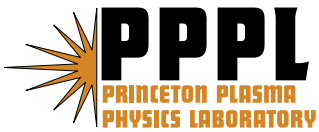

Princeton Plasma Physics Laboratory

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Prepared for the U.S. Department of Energy under Contract DE-AC02-09CH11466.

Princeton Plasma Physics Laboratory

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Considerations for Contractile Electroactive Polymeric Materials and Actuators

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ABSTRACT

Ras Labs produces electroactive polymer (EAP) based materials and actuators that bend, swell, ripple and now contract (new development) with low electric input. This is an important attribute because of the ability of contraction to produce life-like motion. The mechanism of contraction is not well understood. Radionuclide-labeled experiments were conducted to follow the movement of electrolytes and water in these EAPs when activated. Extreme temperature experiments were performed on the contractile EAPs with very favorable results. One of the biggest challenges in developing these actuators, however, is the electrode-EAP interface because of the pronounced movement of the EAP. Plasma treatments of metallic electrodes were investigated in order to improve the attachment of the embedded electrodes to the EAP material. Surface analysis, adhesive testing, and mechanical testing were conducted to test metal surfaces and metal-polymer interfaces. The nitrogen plasma treatment of titanium produced a strong metal-polymer interface; however, oxygen plasma treatment of both stainless steel and titanium produced even stronger metal-polymer interfaces. Plasma treatment of the electrodes allows for the embedded electrodes and the EAP material of the actuator to work and move as a unit, with no detachment, by significantly improving the metal-polymer interface.

Keywords: electroactive, EAP, artificial muscle, plasma treatment, actuator

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INTRODUCTION

Ras Labs, LLC, produces novel, flexible EAP materials and actuators that respond to electricity, then relax back to their original size, weight, and shape when the electricity is turned off, and can be put through motion-relaxation cycles repeatedly. Ras Labs produces flexible EAPs that bend, swell, ripple (first generation materials),^{1,2} and now contract (new development)³ with low electric input. This recent development is an important attribute in the field of electroactivity because of the ability of contraction to produce biomimetic life-like motion. The mechanism of contraction is not well understood. Ras Labs and Princeton Environmental Analytical Radiological Laboratory (PEARL) at the Department of Energy's Princeton University Plasma Physics Laboratory (PPPL) conducted preliminary radionuclide-labeled experiments to follow, in as close to real time as possible, the movement of electrolytes and water when electricity was applied to the contractile EAPs. Fundamentally, the development of strong, flexible, resilient EAP materials, which contract substantially with low electric input, can lead to revolutionary ways of looking at and designing actuators, valves, and other devices where motion is required, particularly where motion must be controlled, energy efficient, and delivered through a compact yet resilient device.

There has been a great deal of interest in the search for materials that can 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 numerous materials. SRI International and its spinoff Artificial Muscle, Inc. holds many patents,^{4,5,6,7,8,9,10,11,12,13,14,15,16,17,18} and publications^{19,20,21,22,23} in this area. Patents are additionally held by the Nippon Zeon Corporation^{24,25} the Nitta Corporation,^{26,27,28} Danfoss,²⁹ and many others. Prof. Shahinpoor,³⁰ Prof. Anderson,³¹ and others use ionic EAPs; however, these materials, including ionic polymer-metal composites (IPMCs), tend to bend when subjected to electric input. The electric fields can be reversed to create oscillation of the EAPs, producing a back-and-forth fishtail type of motion. 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.

The flexible EAP material developed by Ras Labs is capable of pronounced contraction when subjected to an electric impulse, contracting over 80 % (contracts to less than 20 % of its original weight) in less than a minute at 50 V.³ When the electricity is stopped, the flexible EAP relaxes back to its original size and shape. The rapid weight loss during contraction is believed to be primarily due to water leaving the EAP during contraction. How this contraction phenomenon occurs was explored using radionuclides and other experimental approaches.

One of the challenges of using EAPs in actuators is that when they undergo motion, the electrodes, even if embedded, can become detached from the EAP, which causes actuator failure. Plasma treatment and other metal treatments were investigated to improve the interface between the EAP and the embedded electrodes. 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."³² 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. 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.³² By improving the metal-polymer interface, the EAP material and the electrode(s) in the actuator 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.

Most of the theory of EAPs concerns bending, where opposing electrodes are placed on opposite sides of the EAP. When the electricity is turned on, positive ions migrate to the negative electrode and negative ions migrate to the positive electrode. If there is a size differential between the ions in the electrolyte solution, then bending occurs – the greater the size difference between the positive and negative ions in the electrolyte, the greater the degree of bending.

Contraction is not well understood. Tanaka,³³ Osada,³⁴ and others have investigated the contraction behavior of hydrogels from change in pH, change in solvent, and electric input. A radionuclide experiment using sodium-22 (Na-22) and tritium (H-3) was performed to determine the chain of events that occurs when electricity is applied to these novel EAP materials, both in terms of electrolyte flow and water loss during contraction.

EXPERIMENTAL

Electroactive polymeric materials: The EAP materials were synthesized using ion-containing acrylate/methacrylate based monomers, (Aldrich Chemical Co., Inc., 99 %), the initiator cyclohexyl phenyl ketone (Aldrich, 98 %, or Ciba Geigy, Inc.), and a variety of cross-linking agents. Inhibitors were removed using a column of inhibitor removal beads (Aldrich). Typically, one weight percent cyclohexyl phenyl ketone was used. The amount of cross-linking agent(s) varied depending upon the physical properties desired. A custom built, mercury bulb, ultraviolet oven ($\lambda = 300 - 450$ nm) was used to photopolymerize the cross-linked networks for typically 3 to 10 minutes. The reaction mixtures were polymerized in glass vials, test tubes, or UV-transparent molds. For EAP

materials with embedded electrodes, the electrodes were positioned in the monomer mixture prior to the photopolymerization. Once the material had polymerized, electrolyte solution was added to the material, which typically swelled over a finite amount of time, varying from overnight to days to reach final volume. Biphasic and multi-phasic gels were also synthesized, providing different properties for different zones of the EAPs.

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 a simple grid. A HQ Power® adjustable DC-regulated power supply, 0-15V/2A, was used for testing at lower voltages.

Metal electrodes: Stainless steel aircraft grade (McMaster-Carr, ASTM-A580, 302/304, 8860K11) lockwire (0.015 gauge) and foil (0.002 inch thick) and titanium wire (ESPI, Knd1222, G2, 0.001, 0.003, and 0.005 inch diameters) and foil (0.002 inch thick) were used. All metals were degreased prior to plasma treatment.

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 at typically 1 to 2 mTorr. The metal samples were attached to an I-shaped current probe that was 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.

