

# Synthesis and characterization of EDOT-based conducting polymer actuators

N. Vandesteeg<sup>\*a</sup>, P. G. Madden<sup>b</sup>, J. D. Madden<sup>c</sup>, P. A. Anquetil<sup>b</sup>, I. W. Hunter<sup>b</sup>

<sup>a</sup> Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA USA 02139-4307

<sup>b</sup> Dept. of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA USA 02139-4307

<sup>c</sup> Dept. of Electrical and Computer Engineering, The University of British Columbia, 2329 West Mall Vancouver, BC Canada V6T 1Z4

## ABSTRACT

Freestanding films of poly(3,4-ethylenedioxythiophene), PEDOT, were synthesized electrochemically from a solution containing EDOT monomer, tetrabutylammonium hexafluorophosphate, and water in propylene carbonate. The films were tested mechanically under constant stresses ranging from 0.6 to 2.1 MPa and subjected to various electrochemical waveforms while immersed in a bath containing propylene carbonate and an electrolyte. The characterization resulted in observations of ultimate linear strains of 2%, strain rates of 0.003 Hz, and strain to charge densities of  $4 \times 10^{-10} \text{ m}^3/\text{C}$ , comparable to the conventional conducting polymer polypyrrole. In addition to the quantitative analysis, evidence of both anionic and cationic intercalation into the polymer is presented with a discussion of prospective mechanisms and consequences.

**Keywords:** poly(3,4-ethylenedioxythiophene), PEDOT, PEDT, actuator, artificial muscle

## 1. INTRODUCTION

Conventional electroactive polymer actuators exploit volume changes driven by the flux of ions in and out of the bulk material. These ions are forced either chemically or electrochemically and can be used to perform work against an applied load. To date numerous polymers have shown such capability, including polyacetylene, polypyrrole and polyaniline<sup>1</sup>. While some researchers have continued to work with these materials in attempts to improve performance and build devices, others have sought new electroactive polymers that may incorporate conformational changes at the molecular level<sup>2,3</sup>. As these efforts continue, it will remain important to study polymers that actuate via ion intercalation and bulk swelling since changing the oxidation state of a polymer will always require a compensating charge to be transferred from the solution. Furthermore, as polymer actuators increase in complexity, the use of traditional electroactive monomer species as components of larger macromers requires an understanding of the effect of each group.

Poly(3,4-ethylenedioxythiophene), discovered in the 1980s at Bayer AG, is now well established in the field of conducting polymers. Abbreviated often as PEDT or PEDOT, it has been sought for numerous properties including low bandgap, high electrochemical stability, optical clarity in thin films, and good conductivity<sup>4</sup>. Industrially, a blend of PEDOT with poly(styrene sulfonic acid) in water has emerged as an antistatic film forming dispersion, and is currently available from Bayer AG. While other applications have been tried with success<sup>5</sup>, PEDOT has remained isolated from the field of conducting polymer actuators, despite the observations of volume change in bilayers by Inganäs et al in 1996<sup>6</sup>. The scarcity of information, coupled with an interest in discovering how a single 3,4-ethylenedioxythiophene (EDOT) group would contribute to a larger actuating monomer, led to an interest in synthesizing and characterizing PEDOT actuators.

\* Corresponding Author. Tel.: +1.617.258.0533 Fax: +1.617.252.1849 e-mail: vandest@mit.edu

This paper reports on the initial findings of such a study. It presents a short summary of a successful synthetic procedure for preparing freestanding PEDOT films, followed by an overview of initial active linear mechanical characterization of the films. As will be shown, neither the synthesis nor the characterization presents the optimal actuator solution, but rather contributes to an understanding of the potential of this material, which is relatively new to the conducting polymer actuator field.

## 2. SYNTHESIS

PEDOT can be synthesized a number of ways, including direct chemical oxidation, electrochemical oxidation, and transition metal catalyzed couplings common to an organic chemistry laboratory<sup>4</sup>. EDOT is a particularly attractive electroactive monomer, as it is blocked at both  $\beta$  sites which are known to cause structural and electronic defects in polythiophenes and polypyrroles. As such, the resulting polymer should be more regioregular and have larger molecular weights and conjugation lengths. Insolubility problems plague the complete characterization of PEDOT, like many of the other conducting polymers, but its low bandgap and good material properties are often indicative of low defect density and successful polymerization<sup>4</sup>. For use in actuators, electrochemical polymerization was appropriate as it enables the use of any of a number of electrolytes and solvents and would furnish a film already doped with anions. Tests were done with a large cation salt (TBAPF<sub>6</sub>) that has been used previously in polypyrrole actuators where only the anion actively diffuses into and out of the polymer bulk<sup>7,8</sup>. As will be discussed in the next section, it was later discovered that the large cation played an important role in the actuation mechanism.

