The Effect of Temperature Exposure on Polypyrrole Actuation

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ABSTRACT

Polypyrrole actuators offer attractive possibilities due to their large electrochemical stress (>5MPa), moderate to large strain (>2 %) and low voltage operation (<2 V). However, little is known about their temperature dependence response, with nearly all previous tests performed at room temperature. To test the effects of increasing temperature, polypyrrole films in water and propylene carbonate were thermally cycled twice from 22°C to 80°C. Length and actuation were measured before, after and between cycling. Results show that polypyrrole in TBAPF_{6(propylene carbonate)} underwent a 4.8% irrecoverable contraction during the first cycle and lost half it's actuation each cycle. Polypyrrole in NaPF_{6(aq)} showed a 2.1% initial expansion in length on the first cycle followed by a 2.1% contraction on the next cycle, while active strain amplitude dropped from 7.7% to 5.9% to 4.9%. Polypyrrole in NaCl_(aq) has a net contraction of 6% over two cycles with no significant change in it's original 3.5% actuation amplitude. This suggests that although films in NaPF_{6(aq)} have the best initial strain, films in NaCl_(aq) maintain the most consistent strain amplitude in response to temperature on the timescales observed. Strain to charge ratio was found to decrease slightly, but the majority of the loss in actuation for films is correlated with a reduction in charge transfer each cycle. This reduction may result from a reduction in the active volume of film.

INTRODUCTION

Recent work on polypyrrole electrochemically driven actuators has shown dramatic improvement in strains and lifetime [1-3] However, commercial use of polypyrrole requires reliability over a variety of conditions. Of these, use and storage over a range of temperature is critically important but there is very little information on their temperature dependence of their actuation and length. Some work by Anquetil[4] showed vacuum pre-annealed polypyrrole caused a loss in conductivity of 4% but he did not measure actuation before or after annealing, nor did he look at the effect of heating in any solvents. Hara[5] actuated polypyrrole at 60°C, showing increased strain and strain rate but did not look at long terms effects of this temperature or actuation once films were returned to room temperature. Our aim is to look at the effect of multiple exposures up to 80°C on polypyrrole and thereby gain experience and insight into the effects of temperature on actuation.

METHODS

Preparation of PPy Films (Table 1). Polypyrrole(PPy) films were grown galvanostatically using two methods: 1) in propylene carbonate(PC), (Aldrich), tetrabutylammonium tetrafluoroborate (TBAPF₆), (Aldrich), and distilled pyrrole (Aldrich) following the methods of Yamaura at -30 °C, and 2) in methyl benzoate, (Aldrich) and tetrabutylammonium tetrafluoroborate (TBABF₄), (Aldrich) at zero degrees, following the methods of Zama[2,6] The growth setup used was described previously by Madden. [7,8]

Testing of PPy films. Films were cycled in 1.0M NaPF_{6(aq)}, 0.1M TBAPF_{6(propylene carbonate)} and 1.0M NaCl_(aq). During each cycle voltage was ramped from -0.9 to 0.7V and back vs Ag/Ag⁺ using a Solatron analytical SI 1287 at frequencies as low as 0.0025Hz until the strain rate dropped to zero. Measurement of strain was made using an Aurora Scientific Muscle Analyzer at constant 0.1MPa. Following initial cycling at 22°C, solution temperature was raised up to 80°C, held for 30 minutes and cooled back down to 22°C using a Fisher Scientific Circulating bath. Films were subsequently exposed to another set of electrochemical cycles, followed by a temperature cycle and a final set of electrochemical cycles. (See Figure 1 for an example) Note that the frequency of actuation was modified during the experiment in order to ensure strain had stabilized and maximum actuation was achieved. These three different deposition and cycling environments provide a comparison of three commonly used electrolytes and solvents that have relatively high cycle life and show moderate to large strains. [2,9] A parallel set of experiments were performed on films whose conductivity was monitored after thermal cycling. No actuation was performed on these films.