Adhesion testing: Water drop surface contact angle testing was performed using distilled water on untreated and plasma treated metal foils. For T-peel tests, samples were prepared for modified T-peel tests by sandwiching the electroactive monomer mixture between metal foils prior to polymerization, then polymerizing the samples. The modified T-peel tests were conducted on 1 x 5 cm sample strips at TRI/Princeton by peeling and measuring on an Instron® with 75 psig upper and lower jaw grip fixtures with 50 N capacity load cell at 200 mm/min crosshead speed and about 1 mm gauge length. For mechanical tests for the strength of bonding between the embedded electrode and the (modified) EAP material, which was polymerized with the electrode in place, a 9.5 kg counterweight was used while the metal electrode was pulled at a rate of approximately 1 kg/sec and the weight at break/detachment recorded.

Surface analysis: X-ray photoelectron spectroscopy (XPS) was performed on untreated and plasma treated metal foils using a VG Scientific ESCALAB Spectrometer, with a 90° angle between the sample and the analyzer. After the modified T-peel testing, samples where the mode of failure was unclear were analyzed using scanning electron microscopy (SEM), using a high resolution field emission FEI XL30 FEG-SEM equipped with a PGT-IMIX EDX system. After mechanical testing of embedded electrode detachment, samples were analyzed using a stereo dissecting microscope.

Cryogenic and elevated temperature experiments: Cryogenic experiments were performed by subjecting the EAPs to 4.2 K (liquid helium), 77.25 K (liquid nitrogen), 194.65 K (dry ice/isopropyl alcohol bath), and 273.15 K (ice bath). Elevated temperature experiments were conducted up to 410 K.

Radionuclide-labeled experiments: Solutions containing a known amount of H-3 and Na-22 in the form of sodium chloride (NaCl) in water were used. A standard stock solution of Na-22 (NaCl in water) with 9.957 microcuries/g (Isotope Products) was diluted in a 1 g standard stock solution: 99 g unlabeled 0.5 % w/v NaCl solution, producing a final activity of 0.1 microcuries/mL. A standard solution of H-3, 1.010 microcuries in 50 g of water, from PPPL's stock calibration inventory in the Princeton Environmental Analytical Radiological Laboratory (PEARL), was diluted using 8.6 g stock H-3 solution: 91.4 g unlabeled 0.5 % w/v NaCl solution, producing a final activity of 0.001126 microcuries/mL (2500 dpm/mL) in 100 g of water. 20 g of the diluted Na-22 solution was mixed with 20 g of the diluted H-3 solution (total volume of 40 g), with a specific activity of 0.05 microcuries/g Na-22 (111,000 dpm/g) and 0.0056 microcuries/g H-3 (1250 dpm/g). Dried samples of the EAPs were immersed in this aqueous NaCl solution containing both Na-22 and H-3 radionuclides for over 24 hours. The EAPs absorbed the liquid and the overall size of the EAPs increased. Immediately before the contraction experiment, the EAP samples were placed in a solution of unlabeled 0.5 % w/v NaCl solution. The EAPs were activated with electric input (50 V), with aliquots taken from the media surrounding the EAPs at 5, 15, 30, 45, 60, 75, and 90 seconds. For the control experiment, EAPs were placed in an unlabeled 0.5 % w/v NaCl solution and, with no electric input, aliquots were taken from the media surrounding the control EAPs at the same timed intervals. Liquid scintillation chromatography (LSC, Perkin Elmer Tri-Carb Detector) was used to measure H-3 with a standard H-3 in water protocol of 1 mL sample/aliquot for 10 mL aqueous LSC mixture. Gamma-ray spectroscopy (GRS, high resolution Intrinsic Germanium Detector with a beryllium window) was used to measure Na-22 by placing 1 mL sample/aliquot on filter paper in a 47 mm Petri dish and counting with a GRS unit calibrated to this geometry. Following each contraction experiment, the EAP (including control EAPs) were placed in a clean unlabeled 0.5 w/v % NaCl solution for several days. This was done to determine the amount of Na-22 and H-3 left in the EAP after the contraction experiment and also to determine if there is any leaching of the radionuclides from the EAPs.

Encapsulation of the electroactive polymer networks/hydrogels: Poly(vinylidene chloride) copolymer film(s) and other materials were used to coat/cover the EAP materials.

RESULTS AND DISCUSSION

The flexible, contractile EAP materials recently developed by Ras Labs are capable of pronounced contraction when subjected to an electric impulse, contracting over 80 % (contracts to less than 20 % of its original weight) in less than a minute at 50 V (Figure 1).^{3,35,36} When the electricity is stopped, the flexible EAP relaxes back to its original size and shape and this contraction-relaxation cycle can be performed repeatedly with no discernible breakdown of the EAP material.

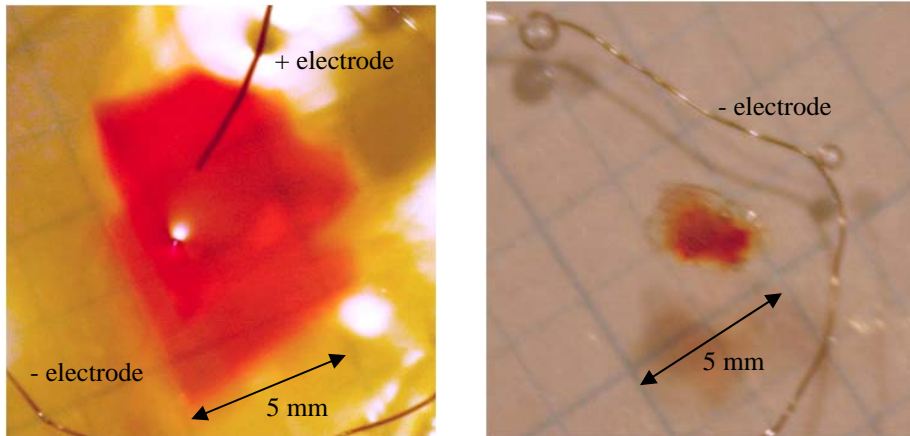


Fig. 1 A. Weight ($t = 0$) = 0.11 g B. Weight ($t = 1$ minute, 50 V) = 0.01 g
Note: Red dye added to (uncoated) EAP to improve visualization. EAP surrounded by electrolyte solution. Electrode removed after experiment for weight determination.

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 2 and 3).

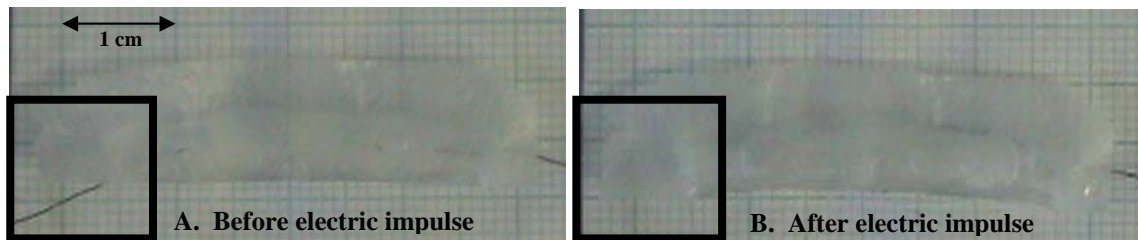


Fig. 2. Coated EAP material with embedded electrodes.