Freestanding films of PEDOT were prepared from a solution containing 0.06 M EDOT, 0.06 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) and 0.6 M water in propylene carbonate (PC)<sup>9,10</sup>. The EDOT was supplied by Bayer AG and was freshly distilled before use, while all other reagents were used as received. The solution was prepared under an argon atmosphere and poured into an electrochemical cell containing a glassy carbon working electrode and copper counter electrode. No effort was made to directly exclude oxygen during deposition, though the electrochemical cell was covered with wax film (Parafilm) to prevent exposure to a steady stream of air. Deposition occurred under a constant current of 0.4 mA/cm<sup>2</sup> at -20 °C. The resulting film was glossy black, varying in thickness from 20 to 70  $\mu$ m and with conductivities between 1 and 8 S/cm. The PEDOT films were readily peeled from the working electrode, but were not allowed to dry and were stored and tested in the electrochemical solution without monomer.

## 3. CHARACTERIZATION

### 3.1 Experimental setup

The testing apparatus depicted in Figure 1 was used for all characterization of PEDOT films. In the apparatus, the polymer is connected both mechanically and electrically on both ends by means of copper alligator clips, which have been coated with polyurethane on the outside to minimize electrochemical interference. The electrochemical solution of 0.05 M TBAPF<sub>6</sub> in PC is contained within a large nylon bath with a stainless steel counter electrode and an Ag/AgClO<sub>4</sub> reference electrode. A potentiostat (Amel, Milan Italy) controls the cell potential or current and is connected to a computer through a data acquisition board. In addition, mechanical information is passed from the load cell (GS Sensors, Ephrata PA USA) into the computer, enabling force feedback and constant stress measurements via the single axis stage (CompuMotor Parker Hannifin, Cleveland OH USA). All techniques were performed with custom Visual Basic applications, including cyclic voltammetry and various isotonic (constant stress) and isometric (constant strain) measurements. For this study, a focus was placed on isotonic testing since it enables the acquisition of key parameters such as strain rate and overall strain achievable against a known load. Isotonic testing also simplifies the calculation of the characteristic ratio of strain to charge density, known to be indicative of actuator performance<sup>11</sup>. For all data presented, negative strains correspond to contraction and positive strains correspond to extension of the film.

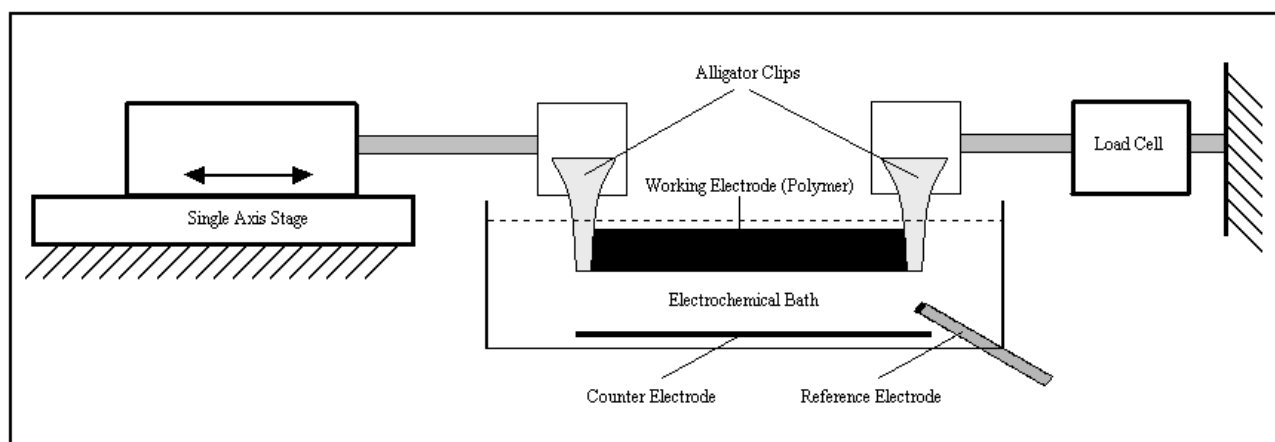


Figure 1: Schematic diagram of polymer testing apparatus.

