Chapter 5: Actuator Characterization: Step Current and Voltage Experiments

The objective of this chapter is to characterize polypyrrole actuator response by applying step voltage and current inputs. Films are held either under constant load (isotonic conditions) or at fixed length (isometric conditions) in electrolyte while the steps are applied. The resulting strains and stresses are recorded. These measurements enable the relationship between input electrical voltage, current and energy and output stress, strain and work, to be obtained as a function of time. Figures of merit, such as strain, strain rate, power to mass, and efficiency are determined, and the form of the electromechanical coupling is discovered. The passive (zero current) mechanical response is obtained, in the form of stress-relaxation, creep and stress-strain relations.

The measurements show that actuator strain is proportional to the charge transferred, and hence that strain rate is proportional to current. Under isometric conditions, changes in stress are also proportional to charge, with the two constants of proportionality being related by the elastic modulus. Voltage and charge transfer are also related, with the polymer acting as a capacitor with a very high charge storage capability $(10^8 \text{ F} \cdot \text{m}^{-3})$, one gram of material having a capacitance of ~100 F. Step current measurements show that the capacitor has a charging time (<500 s for 50 µm thick films) that is likely associated with dopant mass transport into the polymer. These findings are further investigated through modeling and swept sine experiments presented in Chapters 8 through 10.

The experimental procedures are first described, followed by a presentation of results.

5.1 Experimental Methods

Figure 1 shows the bath in which polypyrrole actuators are tested. Films are clamped, as shown, to obtain electrical and mechanical contact. The bath is filled with electrolyte. Displacements are applied to the films under test via a stepper motor driven linear stage, as shown in Figure 2, and forces on the film are measured via a load cell. Feedback from



Figure 2: Image of linear actuator apparatus, showing stepper motor and linear stage used to apply displacements to polypyrrole films held in the bath, shown in Figure 1. The cantilever is used occasionally instead of a clamp, seen in Figure 1, in order to directly observe actuator displacements, as discussed in Chapter 7.

the load cell is used to control motor displacement to produce isotonic conditions.

During step potential measurements, a potentiostat is used to apply voltage steps between the polymer and a reference electrode. The resulting currents, and changes in stress or strain are recorded. The potential of a second reference electrode is recorded to confirm that the potentiostat reference is not drifting and to measure the drop across the polymer film. Step changes in current are applied using a current source, and the resulting voltages, strains or stresses are recorded. Stress/Strain measurements are performed by ramping strain at a fixed rate up to a specified stress level, and back down again. Stress is recorded during the applied ramp. Creep is measured by rapidly ramping film stress by a specified magnitude, holding the stress fixed, and recording the resulting strain following the 'step' in stress. Stress relaxation is similarly measured, but with film length held constant after the initial stress ramp, and stress being recorded.

Figure 3 is a block diagram of the apparatus used in applying step voltages, with the potentiostat circuit represented in Figure 4. Step current experiments are run using the same apparatus, but with the potentiostat replaced by a current source, as shown in Figure 5. The apparatus consists of:

- An electro-mechanical test cell, comprising a bath in which the polymer film is tested, clamps to mechanically and electrically contact the film, a counter electrode, a reference electrode, and a load cell to measure forces on the film, all as shown in Figure 1;
- A potentiostat for applying potentials to the film relative to a reference electrode in step voltage experiments, as depicted in Figures 3 and 4, or a current source used to apply step currents, as shown in Figure 5;
- A stepping motor, motor controller and linear stage for applying displacements to the polymer film;

• Figure 3,

• Figure 4,

• Figure 5.

- A data acquisition card including analog to digital (A/D) channels used to input the force signal, the polymer to reference voltage, the current signal, and the reference to reference voltage to a computer; digital outputs (DIO) used to send step and direction commands to the stepper motor and to command steps in current; and analog outputs (D/A) used to control the potentiostat voltage;
- A computer running a custom Java application, that reads in force levels and outputs motor displacement commands so as to maintain constant force on the film (isotonic mode), commands steps in voltage or current, and records stress, strain, voltage and current. The computer also commands the stepper motor and records data during stress/strain, creep and stress relaxation measurements;

The elements of the apparatus are now described in detail. Results are then presented in section 5.2.

