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Poly(3-methylthiophene) based electrochemical actuators

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ABSTRACT

Polythiophene, one of the most extensively studied conducting polymers, was selected as an actuator material due to its chemical and electrochemical stability both in air and moisture. In this work, poly(3-methylthiophene) based actuators were constructed electrochemically with a tubular geometrical configuration. The actuation behaviour was investigated regarding to the actuation strain generated, the stress produced and work per cycle performed by poly(3-methylthiophene) actuators. The effect of potential sweep rate and different electrolytes (ionic liquid and organic solvent) on the actuation performance were also explored. Poly(3-methylthiophene) actuators show an increase in actuation strain with an increase in applied load.

Keywords: actuators, poly(3-methylthiophene), strain, stress, work per cycle, ionic liquid

1. INTRODUCTION

Electrochemical actuators based on conducting polymers have been investigated extensively. It has been demonstrated that conducting polymers are promising materials potentially applicable to artificial muscles due to their sound strain responses and acceptable isotonic stress and low applied potential. Polypyrrole (PPy) and polyaniline (PAn) as actuator materials have been studied in detail and exhibited ~5% strain and ~12MPa stress^[1-3]. Recently polythiophene has started to draw more attention due to the claims of stability both in air and moisture^[4]. Chan et al^[5] reported a doping induced volume change of electrochemically grown poly(3-alkylthiophene) films. About 2% strain with large creeping was observed by Kaneto and co workers^[6]. However for conducting polymer actuators, there is a common disadvantage that limits the application development: the actuation strain is reduced by repeated cycling between expanded and reduced states as well as when actuators are operated under higher isotonic loads.

In most of the devices the actuation performance is limited by IR drop along the actuators due to poor electrical connection and polymer resistance. To prevent IR drop and thus enhance the actuation performance, a platinum wire is incorporated into the wall of a hollow PPy fibre^[7] and enables the PPy to generate the highest strain rate (10%/s) and work-per-cycle (83kJ/m³)^[8] yet reported. We report here the use of the platinum wire interconnect for polythiophene actuators.

Recent research work has also shown that the cycle life of conducting polymer actuators are greatly improved by operating the devices in ionic liquid (IL) compared to the conventional organic solvents such as propylene carbonate (PC)^[9, 10]. Up to 6000 cycles have been reported with only a decrease of 20% actuation strain when IL was employed as electrolyte. While in PC as electrolyte, actuation strain decreases by 75% after 3500 cycles¹⁰. Furthermore, a smaller decrease in actuation strain with increasing isotonic stress was observed when PPy helix tubes were tested in IL compared with in PC². This can be explained by the Young's modulus results measured at oxidation and reduction states. In IL, Young's modulus changes little with applied voltage within the test range. Contrarily, in PC Young's modulus shifts dramatically at positive and negative potential.

One of the most intriguing aspects of actuation behavior is the effect of applied load on the isotonic actuation strain. The actuation strain of a material can be decayed or be unchanged, or even can be increased with the increasing applied load. The relationship between actuator strain and applied stress has been analyzed by a number of workers^[11-14]. The

difference in Young's modulus between the expanded and contracted states is the key fact to understand the actuation strain stability under increasing load.

In the present work, poly(3-methylthiophene) based actuators have been constructed electrochemically with a tubular geometrical configuration. A platinum wire was embedded into the polymer wall to provide better electrical connection and reduce IR drop along the tube. The actuation performances were investigated both in PC and IL. It is the first time that conducting polymer actuator has reported an increasing actuation strain with the increasing applied loads.

2. EXPERIMENTAL

2.1 Reagents and materials

3-methylthiophene (Met), tetrabutylammonium hexafluorophosphate (TBA.PF₆) and propylene carbonate (PC) were obtained from Aldrich and used as received. Platinum (Pt) wires in 250 and 50 μm diameter were obtained from Goodfellow. The ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(tetrafluorosulfonyl)amide (EMI.TFSA) was synthesized in-house as reported previously^[15].

