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Stochastic System Identification of the Compliance of Conducting Polymers.

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ABSTRACT
Conducting polymers such as polypyrrole, polythiophene and polyaniline are currently studied as novel biologically inspired actuators. The actuation mechanism of these materials depends upon the motion of ions in and out of the polymer film during electrochemical cycling. The diffusion of ions into the bulk of the film causes the dynamic mechanical compliance (or modulus) of the material to change during the actuation process. The mechanism of this change in compliance is not fully understood as it can depend on many different factors such as oxidation state, solvation of the film and the level of counter ion swelling. In-situ measurement of the dynamic compliance of polypyrrole as a function of charge is difficult since the compliance depends upon the excitation frequency as well as the electrochemical stimulus. Pytel et al [1] studied the effect of the changing elastic modulus in-situ at a fixed frequency. In this study we describe a technique to measure the compliance response of polypyrrole as a function of frequency and electrochemistry. A voltage input and a simultaneous stress input was applied to polypyrrole actuated in neat 1-butyl-3-methylimidazolium hexafluorophosphate. The stress input was a stochastic force with a bandwidth of 30 Hz and it allows us to compute the mechanical compliance transfer function of polypyrrole as function of the electrochemistry. Our studies show that the low frequency compliance changes by 50% as charge was injected into the polymer. The compliance changes reversibly as ions diffuse in and out of the film which indicates that the compliance depends upon the level of counter ion swelling.

INTRODUCTION
Electroactive conducting polymers are currently studied as materials that can have a wide range of applications including novel biologically inspired actuators, sensors, valves and pumps. They have a number of attractive properties such as being lightweight, inexpensive and are easy to mold and shape into a wide range of forms. Various electroactive polymers that are activated by ion diffusion are studied for use in a wide variety of applications. The actuation mechanisms in these materials are based on the diffusion of ions in and out of the polymer film. The films are capable of generating large strains of between 5-10% at low voltages (1 to 2 V) which make them ideal elements to build artificial devices that can mimic biological elements [2]. During electrochemical stimulus as charge is injected into the polymer there is an expansion of the polymer film that accounts for a large portion of the overall strain. However, there are a number of underlying mechanisms that can also govern polymer actuator behavior. Changing material properties during the actuation cycle is one such mechanism that has not been studied well. For instance, as ions diffuse into the polymer the compliance of the polymer also changes [1, 3-6]. If the polymer is held in tension then this changing compliance also contributes to the overall strain. This can be best understood from Equation 1 where \( \varepsilon_T \) is the total strain on the polymer, \( \alpha \) is the strain to charge ratio, \( q \) is the charge injected into the polymer, \( Y \) is the compliance which can depend on the charge and excitation frequency and \( \sigma \) is the preload stress.
The overall strain is composed of a volumetric strain that is proportional to the charge injected into the polymer and a component that comes from the changing compliance. Many authors [3-6] have shown that the polymer compliance changes during the actuation cycle, however there are a number of discrepancies about how the compliance changes [1]. There is a need to develop standard techniques that can be used to measure the compliance that can be applied during the actuation process. In this paper we describe novel a technique to make measurements of the compliance of conducting polymers as a function of an electrochemical stimulus and excitation frequency. We do this by computing the compliance impulse response as a representation of the compliance transfer function of the polymer. The impulse response can be convolved with any input stress waveform to predict the resulting strain. We choose to use efficient stochastic system identification techniques to estimate the compliance impulse response of the polymer.

EXPERIMENTAL METHOD

Pyrrole (Aldrich 99%) was vacuum distilled before use. Polypyrrole was electrodeposited on a glassy carbon substrate at -40°C at a constant current density of 0.5 A/m². The deposition solution used was 0.05 M pyrrole in 0.05 M tetraethyl ammonium hexafluorophosphate (TEAPF6) in propylene carbonate. The resulting polypyrrole films were cut in 2 mm × 10 mm strips and tested using a custom built dynamic mechanical analyzer (DMA) [7]. This apparatus allows us to clamp the polymer in tension while applying an electrochemical stimulus using a three electrode cell. The stress generating DMA stage was used to generate a stochastic stress input and the corresponding stochastic strain was measured. The stress input consisted of a stochastic signal having a shaped power spectrum and Gaussian probability density function with mean amplitude of 8 MPa, a standard deviation of 0.5 MPa and a bandwidth of 30 Hz. Linear stochastic system identification techniques [8, 11] were used to estimate the parameters of the compliance impulse response function and the compliance frequency response function of polypyrrole.