5.1.1 The Electromechanical Test Cell

Figure 1 shows the bath in which electrical and mechanical tests are performed on polypyrrole films. The bath is the electrochemical test cell, including the working electrode (the polymer), a reference electrode and a counter electrode, immersed in electrolyte. It is also the mechanical test platform, including a load cell that measures force applied to the film, clamps through which force is transmitted, and a shaft through which displacements are applied. The bath is bolted to a stainless steel optical table, which sits on air bearings to provide vibration isolation.

5.1.1.1 The Bath

The bath itself is a Nylon block (52 mm high \times 170 mm long \times 77 wide) into which a 30 mm deep, 56 mm wide and 140 mm long well has been machined. The bath is bolted to the optical table at the four corners. It serves to contain the liquid electrolyte in which the polypyrrole film is immersed.

5.1.1.2 Electrical and Mechanical Contact with the Polypyrrole Film

Polypyrrole films are clamped at either end within the bath, as shown. Electrical and mechanical contact is made via the two clamps, which have horizontal slots into which the film is placed. The clamps are polyacetal, and consist of two pieces that are bolted together, with the polymer film sandwiched between them. Each piece is 15 mm high, and 40 mm wide. The top piece has an extra 15 mm high section containing a 6.3 mm hole, through which shafts are inserted to make mechanical contact with the linear stage on one side, and the load cell on the other. Setscrews hold the clamps fixed relative to the shafts. Platinum coated stainless steel sheet is also sandwiched between the clamps to provide electrical contact with the polymer. A stainless steel screw is threaded vertically into each clamp to electrically contact each stainless steel sheet.

Two 6.3 mm diameter solid aluminum shafts transmit force beyond the bath. The right hand shaft is 35 mm long, and connects with a load cell, and then on to an aluminum L-bracket (6 mm thick \times 100 mm high \times 50 mm wide) that is bolted to the underlying optical table. The left hand shaft is used to impart displacement. It is 145 mm long, increases in diameter to 9.5 mm to the left of the bath and is bolted to the linear displacement stage, as shown in Figure 2.

5.1.1.3 The Reference Electrode

A silver/silver perchlorate reference electrode is placed next to the film, and centered between the clamps. A second silver/silver perchlorate reference electrode is used to monitor the extent of voltage drop along the length of the film. The electrodes consist of glass tubes each containing a silver wire, and filled with 0.01 M AgClO₄ and 0.05 M $(C_2H_5)_4N$ ClO₄ in propylene carbonate, following the methods of Courtot-Coupez and L'Her (Courtot-Coupez and L'Her 1970). The Ag/Ag⁺ reference is measured to sit at a potential of 0.716 V vs. a standard aqueous calomel reference at room temperature. Details of the reference electrode construction and characterization are given in Chapter 9.

5.1.1.4 The Counter Electrode

A 64 mm wide platinum coated stainless steel sheet is employed as the counter electrode, surrounding the film from three sides, as shown.

5.1.1.5 The Electrolyte

The electrolyte is 0.05 M tetraethylammonium hexafluorophosphate (Aldrich 43,411-6, 99% pure, <u>www.aldrich.com</u>) in propylene carbonate (Aldrich, 31,032-8, 99.7 %, packed under N_2). In one case an aqueous solution is employed. It consists of 18 M Ω electronics grade water containing 0.05 M tetraethylammonium hexafluorophosphate. Reagents are used as shipped, and employed immediately after opening. Nitrogen is bubbled through the solution before use. The electrolyte is chosen because it produces very low background currents (Bard and Faulkner 1980), thereby minimizing parasitic

reactions. Also, it employs the same electrolyte and dopants used during synthesis, thereby minimizing the number of variables.

5.1.2 The Potentiostat

A potentiostat applies current between the working electrode (polymer film) and the counter electrode such that the working to reference electrode voltage difference matches an input command potential. The potentiostat circuit employed is shown in Figure 4, and is similar to circuits described by Bard and Faulkner (Bard and Faulkner 1980). It includes a current buffer to improve reference electrode stability. The voltage drop across a resistor, R_i , in series with the output, is used to measure cell current, and the applied work to reference voltage is measured at the output of the current buffer.