2.2 Instrumentation

The constant current required for polymerisation was applied using an EG and G Princeton Applied Research Model 363 potentiostat/galvanostat. The cyclic potential was applied by a Bioanalytical Systems Inc. CV-27. The actuation test was conducted on an Aurora Scientific Dual Mode Lever System 300B. All the experiment data was processed and recorded by MacLab/4e AD Instruments and computer.

2.2 Poly(3-methylthiophene) (PMet) actuator preparation

The actuator was prepared following similar procedure as described previously⁷. Poly(3-methylthiophene) actuator was grown galvanostatically for 15 hours under a 0.1 mA/cm² current density. The polymerisation solution was PC containing 0.2 M 3-methylthiophene monomer and 0.03 M TBA.PF₆. The temperature was controlled around 0 to 5 °C. A two electrode configuration was used: the working electrode was 250 μm Pt wire core tightly wound by 50 μm Pt wire as helix; the auxiliary electrode was a stainless steel mesh. After polymerization, the 250 μm Pt core was pulled out leaving a PMet/PF₆ tube with the 50 μm Pt wire as helix inside the polymer wall.

2.3 Actuation test

The actuation performance of PMet/PF₆ actuators was tested on a Dual Mode Lever System 300B. A -1.0V to 1.5V triangular waveform at different potential scan rate from 2 to 50 mV/s was applied to the polymer using CV-27. PC containing 0.25 M TBA.PF₆ and IL (EMI.TFSA) were employed as electrolytes. The expansion/contraction of sample was recorded during the test. Isotonic actuation tests were conducted at steadily increasing loads until samples were broken.

2.4 Young's modulus measurements

Young's modulus measurements were conducted on a Dual Mode Lever System 300B while PMet/PF₆ samples were at the expansion and contraction state in different electrolytes: PC and IL. Similar to the actuation test, potential was scanned between -1.0 and 1.5V at 50 mV/s scan rate to drive the polymer at oxidized or reduced state, thus obtained expansion or contraction state. At expansion/contraction state, potential was switched off, and then the sample was gradually stretched to a desirable strain, while the corresponding stress was recorded. The Young's modulus can be obtained from the linear section of the stress vs strain curve using linear regression.

3. RESULTS AND DISCUSSION

Figure 1 and 2 show the CV and actuation strain of PMet/PF₆ at different scan rate in PC and IL as electrolyte. In PC, the actuation strain increased significantly from 0.3% to 0.9%, 1.9% and 2.7% when the potential scan rate was decreased from 50 mV/s to 20 mV/s, 10 mV/s and 2 mV/s, respectively. While in IL, only a slight increasing of actuation strain from 0.4 to 0.5% was observed when the potential scan rate was decreased from 50 mV/s to 20 mV/s and 10 mV/s. When the potential scan rate was decreased to 2 mV/s, the strain was only 0.7%, which indicated less effect of sweeping velocity on actuation strain in the IL.

As is well known, under electrochemical stimulation, the electronic and ion exchanges result in redox processes occurring in polymers that cause polymer volume changes. The anion and/or cation exchanges are the fundamental mechanism of conducting polymer electrochemical actuators. In PC, PMeT/PF₆ expanded at positive potentials and contracted at negative potentials. This behaviour indicates that polymer releases PF₆⁻ during reduction (negative potential) and incorporates PF₆⁻ during oxidation (positive potential). Contrarily in IL, PMeT/PF₆ expanded at negative potentials and contracted at positive potentials. This corresponds with results from polypyrrole actuators¹⁰. In IL, the polymer probably incorporates cations from electrolyte during reduction (negative potential) causing polymer expansion and releases cation during oxidation (positive potential) then resulting in polymer contraction. The redox process may also involve the dopant anion moving in and out of the polymer but cation from electrolyte dominates the actuation performance in IL. Thus the polymer expansion caused by cation incorporation may be partly counteracted by the dopant anion released from the polymer. This mixed ion movement may be one reason why the actuation strain in IL is lower than that in PC.

