CHARACTERIZATION OF THE CORRELATION BETWEEN CURRENT INPUT AND CURVATURE OUTPUT OF POLYPYRROLE TRILAYER ACTUATORS

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Abstract: Conducting polymers (CP) are electro-active polymers and have been used as actuator materials. This paper is intended to characterize the electromechanical correlation between the current input and curvature output of polypyrrole trilayer actuators. A mathematical model is developed using the multilayer bending theory and an analogy between thermal expansion and ion insertion. The experimental results show that both the curvature and current changes along time share a similar tendency to exponential decay. The correlated coefficients are obtained by using least square curve fitting method.

Keywords: Conducting Polymer, Bending Actuator, Current, Curvature.

INTRODUCTION
Conducting polymers (CP) are electro active polymers (EAP) that can be used as actuators or artificial muscles [1-3]. The volume expansion or contraction of CP relies on the ions insertion or extraction to compensate for the electronic charges during redox reactions [4, 5]. During the last decade, a significant amount of research has been conducted on CP-based actuators both theoretically and experimentally, but the relationship between input electrical energy and mechanical output has yet to be fully described. In this paper, polypyrrole (PPy) based trilayer actuators are fabricated and a mathematical model is developed to characterize the electromechanical correlation between the current input and curvature output of polypyrrole trilayer actuators.

EXPERIMENTAL
In this paper, PPy is chosen as the actuating polymer because of its high conductivity, good chemical stability and superior mechanical performance [6]. Sodium dodecylbenzene sulfonate (NaDBS) is used as the electrolyte because it consists of large immobile anions (DBS-) and small mobile cations (Na+) and thus sole cation transportation can be assured.

The polymer is electrochemically synthesized on the 1 mil (25 μm) thick gold coated Kapton HN 100 film. The synthesis parameters are the constant current density of 1 mA/cm² for 30 min, in 0.1 M pyrrole monomer and 0.1 M NaDBS aqueous solution. After synthesis the trilayer actuators are cut into 20 x 1 mm² strips and then tested in 0.1 M NaDBS aqueous solution. The potentiostat controls the input potentials and the potential and current data will be collected to a computer. The real time bending motion is recorded by a CCD camera mounted on top of a microscope and the curvature will be extracted from each captured frame by curve fitting in Image-Pro Plus (Fig. 1).

Fig. 1: Schematic diagram of the set up for curvature measurement.

MODELING
The model is divided in two parts. The first part is a multilayer bending model to relate the bending curvature and actuation strain. This model is derived based on the classic beam bending theory [7]. The resulting curvature \( \kappa \) can be written as

\[
\kappa = \frac{AM_a - BF_a}{B^2 - AD}
\]

where \( A, B \) and \( D \) are the extensional stiffness, bending-extension coupling stiffness, and bending stiffness, respectively. \( F_a \) and \( M_a \) are the force and moment induced by the PPy layer actuation.

\[
A = \int E dz = E_i h_i \sum_{i=1}^{N} m_i n_i
\]  

\[
B = \int E zdz = \frac{E_i h_i^2}{2} \sum_{i=1}^{N} (m_i^2 + 2m_p n_i)
\]
\[
D = \int \varepsilon_2 \varepsilon_2 dz = \frac{E_i h_i}{3} \sum_{i=1}^{N} (m_i^3 + 3m_i^2 p_i + 3m_i p_i^2) n_i \tag{2-c}
\]
\[
F_a = \int E a dz = E_i h_i \sum_{i=1}^{N} m_i n_i \alpha_i \tag{2-d}
\]
\[
M_a = \int E a dz = \frac{E_i h_i^2}{2} \sum_{i=1}^{N} (m_i^2 + 2m_i p_i) n_i \alpha_i \tag{2-e}
\]
where \( m_i = \frac{h_i}{h} \), \( n_i = \frac{E_i}{E} \), \( p_i = \frac{z_i}{h_i} = \frac{1}{\sum_{j=1}^{i-1} h_j} \sum_{j=1}^{i-1} m_j \).

\( h \) is the thickness, \( E \) is the Young’s modulus (the subscript \( i \) denotes the \( i \)th layer, \( 1 \) denotes the bottom layer, and \( N \) denotes the total number of layers).

Since only the PPy layer exhibits the actuation strain \( \alpha \), Eq. 1 can be further written in a coefficient form
\[
\kappa = c_1 \alpha \tag{3}
\]
where the coefficient \( c_1 \) is determined by the thickness ratio \( m_i \) and modulus ratio \( n_i \).

For the second part, it has been reported that the actuation strain \( \alpha \) of conducting polymer is linearly related to the exchanged charge density (charge per volume) \( q \) [8]. The charge consumed by the polymer controls the amount of electrochemical reaction that, in turn, dictates how much the polymer is doped. Since the volume changes in conducting polymers are due to ion/solvent flux, the degree of movement (bending or axial) should be proportional to the current applied. Therefore the actuation strain \( \alpha \) can be written into the following form:
\[
\alpha = c_2 q, \quad (q=Q/B) \tag{4}
\]
where \( c_2 \) is the strain-to-charge coefficient, \( Q \) is the overall consumed charge and \( B \) is the volume of PPy layer.

Combining these two aspects leads to the relationship between the curvature \( \kappa \) and charge density \( q \)
\[
\kappa = c_1 \alpha = (c_1 c_2) q \tag{5}
\]
Eq. 5 relates the electrical input and mechanical output, and will serve as the basis for the following analysis.