For isotonic testing, a relatively simple algorithm was designed to provide fast control over the force feedback loop while simultaneously sampling data and controlling the electrochemical cell through the potentiostat. Force feedback was provided at frequencies between 1 kHz and 10 kHz. The addition of a tolerance on the order of 0.1% of the force prevented the stage from reacting to very small deviations from the desired force. The voltage or current waveform was preloaded into an array before run-time to ensure fast execution, and the input values were all converted after run-time to minimize time spent converting raw data. The resulting software enabled the apparatus depicted in Figure 1 to obtain isotonic measurements using one data acquisition card and one computer interface with complete GUI control.

### 3.2 Stepped potential experiments

Small PEDOT films (typically 15 mm x 4 mm x 30 $\mu$ m) were first immersed in the electrochemical bath and allowed to equilibrate while the open circuit potential (OCP) was monitored via the reference electrode. This equilibration did not take long as the bulk film had been stored in a PC solution of similar salt concentration. Next, the films were held at constant force for 30 seconds to allow for some attenuation of initial creep in the sample and to avoid spikes in the strain measurement upon startup. Following the hold, the films were subjected to a low frequency square potential wave of known magnitude and centered about the OCP. This was done in order to minimize the amount of drift in charge on the material, which introduces a corresponding drift in the strain over the course of the test. Some drift in strain and charge both occurred and samples did not typically return to their original length. Figure 2 presents the results of a series of such tests of one sample at 0.0125 Hz and 1.0 Volt amplitude against various stresses that were cycled from 0.6 to 2.1 MPa and returned to 0.6 MPa.

The results show that at low frequencies, strains on the order of 1% can be achieved with small differences in voltage. Tests of significantly longer duration did not increase the amount of strain observed, as the highest strain produced with PEDOT was roughly 2% and occurred with significant creep and some degradation. Furthermore, it is noted that the relative strains achieved did not differ appreciably within the range of loads applied. This supports a strain based volume-intercalation mechanism in which the electrochemical driving force greatly exceeds the mechanical force holding the polymer. Indeed, larger strains were produced against the largest stresses. This observation suggested that the high strains were perhaps due to an alignment caused during the high stress tests that benefited the performance of the polymer. However, the correlation of strain achieved to stress applied was observed in many samples and for cycles of experiments from low to high stresses and back again. Also noteworthy is the presence of a slight contraction upon the initial application of the negative potential apparent in the data. This is counterintuitive as the principle strain direction is positive during negative potential sweeps in this test and the contractile jump occurs after a long period of contraction with increasing charge. One possible explanation for the anomaly is that both cations and anions may be swelling the film, a topic that will be discussed in greater detail in Section 3.4.