Some key properties of a potentiostat are the maximum voltage and current that can be output, how well and over what bandwidth the output potential matches the command voltage, and the accuracy of current measurement. The accuracy of current measurement is a function of the resistor, R_i , employed in measuring current and the range and resolution of the analog to digital converter used to the voltage drop across R_i . The resistance R_i used depends on the maximum expected current in a given experiment and ranges from 99.6 Ω to 10 k Ω . The 16-bit A/D converter has a resolution of 0.306 mV over a range of ±10 V.

The potentiostat has a bandwidth of 100 kHz, a maximum output current of 1 A, and a cell potential range of ± 20 V. These properties are functions of the cell impedance, the impedance of the current measuring device, and the extent of any parasitic capacitances, as described in section 9.2. The impedances and signal levels used in this chapter are

such that the potentiostat can be treated as ideal (corrections for non-ideal behaviour described in section 9.2 do not need to be applied).

5.1.3 The Current Source

The current source is an HP3245A Universal Source (<u>www.agilent.com</u>). A sequence of output current values is preprogrammed and stored in the HP3245A memory. A digital trigger is used to toggle between current states, enabling steps in current to be applied and removed.

5.1.4 Load Cell and Amplifier

Two load cells are employed to measure force on the polymer film. During the creep and stress/strain tests presented, a 100 N load cell is used (Omega LCCA-25, www.omega.com, ± 30 mN resolution, S-beam) and for small forces a 5 N load cell (Entran ELF-TC13-5, www.entran.com). These cells have four strain gauges that are mounted so as to reject off-axis forces and thermal expansion when configured electrically as a full Wheatstone bridge.

The gauges are wired to an instrumentation amplifier (Vishay, Model 2311 Signal Conditioning Amplifier, Raleigh, North Carolina), which provides variable excitation voltages to the strain gauges (10 Volts used with the 100 N cell, 15 V with the 5 N cell), balances the bridges, and provides an amplified voltage output proportional to force. The force output is low-pass filtered with cut-off frequencies of 10 Hz, 100 Hz or 1 kHz. The filters were used to reduce noise and aliasing.

The load cells are calibrated using a series of known masses. The 100 N cell has a sensitivity of $0.452 \text{ mV} \cdot \text{N}^{-1}$, and the 5 N cell sensitivity is 24.5 mV $\cdot \text{N}^{-1}$.

5.1.5 The Stepper Motor, Controller and Linear Stage

The stepper motor serves to apply displacements to the film in order to maintain constant force. It also provides displacement during passive stress/strain measurements. The stepper is а Compumotor 57-51-MO with 200 steps per revolution (www.compumotor.com). It is driven by a Compumotor LN-Drive, set to microstep at 10,000 steps per revolution. The motor drives a New England Affiliated Technologies LM-50 precision linear stage (<u>www.neat.com</u>), with a 50 mm travel, a lead of 2 mm per revolution, a repeatability of 3 µm, and an accuracy of 15 µm.

The drive accepts digital signal inputs for step, direction and power. Each time the step input is pulsed high, the motor is advanced one micro-step, producing a displacement of 200 nm. Displacements are accurate and repeatable to better than 10 μ m, as measured by performing twenty consecutive 30 mm displacements, which are measured with digital calipers having a 10 μ m resolution. The films measured are all > 16 mm long, so the applied strain is accurate to better than ±0.0007 (10 μ m/16 mm).

5.1.6 Data Acquisition and Output

A National Instruments PCI-MIO16XE-10, (<u>www.natinst.com</u>), installed in the PCI slot of the computer, and attached to a breakout board with BNC connections (BNC-2090, <u>www.natinst.com</u>), provides the analog to digital, A/D, digital to analog, D/A and digital output, DIO, required to measure force, voltages and current, and control the stepping motor, current source and potentiostat. The A/D is configured for ± 10 V inputs, has an input impedance of 100 G Ω in parallel with 100 pF, and samples at up to 100 kHz, at 16 bit resolution (0.3 mV). Similarly the D/A has outputs ± 10 V at up to 100 kHz, at 16 bit resolution (0.3 mV). The digital I/O outputs zero or 5 V at up to 20 MHz.

Separate A/D channels are used to measure polymer to reference voltage, cell voltage, reference to reference potential difference, current and temperature. A D/A channel is used as the command input to the potentiostat during step voltage experiments. A DIO channel is used to toggle the current source between pre-programmed output current states, and two others command steps and the direction input to the stepping motor controller.

