the EAP first in a distilled water environment, followed by placing the EAP into a saturated sodium chloride solution, and observing any changes in the EAP. When the EAP was placed into the saturated NaCl solution, within 2 minutes the EAP contracted 25 %. Within 10 minutes, the EAP contracted by 62 % (Figure 15).
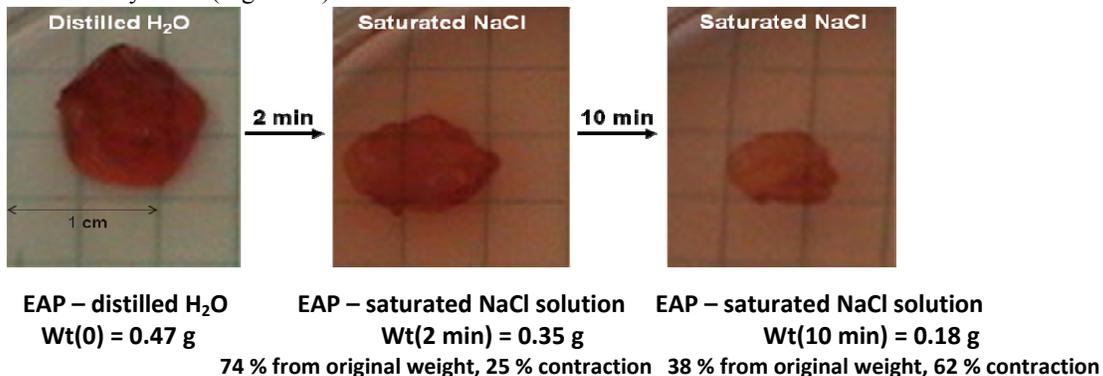

EAP – distilled H$_2$O   EAP – saturated NaCl solution   EAP – saturated NaCl solution
Wt(0) = 0.47 g   Wt(2 min) = 0.35 g   Wt(10 min) = 0.18 g
                    74 % from original weight, 25 % contraction   38 % from original weight, 62 % contraction

Fig. 15. Osmotic effects of contractile EAPs.

The contractile behavior that these EAPs undergo when electrically stimulated is thus a three-fold effect due to the following:

1. The strong negative charged cathode, which is placed external to the EAP, attracts the positively charged cations, such as Na$^+$, out of the EAP.

2. The localized pH effects at the positive charged anode, which is embedded in the EAP, protonates the weak acid groups along the polymer chains of the EAP, making the EAP neutrally charged, so that Na^+ counter ions are no longer attracted to the side groups of the EAP.
3. The osmotic effects following the ion gradient from the rapid cation migration in an electric field cause a large water loss out of the flexible EAP.

All three of these effects cause a rapid and pronounced contraction in selected EAPs. The first two events occur in tandem, followed quickly by the third effect of osmosis, causing a rapid and pronounced contraction in these PMA based EAPs.

Reversing the polarity causes expansion by a similar three-fold effect as follows:
1. The strong negative charged cathode, which is now the internal embedded electrode in the EAP, attracts the positively charged cations, such as Na^+, back into the EAP.
2. The localized pH effects at the negatively charged cathode, which is now embedded in the EAP, deprotonates the weak acid groups along the polymer chains of the EAP, making the EAP negatively charged again, so Na^+ counter ions are attracted back to the side groups of the EAP.
3. The osmotic effects following the ion gradient from the rapid cation migration in an electric field cause a large water gain back into the flexible EAP.

