

In situ observation of dynamic elastic modulus in polypyrrole actuators

Rachel Z. Pytel^a, Edwin L. Thomas^{a,*}, Ian W. Hunter^{b,1}

^a Department of Materials Science and Engineering, Massachusetts Institute of Technology, 6-113, 77 Massachusetts Ave, Cambridge, MA 02139, United States

^b Department of Mechanical Engineering, Massachusetts Institute of Technology, 3-154, 77 Massachusetts Ave, Cambridge, MA 02139, United States

Received 25 September 2007; received in revised form 22 January 2008; accepted 24 January 2008

Available online 30 January 2008

Abstract

Polypyrrole is a leading conducting polymer actuator, but the factors that influence its performance when actuated under load in devices (such as the polymer stiffness) are not yet fully understood. To this end, we have probed the dynamic elastic modulus of polypyrrole *in situ* during actuation in a variety of electrolytes. As part of this study, we demonstrate that the electroactive response in dilute 1-butyl-3-methylimidazolium hexafluorophosphate can be changed from cation- to anion-dominated by adjusting the applied potential waveform. We observe that when conservative electrochemical conditions are applied in order to avoid dual ion movement or significant transfer of neutral solvent, the stiffness is determined by level of counterion swelling. The elastic modulus decreases during the net influx of ions into the bulk polymer and increases as these ions are expelled, regardless of whether the electroactive response is cation- or anion-dominated or whether there is a neutral solvent present in the electrolyte. This effect is quite significant, and we have observed up to a 3× increase in elastic modulus upon actuation in neat 1-butyl-3-methylimidazolium hexafluorophosphate.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Polypyrrole; Actuator; Conducting polymer

1. Introduction

Polypyrrole is one of the most successful conducting polymer actuators to date, and is currently being developed for use in several applications including sensors [1–3], chamber foils [4], microactuators [5–7], valves [2,7], and pumps [8]. Electropolymerized polypyrrole consists of conjugated polypyrrole chains and an ionic dopant. During actuation, polypyrrole is either oxidized or reduced in the presence of a mobile electrolyte, and ions are incorporated or expelled from the bulk polymer in order to maintain charge neutrality. This incorporation or expulsion results in a net volume change or change in stress state of the polymer. Polypyrrole's electroactive response is typically probed either isotonically [9–13], where the polymer is actuated under constant load and its length change is

monitored, or isometrically [14,15], where the polymer is held under tension at a constant length and the change in stress upon actuation is monitored.

In addition to the change in film volume or stress state, it has also been observed that mechanical properties such as the elastic modulus change upon conducting polymer oxidation and reduction. Several authors have held a polypyrrole film in an electrochemical cell at a constant potential, then slowly stretched the film to measure the elastic modulus. However, when comparing these previous works, one is confronted with discrepancies in the way that the modulus changes with oxidation state. In some investigations the modulus was found to be higher in the oxidized state, regardless of whether that state is contracted or expanded [12,16–18]. This has also been observed for poly(3-methyl thiophene) actuators [19]. Alternatively, in other works, a higher modulus was measured in the contracted state than in the expanded state, regardless of which was more oxidized [20,21]. Other authors have observed the same trend for polyaniline fiber actuators [22–24]. Furthermore, in some studies where polypyrrole modulus

* Corresponding author. Tel.: +1 617 253 5931; fax: +1 617 252 1175.

E-mail addresses: elt@mit.edu (E.L. Thomas), ihunter@mit.edu (I.W. Hunter).

¹ Tel.: +1 617 253 3921; fax: +1 617 252 1849.

was probed *in situ* during oxidation and reduction, the modulus did not straightforwardly follow the oxidation or expansion of the polypyrrole film [9,25]. Clearly, the change in polypyrrole's mechanical properties during actuation is a complicated phenomenon that has not yet been fully characterized and understood. Several mechanisms for the change in film's elastic modulus have been proposed, including plasticization due to counterion [20,25] and solvent [9,25,26] swelling, stiffening of the polypyrrole chains due to oxidization [20,25], and ionic crosslinking between charged polymer chains and incorporated anions [17,20]. It is likely that all of these mechanisms can contribute to the change in mechanical properties upon actuation, and that differences in conducting polymer sample geometries, film qualities, electrolyte chemistry, frequency of electrochemical stimulation and frequency of mechanical testing cause different mechanisms to dominate in any particular experiment.

We also observe an electrochemically driven change in polypyrrole film stiffness, and by limiting ourselves to moderate potential windows and short timescales we observe that the level of counterion swelling clearly dominates the elastic modulus. We limit our experiments to these conservative actuator driving conditions in order to probe a parameter space under which polypyrrole actuators can be operated in a predictable manner.