5.1.7 The Computer and Graphical User Interface

The computer used to control the applied force is an IBM 6889 PC running Windows NT 4.0 (www.ibm.com). A custom JAVA interface, depicted in Figure 6, is used to run isotonic and isometric experiments under either stepped voltage or current conditions, and to control stress/strain and creep experiments. The code used is shown in the appendix. The user inputs the measured film dimensions - the length at label 1 in Figure 6, the width at 2, and the thickness, 3 - the force per unit voltage of the load cell/amplifier combination, 4 and the filename to which any data generated is to be saved, 5. Commands may then be executed as follows.

5.1.7.1 Applying Film Displacements

Displacements are applied by first specifying the desired displacement in millimeters in the box indicated by label **6** in Figure 6, and the rate in steps per second at **7**. Clicking 90



the MotorInit button **8** causes the number of steps necessary to produce the desired displacement to be calculated, and the direction of displacement to be determined. Step commands are then sent to the motor controller via the digital output at time intervals determined by the specified step rate **7**, until the specified displacement **6** is completed. Step commands are sent one step at a time, so the maximum step rate is limited by the closed loop response time of the application/operating system/board, which is 2 ms on average. The maximum strain rate is then ~5×10⁻³ s⁻¹ given the 200 nm per step size.

5.1.7.2 Stress-Strain Measurements

To perform a stress/strain measurement, the change in stress (in Pascals) **9** (label in Figure 6) and the strain rate (in strain per second) **10** are provided by the user. Clicking the StressStrain button **11** leads to a ramp in strain at the specified strain rate **10**. The ramp reverses itself once the maximum stress changes by the set amount **9**, displacing the motor at the same rate in the opposite direction, and over the same number of steps. The film stress is recorded during this cycle. When the ramps are completed, time, strain and stress data are saved in the file name specified **5**.

5.1.7.3 Isotonic Experiments

In order to hold films under isotonic conditions the stress, as specified at label **9** in Figure 6, force tolerance **12**, potential amplitude **17** (step voltage case) and duration of the experiment in seconds are specified. There are three parts to determining experiment duration. An initial time is set, **13**, to allow for film creep before current or voltage is applied. Active time, **15**, determines length of the applied steps. Generally a step is applied for the specified time, mirrored about equilibrium for twice the time, and then reapplied, as shown in the plot following this paragraph. The original conditions, namely zero current or the equilibrium, V_{eq} , are reapplied between active times for a specified time, **16**.



Clicking the test button causes strain to be ramped at the prescribed rate 10 until the stress level is reached 9. Thereafter, until the experiment duration has expired (13 + 4.15 + 3.16 seconds), stress is continuously recorded, and strain is ramped up or down, as is appropriate, until the desired stress level, 9, is reached. A step counter is maintained from which net strain is calculated. At the appropriate times a D/A output commands a change in voltage by the specified increment, 17, or a digital output pulse toggles the

current source. Time, stress, strain, current, applied voltage, cell voltage, and reference to reference voltage are recorded at specified intervals, **14**, and saved to file, **5**, at the end of the experiment.

5.1.7.4 Isometric Experiments

Isometric experiments are run using a program that is nearly identical and has the same interface. The only difference is that after the initial stress ramp, the stepping motor is no longer activated.

5.2 Results

The results obtained in performing creep, stress relaxation, stress-strain, step current and step voltage experiments are now presented.

5.2.1 Passive Mechanical Properties

5.2.1.1 Creep and Stress Relaxation

The application of a load to a polymer typically leads to an immediate elastic response, followed by a gradual displacement or creep. Similarly, if a step change in length is applied to a polymer, there is an initial step in force or stress, followed by a gradual relaxation. In an actuator, the goal is generally to control position or force. It is thus important to know the extent of creep and relaxation that occurs in response to changing loads and displacements.

Figures 7 shows the stress relaxation resulting from a 2 % 'step' in displacement. To obtain the result, displacement is increased to 2 % over 4 s, and then held fixed. Figure 8 shows the creep resulting from a 3.5 MPa step in stress. To obtain this result, displacement is increased at a rate of $0.5 \, \text{\%} \cdot \text{s}^{-1}$ until a stress of 3.5 MPa is reached, at which point force feedback is used to maintain constant stress. The resulting strain is plotted in Figure 8 as a function of time.