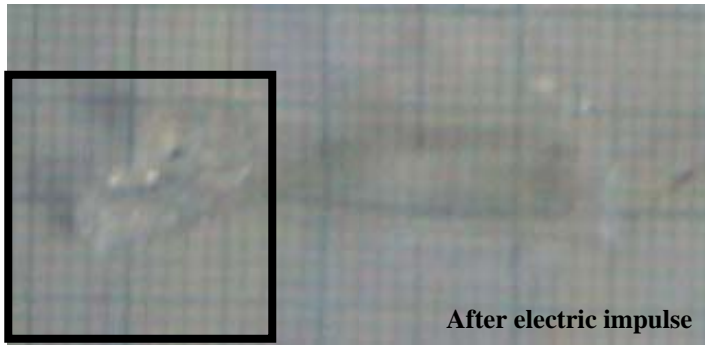


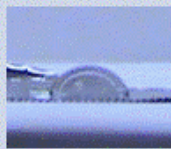


Fig. 3. Damage to EAP material in boxed area.

Note: Coating removed (Fig. 3) to enhance visualization.

Plasma treatment was investigated to improve the interface between the electrode metal and the electroactive material. A CRADA was formed between Ras Labs and PPPL to expand upon improving the attachment of the embedded electrodes to the EAP materials in these actuators using plasma treatment and other treatments to non-corrosive metallic leads. Aircraft grade stainless steel and Grade 2 titanium were subjected to plasma treatment. Several testing methods and surface analyzes were used to determine the metallic surface characterization and strength of the metal-polymer interface.

The water drop surface contact angle test uses a (distilled) water drop on a surface and measures the contact angle. The monomer mixture for the EAP is very hydrophilic. Surfaces with a low contact angle using a water drop are desirable for good metal-polymer cover and adhesion because the monomer mixture then glides uniformly across the metal surface, rather than beading up. The untreated stainless steel had an average water drop surface angle of 81° . Helium and hydrogen plasma treatment did not improve the water drop surface contact angle (117° and 96° , respectively). The nitrogen and synthetic air plasma treatment markedly improved the water drop contact surface angle (26° and 40° , respectively). Using pure oxygen plasma, however, produced the most hydrophilic stainless steel surface (4° contact angle). The untreated titanium had an average water drop surface angle of 81° . Helium, nitrogen, and synthetic air plasma treatment markedly improved the water drop contact surface angle (55° , 47° , and 23° , respectively). Using pure oxygen plasma, however, produced the most hydrophilic titanium surface (5° contact angle).

Table 1. Water Drop Contact Angle Test on Plasma Treated Metal Surfaces

Treatment	Stainless Steel	Titanium	Titanium
Control	81°	81°	
N plasma	26°	47°	
O plasma	4°	5°	

XPS was used to determine the atomic surface composition of plasma treated stainless steel foil by analyzing binding energies for Fe2p, O1s, N1s, and C1s orbitals (Figure 4). For carbon, both the nitrogen and oxygen plasma treatments served to significantly reduce the presence of carbon (C1s C-C peak at 285.3 eV). The presence of carbon is indicative of oils and other organic contaminants. Plasma can strip, sterilize, and super clean metallic surfaces. Nitrogen is difficult to detect using XPS. For nitrogen, there is no discernible peak in the control sample. After nitrogen plasma treatment, a weak peak 396.2 eV (N1s N-Fe peak) was detected. This N-Fe peak was diminished after the oxygen plasma treatment. For oxygen, the oxygen peaks were bimodal, roughly split between the hydroxyl O-H peak (O1s peak at 533.1 eV) and the iron oxide peak (O1s peak at 530.5 eV) (Figure 5). After nitrogen plasma treatment, the O1s peak was markedly elevated, particularly in the oxide region, with a shoulder extending into the hydroxyl region. Again, this is indicative of the nitrogen plasma stripping the metal surface, exposing the iron oxide layer. After subsequent oxygen plasma treatment, the O1s peaks, which were bimodal, were markedly elevated, particularly in the hydroxyl region, indicating an oxygen based chemical modification at the atomic level on the plasma treated stainless steel surface. The high level of hydroxyl groups in addition to a good iron oxide surface should provide for a very hydrophilic metal surface, which was indicated using water drop contact angle tests. For iron, the nitrogen plasma treated sample had the highest peak (Fe2p_{1/2} at 725 eV and Fe2p_{3/2} at 711.5 eV, both peaks from iron oxides). Again, this is indicative of the nitrogen plasma

stripping the metal surface, exposing the iron oxide layer. After oxygen plasma treatment, the iron oxide peaks were slightly diminished, probably due to the pronounced oxygen layer from hydroxyl groups. The nitrogen plasma chemically modified the stainless steel surface somewhat, but more importantly, was paramount in cleaning the metal surface of contaminants. The subsequent oxygen plasma chemically modified the stainless steel surface with oxygen groups in addition to providing for a good, clean iron oxide surface.

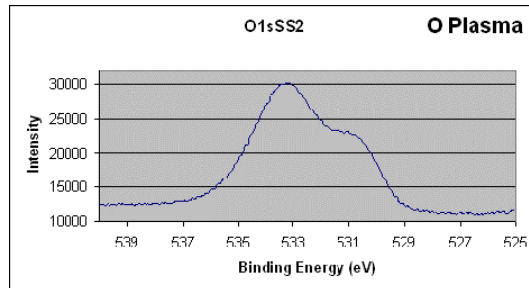
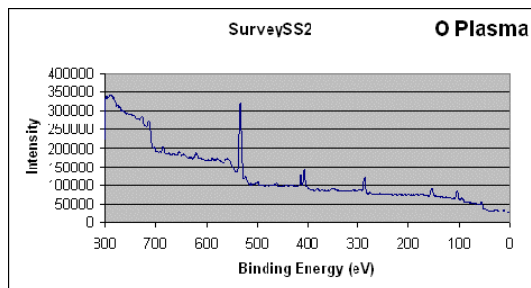
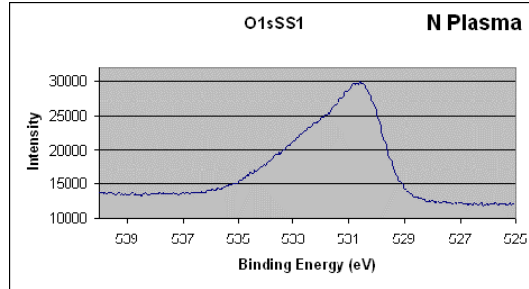
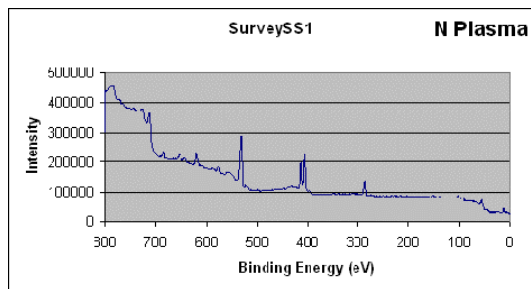
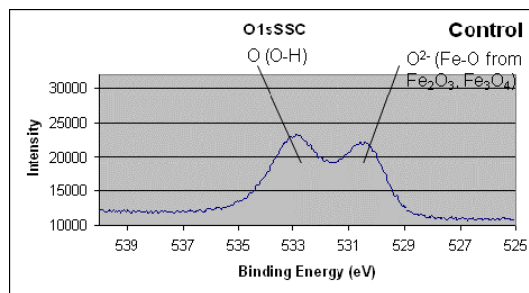
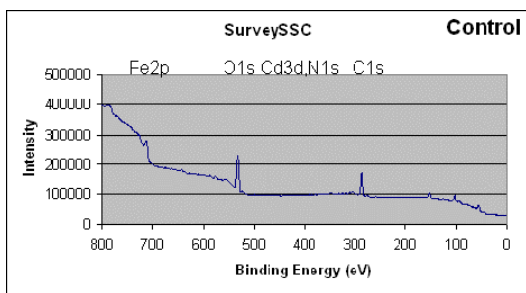