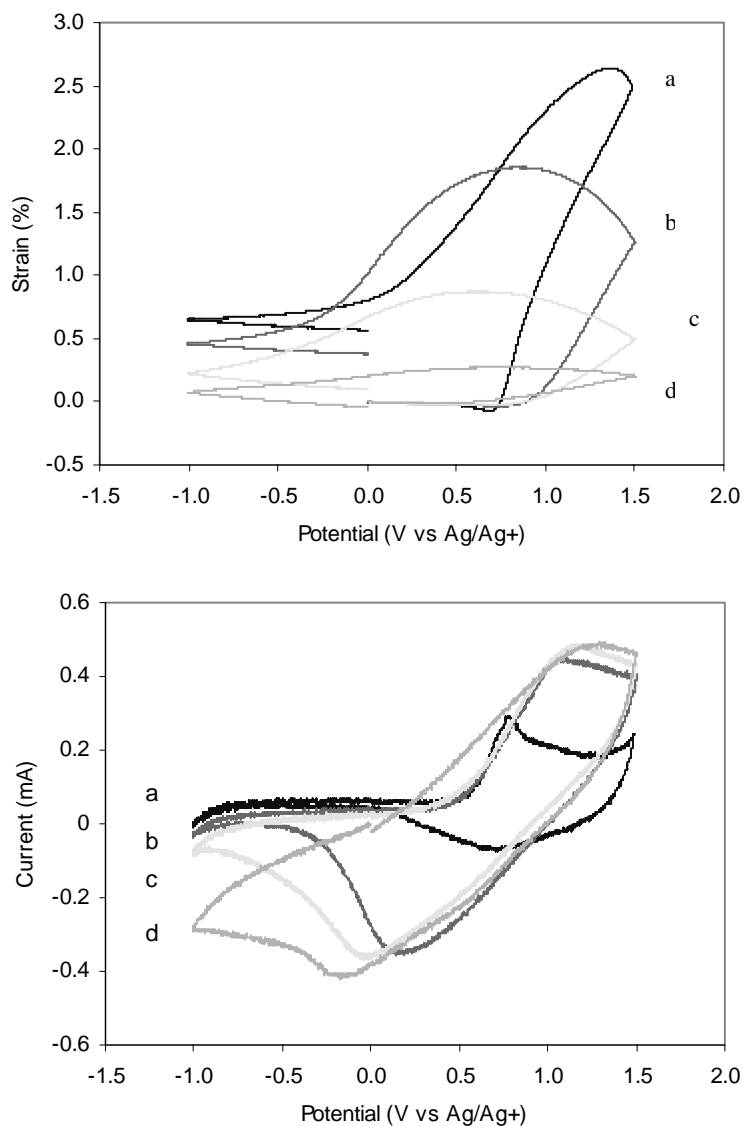


Fig. 1 PMeT/PF₆ helix tube actuation strain and CV in PC at different scan rate: a: 2mV/s, b: 10mV/s, c: 20mV/s, d: 50mV/s

The actuation strain caused by anion or cation exchanging between the polymer and the electrolyte does not only depend on the amount of anion or cation exchanging, but also relate to the diffusion rate of the ionic species. In PC, with

decreasing scan rate, there is sufficient time for more anion incorporate on and release from the polymer. In IL, which is more viscous than PC, the cation or anion movement is restricted by a low diffusion rate, so even at low scan rate, the actuation strain was not increased as much as in PC.

