Load and Time Dependence of Displacement in a Conducting Polymer Actuator John D. Madden, Peter G. Madden, Patrick A. Anquetil and Ian W. Hunter Department of Mechanical Engineering Massachusetts Institute of Technology Cambridge, MA 02139 U.S.A.

ABSTRACT

A number of electromechanical actuators exhibit coupling between displacement and charge. In this paper we explore the relationship between strain and charge as a function of time and load in polypyrrole. A reasonable first approximation is that strain is proportional to the density of charge transferred to these actuators, via an empirically derived proportionality constant known as the strain to charge ratio. The relationship between strain and charge does however exhibit some load and time dependences, which are important to recognize if fine actuator control is to be achieved. In order to study these effects stresses of between 2 MPa and 34 MPa are applied to an electrochemically activated free-standing polypyrrole film. It is shown that the strain to charge ratio exhibits time dependence, dropping by 30 to 45 % from its starting value of $100\pm13\times10^{-12}$ m³·C⁻¹. The drop in strain to charge ratio is consistent with frequency response results, which show a relaxation in the strain to charge ratio. The strain to charge ratio is charge ratio is relatively independent of load. Creep however appears to be accelerated during and following charge transfer. Observation of the electrical response reveals that impedance drops as load is increased.

INTRODUCTION

Conducting polymer actuators convert chemical or electrical energy to mechanical work ¹⁻⁴. In electrical activation the polymer is an electrode in an electrochemical cell, which reversibly contracts as oxidation state is changed. The thermodynamics and kinetics of conducting polymer actuators is becoming increasingly well understood and modeled, allowing response to be controlled and predicted²⁻⁴. Actuator performance characterization is also progressing, demonstrating the displacement of relatively large loads (at least 40 MPa as shown here), with moderate strain (2-6 %) and power (39 W/kg to date), while operating at low voltages (<10 V)³⁻⁵. As a consequence, conducting polymer actuators are being considered as potential alternatives to piezoelectric and electrostatic actuators in microelectromechanical systems⁶, and as a muscle replacement, among other applications.

In conducting polymer actuators, strain, ε , and charge per unit volume, ρ , are often approximated to be directly proportional, via the strain to charge ratio, α :

$$\varepsilon = \frac{\sigma}{E} + \alpha \cdot \rho \,, \tag{1}$$

where σ is stress and *E* is the visco-elastic modulus^{2,4,7}. The strain to charge ratio ranges between 25 and 530 m³·C⁻¹ in non-gels, depending on the polymer used (typically polypyrrole or polyaniline) and on the synthesis and operating conditions³. The modulus, *E*, can usually be approximated as being purely elastic and is typically between 0.5 GPa and 3 GPa, depending on synthesis conditions, processing, and applied potential³.

Equation 1 provides a reasonable first order approximation of conducting polymer response. However, the results from polypyrrole actuators presented here show that the strain to charge ratio is time-dependent. Furthermore, the 'passive' mechanical response, represented by the first term on the right of equation 1, is not independent of the second 'active' term. Finally, there is



Figure 1. Frequency dependence of the strain to charge ratio, α , in an 12.5µm thick film, demonstrating a relaxation centered about 0.04 Hz (open squares). Models depicting α independent of frequency (dashed lines) and α with a relaxation time of 4 s (solid lines) are shown for comparison.

coupling between the applied load and the cell impedance. These interactions need to be characterized to attain fine actuator control.

Work by Della Santa⁸ shows that benzenesulfonate doped polypyrrole actuators exhibit little load dependence of strain to charge, while Kaneto demonstrates significant load dependence in polyaniline ⁹. Frequency domain analysis on the hexafluorophosphate doped polypyrrole used in this study shows that strain to charge becomes time dependent below 0.1 Hz^{3,4}. Further analysis of these data reveal a relaxation in the strain to charge ratio with a characteristic frequency of 0.04 Hz, as depicted in Figure 1. The magnitude of the relaxation is found to be load dependent, the strain to charge dropping at low frequencies by between 50 % at 4 MPa and 75 % at 40 MPa^{3,4}. The present study complements the frequency domain results by enabling creep and plastic deformation to be more readily observed, and by simultaneously observing both the impedance and the electromechanical responses.

Strain to charge ratio is dependent on oxidation state. The load and time dependences are thus investigated using relatively small charge transfers and strains, simplifying analysis. Some authors have also found the visco-elastic modulus to be oxidation state dependent⁸. Previous work has shown that the polypyrrole used in this study does not exhibit significant oxidation state dependence over the potential ranges at which it is typically employed as an actuator³.