Fig. 4 Stainless Steel XPS Spectra

Fig. 5 Stainless Steel XPS Spectra, O1s Region

Titanium was also analyzed by XPS to determine the atomic surface chemistry of plasma treated titanium foil by analyzing binding energies for O1s, Ti2p, N1s, and C1s orbitals (Figure 6). For titanium, both the nitrogen and oxygen plasma treatments served to significantly reduce the presence of carbon (C1s C-C peak at 285.3 eV, in control sample, small C-Ti peak at 282.2 eV). After oxygen plasma treatment, in addition to a small Ti-N peak at 397.3 eV, there was an additional small, broad peak centered around 400.5 eV, which was indicative of an N-O bond (TiO₂ peak). For oxygen, the oxygen peaks were bimodal, roughly split between the hydroxyl O-H peak (O1s peak at 533.1 eV) and the titanium oxide peak (O1s peak at 530.8 eV) (Figure 7). After nitrogen

plasma treatment, the O1s peak was markedly elevated, particularly in the oxide region, with a shoulder extending into the hydroxyl region, which is indicative of the nitrogen plasma stripping the metal surface, exposing the titanium oxide layer. After subsequent oxygen plasma treatment, the O1s peak was markedly elevated, particularly in the hydroxyl region, with a shoulder extending into the oxide region, indicating an oxygen based chemical modification at the atomic level on the plasma treated titanium surface. The high level of hydroxyl groups in addition to a titanium oxide surface should provide for a very hydrophilic metal surface, which was indicated using water drop contact angle tests. For titanium, the nitrogen plasma treated sample had the highest peaks (Ti2p_{1/2} at 465 eV and Ti2p_{3/2} at 459.2 eV, both peaks from TiO₂). Again, this is indicative of the N plasma stripping the metal surface, exposing the titanium oxide layer. After oxygen plasma treatment, the titanium oxide peaks were significantly diminished, probably due to the pronounced oxygen layer from hydroxyl groups. Like the results from stainless steel, the nitrogen plasma was paramount in cleaning the metal surface of contaminants and the subsequent oxygen plasma chemically modified the metal surface with oxygen groups in addition to providing for a clean titanium oxide surface.

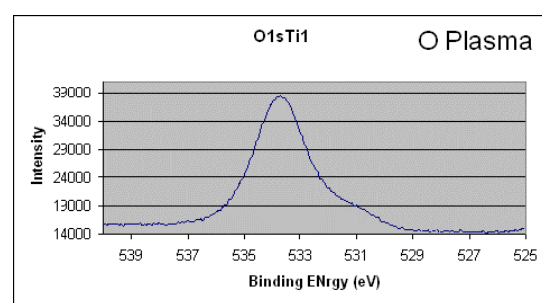
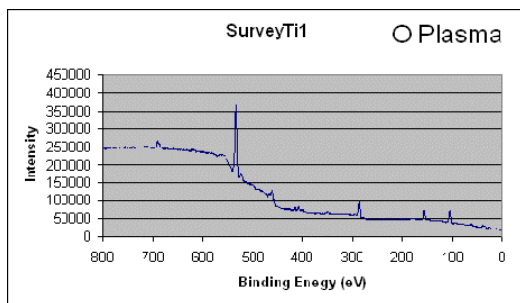
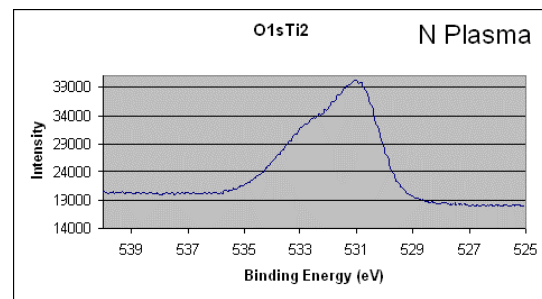
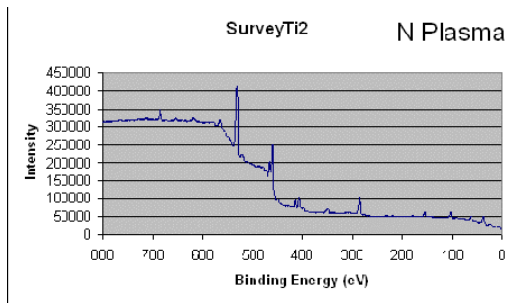
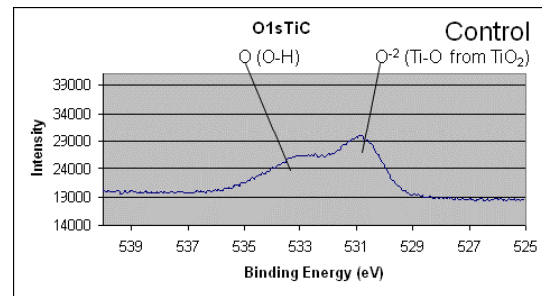
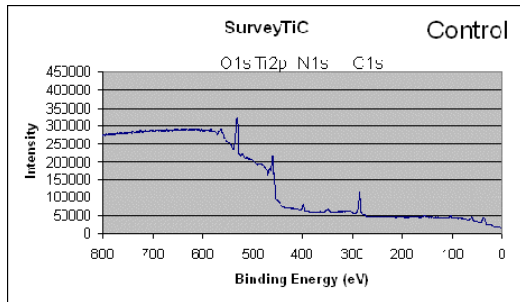


Fig. 6 Titanium XPS Spectra

Fig. 7 Titanium XPS Spectra, O1s Region

Modified T-peel tests were conducted at TRI/Princeton to determine the adhesive strength between the EAPs and stainless steel foil. The mode of failure was determined by visualization and scanning electron microscopy (SEM). The same testing was also performed on titanium foil. All of the plasma treated stainless steel was improved compared to the untreated stainless steel control in terms of strength of adhesion (Table 2). The nitrogen plasma treated titanium was significantly improved in terms of strength of adhesion (Table 3), with an average peak force of 9.846 N compared to the average peak force of 1.810 N for the untreated control.

