Creep and Cycle Life in Polypyrrole Actuators

To be published in Sensors and Actuators A.

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Abstract

Conducting polymer actuators are of interest due to their low voltage operation, and their relatively high strains and forces. However information is incomplete regarding the appropriate operating loads, the extent of creep and cycle life. We report cycle life and creep response in polypyrrole actuators operated in propylene carbonate. Polypyrrole films are found to extend passively by 2 % after 100 minutes at 20 MPa, including about 1 % elastic elongation. Results of creep tests at stresses of up to 60 MPa are presented, showing a non-linear and history dependent response at very high loads. The magnitude of the creep suggests that in situations where position control is desired under varying loads and at times of longer than tens of minutes that the polymer is best operated at loads of < 20 MPa. Polypyrrole films passively cycled at a peak to peak amplitude of 8 MPa under an average load of 10 MPa for one million cycles show no apparent fatigue, suggesting that loading is not limiting cycle life. Films cycled by applying square wave potentials do show a drop in active strain. The strain amplitude decreases from 2 % to 1 % after 7000 cycles and an increased rate of creep is also observed during actuation. When the potential range is reduced such that the initial strain amplitude is 1.5 % the strain drops to 1 % after 32,000 cycles. The reduction in strain amplitude correlates with a decrease in charge transferred, suggesting degradation of the polymer is the cause of the loss in strain amplitude.

1: Introduction

Electroactive polymer actuators are materials that contract or expand in response to input electrical or chemical energy [1,2]. Of these actuators, conducting polymers are amongst the best characterized. They offer low voltage operation (1-10V), moderate to large strain (1-35 %) and high stresses [3-6]. The strains can be similar to those of mammalian skeletal muscle [2], and are one to two orders of magnitude larger than those in piezoceramics. Peak stresses at which actuation is observed reach 34 MPa, one hundred times larger than those in muscle [2]. Typical loads are 5 MPa, about five times lower than those used in piezoceramics. The torque to mass ratio is higher than that of direct drive electric motors. Typically these actuators exhibit only moderate frequency responses. In polypyrrole for example previous work of ours has shown full strain at 2 Hz and small strains up to 30 Hz [7]. The actuators are electrochemically driven with rate of actuation being determined by the current. Current can be limited by mass transport of ions in the film, or by electrode and cell resistances. Redox response in thin films suggests that it is possible to achieve kilohertz frequency response [8] as a result of enhanced mass transport rates, thereby enabling significant improvements in rate if the actuators are appropriately structured [9,10]. The promising properties of polypyrrole actuators has led to a number of applications being developed and prototypes being built including a variable camber propeller and an active Braille screen [11,12].

The results obtained in this paper help show two properties that are important in selecting and implementing polypyrrole actuators. The first is the creep response at high loads and long times. Knowing the extent of elastic and viscous/plastic deformation in response to applied load as a function of time is important in selecting the peak and average loading conditions. For example, if position control is required, it is important to be able to actively change length in order to compensate for creep and change in load. If the extent of creep is greater than the strain that can be induced by the application of voltage, position can no longer be maintained. In this paper creep at very high loads and relatively long time periods is investigated for the first time.

The other property investigated is the cycle life. The first unknown is the effect of passive cyclic loading and whether it is likely to lead to failure. A second set of experiments investigates the number of active cycles that can be achieved, driven by voltage steps. The cycle life will ultimately determine the types of applications appropriate for conducting polymer actuators. For example, a valve used to irrigate crops or lawns that is expected to operate once a day for about ten years will require 4,000 cycles, an artificial urinary sphincter used to replace those damaged after prostate surgery might need 32,000 cycles over ten years and a pump used to help contract the heart once every stroke will need to beat every second for at least 5 years - about 200 million cycles. Can conducting polymers meet these needs?

Conducting polymers are electrically conductive materials. During actuation they are typically electrochemically driven. When potential is applied to an electrochemical cell in which the polymer forms one electrode, charge removed from the polymer is balanced by the insertion of ions. This insertion of ions, and perhaps some solvent insertion and conformational change in the backbone leads to a change in dimension and actuation [13,14]. The redox cycle life of conducting polymers in batteries and electrochemical capacitors is limited [15], and has been shown to be reduced by the presence of water [16,17]. In actuators previous studies have shown that 100,000 cycles can be achieved at small strains [7] and that the cycle life is apparently dependent on the electrolyte employed [18,19]. In this paper we examine the cycle life of polypyrrole actuators at two different starting strain levels. Cycle life is increased when smaller strain is employed. During the cycling potential across the electrode is controlled and the charge is recorded. Before reporting on active cycle life, measurement of creep and of response to mechanical cycling are presented.

2: Methods

The four sets of experiments performed measure creep, tensile strength, passive cycle life and active cycle life.

1. **Creep Tests**. This first set of experiments investigates the mechanical properties of polypyrrole in electrolyte, but without the application of electrochemical potential. A series of creep tests are performed under loads of up to 60 MPa. The behavior is observed at both 24 °C and 44 °C, bracketing the temperatures expected in medical device use. Each application will have a level of creep that is deemed acceptable. These tests provide data on the extent of creep that can be expected, thereby helping the maximum acceptable loading to be determined.
2. **Tensile Strength Tests**. These tests are performed in electrolyte, but without the application of electrochemical potentials, and allow the absolute limit on applied load to be determined.