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Film	Growth environment	Current Density	Time	Thickness	Conductivity	Electrochemical	
		(mA cm ⁻²⁾	(hrs)	(µm)	(S/m ⁻¹⁾	cycling environment	
1	Methyl benzoate	0.2	12	37	1.1.10 ³	Water	
	-0.25M Pyrrole					-1.0M NaPF ₆	
	-0.2M TBABF ₄						
2	Propylene carbonate	0.125	8	10	1.0·10 ⁴	Propylene Carbonate	
	-0.06M Pyrrole					-0.05M TBAPF ₆	
	-0.05M TBAP						
3	Propylene carbonate	0.125	8	10	1.0·10 ⁴	Water	
	-0.06M Pyrrole					-1.0M NaCl	
	-0.05M TBAP						

Table 1: Growth and Actuation Conditions of Polypyrrole films



Figure 1. Thermal and Electrochemical Cycling of Film 1

RESULTS

Change in maximum actuation

Resulting maximum strains for each film are shown in figure 2 (solid bar). Film1 (NaPF₆) showed a gradual decrease in strain from 7.7% to 5.9% to 4.9%. Film 2 (TBAPF₆) showed the most significant decrease in strain going from 1.17% to 0.64% to 0.36% strain. Film 3(NaCl) showed virtually no change in initial strain of 3.5 %.

Reduction in strain amplitude(the difference in strain between the maximum expanded and contracted state of a film), is a combination of reduction in strain to charge ratio and total charge transferred. Comparing the effects of these two factors can give an idea of the mechanism behind decrease in total strain of a film. Strain to charge was estimated by averaging the strain and current over several cycles, and subtracting the parasitic current. The parasitic current was calculated from the stable current obtained near the end of electrochemical cycles where the strain rate had dropped to zero. In this case, changes in strain to charge can account for only a slight amount of the reduction in strain of Film 1 and 2 and strain to charge actually rose in film 3. Given this, the majority of reduction in strain is associated with a net reduction in total charge passed, similar to the effects observed by Madden upon multiple cycling [9]. In this case multiple cycling did not lead to the reduction in strain as the number of cycles was kept well below that causing significant decrease in strain.

To assess whether it was likely that the film was simply breaking down as a result of the elevated temperature a TGA-FTIR (thermal gravimetric analysis – fourier transform infrared spectroscopy) experiment was run on a PF $_6$ grown film. The test indicated that





		Conductivity	Peak	
		-	Strain	Thermal
			Rate	Strain
Film	Cycle	S/m(x10 ³)	%/s	% Strain
1	Pre Thermal	1.1	1.2	-
BF₄film	Post 1 Thermal	1.2	0.83	2.1
in NaPF ₆	Post 2 Thermal	1.2	0.38	-2.1
2.	Pre Thermal	10	0.035	-
PF ₆ film	Post 1 Thermal	10	0.011	-4.8
in TBAPF _{6(PC)}	Post 2 Thermal	5	0.005	-0.4
3	Pre Thermal	10	3.1	-
PF ₆ film	Post 1 Thermal	16	2.2	-3
in NaCl _(aq)	Post 2 Thermal	10	1.72	-3

Table 2. Conductivity, Thermal Strain, Electrochemical Strain, Max Strain Rate

the first significant atmospheric mass loss began at around 180° C, when the propylene carbonate began to evaporate and the PF₆ decomposed, and there was no indication of thermal decomposition of the backbone until much higher temperature. This suggests that if there are any chemical changes to the polymer at 80° C they are the result of reactions with ions, solvent and polymer already present within the films.

Rate of Actuation

More significant than change in strain is the drop in the rate of actuation. (see Table 2) This was calculated by measuring the change in strain in the first second after voltage was switched. Proportionally, the largest change was seen in Film 2 which dropped 7-fold, from a peak strain rate of 0.035%/s to 0.005%/s. Film 1 had a 4-fold drop from 1.2%/s and even film 3 which showed no net change in total actuation had a significant reduction in peak strain rate from 3.1%/s to 1.72%/s.

Temperature Induced Change in Conductivity and Contraction

The films whose conductivity was monitored in a parallel set of experiments showed some variation in conductivity as shown in Table 2. The change in resistance is not enough to explain the change in rate of actuation.