Table 2. Average Peak Forces for Modified T-Peel Test of Polymer-Stainless Steel

Plasma Treatment	Mean Peak Force (N)
Control	2.736
Nitrogen	3.350
Synthetic Air	4.430
Helium	5.098
Hydrogen*	5.326

* Mode of failure was at the interface and polymer in contact with H plasma treated surface was opaque and hard, rather than a soft hydrogel, which is undesirable.

Table 3. Average Peak Forces for Modified T-Peel Test of Polymer-Titanium

Plasma Treatment	Mean Peak Force (N)
Control	1.810
Helium	3.374
Synthetic Air	4.050
Nitrogen	9.486

After the modified T-peel tests, the metal strips were observed to determine mode of failure. In most cases, from visualization, the failure was within the polymer layer. In a few samples, it was difficult to determine the mode of failure from visualization, so SEM was used to determine mode of failure for areas that appeared, to the naked eye, to be stripped of polymer (Figure 8). Using SEM, the mode of failure for the synthetic air plasma treated stainless steel appeared to be within the polymer layer (Micrograph A). For titanium, in most cases the mode of failure was within the polymer layer from visualization. In some of the nitrogen plasma treated titanium samples, areas that appeared visually to be stripped of polymer were determined by SEM to be interfacial failure (Micrograph E).

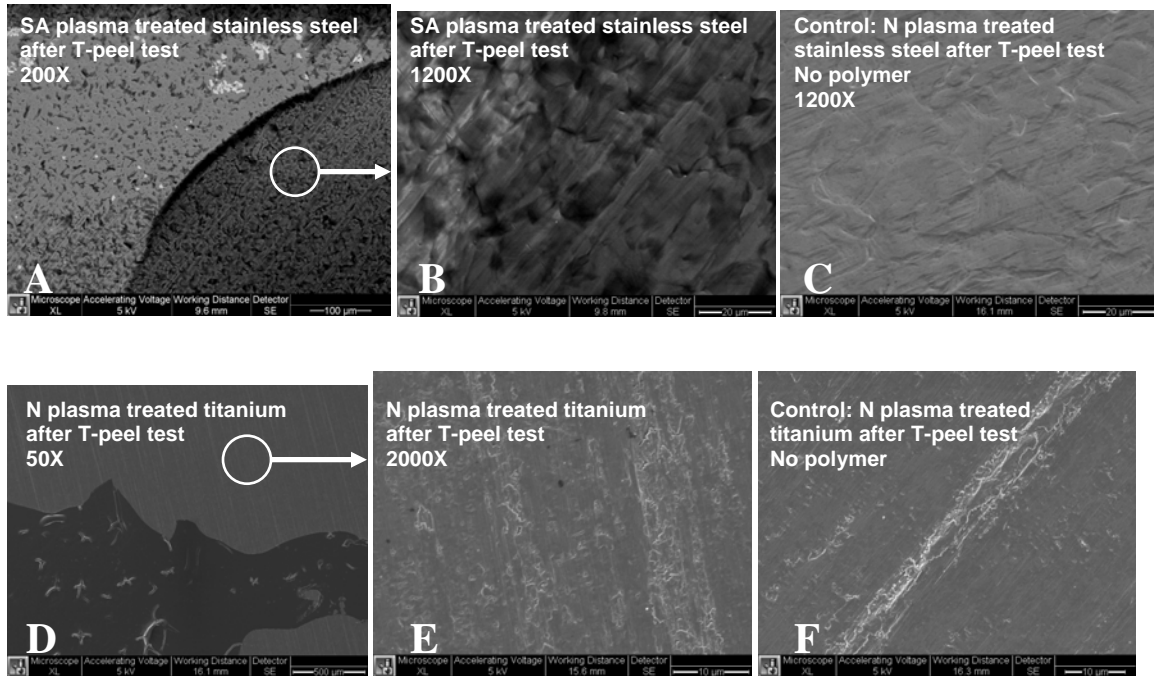


Fig. 8. SEM micrographs to determine mode of failure for selected stainless steel and titanium samples.

For mechanical testing of the bond strength between the embedded electrode and the (modified) EAP material, which was polymerized with the electrode(s) in place, a heavy counterweight was used while the electrode was pulled at a consistent rate until the electrode broke free and detached from the polymer (Figure 9). For stainless steel and for titanium, oxygen plasma treatment produced the best metal-polymer interfaces (Tables 4 and 5).

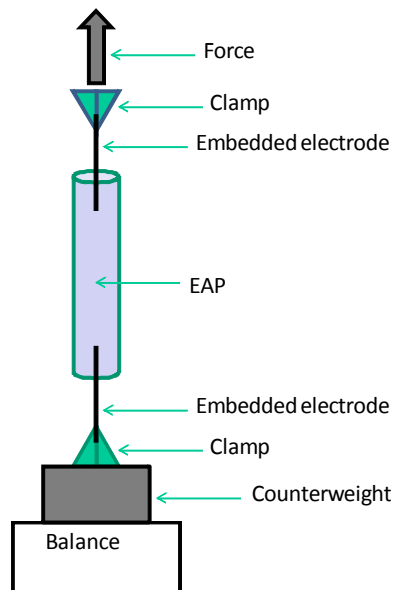


Fig. 9. Mechanical Testing to Determine Strength of Polymer-Metal Interface.

After the mechanical testing of the bond strength between the embedded electrode and the EAP material, the metal wires were observed to determine mode of failure using visualization and a stereo dissecting microscope (Table 6). In most cases, the failure was at the interface. For a few wire samples, the mode of failure was a mixed mode between interfacial failure and failure within the polymer layer.

Table 4. Stress Test to Break of Plasma Treated Stainless Steel Electrodes in EAP Actuators

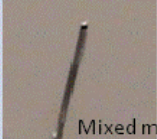

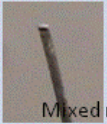

Sample	Weight to break (g)	Distance (cm)	Stress (N/m ² = kg/ms ²)	<Stress> (N/m ²)
Control 1	1,100	0.9	122	125
Control 2	2,300	1.8	128	
N plasma 1	610	0.8	76.2	76
N Plasma 2	920	1.2	76.8	
O plasma 1	3,700	1	370	349
O plasma 2	5,900	1.8	328	

Table 5. Stress Test to Break of Plasma Treated Titanium Electrodes in EAP Actuators

Sample	Weight to break (g)	Distance (cm)	Stress (N/m ² = kg/ms ²)	<Stress> (N/m ²)
Control 1 [†]	183	1	18.3	
Control 2	5,600	1.3	431	431
N plasma 1	6,800	1.5	453	476
N Plasma 2	7,500	1.5	500	
O plasma 1	6,300	1	630	746
O plasma 2	6,900	0.8	862	

[†] Control 1 not used in average data set.