3. **Passive Cycle Life**. In these tests, the applied load is cycled with the film immersed in electrolyte, but without the application of electrochemical potential. These results help determine the upper limits on cyclic loading in the absence of electrochemical activity.
4. **Active Cycle Life**. Applied load is held constant while the electrochemical state is cycled, and the current, and strain are observed. These tests help determine the limits on electrochemically driven (active) cycling.

2.1 *Apparatus*

The first four tests were performed using a Perkin Elmer Dynamic Mechanical Analyzer, DMA 7e (http://instruments.perkinelmer.com). It allows tensile tests to be performed on films at programmable temperatures.

An instrument with the ability to control the sample electrochemistry while performing mechanical tests was built for the purpose of the tests and is now described.

2.1.1 Description of the Isotonic Testing Apparatus

The isotonic testing apparatus (ITA) is composed of two modules: the upper module containing force and displacement sensors, the actuators, the upper clamp and probe; and the lower module composed of the lower clamp and bath. The ITA is shown in Figure 1 below. Sample films are held vertically between two clamps within a bath, which is part of the lower module. Force is applied to the sample via a voice coil actuator (Bruel and Kjaer minishaker Model 4810, www.bkhome.com). An aluminum rod connects the voice coil actuator to the upper clamp. In series with the clamp is a load cell, enabling the applied force to be recorded (Entran ELFS-T3E-10N load cell www.entran.com, with Vishay 2311 Signal Conditioning Amplifier www.vishay.com). An LED placed along the rod provides a photon source for a position sensitive photodiode (PSD), thereby enabling position measurement (Pacific Silicon Sensors, www.pacific-sensors.com, PSS-DL100-7PCBA duolateral (2-axis) position sensing module, with PSS-DL-100 position sensing photodiode (PSD)). The applied force is under computer control via a data acquisition board (Allios 16-bit A/D, D/A, 50 kHz sampling) and a voltage to current amplifier. The graphical user interface is written in Visual Basic 6.0 (www.microsoft.com) and includes a digital control algorithm for maintaining a desired force. Vertical sample positioning is performed via a stepper motor and linear stage (Parker linear stage with a Zeta57-51-MO stepper motor and a Compumotor Zeta6104 Indexer Drive connected to the RS-232 port, http://www.compumotor.com), while horizontal alignment is achieved via the lower micrometer driven stage.

Electrochemical potential is under computer control via the data acquisition board and a potentiostat (Amel, model 2053). The graphical user interface enables input of shaped potentials at user controlled rates. The shaped potentials maximize response rate while minimizing sample degradation [7]. This method also accounts for the effect of any series resistance in the electrical circuit, thus providing enhanced experimental repeatability.