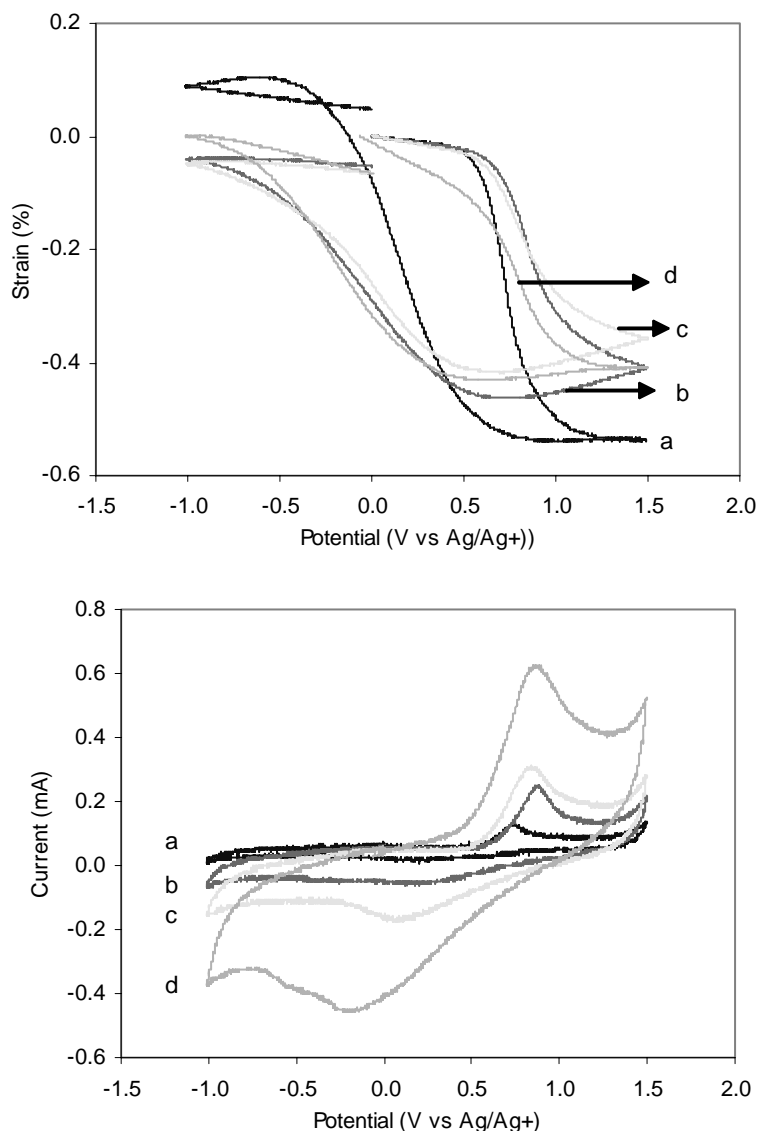


Fig. 2 PMeT/PF₆ helix tube actuation strain and CV in IL at different scan rate: a: 2mV/s, b: 10mV/s, c: 20mV/s, d: 50mV/s

Figure 3 illustrates the relationship between the applied stress and the actuation strain of PMet actuators in PC and IL as electrolyte. Similar to the previous reported results^{2,13}, a linear decrease in strain from 1.5% to 0.1% occurs in PC under the increasing applied load. While in IL, it is of interest to note that the actuation strain is slightly increased from 0.4% to 0.6% with increasing stress. This is a very promising result that can overcome the barrier limiting the application development caused by strain decline. It has been reported by Lu and co workers⁹ and Ding et al¹⁰ that the use of IL as electrolyte can significantly improve the actuation performance both in terms of lifetime cycles and under load. The present work is the first report that the actuation strain produced by a conducting polymer actuator increases under increasing load before fracture.

The relationship between the actuation strain and the applied stress was first analyzed by Baughman¹¹ and more in detail by Spinks¹³ and Tahhan et al¹⁴. The total strain is the sum of the strain from electrochemical stimulation and the strain from external force. From this analysis, the following equation can be obtained:

$$\Delta l_f = \Delta l_0 + (f l_0 / A) (1/Y_d - 1/Y_o) \tag{1}$$

Where Δl_f is the displacement with a load f ; Δl_0 is the displacement without load; l_0 is the sample length at the contraction state without load, Y_d is the Young's modulus at the expanded state, Y_o is the Young's modulus at the contracted state.

