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# *In situ* observation of dynamic elastic modulus in polypyrrole actuators

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**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.

*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

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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

Pyrrole (Aldrich 99%) was vacuum distilled before use. All other materials were used as received. Polypyrrole was electrodeposited at −40 °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 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 mm × 230 mm × 0.03 mm) were peeled off the working electrode, and small samples (8 mm × 2 mm) were then cut for active testing. The conductivity of the small samples was measured with a standard four-point probe, and was approximately $3 \times 10^4$ 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

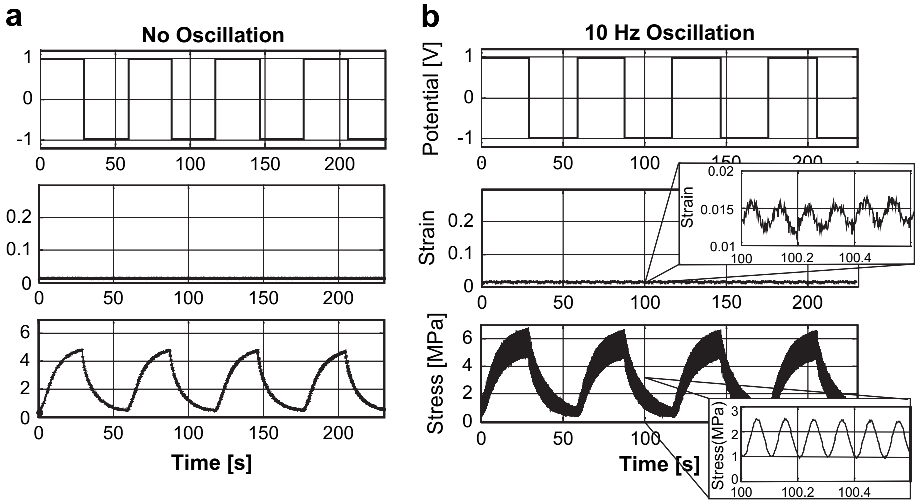

Fig. 1. Electroactive response under constant and oscillatory strain. (a) Testing in BMIMPF6 with constant strain input. The film was held in tension at an initial strain of 1.4%, resulting in an initial stress of 0.5 MPa. A +1 V potential square wave was applied at a frequency of 0.0167 Hz, and the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

was held in the electrolyte at approximately 1% strain, and the same potential square wave was applied. During the electrochemical cycling a small (amplitude = 0.003) sinusoidal perturbation in strain was applied to the film at 10 Hz (approximately 600× higher than the frequency of the applied potential). This resulted in a high-frequency stress response superimposed on the low frequency active stress (Fig. 1b). We have not yet sufficiently probed the effect of frequency on the elastic modulus of polypyrrole, but it is likely that testing frequency contributes to differences in polypyrrole response in previous investigations. Future work will include *in situ* observation of the elastic modulus over several orders of frequency.

## 3. Results and discussion

### *3.1. Cation- and anion-dominated actuation*

When BMIMPF6 is diluted in propylene carbonate, the potential waveform can be adjusted such that movement of the $\mathrm{BMIM}^+$ cation or the $\mathrm{PF}_6^-$ anion can be observed in the electroactive response. Dual ion movement has been observed in many electrolyte systems [27–32], but for this study we specifically choose potentials and timescales at which one ion clearly dominates the response. For example, if the potential is switched between 0 V and −1 V, one observes a stress response dominated by the $\mathrm{BMIM}^+$ cations. This response is shown in the isometric test, as is shown in Fig. 2a, where the stress increases as the charge increases (as $\mathrm{BMIM}^+$ cations leave the film during oxidation), and the stress decreases as the charge decreases (as $\mathrm{BMIM}^+$ cations enter the film during reduction). The opposite response is observed when one switches the potential between 1 V and 0 V, as is shown in Fig. 2b. Here the stress decreases as the charge increases (as $\mathrm{PF}_6^-$ enter the film during oxidation), and the stress increases as the charge decreases (as $\mathrm{PF}_6^-$ leave the film during reduction).