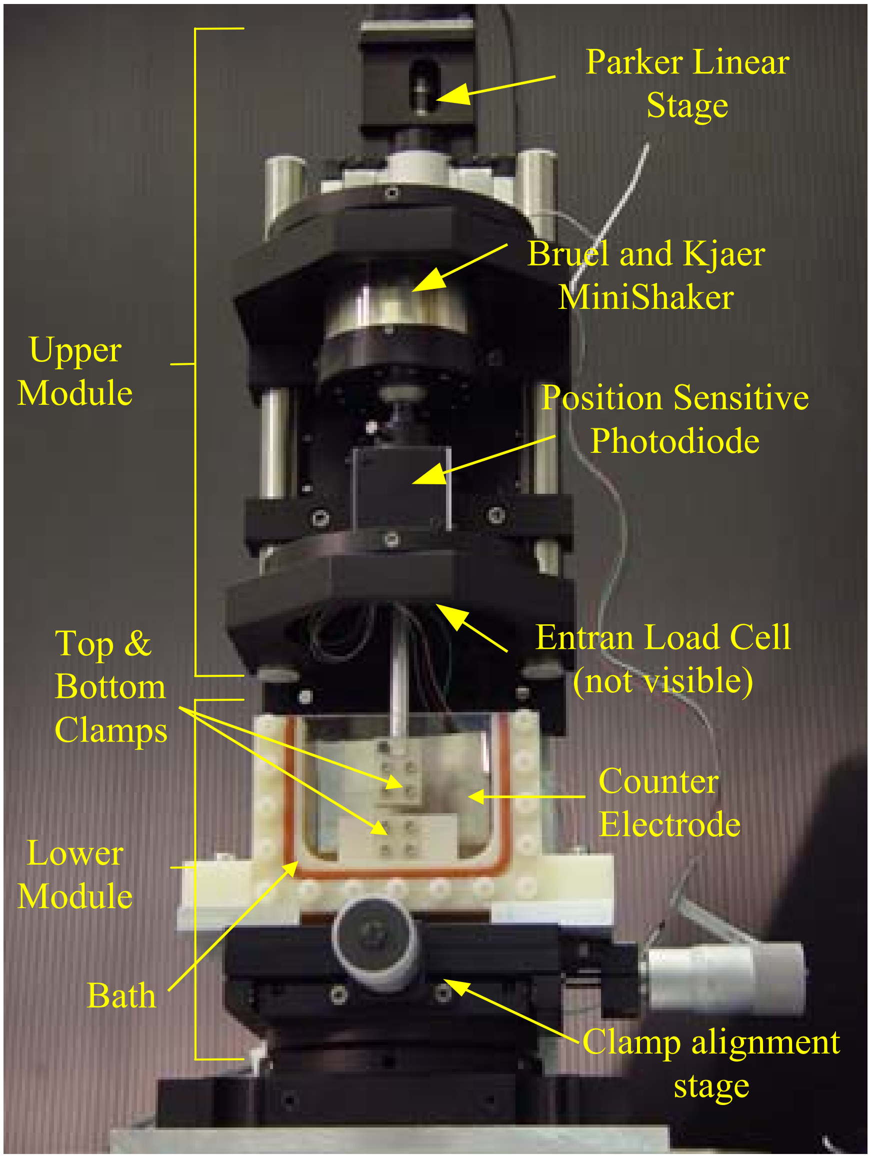

Figure 1: Testing apparatus, including a solution containing bath (white).

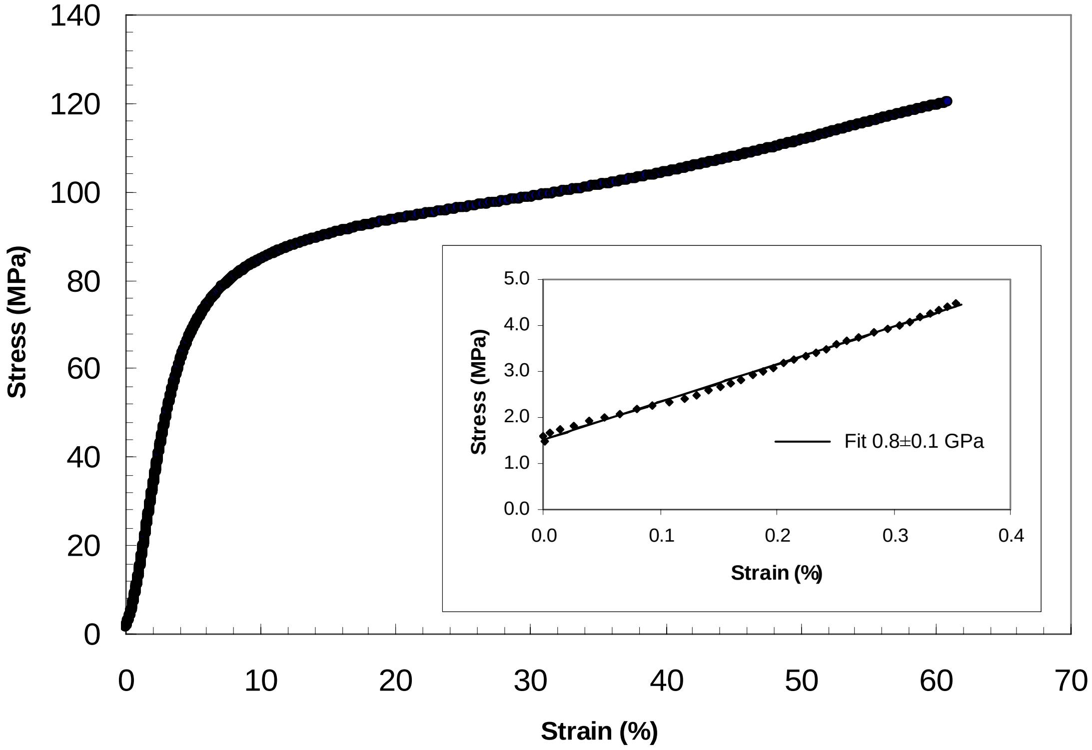

Figure 2: Tensile strength of a polypyrrole film drawn at 5 MPa/min.

2.2 *Synthesis*

Films were synthesized by electrodeposition following previously established procedures [9,20]. 0.05 M pyrrole in 0.06 M tetraethylammonium hexafluorophosphate/propylene carbonate with 1 wt% water is galvanostatically deposited at 0.125 mA/cm^2 onto polished glassy carbon substrates at -40 °C. Films are typically 15 micrometers thick, and are cut to be 15-35 mm long and 1.5-2.5 mm wide. These films are peeled from the electrode by hand. Conductivities of the as grown films are 350±50 S/cm. Films employed in mechanical and electro-mechanical tests are soaked in electrolyte prior to use because it has been found that dry films have a higher modulus, do not initially respond as quickly, and swell considerably upon immersion in propylene carbonate electrolyte [21].

3: Experiments and Results

3.1 *Tensile Strength*

The tensile strengths of polypyrrole films were measured using the Perkin Elmer DMA 7e. The tensile strength of the 16±2 μm thick, 1.7±0.1 mm wide and 4.77±0.01 mm long film drawn at 5 MPa/min is found to be 120±17 MPa, as shown in Figure 2, and the elastic modulus at small strains is 0.8±0.1 GPa. The results were obtained for a freshly grown film while in propylene carbonate containing 0.1 M tetraethylammonium hexafluorophosphate. Tensile strength is found to vary depending pre-treatment (dried vs. soaked), degree of alignment of the film with the clamps, and previous testing history. For example tensile strength in dry films reaches 150 MPa, while films soaked for prolonged periods in propylene carbonate can exhibit tensile strengths as low as 30 MPa. The important result for the current analysis is that in polypyrrole films grown as described the tensile strength is not limiting the stress at which the films actuate. As discussed below, it is the extent of creep that limits operating loads.