Creep and stress relaxation have time constants of approximately 100 s. The total creep over 800 s is 0.002, and the stress drops by 1.7 MPa over 600 s. Both creep and stress relaxation increase as the applied loads and displacements increase. In Chapter 10 it is shown that a linear visco-elastic model is effective in describing the mechanical response over similar time scales.

5.2.1.2 Stress-strain

Figure 9 shows the stress-strain relationship obtained at a strain rate of $0.5 \,\% \cdot s^{-1}$ over a total strain of 0.45 %. Very little hysteresis is observed at this strain rate, indicating that the material is behaving elastically over the ~2 s measurement timescale. The elastic modulus increases with strain, partly due to imperfect alignment of the film, averaging 0.8 GPa over the full range of strain.

5.2.1.3 Gauge Factor

The displacement dependent resistance of conductive materials is employed in load cells and strain gauges. The materials used in strain gauges and load cells are characterized by their gauge factor, K, defined as the ratio of relative change in resistance, R, to relative change in length, l:

$$K = \frac{\Delta R / R}{\Delta l / l}.$$
 1

The relative change in length is strain. In this section, the gauge factor of polypyrrole is measured, and compared with those of other materials, as summarized in Table 1.

Resistance changes are measured by applying a constant current lengthwise along a film and measuring the voltage drop. The voltage drop is shown as a function of strain in Figure 10. The gauge factor is readily calculated from this data. Since constant current is being input, the numerator of Equation 1 is proportional to the relative change in voltage. The curvature seen in Figure 10 indicates that gauge factor is a function of strain in polypyrrole. The average value is 4 and *K* exceeds 6 near 1 % displacement. Table 1 compares polypyrrole strain gauge properties with those of constantan and doped silicon,

Table 1

both of which are commonly used in strain gauges. The principal advantage of polypyrrole is the large accessible strain range. A disadvantage is the significant creep observed under large loads.

The moderate gauge factor of polypyrrole is encouraging because it suggests that the actuator itself, or an adjacent member of the same material, can be used to record force and displacement.

5.2.2 Electromechanical Response

5.2.2.1 Step Current

A sequence of step currents is used to analyze polypyrrole electrical and mechanical responses under constant load (isotonic conditions). Figure 11 is an example of one such measured response. The polypyrrole film used in obtaining the results shown is 53 μ m thick, 82.5 mm long and 7.6 mm wide, and is held under a constant 5 MPa load over the 8000 s duration of the experiment. The distance between clamps holding the polymer is 44.5 mm.

Current is zero for the first 3000 s, over which period no change in voltage is observed. Creep is evident over this initial time. A current of 0.3 mA is applied for 1000 s (the polymer is the positive electrode). When current is applied the voltage steps, as would be expected for a resistor. Thereafter, until the step is reversed, steady increases in voltage and polymer length are observed. 4000 s after the initial application of stress, the current is set to -0.3 mA. Again, a step in voltage is observed, this time in a negative direction and with twice the amplitude. The strain and voltage then decrease with time at a constant rate until the step current is again reversed.

The step response suggests that strain, ε , is proportional to charge transferred, Q. Anticipating that the strain is in fact proportional to the charge transferred per unit of polymer volume, the proportionality is expressed in terms of the charge density, ρ :

$$\varepsilon = \alpha \cdot \rho$$
, 2

where α is the strain to charge ratio, and has units of volume per charge. Fitting a line to the data in Figure 11 yields a value of α =1.2±0.1 m³·C⁻¹, where the uncertainty accounts for the standard deviation of the fit, and the slight differences in slope observed at each step.

Expressed in terms of elementary charge, the volume change is 7×10^{-29} m³ per charge transferred, or 0.07 nm³. A sphere of equivalent volume has a diameter of between 0.5 and 0.6 nm. The diameter^{*} of the PF₆⁻ anion is roughly 0.5 nm, suggesting that swelling is proportional to ion size.

Figure 12 shows that strain rate increases linearly with the magnitude of applied current, confirming the direct proportionality between strain and charge.

The polypyrrole films elongate when the current is positive, and the polymer is oxidized. Pei and Inganäs have shown that in polypyrrole, oxidation leads to elongation if anions are transferred from the electrolyte to balance charge, and contraction is observed if cations are expelled from the polymer (Pei and Inganas 1992; Pei and Inganas 1993). The positive strain to charge ratio obtained suggests that the hexafluorophosphate ions are exchanged during doping, rather than the bulky tetraethylammonium cations.