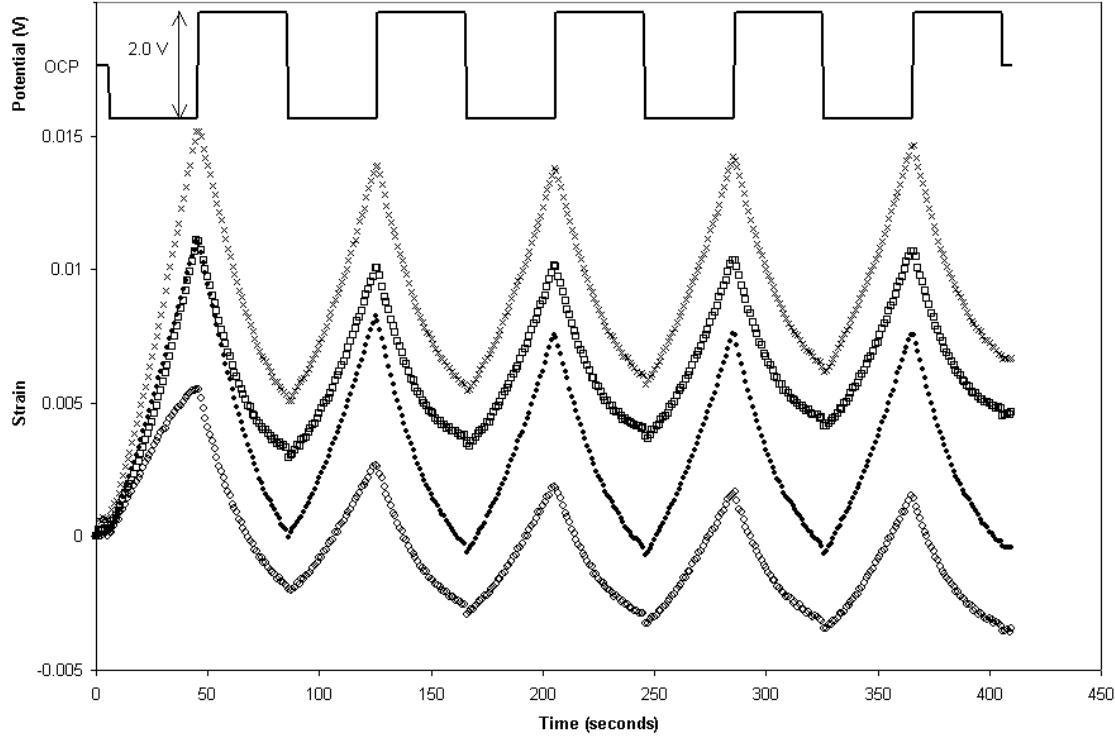


Figure 2: Isotonic data obtained against loads from 0.6 to 2.1 MPa. diamonds: 0.6 MPa, dots: 1.5 MPa, squares: 1.8 MPa, crosses 2.1MPa.

### 3.3 Stepped current experiments

During constant current control, care must be taken to avoid over-oxidizing the film, which leads to degradation and loss of performance in the polymer. This occurs because more voltage is applied to maintain the current as the film reaches saturation. The constant potential tests in Section 3.2 do not risk over-oxidation since the current decreases with time, approaching the small leakage value of the electrochemical cell. In spite of the risks, however, constant current control provides an excellent way to measure the actuation mechanism by maintaining a constant flux of ions.

For this set of experiments, similarly sized films were used. In order to prevent the application of high voltages, a check was added to the software to enable the current to be lowered during the test if a voltage threshold was exceeded. Figure 3 presents the results of a number of such tests in which square current waves of increasing amplitude were applied to a film held at 1.0 MPa. The voltage limit was set to  $\pm 3.0$  V and no degradation was observed at 0.1 Hz, reflecting the well-known electrochemical stability of PEDOT<sup>12</sup>. At higher voltages and lower frequencies, a trail of dark material was observed to flow from the polymer to the counter electrode, indicating degradation and confirming the observation that high voltages can only be applied to conducting polymer actuator systems for short times<sup>13</sup>.