SYNTHESIS

The synthesis follows the methods of Yamaura and colleagues¹⁰. Free-standing polypyrrole films are electrodeposited to produce high conductivity films $(2-4.5 \times 10^4 \text{ S} \cdot \text{m}^{-1})$, with good mechanical properties (> 40 MPa tensile strength, 0.8 GPa elastic modulus wet)^{3-5,11}. Films are

grown from a solution of 0.06 M freshly distilled pyrrole monomer (<u>www.aldrich.com</u>) and 0.05 M tetraethylammonium hexafluorophosphate (Aldrich) in propylene carbonate at -40 °C. Polypyrrole is deposited galvanostatically on to a polished glassy carbon substrate (<u>www.alfaaesar.com</u>) at a current density of 1.5 A·m⁻², resulting in a 53 µm thick film.

EXPERIMENT

In order to analyze the time and load dependence of the strain to charge ratio, a polypyrrole film is held under constant load while currents are applied. The resulting displacements and voltages are recorded at 5 s intervals and analyzed. The sequence of applied stresses, rising in increments of 4 MPa from 2 MPa to 34 MPa, is shown in Figure 2. The resulting strains are also shown. A 0.3 mA current is applied 4000 s after the application of each step in stress. The initial period with no current allows the rate of creep to reach a steady rate. The current is switched off after 250 s, and then reversed after a further 250 s. The -0.3 mA current is held for 500 s, followed by 250 s of zero current and finally 250 s at +0.3 mA. There is no net charge transfer to the polymer.



Figure 2. Applied stress of between 2 MPa and 34 MPa and the resulting strain in a 53 μ m thick polypyrrole film. The film is charged and discharged using ± 0.3 mA step currents initiated 4000 s after the application of each step in stress. Charge induced strain shows a characteristic triangular wave response.

APPARATUS

Mechanical testing is performed on a 2.5 mm wide, 37 mm long film using an apparatus described in greater detail by Madden^{3,5,11}. The film is clamped at either end to obtain electrical and mechanical contact, leaving a 33.5 mm length between clamps. It is submerged in propylene carbonate electrolyte containing 0.05 M tetraethylammonium hexafluorophosphate. Displacements are applied to the films under test via a stepper motor driven linear stage and forces on the film are measured via a load cell. Feedback from the load cell is used to control motor displacements that maintain isotonic (constant force) conditions. A stainless steel sheet provides a counter electrode and a silver/silver perchlorate electrode provides a reference relative to which the polypyrrole potential is measured. Computer controlled currents are applied between the polypyrrole film and the counter electrode. Voltage, current, displacement and force are recorded via 16-bit analog to digital converters.

LOAD DEPENDENCE OF ELECTROCHEMICAL IMPEDANCE

Figure 3 shows the potential applied between the polypyrrole film and the reference electrode during the sequence of current steps. The application of a current step leads to a voltage step, followed by a monotonic increase or decrease in voltage, depending on the sign of the current. The form of the response is typical of hexafluorophosphate-doped polypyrrole in this potential range^{3,4} and is characteristic of systems behaving as a resistance in series with a finite diffusion element. In polypyrrole actuators the resistance is the sum of the electrolyte and metal to



Figure 3. Polypyrrole actuator voltage applied during step current charging. While current is applied the magnitude of the applied potential decreases as load is increased, particularly during the positive current steps.

polymer contact resistances, and the finite diffusion term describes the mass transport of hexafluorophosphate ions to and from the polymer.

The primary effect of increased load is to reduce the electrical impedance. The potential difference required to drive current in the cell drops by at least 100 mV between 2 MPa and 34 MPa under positive currents and 50 mV at negative currents (accounting for the shift in initial potential). A slight increase in effective capacitance is also evident at positive currents. The voltage shift is reproducible, eliminating polymer degradation as a cause. The difference rapidly vanishes when current is switched off, suggesting that a kinetics/mass transport related mechanism is responsible. There is strong evidence that the primary rate limiting mechanisms are contact, polymer and electrolyte resistances and mass transport within the polymer ^{3,4}. The results suggest that the resistance and/or the rate of ionic transport are functions of load. These mechanisms cannot be effectively distinguished using the present data because of the relatively low sampling rate, and hence a determination of the cause will have to await further experimentation. The interdependence of load and impedance could provide an effective means of force measurement.

The potential undergoes a gradual -15 mV shift over the course of the experiment. Part of this shift may be the result of a generator effect, the inverse of the elecromechanical coupling that produces work. Modeling predicts that stress induced potential differences are described by the product of stress and the strain to charge ratio ^{3,4}. At $\sigma = 34$ MPa and assuming a strain to charge ratio of $\alpha = 10^{-10}$ m³·C⁻¹, the stress induced potential difference is estimated to have a magnitude of approximately 3 mV, significantly smaller than the observed negative 15 mV shift.