Liquid salts such as neat BMIMPF6 can also be used as electrolytes without addition of neutral solvent, and have shown excellent stability and improved performance over solvated electrolytes for conducting polymer actuators [33–35]. In neat BMIMPF6, the $\mathrm{BMIM}^+$ cations dominate the electroactive response over a very wide potential range [29,33,35]. This means that as the film is reduced, $\mathrm{BMIM}^+$ cations enter the film and the film expands. We use neat BMIMPF6 as an electrolyte containing no neutral solvent to minimize any modulus change caused by solvent transfer analogous to the osmotic effect described by Bay et al. [26]. Finally, we use TBAPF6/PC in this study to provide an electrolyte without a liquid salt component. Under the conditions applied in this study, the electroactive response is dominated by the $\mathrm{PF}_6^-$ anions for the TBAPF6/PC system. That is, when the polymer is reduced, anions leave the film and the film contracts.

### *3.2. Change in modulus upon actuation*

The high-frequency stress response was isolated by subtracting the isometric active stress (the last curve in Fig. 1a) from the stress response under oscillatory strain (the last curve in Fig. 1b). The modulus ($E(t)$) is calculated by dividing the high-frequency

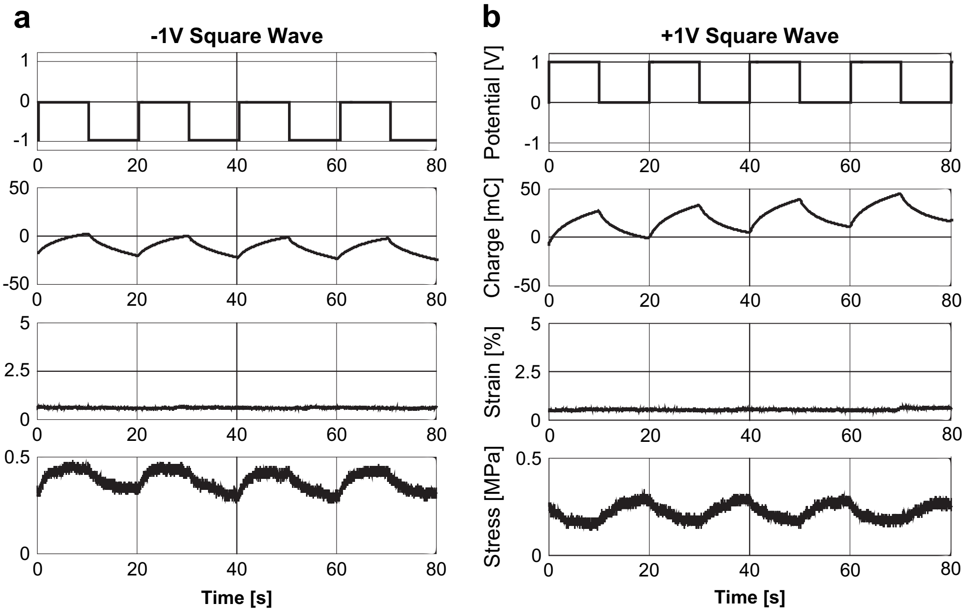

Fig. 2. Isometric testing in BMIMPF6/PC. Parts (a) and (b) were conducted on the same film, without removal from the apparatus. (a) The film was held in tension at a constant strain of 0.6%, resulting in an initial stress of 0.32 MPa. A −1 V potential square wave was applied at a frequency of 0.05 Hz. The active stress increases upon oxidation and decreases upon reduction. (b) The film was held in tension at a constant strain of 0.6%, resulting in an initial stress of 0.25 MPa. A +1 V potential square wave was applied at a frequency of 0.05 Hz. The film was cycled over this potential window for approximately 15 cycles before the data shown here, allowing the system to transition to from cation- to anion-dominated. The active stress decreases upon oxidation and increases upon reduction. The decreased stress at 0 V when compared to part (a) is due to a higher degree of counterion swelling.