3.2 *Creep Tests*

The application of a load to polypyrrole leads to an elastic deformation and creep. In this work we refer to creep as strain that occurs subsequent to the immediate spring-like deformation when a step in load is applied. Much of what is referred to as creep is recoverable, as will be seen, but some is plastic deformation - it is not recoverable. The extent of these elastic and creep displacements will often determine the maximum acceptable load.

Previous work on polypyrrole by us and others over timescales of up to 1000 s suggests that the creep in polypyrrole is linear and viscoelastic in nature [9,22]. Linear viscoelastic materials are relatively easily modeled, and their responses may then be predicted. A series of creep tests taking place over 12,000 s and at loads of between 10 MPa and 60 MPa demonstrate a non-linear, history dependent behavior on these time scales.

3.2.1 Methods

In the creep testing procedure films are held in the PerkinElmer DMA in propylene carbonate under a 2 MPa load. Step loads of up to 60 MPa are subsequently applied for 100 minutes and the resulting responses recorded.

3.2.2 Results

Figure 3 depicts two creep responses taken on one sample. During these tests the stress is stepped from 2 MPa to 20 MPa, where it is held for 100 minutes, and then returned to 2 MPa while recording strain. The lower curve results from the same test performed 6 days later. Note that the rate of creep is reduced by a factor of 3 from the original measurement. This reduction in creep may be due to a gradual stretch alignment of the film in the axial direction, making deformation more difficult. In a time invariant system the responses should be identical, but instead clearly demonstrate that the film mechanical properties are dependent on the load history.

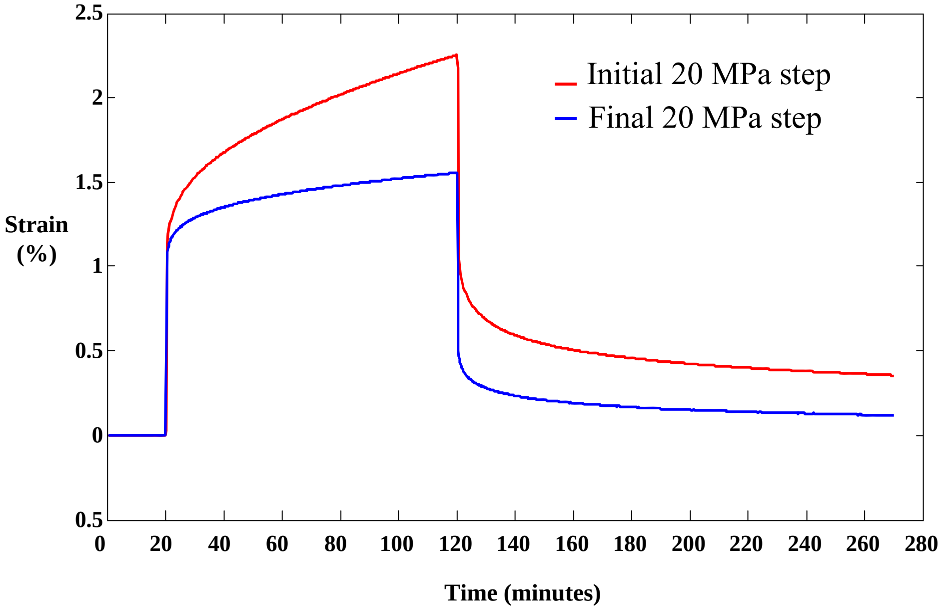

Figure 3: History Dependence of Creep in a polypyrrole film. An initial load of 2 MPa is applied. Stress is then increased to 20 for 100 minutes, and returned to 2 MPa for the final 150 minutes. The red curve data was taken two days after immersion of the sample in propylene carbonate, and the blue curve data was obtained a further 6 days later. Measurements were performed at 24 ºC.

Figure 4 shows the superimposed strain from a sequence of creep tests recoded at a temperature of 24 ºC, all of which are normalized by the magnitude of the step in applied stress. In the case of a linear time-invariant system, the curves will all match. The fact that they do not match shows that the response is either non-linear, time varying or both. The blue curve is a step response taken at 10 MPa. The green curve is the result of a subsequent step to 30 MPa taken the following day. The relative creep is greater at the higher stress. However 2 days later the film creep at 40 MPa (magenta) is similar to the original 10 MPa data. In the final measurement at 60 MPa (turquoise) the film shows the highest relative creep.

The polypyrrole creep response is clearly history dependent and non-linear at the very high loads employed in this study. The sequence of results shown in Figures 3 and 4 show that after enduring high stresses over significant periods of time (~100 minutes), creep can be substantially reduced. This effect may be useful as a pre-treatment in cases where high load operation is required with minimal creep, although exposure to high loads could also reduce electrochemically induced strain [23]. The final loading at 60 MPa in Figure 4 shows that even with stress pre-treatment, long term operation at extremely high loads is impractical. The results also show that much of the creep is recoverable, though not all. The extent of creep recovery is relevant to position control under varying loads as it indicates the extent to which the structure will return to its original position after unloading.