^{*} Van der Waals diameters are estimated from CambridgeSoft's CS Chem3D Pro Version 4.0, © 1997, www.chemoffice.com.

Figure 13 shows the effect of changing solvent. The same electrolyte concentration is used but in water rather than in propylene carbonate. The strain to charge ratio is more than double at $3 \times 10^{-10} \text{ C}^{-1} \cdot \text{m}^3$. The increased strain to charge ratio may be due to the insertion of entrained solvation spheres, or the result from the decreased hydrophobicity as the material is oxidized.

Clearly ion size is not sole determinant of the strain to charge ratio in polypyrrole. Further evidence of solvent dependence is obtained from measurements of polypyrrole films that are doped with large, immobile anions. The strain to charge ratio of dodecylbenzenesulfonate doped polypyrrole in 0.1 Μ aqueous sodium dodecylbenzenesulfonate (DBS) is -2.3×10⁻¹⁰ C⁻¹·m³ (Madden, Brenan and Dubow 1997). Della Santa and colleagues find the strain to charge ratio of benzenesulfonate (BS) doped polypyrrole run in 0.1 M sodium BS in an acetonitrile and water mixture, to be an order of magnitude smaller, at $-3 \times 10^{-10} \text{ C}^{-1} \cdot \text{m}^3$ (Della Santa, DeRossi and Mazzoldi 1997).

Does the strain to charge ratio depend on the applied stress? Figure 14 shows the results of an experiment using a sequence of current steps, similar to those shown in Figure 11. except that the experiment is repeated at nine isotonic states equally spaced between 2 MPa and 34 MPa. At each isotonic state, no current is applied during the first 4000 s. A current of 0.3 mA is then applied for 500 s, followed by a current of -0.3 mA applied for 1000 s, followed again by a current of 0.3 mA for 500 s. The film employed is 2.5 mm wide, 33.5 mm long between clamps, and 52 μ m thick. The strains resulting from the periods of applied current are analyzed to obtain estimates of the strain to charge ratio at each applied stress. At high stresses, the rate of creep is significant even after 4000 s of

equilibration. The creep effect is subtracted in estimating strain to charge by assuming that the creep rate prior to the beginning of application of current is maintained. The strain to charge ratio is found to drop slightly above 15 MPa, with the decrease reaching 30 % at 34 MPa. The large creep observed at stresses above 10 MPa will limit the use of polypyrrole actuators, as prepared in this study, at such loads.

The voltage produced in response to a step change in current has the same form as the response of a resistor and capacitor in series. The apparent resistance of the response shown in Figure 11 is 5000 Ω . The electronic resistance of the polymer film is 2 Ω , so the electrolyte is likely responsible. The capacitance is measured by fitting a line to the voltage response of Figure 11, as shown in Figure 15. The measurement of capacitance is done for three films. The capacitance per unit volume is found to be 1.3 ± 0.1 F·m⁻³, the uncertainty expressing the variation between films and the uncertainties in film dimensions. The initial curvature in the voltage slope seen in Figure 15 is evidence of the diffusion limited charging time. Figure 16 shows the typical short time voltage curve in response to a step in current. The red line shown is the form of the response expected for diffusion limited charging, following the model presented in Chapter 8.

The volumetric capacitance is enormous, as emphasized in Table 2, where it is compared with those achieved in standard electronic components. The very high capacitance is likely due to the storage of charge throughout the polymer, and not simply at an interface, as is the case with the other capacitor technologies listed in Table 2. The main limitations of the polypyrrole capacitor are the low voltage range, as will be discussed later in this section, and the diffusion limited charging time, discussed in Chapters 8 and 10. The super-capacitance of polypyrrole is also susceptible to leakage currents

Table 2

(Arbizzani, Mastragostino and Meneghello 1996; Arbizzani, Mastragostino and Scrosati 1997).

Equation 2 predicts that if current is zero, and hence no electrical energy is being expended, then there will be no displacement, and hence no work done. The results in Figure 17 show that strain rate is nearly zero when current is zero. Note that no work is expended in order to maintain a force. Mammalian muscle, and electric motors on the other hand must be expend energy to maintain force, even when no work is being done.