Each of the films showed a net change in length due simply to the thermal cycling. Film 1 in NaPF₆(aq) showed a net expansion on the first thermal cycle of 2.1% followed by a contraction of 2.1% on the second cycle, as seen in Figure 1. The rate of contraction observed during the second cycle appears to be fairly constant, suggesting that contraction is not complete. Film 2, cycled in propylene carbonate, shows the quickest contraction beginning at 45°C for a total of 4.8% during the first thermal cycle and 5.2% overall. Film 3, cycled in an NaCl_(aq) aqueous solution showed a more gradual contraction of 3% on both the first and second cycles for a total contraction of 6%. Irreversible contraction upon exposure to heat is typical of polymer networks, which are seldom in thermal equilibrium, and is called the Gulch-Joule Effect.[10] The thermal contractions present an engineering challenge since they are similar in magnitude to active strain. Holding the films at high temperatures for longer times leads to saturation of this contraction, and thus thermal pre-treatment may be advisable in cases where it does not have a dramatic impact on active strain.

DISCUSSION

Drop in maximum actuator strain

There are three possible mechanisms for the reduction in active strain of films 1 and 3 after thermal cycling. These include (1) a change in mechanism of actuation or structure of the film e.g., increased stiffness or cross-linking that reduce strain, (2) structural changes or thermal degradation of the film preventing oxidation and reduction and (3) changes in the film structure that lead to a reduction in strain rate. The observed irreversible contraction induced by heating the films suggests a chance in structure. This likely represents a reconfiguration of film polymers into more energetically favourable states and could lead to regions of the film being less accessible to ions. However, if changes in structure are responsible for a change in the mechanisms of actuation, one would expect the strain to charge ratio and change in strain suggests that the primary reason for drop in voltage induced strain is the decrease in total charge transfer, either due to rate effects, degradation or reduction in accessibility of ions. Rate effects are probably not the cause of the reduced active strain because these were largely compensated for waiting for saturation in the total strain.

Supporting thermal degradation of the film are experiments by Sakkapoulous that model chemically synthesized polypyrrole as conductive grains surrounded by an insulating matrix. [11] [12] [13]As polypyrrole is thermally aged, conductive areas shrink at a rate dependent on the temperature, doping ion and atmosphere. Mechanisms of this loss include dedoping, oxidation/hydrolysis/scission of chains and cross-linking. These effects have been measured at temperatures as low as 22°C. Although this degradation may be occurring, the relatively small change in conductivity and the short timescales compared to those of Sakkapoulous suggest that this is not the dominant mechanism.

Changes in Rate

Two possible causes for the reduction in strain rate are reductions in either ionic mass transport or electrical conductivity. While electrical conductivity was not measured insitu, measurements on films following cycling and actuation as well as those shown in Table 2 suggest that this was not the dominant effect. This leaves the likelihood there is a change in mass transport rate within the film causing a decrease in ionic conductivity. A more tightly packed polymer would impede mass transport and possibly lead to the formation of regions within the polymer that are inaccessible to charge.

Engineering Solutions

Reduction in active strain, strain rate and film contraction caused by temperature changes present obstacles to commercial use of polypyrrole actuators. It is quite likely that the effects observed by thermal cycling are reproduced in polymers operated only at

room temperature, but simply over longer time periods. Considering that thermal contractions and expansions for these films are on the same order or larger than total strain, either efforts to minimize these contractions or use of designs that are unaffected by thermal contractions are necessary. Work has shown that pre-annealing in vacuum causes a net contraction of tetraethylammonium tetrafluouroborate(TEAP) grown films of 5%.[4] This pre-annealing eliminates almost all the thermal contraction in propylene carbonate and further experiments to determine whether it does the same in other solvents should be done. If rate is important, films can be cycled galvanostatically, similar to techniques used by Spinks.[14] This approach may improve consistency of cycle life and should initially negate the rate effects of thermal aging, providing the overpotentials needed are not so large that deleterious reactions are induced. Alternatively, if the fastest possible rate is of interest, then a resistance compensation approach is desirable [15]. Since reduction in active strain is a function of electrolyte employed, in order to minimize reduction in active strain, other combinations of electrolytes should be tested.

CONCLUSIONS

This study showed that thermal cycling of polypyrrole causes significant inactive strain, and reduces electrochemical strain and strain rate of films. The primary cause for the loss in strain is a reduction in the total charge transfer. All the films show a significant reduction in strain rate while a PF_6 grown film in $NaCl_{(aq)}$ shows relatively high thermal actuation stability. Design using bilayers or galvanic cycling could minimize some of the effects of thermal cycling and offer more stable performance.

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