4. CONCLUSIONS

Ionic electroactive materials have been synthesized, where the strength and electroactivity can be tailored by controlling the extent of cross-linking and other synthetic strategies. These EAP based materials and actuators can undergo rapid and pronounced contraction. Reversing the polarity of selected EAPs produces contraction-expansion cycles. Voltage step functions – high voltage followed by low voltage – were applied to these contractile EAPs. Using a variety of voltages produced varying amounts of contraction. This has enormous potential for biomimetic applications. A combination of high and low voltages could produce gross and fine motor skills, respectively, providing both large motor control and fine motor control (fine manipulation) within the same actuator unit. The ability to modulate the level of movement in these EAPs by simply adjusting the voltage level could also be linked with biofeedback. Research and development to significantly improve the polymer-electrode interface has been performed, with significantly better adhesion between the electrode(s) and the EAP, particularly for stainless steel and titanium treated with oxygen plasma. Different electrode geometries were also investigated, with greatly improved durability using spiral shaped electrodes. The goal is for both the electroactive smart material and the embedded electrodes to move as a unit, analogous to our muscles, nerves, and tendons moving together. Molecular modeling and experimentation were performed to determine how and why these EAPs contract. Without electric input, the positively charged cations remain very tightly bound to the ionic EAPs. Once electricity is applied to these EAP based materials and actuators, cations and water move very rapidly from a three-fold effect due to ion migration, localized pH effects at the electrodes, and osmosis, producing a rapid pronounced contraction of the EAP. These recent developments, and fundamentally, the thorough understanding of this contraction phenomenon, are important in the field of electroactivity because of the ability of contraction and contraction-expansion to produce biomimetic life-like motion.

ACKNOWLEGEMENTS

REFERENCES

[1] Pelrine, R. E., Kornbluh, R. D., Stanford, S. E., Pei, Q., Heydt, R., Eckerle, J. S., and Heim, J. R., "Electroactive polymer devices for moving fluid," US Patent 7,064,462, SRI International (2006).
[2] Pei, Q., Pelrine, R. E., and Kornbluh, R. D., "Electroactive polymers," US Patent 7,049,732, SRI International (2006).
[3] Pelrine, R. E., Kornbluh, R. D., and Pei, Q., "Electroactive polymer transducers and actuators," US Patent 6,940,211, SRI International (2005).

[4] Pelrine, R. E., Kornbluh, R. D., and Eckerle, J. S., "Energy efficient electroactive polymers and electroactive polymer devices," US Patent 6,911,764, SRI International (2005).

[5] Kornbluh, R. D., and Pelrine, R. E., "Variable stiffness electroactive polymer systems," US Patent 6,882,086, SRI International (2005).

[6] Pei, Q., Pelrine, R. E.., and Kornbluh, R. D., "Electroactive polymers," US Patent 6,812,624, SRI International (2004).

[7] Pelrine, R. E., Kornbluh, R. D., and Pei, Q., "Electroactive polymer transducers and actuators," US Patent 6,781,284, SRI International (2004).

[8] Pelrine, R. E., Kornbluh, R. D., Eckerle, J. S., Stanford, S. E., Oh, S., and Garcia, P. E., "Biologically powered electroactive polymer generators," US Patent 6,768,246, SRI International (2004).

[9] Pelrine, R. E., and Kornbluh, R. D., "Non-contact electroactive polymer electrodes," US Patent 6,707,236, SRI International (2004).

[10] Pelrine, R. E., Kornbluh, R. D., Pei, Q., and Joseph, J. P., "Electroactive polymer electrodes," US Patent 6,583,533, SRI International (2003).

[11] Pelrine, R. E., and Kornbluh, R. D., "Electroactive polymer devices," US Patent 6,545,384, SRI International (2003).

[12] Pelrine, R. E., Kornbluh, R. D., Pei, Q., and Joseph, J. P., "Electroactive polymer electrodes," US Patent 6,376,971 (2002).

[13] Pelrine, R. E., Kornbluh, R. D., Oh, S., and Joseph, J. P., "Electroactive polymer fabrication," US Patent 6,543,110 (2003).

[14] Lacour, L. P., Prahlad, H., Pelrine, R., and Wagner, S., *Sensors and Actuators A: Physical*, 111(2-3), 288-292 (2004).

[15] Pei, Q., Pelrine, R., Stanford, S., Kornbluh, R., and Rosenthal, M., *Synthetic Metals*, 135-135(4), 129-131 (2003).

[16] Pelrine, R., Kornbluh, R., Pei, Q., and Joseph, J., *Science*, 287(5454), 836-839 (2000).

[17] Pelrine, R., Kornbluh, R., Joseph, J., Heydt, R., Pei, Q., and Chiba, S., *Mater. Sci. and Eng.: C*, 11(2), 89-100 (2000).

[18] Ashley, S., *Sci. Amer.*, 289(4), 52-59 (2003).

[19] Nanba, T., Kimura, K., Kobayashi, H., and Shimomura, T. "Polymer gels with fast response to electric stimulation," JP Patent 03234770 A2, Nippon Zeon Co. (1991).