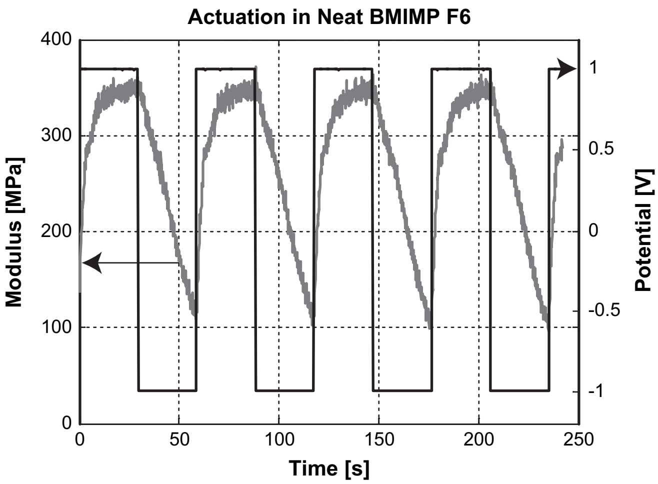

Fig. 3. Polypyrrole Modulus ($E(t)$) in neat BMIMPF6. The magnitude of the high-frequency response was divided by the magnitude of the applied oscillatory strain to calculate the modulus. Under these conditions, the modulus increases over 200% upon oxidation and decreases to its original value upon reduction.

stress response by the high-frequency applied strain perturbation, and is shown in Fig. 3. We do not separate this modulus into real and complex parts, as we do not observe a change in phase lag between the applied oscillatory strain and resulting oscillatory stress even as the oscillatory stress magnitude changes.

As shown in Figs. 3 and 4, we observe an elastic modulus of approximately 100–350 MPa for polypyrrole tested at 10 Hz during actuation, while our as-deposited polypyrrole films tested statically (via a stress ramp of 5000 kPa/min) in air have an average modulus of 300 MPa. This is typical for polypyrrole/$PF_6^-$ films produced from the recipe described earlier. Variables in the polypyrrole deposition such as purity of monomer, choice of solvent, electrolyte, electrode material, deposition current density and deposition temperature will all affect the quality and mechanical properties of the polypyrrole samples, while differences in the sample geometry, testing rate and environment will affect the measured modulus [36–42]. These variables make it quite difficult to compare previously published works in this area (e.g. moduli from 400 MPa to 3400 MPa have been reported for polypyrrole films [18,20,21]), and we simplify our investigation by studying one commonly used polypyrrole system ($PF_6^-$-doped polypyrrole films synthesized from propylene carbonate solution) [13,36,43–45] under electrochemical conditions that produce a significant but straightforward electroactive response.

In neat BMIMPF6, we observe a 30% decrease in modulus while the film is held at a negative potential for 10 s, as shown in Fig. 4a. The modulus then increases as the film is re-oxidized, returning to its original value. Alternatively, when actuating in TBAPF6/PC, the modulus decreases 10% during oxidation and increases during reduction as shown in Fig. 4b. In both of these cases, the modulus decreases as ions are brought into the film, and increases as ions are expelled. These results are notably different from previously published static experiments, where the modulus of a polypyrrole fiber was observed to increase only slightly (1%) when film was oxidized in a liquid salt solution and to increase significantly (300%) upon oxidation in TBAPF6/PC [12,34].