Figure 18 shows the effect of current on stress when films are held under isometric (constant length) conditions. The experiment is very similar to that shown in Figure 11, except that it is performed at constant length. The change in stress is proportional to current, except at high stress where it appears that some creep is occurring. The constant of proportionality between stress, σ , and charge density is found to equal the strain to charge ratio multiplied by the elastic modulus, namely:

$$\sigma = E \cdot \alpha \cdot \rho \,. \tag{3}$$

Once again the change in voltage is proportional to charge, after an initial charging time. The charging time becomes particularly obvious under zero current conditions. The observed change in voltage at zero current is attributed to discharging of the double layer capacitance at the interface between the polymer and the electrolyte, as dopants diffuse in or out of the material. The diffusion model is discussed in Chapter 8.

The results presented thus far show that strain is proportional to charge, and that, after an initial diffusion time, voltage is also proportional to charge. Also it is shown that stress is proportional to charge under isometric conditions. Thus the strain is a function of the charge density, the strain to charge ratio, the applied load and the elastic modulus, *E*:

$$\varepsilon = \frac{\sigma}{E} + \alpha \cdot \rho = \frac{\sigma}{E} + \alpha \cdot C_V \cdot (V - I \cdot R), \qquad 4$$

where a linear elastic stress-strain relationhip is assumed for simplicity. The rightmost term substitutes the capacitance per unit volume, C_V , and the applied voltage, V, for the charge density. The *I*·*R* term accounts for voltage drop across the resistance, R, due to the applied current, I. It is known that polypyrrole switches to an insulating state if sufficiently reduced, and degrades when sufficiently oxidized (Doblhofer and Rajeshwar 1998; Feldman, Burgmayer and Murray 1985b). The potential range over which Equation 4 applies is thus limited.

Figure 19 shows the strain and voltage in response to steps in applied current. The voltage range is +0.6 V to -1 V vs. Ag/AgClO₄. Note that the voltage increase at positive applied current plateaus at approximately +0.6 V. At this potential, and after several hundred seconds, signs of degradation are visible, with wisps of black material being released into the electrolyte from the polymer. The strain to charge ratio increases as the potential approaches +0.6 V vs. Ag/AgClO₄ and a 6.5 % strain is achieved. Of this, 6 % is recoverable on reversing the current. If the current is not reversed, then a 20 % film extension is achieved before mechanical failure as shown in Figure 20. Reversal of the current leads to a nearly perfectly capacitive response down to -1 V, but the strain to charge exhibits significant curvature. These and other similar experiments suggest that

the range of capacitive response is from -0.8 V to +0.4 V vs. Ag/AgClO₄, and that strain and charge are directly proportional over the same range of applied potentials. A cyclic voltammogram of polypyrrole between -0.8 V to 0.4 V at a voltage rate of 5 mV/s confirms the capacitive nature of the film in this range, as shown in Figure 21. Near the extremes of voltage, the magnitude of current increases slightly showing that noncapacitive processes are occurring.

The voltage range over which the capacitive impedance, and capacitance-like electrical to mechanical coupling hold, corresponds to a range of potentials over which polypyrrole is highly conductive (Feldman, Burgmayer and Murray 1985a). The oxidation state, changes by approximately 30 % over this voltage range^{*}.

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^{*} As calculated by taking the ratio of the total charge transferred per unit volume required to span the potential range, and dividing by the initial dopant concentration per unit volume. The initial dopant concentration is 0.35 charges per monomer (Yamaura, Hagiwara and Iwata 1988), which is converted to charge per volume using the film density and the relative molecular weights of the dopant and monomer.

5.2.2.2 Step Voltage Response

Experiments similar to those of the previous section are performed, but step voltages are applied instead of step currents, as shown in Figure 22. A step in voltage results in a spike in current and a rapid change in stress. As current diminishes so does the rate of change in stress. Again, changes in stress and strain are directly proportional to charge density, with α =1.2±0.3×10⁻¹⁰ C⁻¹·m³. Note that voltage determines the final stress state in Figure 22. Such a response is expected, since charge and voltage are related via the volumetric capacitance, and therefore setting the voltage also determines the final state of stress or strain.

Figure 23 shows that the current scales linearly in response to steps in voltage. This is an indication that a model that is dynamically linear in nature may provide a good description of the polymer and cell impedances.