Figure 5. Strain in response to step currents at 2 MPa, 18 MPa and 34 MPa loads. The estimated creep has been subtracted. Note the apparent reversal of the strain to charge ratio at the end of the -0.3 mA segment at 34 MPa, and the fact that the strain has not returned to zero under the 2 MPa and the 34 MPa loads, despite the return of the polymer to its original charge state.

LOAD DEPENDENCE OF THE STRAIN TO CHARGE RATIO

Figure 2 shows the polypyrrole strain induced by the combination of load and applied current. The strain data is overlaid in Figure 4, where time and strain are reset to zero immediately prior to each step in stress. Note that the elastic modulus (inversely proportional to the magnitude of the change in strain immediately upon application of stress) is relatively independent of load. The magnitude and rate of creep increase with load. The negative strain rate observed in the 2 MPa data is due to creep recovery, indicating that the polypyrrole sample maintains a memory of prior tests.

The application of current induces clearly visible ramps in strain. The rate of creep is nevertheless significant relative to the active strain. In order to separate the influences of creep from those of charge the magnitude of the creep is estimated by fitting a line to the strain responses between 3000 s to 4000 s, and extrapolating, as shown in Figure 4. The estimated creep is then subtracted from the measured strain to estimate the charge related strain, Figure 5. For clarity, only the strains at 2 MPa, 18 MPa and 34 MPa are shown.

The strain to charge ratio is estimated by employing a linear least squares fit to the strain data, thereby determining strain rate. The fit strain rate is divided by current and multiplied by volume to obtain the estimated strain to charge ratios plotted in Figure 6. In the figure α 1 is estimated from the slopes upon initial application of +0.3 mA, α 2 is the estimated strain to

charge during the application of -0.3 mA, and α 3 is the strain to charge ratio estimated from the final application of 0.3 mA. The α 1initial points are estimated from the measurements made within the first 30 s after the application of the first +0.3 mA step.

No clear relationship between strain to charge ratio and stress is observed, apart from $\alpha 3$ which exhibits a weak reduction in strain to charge with increasing load, as shown by the trend line in Figure 6. The mean strain to charge ratios taken across all stress levels are listed in Table I. The largest strain to charge ratio is $\alpha 1$ initial, which is 30 to 45% larger than $\alpha 1$. The greater strain to charge observed at short times is consistent with the frequency response results in Figure 1. The strain to charge ratios $\alpha 2$ and $\alpha 3$ are 30% smaller than $\alpha 1$. This may be due to some potential dependence of the strain to charge ratio, or further time-dependent behavior.

Stress	αl	αl initial	02	03
(MPa)	$(m^{3} \cdot C^{-1}) \times 10^{12}$			
Mean±variance ^{1/2}	60±4	100±13	41±2	40±8

Table 1: Strain to charge ratio from least squares fit, averaged across all stress levels.

Finally, note that despite the fact that the net charge transfer is zero, and that the extrapolated creep has been subtracted, the net active strain is greater than zero at 34 MPa and less than zero at 2 MPa. In the 2 MPa case the undershoot is largely the result of creep occurring during the phases between applications of current. Charge transfer appears to have accelerated creep, which in this case, due to memory of previous stress states, is working against the applied load.

The 34 MPa response shows a reversal of the measured strain to charge ratio, $\alpha 2$, 400 s after



Figure 6. Measured strain to charge ratio vs. load. The strain to charge ratio shows little load dependence. Time dependence is evident from the difference between the initial strain to charge ratio, α linitial, and the average strain to charge over 250 s, α l. The line is a fit aimed at descring the dependence of the strain to charge ratio, α 3, and load.

the application of current, which contributes to a strain overshoot. The voltage response in Figure 3 shows no evidence of new electrochemical processes that might be responsible for the reversal. Instead it appears that changes in ion concentration within the polymer, resulting from the applied current, may accelerate the progress of molecular rearrangement associated with creep.

CONCLUSIONS

Loads of between 2 MPa and 34 MPa are applied to a hexafluorophosphate-doped polypyrrole film. Step currents are applied over 250 s to 500 s to induce strain, and thereby enable the study of the load and time dependence of the strain to charge ratio. The strain to charge ratio in hexafluorophosphate-doped polypyrrole is shown to exhibit time dependence but little load dependence. However, the transfer of charge to or from the polymer appears to induce creep. Finally, the application of load is also observed to decrease the electrochemical impedance of the cell employed to actuate the polypyrrole.

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