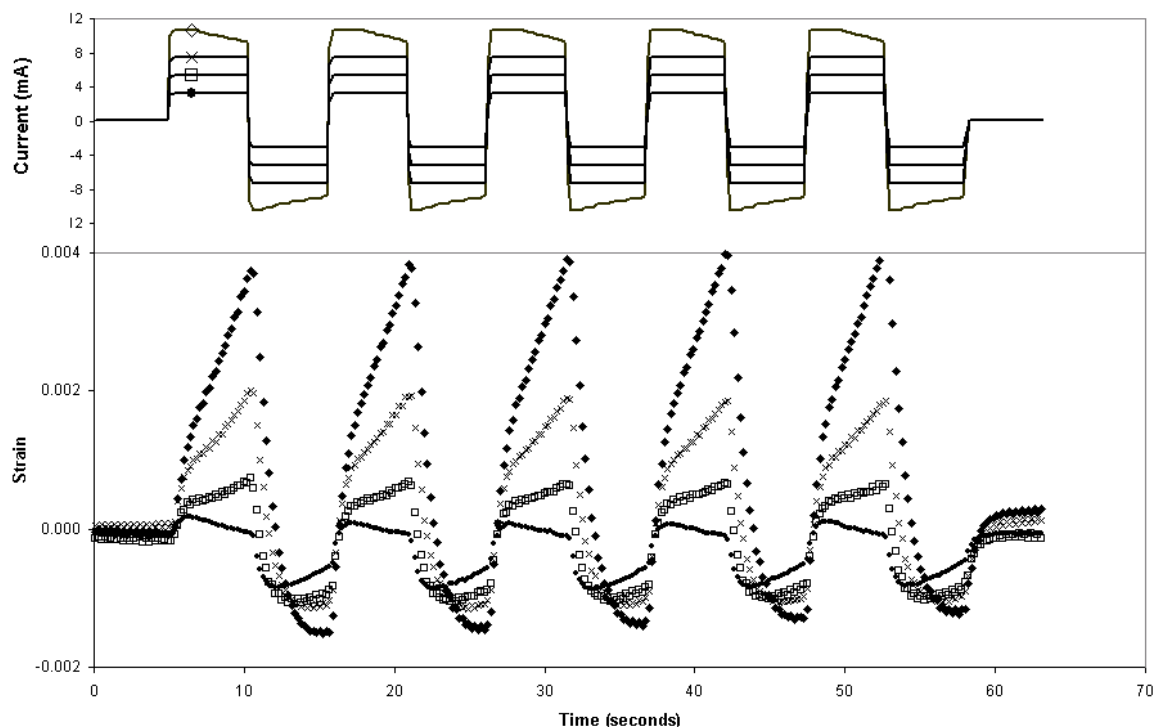


Figure 3: Isotonic data obtained for constant current waves of varying amplitudes at 1 MPa load. dots: 3 mA, squares: 5 mA, crosses: 7mA, diamonds, 10mA.

From the data it is clear that more current input results in greater strains against 1.0 MPa. Furthermore, the response of the polymer to galvanic switching is fast. At high currents, the imposed limit of  $\pm 3.0$  V is reached and the current is reduced as shown in the upper portion of Figure 3 (diamonds). At the onset of the change in polarity, the peak strain rates in PEDOT are measured to be 0.003 Hz, from the data in Figure 3. This speed appears to be independent of the magnitude or direction of the change. The average strain rate achieved in Figure 3 for the sample driven at 10 mA is 0.001 Hz, approximately one order of magnitude lower than polypyrrole and two orders of magnitude below mammalian skeletal muscles<sup>13</sup>. Similarly, for the fastest contraction at 10mA, a calculation of strain rate to rate of charge injection gave a strain to charge density ratio of  $2.3 \times 10^{-10} \text{ m}^3/\text{C}$  while the strain to charge density ratio over the entire half wave was  $1.0 \times 10^{-10} \text{ m}^3/\text{C}$ . These values were characteristic of strain to charge densities calculated throughout the testing, the highest of which was  $4.3 \times 10^{-10} \text{ m}^3/\text{C}$ , approximately the same as calculated for  $\text{PF}_6^-$  doped polypyrrole<sup>3,14</sup>.

The shape of the strain curve observed in Figure 3 was not anticipated. For coupling of strain and charge with a single ion diffusing in and out, a square current wave should produce a triangular strain response, similar to the one obtained in Figure 2. However in Figure 3, the initially fast response slows and is followed by different responses depending on the conditions. For the anodic current, initial response slows to a reduced rate in the same direction for high currents (5 mA, 7 mA, and 10 mA) but slows and then changes direction at low current (3 mA, Figure 3). For the cathodic current, the contraction at all current levels slows to zero and changes direction as the polymer film begins to extend. This transition to extension occurs the most rapidly in the sample driven at 3mA and follows sequentially to the sample driven at 10 mA.

### 3.4 Dual ion movement

An inspection of the isotonic PEDOT data revealed that not only had the strain frequently reversed direction during a half wave as shown in Figure 3, but that both the cation and anion had at some time provided the dominant role in actuation. Indeed a closer look at Figures 2 and 3 reveal that cathodic and anodic currents respectively can drive elongation of the film. Numerous attempts to repeat the data presented were successful,

including single films that reproduced both behaviors. The ability to switch from anionic contraction to elongation was also observed during a carefully selected set of experimental conditions. In the first of two runs, a 10 mA controlled current square wave was applied at 0.07 Hz for 10 cycles against a load of 1.0 MPa, similar to the experiment described in Section 3.3. Immediately thereafter, a second test was performed in which all conditions remained the same except that the polarity was reversed (negative current first). The results of a typical second run are shown in Figure 4.