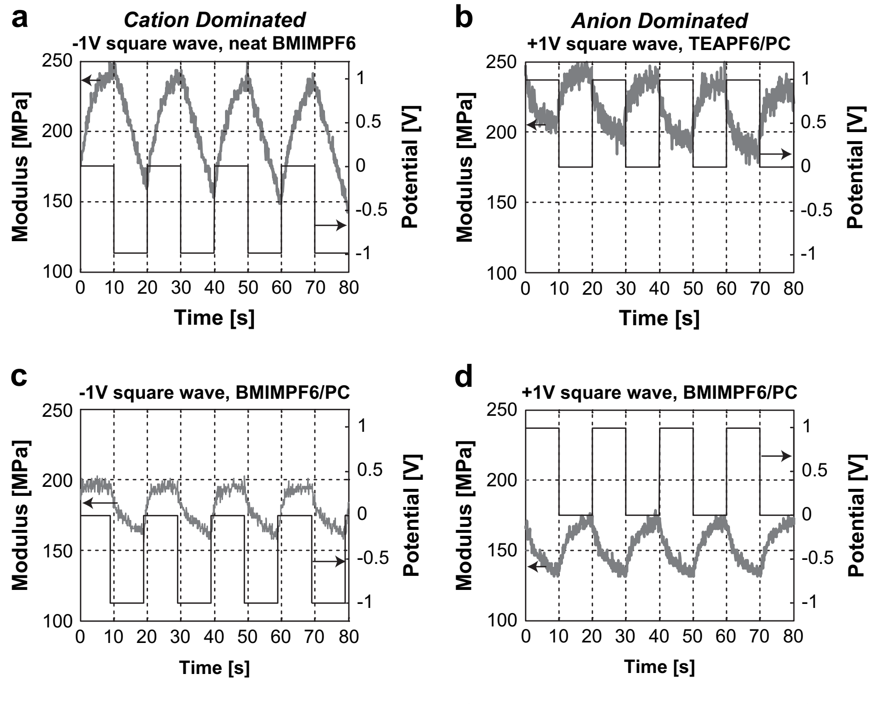

Fig. 4. Dynamic elastic modulus ($E(t)$). $E(t)$ was calculated by dividing the high-frequency stress response by the high-frequency strain input. In (a) and (c), $BMIM^+$ cations dominate the electroactive response. In (b) and (d), $PF_6^-$ anions dominate the electroactive response. (a) −1 V potential square wave in BMIMPF6, $E(t)$ increases 56% during oxidation; (b) +1 V potential square wave in TBAPF6/PC, $E(t)$ increases 21% during reduction; (c) −1 V potential square wave in BMIMPF6/PC, $E(t)$ increases 22% during oxidation; (d) +1 V potential square wave in BMIMPF6, $E(t)$ increases 26% during reduction.

However, the previous TBAPF6/PC work was performed under static conditions, using a two-electrode configuration. A two-electrode cell does not provide sufficient control over the charge state of the polymer, and when the same group probed elastic modulus in a three-electrode cell they observed a softening of polypyrrole over part of the oxidation sweep in TBAPF6/PC [9]. For this study we use a three-electrode cell to control the potential at the polymer film, and by narrowing the potential limits and length of potential holds we avoid the dual ion movement and neutral solvent transfer that has complicated the electroactive response in previous three-electrode studies of polypyrrole in TBAPF6/PC [9,25].

When a $-1$ V potential square wave is applied to a film in BMIMPF6/PC, we observe an electroactive response dominated by the $BMIM^+$ cations (Fig. 2a). The modulus response for this system is shown in Fig. 4c. The direction of modulus change is similar to the neat BMIMPF6 system which is also dominated by the $BMIM^+$ cations, in that there is an increase in modulus upon oxidation and decrease upon reduction. When a $+1$ V potential square wave is applied to a polypyrrole film in BMIMPF6/PC, we observe an electroactive response dominated by the $PF_6^-$ anions (Fig. 2b). The modulus response is similar to that of the TBAPF6/PC system, the other system dominated by the movement of $PF_6^-$ anions, and is shown in Fig. 4d. In all cases, regardless of the presence of solvent or liquid salt, the modulus decreases as ions enter the film and increases as ions are expelled. We attribute the decrease in elastic modulus with increasing ion concentration to a plasticization of the polypyrrole film by the small electrolyte molecules. Plasticization resulting from counterion incorporation has been reported during static experiments [20,22], but has not been previously shown to dominate the *in situ* oxidation–reduction modulus response. In our case the polymer is not equilibrated at a particular potential and then tested, instead the change in modulus is observed in real time with the changing counterion swelling of the film.

Under the conditions shown in Fig. 3, the modulus increases to three times its original value upon expulsion of counterions and contraction of the film. A change in this magnitude will significantly affect the amount of work a polypyrrole actuator will be able to produce under load. The implications that a change in elastic modulus will have on actuation have been discussed at length in the literature [12,14,22,46,47], and it has been shown that a larger work-per-cycle can be achieved by an actuator whose modulus increases upon contraction than by one whose modulus decreases or remains constant [14]. Our results show that the conditions applied in this study allow us to operate in this desirable actuation regime.

## 4. Conclusions

By actuating in different electrolyte solutions we have shown that it is possible to operate polypyrrole actuators under conditions where the elastic modulus of polypyrrole is dominated by the degree of counterion swelling for both cations and anions, for both solvated and solvent-free electrolytes. The change in elastic modulus with swelling begins as soon as the potential is switched and can increase by over 200% over the course of 30 s. Awareness of this variation in modulus is critical to developing the mechanics and loading conditions of polypyrrole-driven devices, as well as understanding the theoretical and practical active stresses and strains one can achieve in a given electrochemical environment.

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