What loading conditions are appropriate for actuation? If position control is desired over a wide range of loads it is important the deformation resulting from the application of a load not exceed the active strain. Otherwise the change in load cannot be compensated for. During the first 20 MPa load, the upper curve in Figure 3, the combined elastic and creep deformation at 20 MPa is nearly 2.3 % after 100 minutes. Such creep is near the limit of actuation expected in polypyrrole synthesized and actuated in propylene carbonate/tetraethylammonium hexafluorophosphate electrolyte, and thus presents an upper limit on operation under position control. As noted above, the subsequent cycle (lower curve in Figure 3) shows that creep can be substantially reduced after prolonged exposure to high loads. Such treatment may be useful in situations where high loads are necessary, and could allow position control at such high loads. Note that the maximum load under which position control is suitable depends on the operating time – for short times large loads can be sustained without large creep, whereas over longer times (tens of minutes), creep becomes significant. The data in Figures 3 and 4 provide some guidance as to the extent of creep that can be expected. If force control is desired then very high loading can be employed (potentially in excess of 60 MPa). Such loading is unprecedented in polypyrrole actuators.

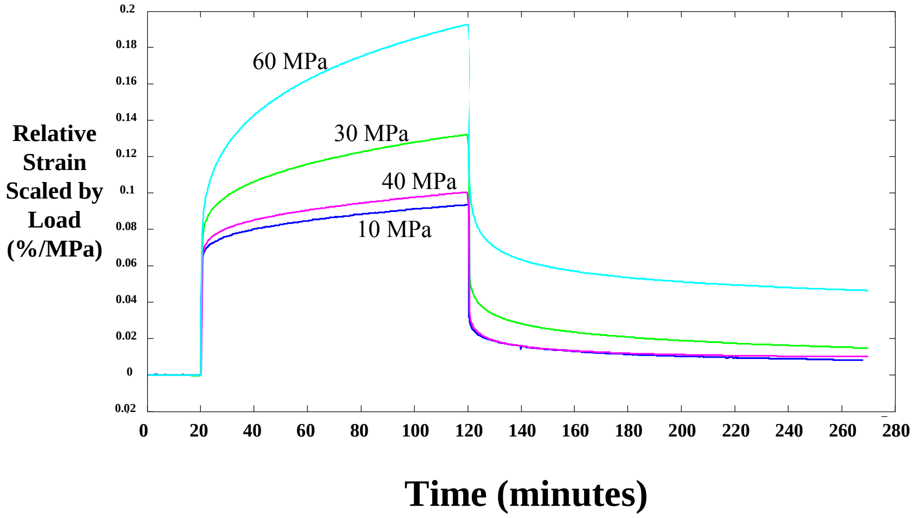

Figure 4: Further History Dependence of Creep in a Polypyrrole Film. An initial load of 2 MPa is applied. Stress is then increased to between 10 MPa and 60 MPa for 100 minutes, and returned to 2 MPa for the final 150 minutes. The blue curve data was taken four days after immersion of the sample in propylene carbonate, followed by the 30 MPa data (green), and then the 40 MPa creep test, and finally the 60 MPa test.

3.2.3 Temperature Dependence

Temperature has a large influence on the speed of passive mechanical response/creep. Figure 5 shows the response at 44 °C and at 24 °C. The creep is much faster at the higher temperature. This is most evident when the ratios of total stress and strain (referred to in Figure 5 as static modulus) are plotted versus time on a log-log scale. The similarity of the two curves in the log-log domain suggests that time-temperature equivalence may apply. If operation is expected at a variety of temperatures then the need for compensation under position control will be greater at higher temperatures, and the time over which loads can be held will be shorter. This will be important for operation in vivo for example, where creep will be accelerated relative to room temperature.

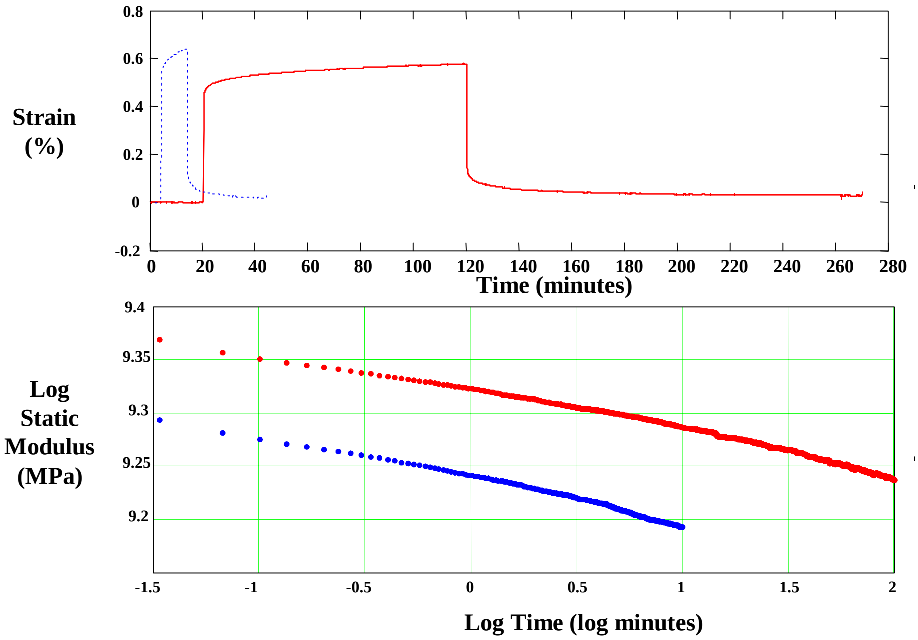

Figure 5: Temperature dependence of creep. Stress is stepped between 2 MPa and 10 MPa in a sample at 44 °C (blue) and 24 °C (red). The 10 MPa stress is held for 10 minutes at 44 °C and 100 minutes at 24 °C, after which stress is returned to 2 MPa. The top plot is the strain versus time, the bottom plot is the ratio of stress to strain over time.