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5.2.3 Efficiency

Thus far it has been shown that strain is proportional to charge over a limited range of potentials, as is voltage once an initial charging period has elapsed. The implications for efficiency are now explored.

The efficiency of electrical to mechanical energy conversion, e, is:

$$e = \frac{\int F \cdot dx}{\int V \cdot dQ} = \frac{\int \sigma \cdot d\varepsilon}{\int V \cdot d\rho},$$
 5

where *F* is force, *x* is displacement, *V* is applied voltage, *Q* is charge, σ is stress, ε is strain and ρ is charge density. Assuming that strain is proportional to charge density via the relationship:

$$\mathcal{E}=\alpha\cdot\rho,$$
 6

the efficiency is re-expressed as:

$$e = \frac{\int \sigma \cdot \alpha \cdot d\rho}{\int V \cdot d\rho} \,. \tag{7}$$

If changes in charge state or voltage are made slowly, or in thermodynamic terms, reversibly, so that dissipation across resistances is minimal, and charging is nearly complete, the voltage and charge density are related to the volumetric capacitance, C_v , by the relationship:

$$V \cdot C_V = \rho.$$
 8

Substituting for ρ in Equation 7 using Equation 8 gives:

$$e = \frac{2 \cdot \int \sigma \cdot \alpha \cdot dV}{V^2} \,. \tag{9}$$

At fixed load the efficiency is predicted to be:

$$e = \frac{2 \cdot \sigma \cdot \alpha}{V} \,. \tag{10}$$

The efficiency is maximized when large loads are displaced at small voltages, and the material exhibits large strains per unit charge. The voltage dependence in Equation 8 can be understood by realizing that the addition of each charge produces the same amount of work under constant load conditions, but requires progressively larger amounts of electrical energy to insert due to the capacitive nature of the impedance.

The strain to charge ratio for polypyrrole as synthesized in this study is α =1.2×10⁻¹⁰ m³·C⁻¹, and loads range between 1 and 34 MPa, making the numerator 8 mV at best. However, given the large creep observed at such high loads, a maximum load of 10 MPa is more realistic, making the numerator 2.5 mV.

Strain and voltage are proportional after the initial charging time, via the relationship:

$$\varepsilon = \alpha \cdot C_V \cdot V \quad , \qquad \qquad 11$$

obtained by combining Equations 6 and 8, which relate strain and charge, and voltage and charge, respectively. A 1 V applied potential produces a ~1% strain, given the volumetric capacitance of $C_V=10^8$ F·m⁻³. The predicted efficiency for a 1 % displacement at a 10 MPa load is then 0.25 %. The low predicted efficiency is a consequence of the fact that most of the electrical energy input is stored. In order to combine large strains

and high efficiency without changing the polymer or the electrolyte, the stored electrical energy must be recovered.

Equations 9 and 10 predict that efficiency is maximized at small voltages and strains. These equations must break down at voltages that are ~2.5 mV, and corresponding strains of ~10⁻⁵ from Equation 11, because otherwise the efficiency would be greater than unity. Some coupling between the electrical and mechanical behaviors must be incorporated, as discussed in Chapter 8. This <u>coupling</u> is not required at higher voltages and strains because the electrical energy is much larger than the mechanical energy in such cases.

5.3 Discussion and Summary

Step voltage and current measurements show that over a potential range of -0.8 V to +0.4 V vs. Ag/AgClO₄, strain is directly proportional to charge density, via the strain to charge ratio, $\alpha = 1.2 \pm 0.1 \times 10^{-10}$ m³·C⁻¹. Changes in stress observed when the film is held under isometric conditions show the same form of charge dependence, but scaled by the actuator elastic modulus. The voltage is also proportional to charge density, after an initial charging time. The capacitance per unit volume, which relates voltage and charge density, is found to be $1.3\pm0.1\times10^{8}$ F·m⁻³.

Strain to charge ratio is found to be a function of solvent used, doubling when propylene carbonate is replaced with water.

The electrical energy input is shown to be very large compared to the mechanical energy output, producing electrical to mechanical conversion efficiencies of less than 1 %. The efficiency is significantly improved if stored electrical energy is recovered, as discussed in Chapters 8 and 10.

Thus far discussion and results have focused on the material in or near steady state.

Chapters 7, 8 and 10 explore the limits on strain rate and power to mass. First, however,

Chapter 6 presents methods of operating actuators outside of a liquid environment.

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