2. Experimental

2.1. Polypyrrole preparation

Pyrrrole (Aldrich 99%) was vacuum distilled before use. All other materials were used as received. Polypyrrole was electrodeposited at $-40\text{ }^{\circ}\text{C}$ at a constant current density of 0.5 A/m^2 . The deposition solution contained 0.05 M pyrrole, 0.05 M tetraethylammonium hexafluorophosphate (TEAPF6)

and $1\text{ vol}\%$ water in propylene carbonate. Copper foil was used as a counter electrode, and the polypyrrole film was deposited onto a polished glassy carbon working electrode over the course of 18 h . After synthesis, large area films ($70\text{ mm} \times 230\text{ mm} \times 0.03\text{ mm}$) were peeled off the working electrode, and small samples ($8\text{ mm} \times 2\text{ mm}$) were then cut for active testing. The conductivity of the small samples was measured with a standard four-point probe, and was approximately $3 \times 10^4\text{ S/m}$.

2.2. Polypyrrole testing

To probe the electrochemical dependence of polypyrrole's elastic modulus, we test films in three different electrolyte systems: neat 1-butyl-3-methylimidazolium hexafluorophosphate, (BMIMPF6), an 0.05 M solution of 1-butyl-3-methylimidazolium hexafluorophosphate in propylene carbonate (BMIMPF6/PC) and an 0.05 M solution of tetrabutylammonium hexafluorophosphate in propylene carbonate (TBAPF6/PC). Polypyrrole samples were clamped into a custom-built electrochemical dynamic mechanical analyzer developed by Vandesteeg [15]. This apparatus allows one to clamp the polypyrrole film under tension as the working electrode in a three-electrode electrochemical cell, and measures the electroactive response that occurs upon application of a potential waveform. A silver wire reference electrode was utilized for these experiments. Initially, the film was slackened, submersed into electrolyte, and "warmed up" by cyclic voltammetry until the current response stabilized. After warm up, the films were placed into tension at a strain of approximately 1% , and a potential square wave was applied. The resulting change in stress was measured and considered the "active stress," that is, the stress caused by electrochemical actuation (Fig. 1a). The film's modulus was then immediately measured under an oscillatory strain input, without removal from the apparatus. The film

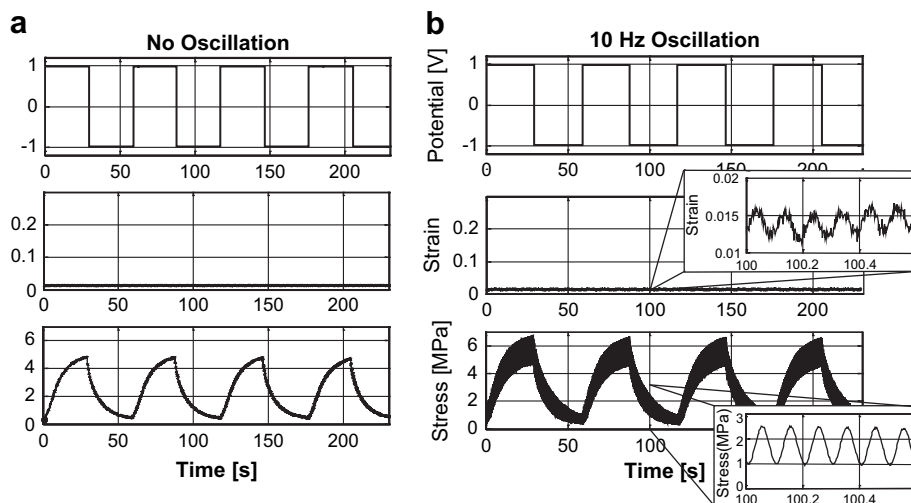


Fig. 1. Electroactive response under constant and oscillatory strain. (a) Testing in BMIMPF6 with constant strain input. The film was held in tension at an initial strain of 1.4% , resulting in an initial stress of 0.5 MPa . A $+1\text{ V}$ potential square wave was applied at a frequency of 0.0167 Hz , and the stress response was measured. (b) Testing in BMIMPF6 with oscillatory strain input. The film was held in tension at an initial strain of 1.4% , resulting in an initial stress of 0.5 MPa . A sinusoidal perturbation in strain with an amplitude of 0.003 and frequency of 10 Hz was applied. A $+1\text{ V}$ potential square wave was applied at a frequency of 0.0167 Hz , and the stress response was measured.

Download English Version:

<https://daneshyari.com/en/article/5187643>

Download Persian Version:

<https://daneshyari.com/article/5187643>

[Daneshyari.com](https://daneshyari.com)