3.3 *Passive Cycle Life*

Another failure mechanism is fatigue, which is induced in response to cycling. Samples soaked in propylene carbonate were held for 6000 minutes at 10 MPa, and a dynamic load of ±4 MPa was applied at 3 Hz. The test was run at 24 °C and repeated at 37 °C. Results show that the samples easily withstand 10^6 cycles, far more than will be demonstrated in active cycling. Steady creep is not enhanced by cycling.

3.4 *Active Cycle Life*

The aim is to determine how actuator performance changes with the number of redox cycles.

3.4.1 Methods

In these experiments films are clamped into the isotonic test rig (Figures 1). The modulus is measured. Films are then subjected to a constant load. After 50-100 s a train of excitation pulses is begun, as shown in Figure 6. These pulses are designed to maximize strain rate, while avoiding overcharging of the films [7]. The resulting currents and strains are recorded, and the charge is calculated. Tests are continued until a substantial reduction in performance is observed.

3.4.2 Results

Active cycle life is substantially shorter than ‘passive’ cycle life. A number of experiments were run using films having a thickness of 15 µm, at applied loads of between 2.5 MPa and 10 MPa, and at frequencies of 0.2 Hz to 1 Hz. The larger the charge transfer and strain the shorter the cycle life. Two examples of cycle life are shown – one at 2% strain, showing short life (< 10,000 cycles), and the other at moderate strain (1.5 %), exhibiting higher cycle life (32,000 cycles).

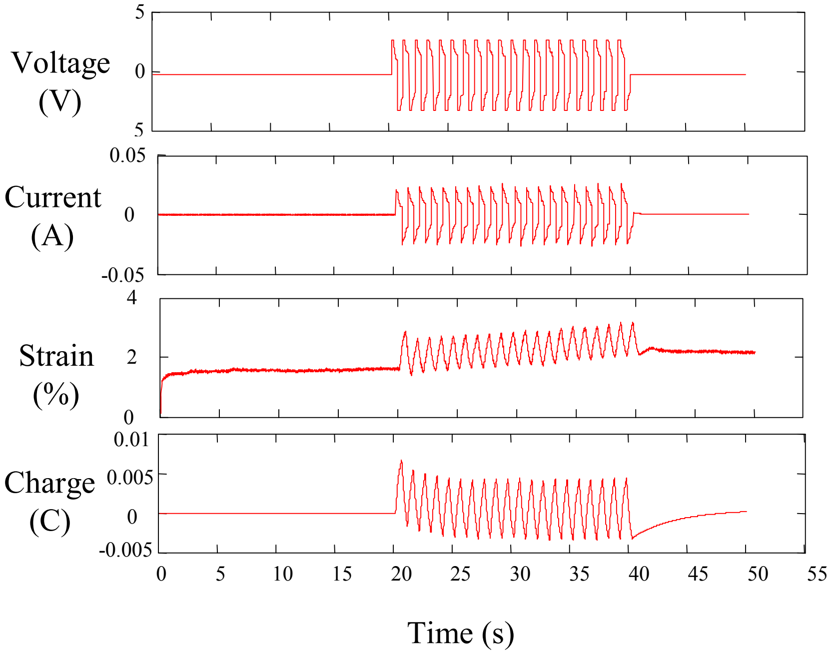

Figure 6: Example of isotonic electrochemical cycling at 5 MPa.

3.4.2.1 Low Frequency, Large Strain

In this procedure cycling potentials are applied to a polypyrrole film at 0.24 Hz and under a constant 2.5 MPa stress, as depicted in Figures 7 and 8. Resistance compensation is employed, with the applied potential being shaped, as seen in Figure 8, such that the estimated double layer potential is maintained between 0.4 V and –0.8 V (1.2 V amplitude) vs. Ag/AgClO$_4$ [7]. The strain initially exceeds 2 %. Figure 7 presents the final 7000 cycles of the total 10600, with the top graph showing the strain amplitude and creep, and the bottom plot depicting the strain and charge transfer amplitudes. Strain and charge amplitudes are obtained by subtracting the gradual change in strain and charge using a polynomial fit (removing low frequency changes) and then using a peak identification algorithm to find the amplitude of the strain and charge at 0.24 Hz. The charge has been scaled for easier comparison with strain. Based on the amount of charge transferred per unit sample volume and the typical initial doping state (as grown) it is estimated that the charge state is switched between approximately 0.3 and 0.2 charges per monomer, a range over which very little change in polymer conductivity is observed. This charging level persists for the first ~ 7000 cycles, after which it drops off.