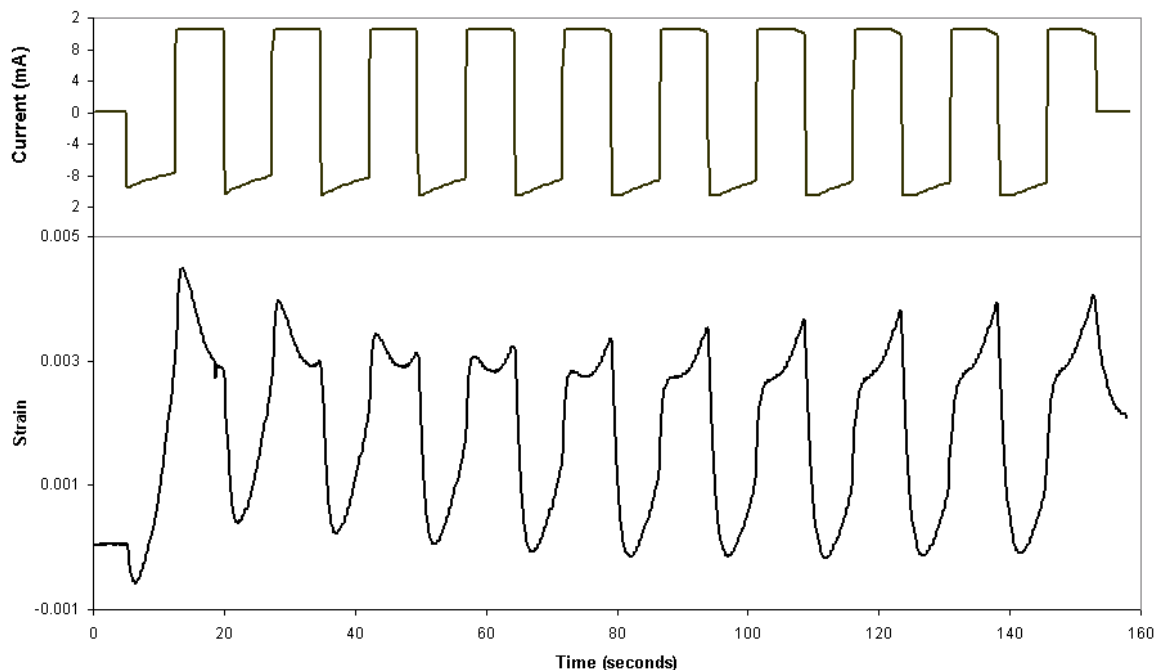


Figure 4: Isotonic data showing inversion of ionic behavior from anionic swelling to cationic swelling.

Comparing the data in Figure 4 to that in Figure 3, representative of the first portion of the experiment, reveals that the first strain event (during the cathodic current) in Figure 4 is the chronological inverse of the final strain event in Figure 3 for the test run at 10 mA. Thus, in the series of two tests, a long period of contraction with a short extension at the end is followed by a short contraction and long period of extension, both during cathodic currents. One might expect the inverse behavior to continue during the entire test, with Figure 4 as the mirror image of Figure 3. However, following a small contraction during the anodic sweep, the contraction continues for nearly half of the cathodic sweep of the 2<sup>nd</sup> cycle. Over time, the anodic current also develops a bi-directional response such that by the 4<sup>th</sup> cycle, both anodic and cathodic sweeps are producing contractions followed by extensions. By the 7<sup>th</sup> cycle, the anodic current has returned to its role shown in Figure 3 of elongating the film, thereby completely reversing the ionic behavior of the film within the test depicted.

#### 4. DISCUSSION

While the synthesis was successful in that it produced a freestanding film that actuated, it is by no means an optimized process. A different salt introduced during deposition might lead to a single ion actuation process as seen in polypyrrole with many solute systems<sup>11,13</sup>. The deposition parameters of current density and temperature were chosen from the references cited<sup>9,10</sup>, but no systematic variations have been tried. This presents a useful opportunity for further work with PEDOT films. In the characterization experiments presented herein, while actuation was observed, none of the properties presented a significant gain in the performance of conducting polymer actuators. Strain rates, maximum strains, and the strain to charge ratio were all affected by the

directional change in the response of the film, causing large variation between the peak and average properties measured.