**DISCUSSION**

The primary actuation mechanism of CP-based actuators is the ion transportation to compensate for the electronic charges during redox reactions. As shown in Eq. 6 and Fig. 2, the DBS doped PPy will expand by applying a negative potential (reduced), and contract by a positive potential (oxidized). The curvature increase from the reduced state to the oxidized state, which indicates a volume contraction in the PPy layer and the bilayer bends to the PPy side.

\[
PPy^\alpha(\text{DBS}^-) + Na^+ + e^- \rightarrow \text{PPy}^\beta(\text{NaDBS}) \tag{6}
\]

The PPy/Au/Kapton trilayer actuator is stimulated by a potential square wave between 0 V and -0.5 V with a cycle time of 60 sec. Both the anodic and cathodic scans are performed. For the anodic scan the potential is stepped from -0.5 V to 0 V and held for 30 sec, while for the cathodic scan the potential is stepped from 0 V to -0.5 V and held for 30 sec.

As shown in Fig 3(a), the curvature and current share a very similar tendency to exponential decay. If
we consider the actuator as a capacitor, the whole electrochemical cell is equivalent to a RC circuit. Therefore, the consumed charge can be obtained by integrating the current with respect to time. Fig. 3(b) shows that the relationship between the curvature and charge is quite close to a linear line, which validates the model we derived before.

To solve the electromechanical coupling coefficients \( c_1 \) and \( c_2 \), the PPy modulus \( E_3 \) needs to be known. Although various values have been reported [9-11], the exact value is unknown. Here the value will be determined from the actuation strain \( \alpha \).

Eq. 3 can be rewritten in the following form

\[
\alpha_{\text{max}} = \frac{\kappa_{\text{max}}}{c_k}
\]

(7)

where \( \alpha_{\text{max}} \) is the maximum actuation strain and \( \kappa_{\text{max}} \) is the maximum curvature. Then \( E_3 \) is set to a variable with a possible range of 10~1000 MPa, with gold modulus \( E_2 \) of 54 GPa [12] and other material properties listed in Table 1.

### Table 1. Material properties for the trilayer actuators

<table>
<thead>
<tr>
<th>Layer No. ( i )</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Kapton</td>
<td>Au</td>
<td>PPy</td>
</tr>
<tr>
<td>Thickness ( h_i ) (µm)</td>
<td>25</td>
<td>0.02</td>
<td>25</td>
</tr>
<tr>
<td>Young’s modulus ( E_i ) (GPa)</td>
<td>2.5</td>
<td>54</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Fig. 4: The maximum actuation strain \( \alpha_{\text{max}} \) as a function of PPy modulus \( E_3 \).

As shown in Fig. 4, when \( E_3 \) equals 80 MPa, the magnitude of \( \alpha_{\text{max}} \) is around 2% (in compression), which agrees well with the typical PPy actuation strain value.

Note in this paper the PPy modulus is considered constant during the potential scans. This assumption is assured based on the report of Spinks et al. [11]. It is said that PPy modulus will change when the applied potential is beyond certain threshold (± 2 V). Within this potential threshold, the PPy modulus can be treated as constant (around 80 MPa).

After the PPy modulus is obtained, the two electromechanical coupling coefficient \( c_1 \) and \( c_2 \) during the whole scan can be calculated based on Eq. 5 and experimental curvature and consumed charge data. The calculation is carried out by two approaches: by the least square curve fitting for the whole potential scan (Fig. 3(a)), and by the slope of \( \kappa \)-Q plot (Fig. 3(b)).

As shown in Table 2, the coefficient \( c_1 \) for the anodic scan gets an average of -2.30 mm\(^{-1}\) with a standard deviation of 0.03 mm\(^{-1}\) from the curve fitting method. While the \( c_1 \) calculated from the slope of \( \kappa \)-Q plot is -2.25 mm\(^{-1}\), this results in an error of only 2.18% against the value from the previous method. The values of \( c_1 \) for the cathodic scan also show a similar tendency. It indicates that \( c_1 \) can be approximated by a constant for simplification.

For the strain to charge ratio \( c_2 \), Madden et al. [6] found that it ranged between 0.3~5 × 10\(^{-10}\) m\(^3\)/C for PPy and polyaniline (PANI) actuators. Our results agree well with this range.

### Table 2. Summary of the coupling coefficients

<table>
<thead>
<tr>
<th>Scan</th>
<th>Anodic (0 V)</th>
<th>Cathodic (-0.5 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_1 ) (mm(^{-1}))</td>
<td>-2.25</td>
<td>-2.25</td>
</tr>
<tr>
<td>by ( \kappa )-Q slope</td>
<td>-2.30±0.03</td>
<td>-2.32±0.05</td>
</tr>
<tr>
<td>Error (%)</td>
<td>2.18</td>
<td>2.95</td>
</tr>
<tr>
<td>( c_2 ) (m(^3)/C)</td>
<td>-3.81 × 10(^{-10})</td>
<td>-3.33 × 10(^{-10})</td>
</tr>
</tbody>
</table>

### CONCLUSION

The electromechanical correlation of PPy-based trilayer actuators has been studied, resulting in the establishment of a mathematical model to relate the electrical input and mechanical output. It is demonstrated that multilayer bending theory and thermal expansion-ion insertion analogy is applicable to CP-based actuators. By tuning the material properties and model coefficients, it is possible to improve the actuator design and performance for specific applications.

Future work involves: (1) fabricate new type of actuators with more stable performance, such as ionic liquid-based actuators that can work in air; (2) improve the model by including the ion diffusion effect, polymer relaxation behavior, (3) characterize the actuator dynamic performance in frequency domain, and (4) evaluate the actuator force or moment output to provide more information for the actuator design.
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