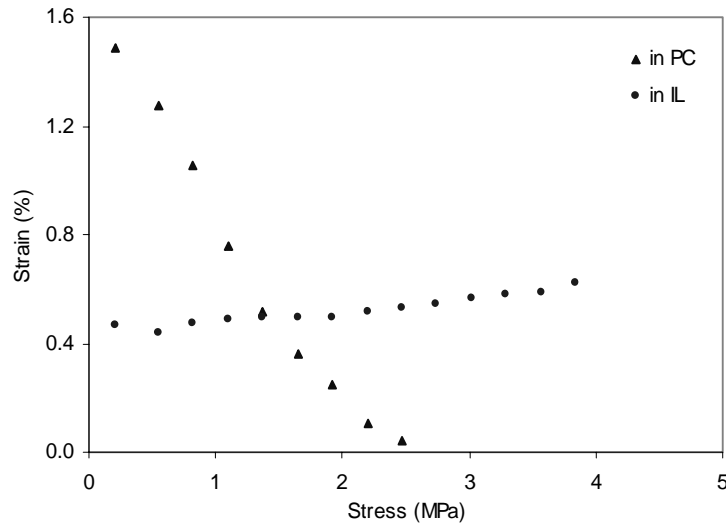


Fig. 3 PMet helix tube strain under isotonic condition at different stress levels in both PC and IL electrolyte. Potential scanned between -1.0 to 1.5V (vs Ag/Ag+)

From equation (1) it can be seen that the Young's moduli changes at the contraction and expansion states determine the slope of the actuation strain vs stress line. If $1/Y_d > 1/Y_o$, (i.e. $Y_d < Y_o$), the actuation strain will increase with the increasing load. On the other hand, if $1/Y_d < 1/Y_o$, (i.e. $Y_d > Y_o$), the actuation strain will decrease with the increasing load.

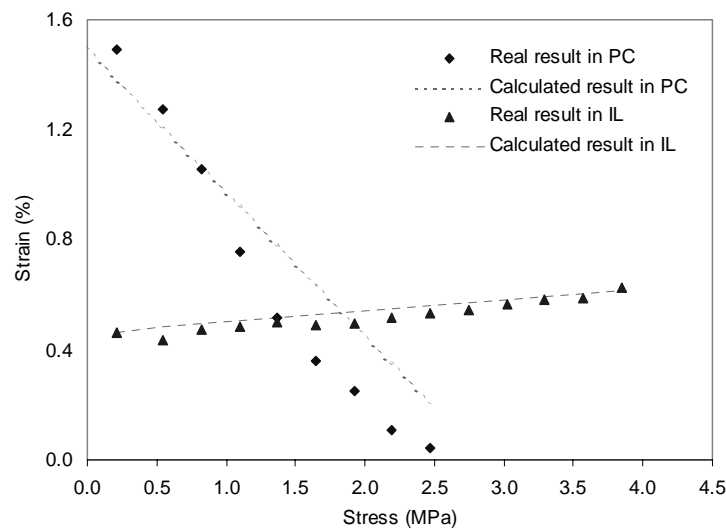


Fig. 4 Experimental actuation strain produced by PMet helix tube and the calculated strain from Young's modulus modeling

The Young's modulus of PMet helix tubes were measured in PC and IL when the samples were at the contracted and expanded states. Table 1 summaries the Young's modulus measurement of PMet samples in PC and IL.

Table 1 Young's modulus of PMet helix tube measured in PC and IL

PMet helix tube actuator	Y_d Expanded state (MPa)	Y_o Contracted state (MPa)
In PC	109.4	69.6
In IL	70.5	72.5

In PC as electrolyte, the Young's modulus changes significantly between the expanded and contracted states. As a result, the polymer sample elongates when the polymer is switched between the reduced state and oxidized states. This elongation will partially counteract the sample contraction when it is at the reduction state. In IL as electrolyte, the Young's modulus changes little between expanded and contracted states. Consequently, the sample displacement due to oxidation and reduction will be almost independent of the applied load. Given the Young's modulus at contracted state (72.5 MPa) is slightly greater than at expanded state (70.5 MPa), the sample displacement under loads will be increased slightly with the increasing loads.

According to equation (1) and Young's moduli in table 1, the calculated results of strain under increasing load were given as dotted lines in Figure 4. It can be seen that the calculated results are very close to the experimental results. The slight shift between the real result and calculated result in PC is due to the polymer degradation when cycled in PC electrolyte.

The work performed per expansion/contraction cycle is another important parameter to evaluate the performance of actuators. The work per cycle (W) is defined as:

$$W = f \Delta l_f \tag{2}$$

Where Δl_f is the displacement produced by one expansion/contraction cycle under a load f . Figure 5 shows the work per cycle performed by PMet helix tubes when operated in PC and IL as electrolytes. In PC, the work per cycle and applied stress curve shows a parabolic behaviour. In contrast, when an actuator is operated in IL, the work per cycle is increased linearly with the increased applied stress. The maximum work per cycle achieved in IL (24 kJ/m^3) is about 3 times that achieved in PC (8.7 kJ/m^3).