[20] Hirako, Y., Suzuki, M., Hirai, T., and Watanabe, M., "Polymeric actuators," JP Patent 2001258275 A2, Nippon Zeon Co. (2001).

[21] Kurita, Y., Ueda, T., Kasazaki, T., and Hirai, T., "Polyurethane elastomer actuator," US Patent 5,977,685, Nitta Corporation (1999).

[22] Amaike, Y., Ueda, A., Suzuki, M., Hirai, T., and Watanabe, S., "Polymer actuator," JP Patent 2000049397 A2, Nitta Corporation (2000).

[23] Maeda, K., Hirikawa, Y., and Tanaka, T., "Polymer gels showing anisotropic changes to external stimuli and manufacture thereof," JP Patent 07216244 A2, Nitta Corporation (1995).

[24] Rasmussen, L., "Electrically Driven Mechanochemical Actuators that can act as Artificial Muscle," US Patent Application 11/478431 (2005).

[25] Rasmussen, L., "Process for Producing an Electrically Driven Mechanochemical Actuator," U.S. Patent 5736590 (1998).

[26] Rasmussen, L., "Electroactive Materials and Electroactive Actuators that Act as Artificial Muscle, Tendon, and Skin," US Patent Application 12/319804 (2009).

[27] Rasmussen,L., Erickson, C.J., Meixler,L.D., Ascione,G., Gentile C.A., Tilson, C., Abelev,E., "Considerations for Contractile Electroactive Polymeric Materials and Actuators," *Polym. Int.*, 59(3): 290-299 (2010).

[28] Shapiro, B. and Smela, E., "Bending Actuators with Maximum Curvature and Force and Zero Interfacial Stress," *J. Intell. Mater. Sys. Struct.,* 18(2), 181-186 (2006).

[29] Maw, S., Smela, E., Yoshida, K., Sommer-Larson, P., and Stein, R. B., "The Effects of Varying Deposition Current Density on Bending Behavior in PPy(DBS)-Actuated Bending Beams," *Sens. Act. A*, 89, 175-184 (2001).

[30] Tanaka, T., Nishio, I, and Sun, S. T., "Collapse of Gels in an Electric Field," *Science*, 218, 467-469 (1982).

[31] Osada, Y., "Conversion of Chemical Into Mechanical Energy by Synthetic Polymers," *Advances in Polymer Science 82*, © Springer-Verlag Berlin Heidelberg (1987), 3-46.

[32] Wang, X. and Smela, E., "Experimental Studies of Ion Transport in PPy(DBS), *J. Phys. Chem. C*, 113(1), 359-368 (2009).

[33] Wang, X. and Smela, E., "Experimental Studies of Ion Transport in PPy(DBS)," *J. Phys. Chem. C.*, 113(1), 369-381 (2009).

[34] Wang, X., Shapiro, B., and Smela, E., "Visualizing ion transport in Conjugated Polymers," *Adv. Mater.*, 16(18), 1605-1609 (2004).

[35] Rasmussen L., Schramm D., Meixler L.D., Gentile C.A., Ascione G., Tilson C., Pagdon K., "Considerations for Contractile Electroactive Materials and Actuators," *SPIE EAPAD 2010, Proc. of SPIE* 7642: 76420Z-1-76420Z-9 (2010) doi: 10.1117/12.847176

[36] http://www.astp.com/plasma/pl_examples.html .

[37] Masiak, M., Hyk, W., Stojek, Z., and Ciszkowska, M., "Structural Changes of Polyacids Initiated by Their Neutralization with Various Alkali Metal Hydroxides. Diffusion Studies in Poly(acrylic acid)s," *J. Phys. Chem. B,* 111, 11194-11200 (2007). doi: 10.1021/jp0711904

[38] CRC Handbook of Chemistry and Physics, CRC Press, NY (2008).

[39] Wu Y., Joseph, S., Aluru N.R., "Effect of Cross-Linking on the Diffusion of Water, Ions, and Small Molecules in Hydrogels," *J. Phys. Chem. B,* 113*,* 3512–3520 (2009). doi: 10.1021/jp808145x

[40] Mudry B., Guy,R.H., Delgado-Charro, M.B., "Transport Numbers in Transdermal Iontophoresis," Biophy. J., 90, 2822–2830 (2006). doi: 10.1529/biophysj.105.074609