Table 6. Mode of Failure for Stress Test to Break

Sample	Mode of Failure	Selected Pictures
Stainless Steel C-1, C-2, C-3, C-4, C-5, C-6	Interface, mostly interface, mostly interface, interface, interface, mostly interface	—
Stainless Steel N-1, N-2, N-3	Interface, mixed mode, interface	—
Stainless Steel N-O-1, N-O-2, N-O-3, N-O-4	Interface, mixed mode, Interface, interface	 Mixed mode
Stainless Steel O-1, O-2	Interface, interface	 Interfacial
Titanium C-1, C-2	Interface, mixed mode	 Mixed mode
Titanium N-1, N-2	Mostly interface, mostly interface	—
Titanium N-O-1, N-O-2	Mostly interface, interface	—
Titanium O-1, O-2	Interface, interface	 Interfacial

Cryogenic experiments were performed by subjecting contractile EAPs to 4.2 K using liquid helium, 77.25 K using liquid nitrogen, 194.65 K using a dry ice/isopropyl alcohol bath, and 273.15 K using an ice bath. After the EAP was exposed to 4.2 K by attaching to a probe and lowering into a Dewar of liquid helium, then thawed, the EAP contracted down to 54 % from its original weight when exposed to 50V (0.013 g to 0.07 g). After the EAP was exposed to 77.25 K using liquid nitrogen, then thawed, the EAP contracted down to 24 % of its original weight when exposed to 50 V (0.25 g to 0.06 g). After the EAP was exposed to 194.65 K using a dry ice/IPA bath, the EAP contracted down to 40 % of its original weight when exposed to 50 V (0.10 g to 0.04 g). Exposing these contractile EAPs to even extremely cold temperatures did not affect their ability to contract when electrically stimulated. Elevated temperature experiments were conducted up to 410 K using a hot oil bath. The EAP was fine to 373 K (100°C), but above 408 K (135°C), the EAP began to physically distort.

Most of the theory of EAPs concerns bending. Contraction is not well understood. A radionuclide experiment was performed to determine, in as close to real time as possible, the chain of events that occurs when electricity is applied to EAP materials, both in terms of water loss and electrolyte flow during contraction (Figure 10). EAP samples were immersed in aqueous solutions containing known concentrations for both H-3 and Na-22 radionuclides and allowed to swell/equilibrate. For the electroactive experiment, EAP samples were then placed in an unlabeled aqueous NaCl solution and subjected to electric input. Aliquots of the surrounding solution were removed in timed intervals during the electric input. Control experiments were also performed, where no electricity was applied to sample EAPs while aliquots were removed in the same timed intervals. LSC was used to detect tritium levels and GRS was used to detect Na-22 levels.

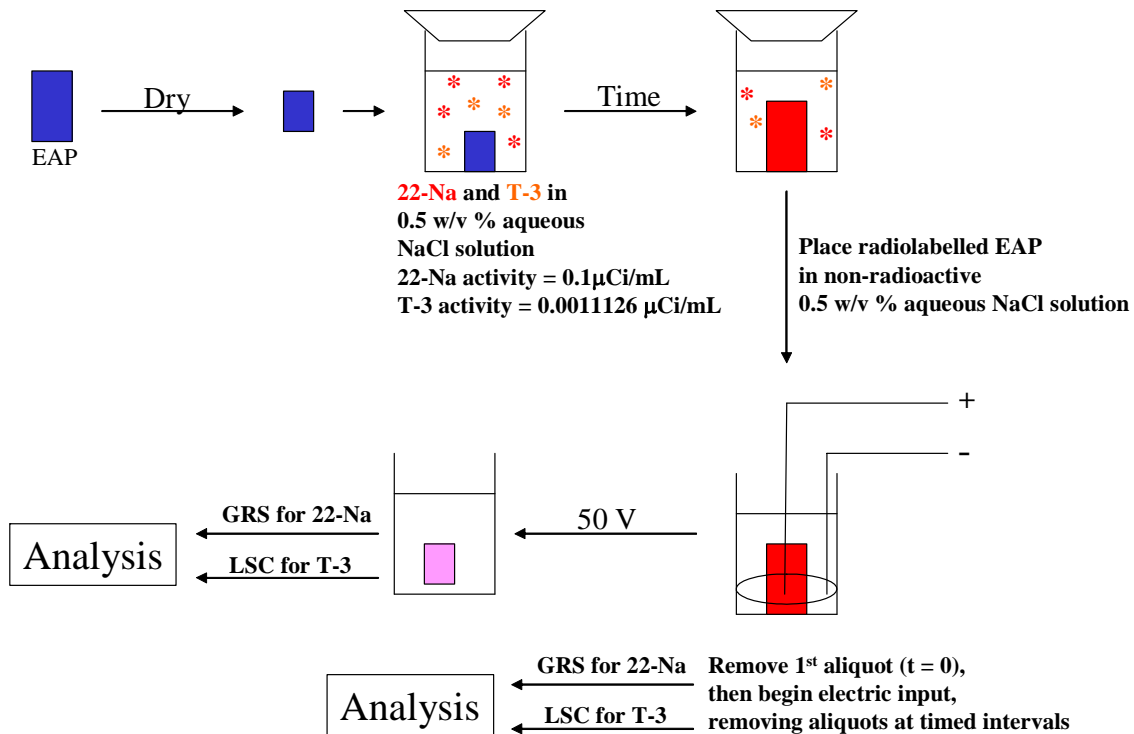


Fig. 10. Radionuclide experiment to follow EAP contraction.

The results from this preliminary radionuclide experiment indicate that during the electric input, Na-22 leaves the contractile EAP very quickly, with significant outflow of the positive sodium ions towards the negative electrode within 5 seconds. The outflow plateaus around 75 seconds. Based on the control (no electric input), the Na-22 is retained very tightly to the EAP material, while the tritium has some baseline mobility in and out of the EAP. Once the EAP is activated by electricity, the positive sodium ions and water move very quickly and simultaneously out of the EAP material, leading to a very fast, pronounced contraction (Figure 11 and Figure 1). Indeed, it appears that electricity is required in order for sodium ions to flow out of these contractile EAPs.

Following water loss by volume change and weight conversions in real time show a similar trend (Figure 12).