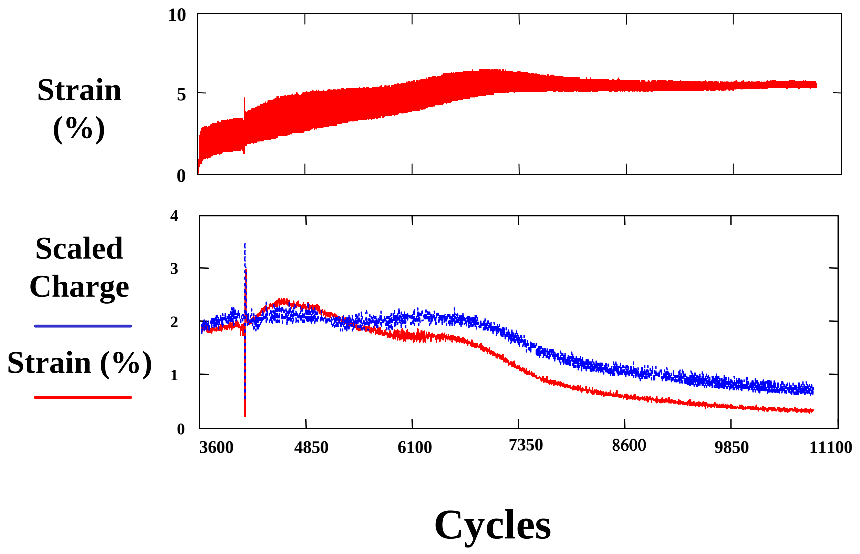

Figure 7: Final 7000 cycles of a 10600 cycle active test performed at 0.24 Hz and at 2.5 MPa. The top plot depicts strain vs. cycles. The bottom plot shows the 0.24 Hz strain amplitude and charge density amplitude as functions of time. The charge density is scaled by an estimated strain to charge ratio of 2.5×10^{-10} $m^3\cdot C^{-1}$ to show the correlation between charge density and strain.

A drop in the strain amplitude below 1 % is evident after 7100 cycles. The drop in amplitude is associated with a drop in charge transfer. The correlation suggests that a reduction in charge transfer is substantially responsible for the drop in amplitude. The reduction in charge may be due to increased sample or cell resistance, reduced mass transport of ions within the sample, a reduction in the kinetics of charge transfer or irreversible sample degradation. No significant change in solution or film resistance is observed, pointing to one of the other factors as the cause of the degradation in performance. Immediately following cycling the period of the applied square wave potential was greatly increased but the strain did not increase significantly. This observation suggests that a change in mass transport rates or kinetics is not limiting the strain amplitude. Instead it seems likely that the number of redox sites has been reduced, and irreversible degradation has occurred.

Substantial creep is observed during the cycling. The 3.5 % net strain observed over 100 minutes in Figure 7 is larger even than the 2.25 % creep observed over the same time period at 20 MPa (Figure 3). Similarly high creep rate is observed in the results shown in Figures 6 and 9(top). The rate of creep drops fairly abruptly as the charge per cycle and strain amplitude drop (Figures 7 and 9), suggesting that the mass transport within the polymer activates creep. This coupling between the mechanisms of creep and of actuation has previously been reported by our group [24], where it is seen that the direction of this creep depends on the previous load history.

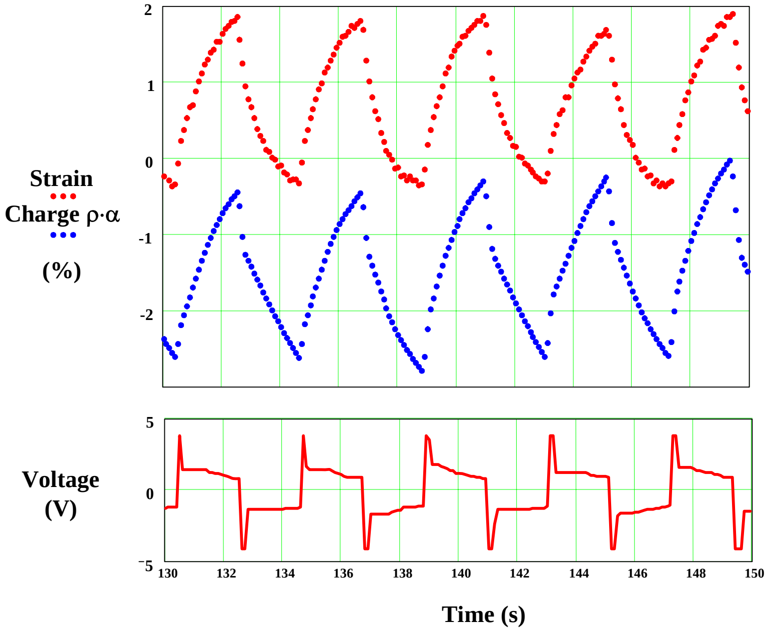

Figure 8: Example cycles at 0.24 Hz obtained early in the 10600 cycle test sequence. Charge density is scaled by a strain to charge ratio of 2.5×10^{-10} $m^3\cdot C^{-1}$.