The bi-directional response renews the discussion over possible internal mechanisms causing actuation. In 1996, Inganäs et al suggested that the PEDOT response was due to conformational changes appearing at specific potentials<sup>6</sup>. Otero et al have suggested a combination of structural relaxation and ion exchange for the volume change observed in polypyrrole<sup>15</sup>. The work presented above, however, would indicate that dual ion movement might also lead to elongation and contraction at a single potential since there was no direct correlation between the sign of the current and the sign of actuation. The dual ion mechanism follows straightforwardly from the conjecture that a film subjected to a positive potential or current will positively charge the capacitive double layer found on the surface of the film. This charge may be compensated by imbibing the polymer with anions or expelling the cations, phenomena which lead to the opposite mechanical result for a free-ended film under constant stress. The possibility of either ion diffusing in and out of the polymer independently suggests that the coordinated salt may also be able to move in and out of the film (salt draining) as discussed by Pei and Iganäs in 1992<sup>16</sup> and Wallace et al in 1995<sup>8</sup>, enabling strain to occur without current flow. Salt draining may then be responsible for the nonzero strains seen during the zero-current rest period at the end of the experiments in Section 3.3, though this data is inconclusive due to the creep that occurred during the experiments.

A successful model of the actuation mechanism of TBAPF<sub>6</sub> in PEDOT is currently being developed with parameters that correctly describe the three time constants associated with species movement. Diffusion data for both cation and anion, as well as the combined salt, are required and can be elucidated from studies with a Quartz Crystal Microbalance (QCM) similar to those performed by Oyama et al in 1994<sup>17</sup>. The diffusion of ionic species would depend on the concentrations within the polymer and the capacitive double layer, while the diffusion of salt species would depend on the concentration difference between polymer and bulk solution. Some measure of the ability of the ionic species in the polymer to recombine and form the salt, such as an equilibrium relation and constant, would couple the salt movements to the ionic movements. Lastly, a basic relation between the charge injected into the polymer and the relative ionic movements would enable the actuation mechanism to be related to the electrochemical environment imposed on the film.

From this model it would be possible to see the responses dependent on both time and experimental history, obtained throughout the experiments presented herein and most dramatically shown in Figure 4, by correctly analyzing the driving forces for ionic diffusion as well as salt diffusion. It would also anticipate the response of the polymer to a particular potential for actuator design purposes and allow for the application of the appropriate stimulus to afford actuation in a desired direction. This technique would then succeed in exploiting the bi-directional response first seen in Figure 2. During the switch to negative potentials, the contracting film continued to contract, despite the change in current direction. The ability to swell a polymer with both ions could greatly increase the total strains attainable within one polymer-solute system as one intercalated ion is followed by the other, turning a characterization difficulty into a practical advantage for conducting polymer actuators.

## 5. CONCLUSIONS

Successful electrochemical synthesis of freestanding PEDOT films, with conductivities as high as 8 S/cm, enabled a study of their electrochemical actuation in TBAPF<sub>6</sub> and PC. Strains as high as 2% against a load of 1.0 MPa were observed on a characterization apparatus capable of maintaining force and voltage feedback while applying a predetermined waveform. Strain rates of 0.003 Hz and strain to charge density ratios of  $4 \times 10^{-10} \text{ m}^3/\text{C}$  were measured during tests performed at constant stress under galvanic control. Unexpectedly, the polymer films both contracted and expanded in response to single anodic and cathodic currents. This direction of response could be changed from one experiment to the next and even during the course of a single experiment. A mechanism involving diffusion of anions, cations, and the combined salt in and out of the polymer was presented to explain the vast differences observed in the behavior of PEDOT. While research on electroactive polymer actuators continues to blossom and expand to new and more complicated materials, it remains important to investigate the properties of those materials readily available. This study presents one of the first investigations of linear actuation in PEDOT, arguably the most commercially successful conductive polymer available today.

## ACKNOWLEDGEMENTS

Financial support for this work was partially provided by the Office of Naval Research and the National Science Foundation.