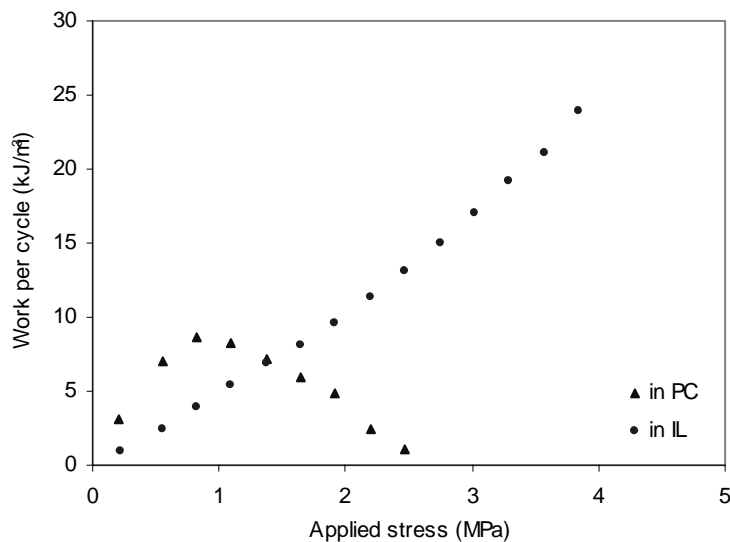


Fig. 5 The work per cycle for PMet/PF₆ helix tube at different applied stress levels in PC and IL

According to the analysis of the relationship between the actuator displacement and Young's modulus and equation (1), the work per cycle is expected to be:

$$W = f \Delta l_0 + (f^2 l_0 / A) (1/Y_d - 1/Y_0) \quad (3)$$

Using equation (3), the predicted work per cycle are also shown as the dashed lines and compared with the real results in figure 6. Again in PC, and the calculated work per cycle is higher than the real work performed by actuator. This difference is due to the polymer degradation when cycled in PC electrolyte. In IL the calculated work per cycle almost exactly matches the measured values.

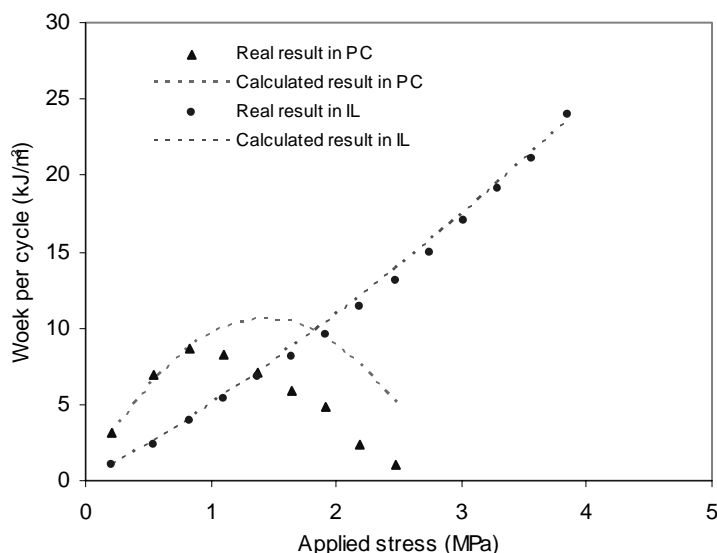


Fig. 6 Real work per cycle performed by PMet/PF₆ helix tube

4. CONCLUSIONS

Practical application of actuator devices require that actuators to be operated under load. Most of the studied actuators based on PPy and PAn display a decreased actuation strain when external loads are applied to the actuators. In this study, for the first time actuators based on poly(3-methylthiophene) with a tubular hollow configuration and a platinum wire helix embedded exhibit an increasing actuation strain with the increasing applied stress when operated in ionic liquid (EMI.TFSI). Based on this unique property, poly(3-methylthiophene) is a promising material for developing the electrochemical actuator application as artificial muscles.

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