3.4.2.2 Moderate Frequency and Strain

In these tests 1 Hz square wave potentials are applied to polypyrrole films under a constant 5 MPa stress, as depicted in Figures 6 and 9. The double layer potential is maintained between 0.16 V to –0.69 V (0.85 V amplitude) vs. $Ag/AgClO_4$, employing the same inputs as presented in Figure 6. Strain exceeds 1.5 % during the initial 10,000 cycles, and is above 1 % for 32,000 cycles. Over these initial 32,000 cycles the charge transfer is about 25 % of the charge transfer expected when proceeding from fully oxidized to fully reduced. After 45,000 cycles, the magnitude of strain falls below 0.3 %. Once again changes in strain amplitude are correlated with the extent of charge transferred. The increased cycle life beyond that observed at 0.24 Hz may be due to the reduction in the potential excursion, and/or the reduction in the extent of charge transferred. The 32,000 cycles obtained at strains of greater than 1 % are ample for many disposable dispensing devices and toys, and for some low cycle medical applications such as artificial urinary sphincters.

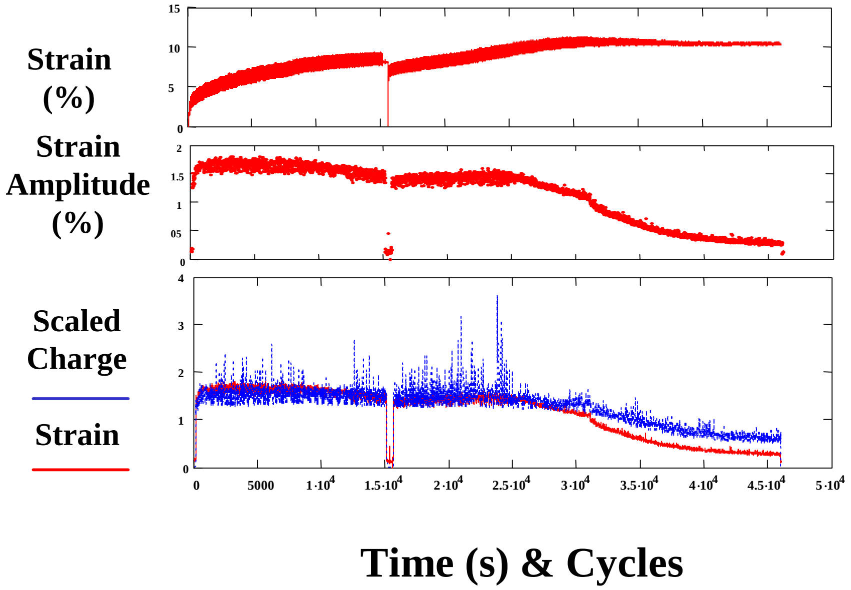

Figure 9: Cycle testing at 1 Hz. The upper plot depicts strain vs. time. The middle plot shows the strain amplitude as a function of time. In the lower plot the charge density is scaled by an estimated strain to charge ratio of 2.5×10^{-10} $m^3\cdot C^{-1}$ to show the correlation between charge density and strain amplitude. The cycling in potential was stopped briefly after 15,000 cycles in order to save the accumulated data.

The investigation of cycle life has demonstrated that 32,000 cycles of amplitude of at least 1 % can be obtained at a 1 Hz excitation. The result provides an important measure of the number of cycles that can be expected. The performance achieved in these cycles is good relative to the best achievable, with work densities during initial actuation cycles exceeding 75 kJ/m^3 (product of load and strain) or 58 J/kg, comparing favorably to the best reported elsewhere [25]. By reducing strain amplitude it is likely that further improvements in lifetime will be achieved [7].

Degradation may be a function of the time spent at the potential extremes. If position control is required in which the actuator spends much of its time at an extreme of its range, it is possible that lifetime will be reduced.

Changing electrolyte may increase life as observed in polypyrrole actuators operated under very similar conditions to those reported here [18,19]. It is shown that strains in polypyrrole drop linearly from 1.5 % strain to 0.3 % over the course of 4000 cycles when propylene carbonate/tetraethyl ammonium hexafluorophosphate electrolyte is used. Switching to ionic liquid electrolytes extends cycle life such that the response drops from 1.5 % to 1 % over 6000 cycles. (The full strain is recoverable after resting the ionic liquid driven actuators.) In electrochromic applications in redox it has been shown that one million full redox cycles can be achieved in ionic liquids [18]. Although ionic liquids offer a promising approach for further improving cycle life, they are at present expensive and hard obtain, compared with propylene carbonate.

4: Conclusions

Results are presented on the passive mechanical properties, cycle life, and electrochemical cyclability of polypyrrole. One million passive stress cycles at 8 MPa amplitude are easily achieved at 24 °C and 37 °C. The fundamental limit on durability is not the passive cycle life, but rather the active response. 7,100 and 32,000 cycles were obtained at 0.24 Hz and 1 Hz respectively. Reduction in strain is correlated with a reduction in charge transfer, suggesting that irreversible reactions limit performance. Although the maximum tensile strength is 120 MPa, creep behavior suggests that sustained loads of over 20 MPa are impractical if position control is to be maintained. The passive mechanical response is found to be history dependent at such high loads. Creep is reduced and stiffness increased with time under load. Increasing temperature and actuation both increase the rate of creep.

Acknowledgements
This work was supported in part by an Office of Naval Research SBIR contract. Work was performed by the authors at Molecular Mechanisms LLC.

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