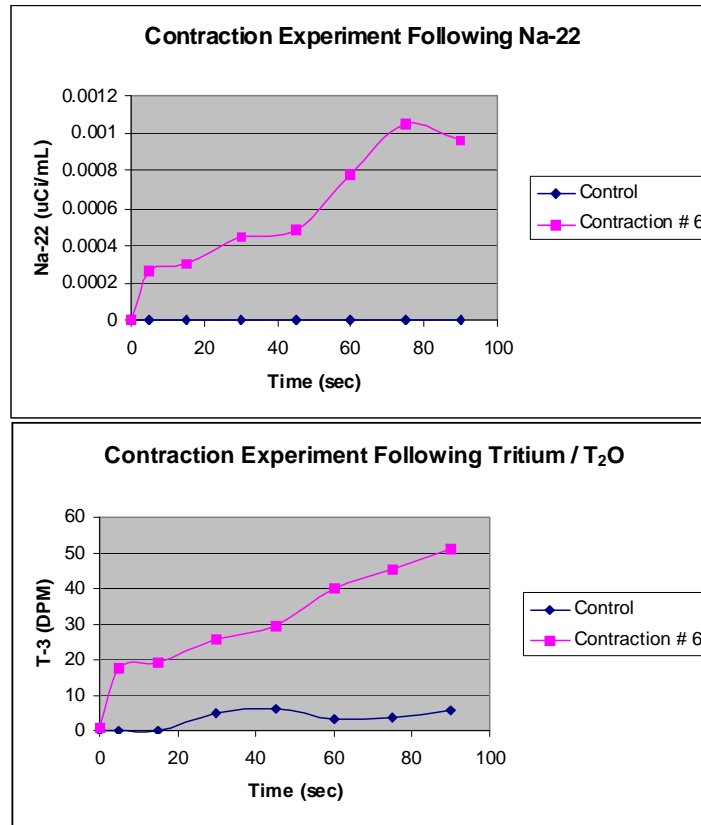


Fig. 11. Radionuclide-labeled contraction experiments.

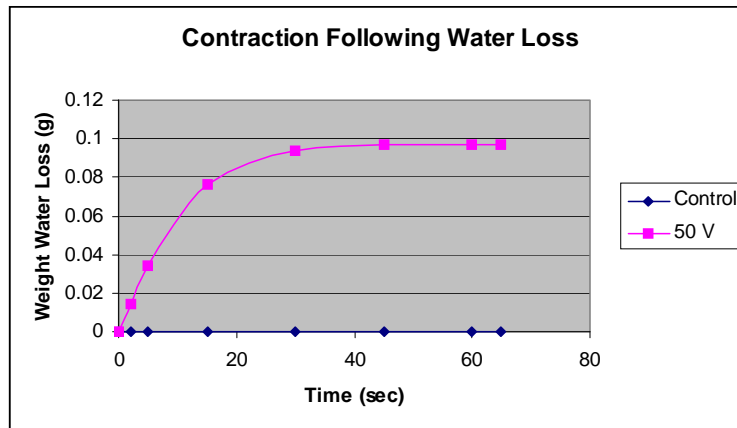


Fig. 12. Contraction following water loss.

After the electric input part of the radionuclide-labeled experiment, the EAPs were placed in fresh unlabeled aqueous sodium solution, allowed to equilibrate for several days, and then aliquots taken from each equilibration media (Figure 13). GRS found no Na-22 activity in the equilibration media, while tritium levels were fairly high, particularly for the control (Table 7). Again, this indicates that the Na-22 is very tightly

bound to the contractile EAPs when there is no electricity. Currently, GRS is being used to analyze the EAPs themselves (the contraction experimental samples and controls), which is well after the contraction part of the experiment, to account for the location of all 22-Na, particularly in the controls which had no electric input.

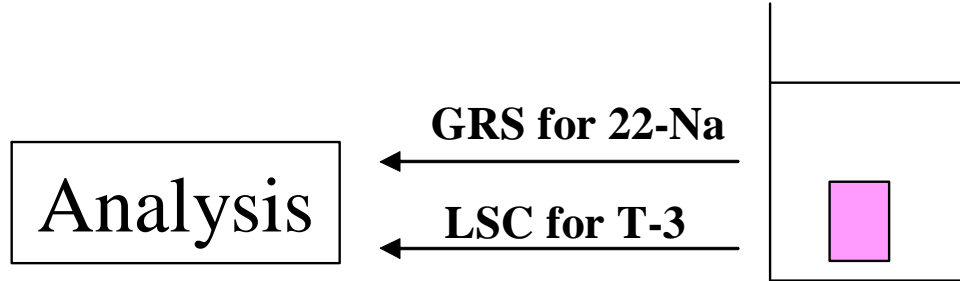


Fig. 13. Radionuclide equilibration following contraction.

Table 7. Radionuclide-labeled equilibration results following contraction experiment.

Sample	Na-22 (DPM)	T-3 (DPM)	Normalized T-3 [†]
Control	0	53.60	100
Contraction EAP	0	20.85	34

[†] Normalized with respect to the control and to the initial weight of the EAPs.

The last step in producing a prototype actuator was to encapsulate the electroactive materials, with electrolyte solution(s) and embedded electrodes in place, with a thin, flexible, moisture-barrier coating, analogous to skin (Figure 14) to prevent evaporation and leakage of the electrolyte solution from the EAPs. The coating step can be repeated as needed to give good coverage, however, too thick an overall coating impedes movement. Elasticity of the coating is also very important, because if the coating is too stiff, movement is impeded.

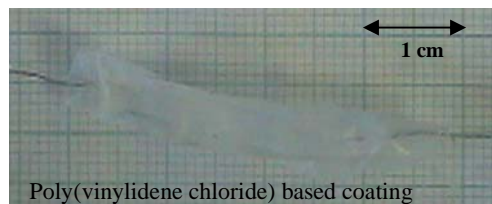


Fig. 14. Encapsulated electroactive materials with embedded electrodes.

CONCLUSIONS

EAPs with good strength, flexibility, and electroactivity, particularly contraction, have been developed, with the ability of some of these EAP materials to contract over 80 % (less than 20 % of their original weight) within 1 minute at 50 V, and then return to their original size and shape when the electric input is stopped. Research and development to significantly improve the polymer-electrode interface has been performed, with significantly better adhesion between the embedded electrode(s) and the EAP. Based on the water drop surface contact angle tests and mechanical testing, oxygen plasma treated stainless steel and titanium produced significantly improved polymer-metal interfaces. For both stainless steel and titanium, XPS confirmed the presence of a good, clean oxide layer with a large presence of elemental oxygen in the form of hydroxyl groups after oxygen plasma treatment, which significantly increased the hydrophilicity of these metal surfaces. The goal is for both the electroactive material and the embedded electrode(s) to move as a unit, analogous to our muscles, nerves, and tendons moving together. In this analogy, the EAP material serves as the artificial muscle, and the plasma treated electrode(s) serves as both a tendon, connecting the EAP to a lever, and as a nerve, delivering electric stimulus to the EAP. Thin elastomeric coatings, which also serve as a moisture barrier, act as skin, preventing evaporation and leakage of the electrolyte solution(s) and potentially allow these actuators to be fully operational anywhere. Using radionuclides, the electrolyte and water flow could be followed as contraction occurred. The positive sodium ions are very tightly associated with the ionic EAP, unless there is electric input. Once the EAP is electrically activated, the sodium ions rapidly leave the EAP towards the negative electrode, simultaneously bringing water molecules with them, leading to a rapid and pronounced contraction. This understanding of EAP contraction theory based on solid experimental results is being applied to synthesize EAPs and prototype actuators with enhanced strength, flexibility, energy efficiency, durability, and electroactivity, particularly contraction.