## REFERENCES

- <sup>1</sup> R.H. Baughman, "Conducting polymer artificial muscles", *Synth. Met.* **78**, 339-353, 1996.
- <sup>2</sup> P. A. Anquetil, H.-H. Yu, J. D. Madden, P. G. Madden, T. M. Swager, I. W. Hunter, "Thiophene-based conducting polymer molecular actuators," *Smart Structures and Materials 2002 Electroactive Polymer Actuators and Devices (EAPAD)* **4695**, 424-434, Society of Photo-Optical Instrumentation Engineers, Bellingham WA, 2002.
- <sup>3</sup> M. J. Marsella, R. J. Reid, "Toward Molecular Muscles: Design and Synthesis of an Electrically Conducting Poly[cyclooctatetrathiophene]," *Macromolecules* **32**, 5982-5984, 1999.
- <sup>4</sup> L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, "Poly(3,4-ethylenedioxythiophene) and Its Derivative: Past, Present, and Future," *Adv. Mater.* **12**, 481-494, 2000.
- <sup>5</sup> see for example: Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, "Poly(3,4-ethylenedioxythiophene) as a hole conductor in solid state dye sensitized solar cells," *Synth. Met.* **131**, 185-187, 2002. or others covered in Ref. 4.
- <sup>6</sup> X. Chen, K.-Z. Xing, O. Inganäs, "Electrochemically Induced Volume Changes in Poly(3,4-ethylenedioxythiophene)," *Chem. Mater.* **8**, 2439-2443, 1996.
- <sup>7</sup> Q. Pei, O. Inganäs, "Electrochemical Applications of the Bending Beam Method. 2. Electroshrinking and Slow Relaxation in Polypyrrole," *J. Phys. Chem.* **97**, 6034-6041, 1993.
- <sup>8</sup> M. R. Gandhi, P. Murray, G. M. Spinks, G. G. Wallace, "Mechanism of electrochemical actuation in polypyrrole," *Synth. Met.* **73**, 247-256, 1995.
- <sup>9</sup> A. Aleshin, R. Kiebooms, R. Menon, A.J. Heeger, "Electronic transport in doped poly(3,4-ethylenedioxythiophene) near the metal-insulator transition," *Synth. Met.* **90**, 61-68, 1997.
- <sup>10</sup> I. Giurgiu, K. Zong, J. R. Reynolds, W.-P. Lee, K. R. Breneman, A. V. Saprigin, A. J. Epstein, J. Hwang, D. B. Tanner, "Dioxypyrrole and dioxothiophene based conducting polymers: properties and applications," *Synth. Met.* **119**, 405-406, 2001.
- <sup>11</sup> A. Della Santa, D. De Rossi, A. Mazzoldi, "Characterization and modeling of a conducting polymer muscle-like linear actuator," *Smart Mater. Struct.* **6**, 23-34, 1997.
- <sup>12</sup> C. Kvarnstrom, H. Neugebauer, A. Ivaska, N. S. Sariciftci, "Vibrational signatures of electrochemical p- and n-doping of poly(3,4-ethylenedioxythiophene) films: an in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) study," *J. Molec. Struct.* **521**, 271-277, 2000.
- <sup>13</sup> J. D. Madden, R. A. Cush, T. S. Kanigan, I. W. Hunter, "Fast contracting polypyrrole actuators," *Synth. Met.* **113**, 185-192, 2000.
- <sup>14</sup> J. D. Madden, R. A. Cush, T. S. Kanigan, C. J. Brenan, I. W. Hunter, "Encapsulated polypyrrole actuators," *Synth. Met.* **105**, 61-64, 1999.
- <sup>15</sup> T. F. Otero, H.-J. Grande, J. Rodriguez, "Reinterpretation of Polypyrrole Electrochemistry after Consideration of Conformational Relaxation Processes," *J. Phys Chem. B* **101**, 3588-3697, 1997.
- <sup>16</sup> Q. Pei, O. Inganäs, "Electrochemical Applications of the Bending Beam Method. 1. Mass Transport and Volume Changes in Polypyrrole during Redox," *J. Phys. Chem.* **96**, 10507-10514, 1992.
- <sup>17</sup> K. Takeshita, W. Wernet, N. Oyama, "Electrochemical Quartz Crystal Microbalance Investigation of a Poly(pyrrole)/Sulfated Poly(b-hydroxyether) Composite Film," *J. Electrochem. Soc.* **141**, 2004-2009, 1994.