To find the impulse response 40 point auto and cross correlation function estimates were made of the stress and strain and were used to fill the elements of Equation 1, where $R_{xx}$ is a Toeplitz matrix of the autocorrelation function values, $R_{xy}$ is the cross correlation function estimates and $h_{xy}$ is the of samples of the impulse response function to be determined. We solve for $h_{xy}$ using a Toeplitz matrix inversion implemented in MATLAB. The dynamic compliance frequency response function may then be determined from the Fourier transform of $h_{xy}$ and is normally referred to as the transfer function with magnitude and phase. The coherence squared function [8] can be used to gauge the quality of the system identification procedure. It is determined using Equation 2, where $S_{xy}(j\omega)$, $S_{xx}(j\omega)$ and $S_{yy}(j\omega)$ are the cross, stress and strain power spectral densities respectively. If there is any sensor noise or non linearity within the system the coherence squared will be less than one.
\[ \text{coh}^2(j\omega) = \frac{|S_{xy}(j\omega)|^2}{|S_{xx}(j\omega)| |S_{yy}(j\omega)|}, \quad 0 \leq \text{coh}^2(j\omega) \leq 1 \quad (3) \]

**Mechanical Testing**

An initial test was conducted to measure the compliance without any electrochemical stimulus. This test was used to calculate the compliance impulse response using the stress input described in the above section. The data was sampled at 1000Hz.

**Electrochemical Mechanical Testing:**

In this test two separate inputs are used to excite the polymer, an electrochemical potential and a stochastic stress. A three electrode electrochemical cell was coupled with a dynamic mechanical analyzer [7] to generate the inputs. A silver wire was used as a reference electrode and the tests were conducted in neat 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6). The samples were warmed up by cyclic voltametry until the electrochemical response was stabilized. The voltage input was a triangle wave between -0.8 V to 0.8 V and a rate of 20 mV/s. The stress input was the same as described in the mechanical testing section above. The resulting strain was a high frequency strain superimposed on a low frequency strain (Figure 3). The stress and strain data were filtered using a 2\textsuperscript{nd} order low pass butterworth anti aliasing filter implemented in hardware with a cut off frequency at 100Hz.

**RESULTS AND DISCUSSION**

**Mechanical Characterization**

Figure 1 shows the calculated compliance impulse response of polypyrrole. The impulse response rises to 200 GPa\(^{-1}\) and falls to zero within 20 lags or 0.02s. This indicates that the 40 point impulse response was sufficient to fit the data.

![Figure 1](image.png)

**Figure 1:** Left: The calculated compliance impulse response of polypyrrole. Right: The compliance frequency response of polypyrrole calculated using Gaussian stress strain data and Equation 1.

Figure 1 also shows the frequency domain equivalent of compliance impulse response also known as the transfer function. This indicates that the system is at least 3\textsuperscript{rd} order. The low frequency compliance was 2 GPa\(^{-1}\) which corresponds to an elastic modulus of 500 MPa. This
matches with prior studies conducted on the same material [1]. There was a gradual reduction in the compliance until 100 Hz, after which there was a large drop in the compliance.

**Figure 2**: Coherence squared of the stress strain data. This indicates that a linear model is sufficient to model the compliance data up to 100Hz.

However, the coherence squared (Figure 2) estimate was close to one only until 100 Hz after which there was a large drop. This would indicate that the compliance response shown in Figure 1 was only valid up to 100 Hz. Since the coherence was close to one until 100 Hz, a linear model represented by the compliance impulse response was sufficient to model the data. Our input stress is within a range of 5-10MPa and it should be noted that the response calculated is accurate within that stress range.

**Electrochemical Characterization**

Ionic liquids such as BMIMPF6 can be used as solvents for actuation. In neat BMIMPF6 the BMIM⁺ cation tends to diffuse into the polymer over a wide range of potentials [1, 9-10]. Therefore the expansion of the polypyrrole occurs during reduction when the cation diffuses into the film. We do not use any solvent to avoid any changes to the compliance due to solvent transfer [1].

**Figure 3**: Polypyrrole being excited using a triangle wave voltage input that varies at 10mV/sec and the stochastic stress input. The output strain has a low frequency volumetric component proportional to the charge superimposed on a high frequency strain.

Figure 3 shows polypyrrole being excited by 2 inputs, a high frequency stochastic stress wave and a low frequency voltage waveform. The resulting strain was composed of a low frequency strain proportional to the charge injected into the polymer and a high frequency strain due to input stress. The resulting stress and strain data was sectioned into sequences of 15 seconds and
The impulse response and frequency response for each of the sections was calculated. Since the frequency of the applied voltage was low, there was little change to the compliance during this 15 s interval.

![Graph showing compliance vs charge](image)

**Figure 4:** The low frequency compliance of the polypyrrole as a function of charge injected into the polymer.

The compliance impulse responses are strongly correlated with the charge injected into the polymer. The low frequency gain of the transfer function shows the most significant change. Figure 4 shows the changing low frequency compliance due to charge injection. As the BMIM$^+$ diffuse into the polypyrrole the low frequency compliance changes significantly by 40-50% during each cycle. The BMIM$^+$ seems to only change the low frequency component of the compliance transfer function and does not affect the natural frequency or the damping of the compliance.

**CONCLUSIONS**

We have used a novel technique to measure the compliance transfer function of polymers. Based on the coherence squared estimate the compliance transfer function was found to be valid up to 100 Hz. We have also shown that the compliance impulse response function changes as BMIM$^+$ ions are driven in and out of the polymer. The low frequency polymer compliance changes by as much as 40-50% as ions diffuse through the polymer. There is no discernable effect of the ions on the natural frequency or the damping of compliance transfer function. Future tests will include the use of solvents and other ions to see how they affect other features of the transfer function.

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