ACKNOWLEDGEMENTS

This work was supported in part by the Department of Energy, US DOE Contract No. DE-AC02-CH0911466. We would also like to thank Don Harper and Kimun Park at TRI/Princeton for performing the modified T-peel tests, Prof. Robert J. Cava and Anthony Williams of the Department of Chemistry's Solid State Chemistry Lab at Princeton University for their help with extremely low temperature experiments, and Dr. Jane Woodruff and Prof. Nan Yao at the Princeton University Imaging and Analysis Center (IAC) for performing the scanning electron microscopy.

REFERENCES

- ¹ L. Rasmussen, "Electrically Driven Mechanochemical Actuators that can act as Artificial Muscle," US Patent Application 11/478431 (2005).
- ² L. Rasmussen, "Process for Producing an Electrically Driven Mechanochemical Actuator," U.S. Patent 5736590 (1998).
- ³ L. Rasmussen, "Electroactive Materials and Electroactive Actuators that Act as Artificial Muscle, Tendon, and Skin," US Patent Application (2009).
- ⁴ Heim, J., "Electric Polymer Actuated Devices," US Patent Application 11/933,277, Artificial Muscle (2007).
- ⁵ 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).
- ⁶ Pei, Q., Pelrine, R. E., and Kornbluh, R. D., "Electroactive polymers," US Patent 7,049,732, SRI International (2006).
- ⁷ Pelrine, R. E., Kornbluh, R. D., and Pei, Q., "Electroactive polymer transducers and actuators," US Patent 6,940,211, SRI International (2005).
- ⁸ 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).
- ⁹ Kornbluh, R. D., and Pelrine, R. E., "Variable stiffness electroactive polymer systems," US Patent 6,882,086, SRI International (2005).
- ¹⁰ Pei, Q., Pelrine, R. E., and Kornbluh, R. D., "Electroactive polymers," US Patent 6,812,624, SRI International, 2004.
- ¹¹ Pelrine, R. E., Kornbluh, R. D., and Pei, Q., "Electroactive polymer transducers and actuators," US Patent 6,781,284, SRI International, 2004.
- ¹² 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.
- ¹³ Pelrine, R. E., and Kornbluh, R. D., "Non-contact electroactive polymer electrodes," US Patent 6,707,236, SRI International, 2004.
- ¹⁴ Pelrine, R. E., Kornbluh, R. D., Pei, Q., and Joseph, J. P., "Electroactive polymer electrodes," US Patent 6,583,533, SRI International, 2003.
- ¹⁵ Pelrine, R. E., and Kornbluh, R. D., "Electroactive polymer devices," US Patent 6,545,384, SRI International, 2003.
- ¹⁶ Pelrine, R. E., Kornbluh, R. D., Pei, Q., and Joseph, J. P., "Electroactive polymer electrodes," US Patent 6,376,971, 2002.
- ¹⁷ Pelrine, R. E., Kornbluh, R. D., Oh, S., and Joseph, J. P., "Electroactive polymer fabrication," US Patent 6,543,110, 2003.
- ¹⁸ Pelrine, R. E., Kornbluh, R. D., Pei, Q., Oh, S., Joseph, J. P., "Electroactive polymers and their use in devices for conversion of electrical to mechanical energy," US Patent 6376971 B1 (2002), WO Patent 2001006579 A2 (2001), EP Patent 1221180 A2 (2002), JP Patent 2001524278 T2, 2001.
- ¹⁹ Lacour, L. P., Prahlad, H., Pelrine, R., and Wagner, S., *Sensors and Actuators A: Physical*, 111(2-3), 288-292 (2004).
- ²⁰ Pei, Q., Pelrine, R., Stanford, S., Kornbluh, R., and Rosenthal, M., *Synthetic Metals*, 135-135(4), 129-131, 2003.
- ²¹ Pelrine, R., Kornbluh, R., Pei, Q., and Joseph, J., *Science*, 287(5454), 836-839, 2000.
- ²² Pelrine, R., Kornbluh, R., Joseph, J., Heydt, R., Pei, Q., and Chiba, S., *Mater. Sci. and Eng.: C*, 11(2), 89-100, 2000.
- ²³ Ashley, S., *Sci. Amer.*, 289(4), 52-59, 2003.
- ²⁴ 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.
- ²⁵ Hirako, Y., Suzuki, M., Hirai, T., and Watanabe, M., "Polymeric actuators," JP Patent 2001258275 A2, Nippon Zeon Co., 2001.
- ²⁶ Kurita, Y., Ueda, T., Kasazaki, T., and Hirai, T., "Polyurethane elastomer actuator," US Patent 5,977,685, Nitta Corporation, 1999.

-
- ²⁷ Amaike, Y., Ueda, A., Suzuki, M., Hirai, T., and Watanabe, S., "Polymer actuator," JP Patent 2000049397 A2, Nitta Corporation, 2000.
- ²⁸ 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.
- ²⁹ Benslimand, M.Y., Gravesen, P., "Elastomer Actuator and method of making an actuator," US Patent Application 11/890,381, 2007.
- ³⁰ Shahinpoor, M., Kim, K. J., and Mojarad, M., "Artificial Muscles: Applications of Advanced Polymeric Nanocomposites," Taylor & Francis Group, LLC © 2007.
- ³¹ Anderson, I. A., Calius, E.P., Gisby, T., Hale, T., McKay, T., O'Brien, B., and Walbran, S., *EAPAD 2009 Proc. of SPIE*, Vol. 7287, 72871H-1, 2009.
- ³² http://www.astp.com/plasma/pl_examples.html .
- ³³ Tanaka, T., Nishio, I, and Sun, S. T., "Collapse of Gels in an Electric Field," *Science*, 218, 467-469, 1982.
- ³⁴ Osada, Y., "Conversion of Chemical Into Mechanical Energy by Synthetic Polymers," *Advances in Polymer Science* 82, Springer-Verlag Berlin Heidelberg, 3-46, © 1987.
- ³⁵ L. Rasmussen, EAP-in-Action live demonstration of Ras Labs contractile electroactive materials, *SPIE EAPAD 2009 11th Smart Structures and Materials Conference*, San Diego, CA, 3/9/2009, http://ndeaa.jpl.nasa.gov/nasa-nde/lommas/eap/EAPIA/EAP-in-Action_2009.htm.
- ³⁶ L. Rasmussen, C. J. Erickson, and L. D. Meixler, "The Development of Electrically Driven Mechanochemical Actuators that Act as Artificial Muscle," *SPIE Electroactive Polymers and Devices (EAPAD) 2009, Proc. of SPIE*, Vol. 7287, pp. 7287E1-72871E-13, 2009.

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