

The Relation of Conducting Polymer Actuator Material Properties to Performance

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Abstract—Materials used in many branches of engineering are of low molecular weight and not flexible. As we develop more sophisticated engineering devices one can look to nature for inspiration and advocate the use of high molecular weight flexible materials. Conducting polymer actuators will soon be used in applications where traditional low molecular weight actuator systems are incapable of mimicking the functionality provided by nature's muscle. To incorporate conducting polymer actuators into engineering systems it is of high importance to not only model and predict the behavior of these actuators but also understand the implication of material properties to performance. In this paper, the importance of fundamental actuation mechanisms and the fundamental material properties of conducting polymer muscles such as ionic diffusion rate, electrochemical operating window, strain to charge ratio, ratio of charge carried by positive versus negative ions, and salt draining are discussed and their effect on performance is demonstrated. The relevance of engineered geometry on the performance of conducting polymer muscles is also shown. Our understanding of what limits the performance of existing conducting polymer actuators provides directions for the improvement of the next generation of conducting polymer actuators.

Index Terms—Actuators, artificial muscle, conducting polymers, diffusive elastic model.

I. INTRODUCTION

MATERIALS used in many branches of engineering are of low molecular weight, are not flexible, and their application for the creation of biomimetic systems is limited. For example electromagnetic or turbine motors are excellent for producing rotary motion but prove to be limited when recreating the complicated movements of biological systems such as caudal or pectoral fish fins that generate unsteady flows.

Conducting polymer actuators, on the other hand, offer muscle-like properties that could be useful for the creation of biomimetic devices. Such high molecular weight actuators based on polypyrrole, for example, generate large forces per cross-sectional area (40 MPa peak) with impressive power to mass ratios (150 W/kg), with low actuation voltages (~ 1 V).

These materials are relatively new as actuator materials, having been proposed by Baughman in 1991 [4]. For a gen-

eral review of conducting polymers as they might be used in biomimetic systems, the reader is referred to [19]. There are also several books that cover the field of conducting polymers in general [23], [33] and reviews of conducting polymer actuators have been published as well [22], [25].

In conducting polymer actuators contraction and expansion results from ions diffusing into and out of the polymer from a surrounding electrolyte. We show that the performance of actuators is often limited at a fundamental level by material properties. To get the very best performance from a given class of actuators, it is crucial to understand, select, and design these materials with optimized properties. In this paper, the limits of the performance of conducting polymer actuators are related to specific material properties. It is hoped that a better understanding of which material properties limit actuator performance will impact and direct research toward new conducting polymer materials.

In Section II we first recapitulate the diffusive elastic metal (DEM) model for the behavior of conducting polymers developed by J. Madden [13], [15], [16]. The model is then used in Section III to forge links between specific material properties and performance. For instance, the rate of diffusion of ions into the polymer determines the limit of the strain rate. Any material properties that affect the diffusion rate have a direct effect on actuator performance.

Section IV discusses the importance of material properties that affect behavior in situations not completely described by the DEM model. For example, voltage changes due to resistance in the polymer and creep are not modeled by the DEM. Note that the model is also derived for single ion diffusion into and out of the polymer.

Finally, Section V presents a comprehensive overview summary of material properties affecting actuation.

II. DIFFUSIVE ELASTIC METAL MODEL

The diffusive elastic model describes the electrical and mechanical behavior of a thin film of conducting polymer placed in an electrolyte solution (Fig. 1). A counter electrode (which can also be conducting polymer) is also placed in solution so that the electrochemical potential of the polymer film can be controlled. The model accurately predicts the electrical behavior of the conducting polymer polypyrrole in a liquid electrolyte at frequencies from 10^{-3} up to 10^5 Hz [16].

The solution itself is made up of a solvent (often water or propylene carbonate) with a dissolved salt such as tetraethylammonium hexafluorophosphate (TEAP). TEAP is made up of a large cation [tetraethylammonium, $N(C_2H_5)_4^+$] and a much smaller and more mobile anion [hexafluorophosphate, PF_6^-].

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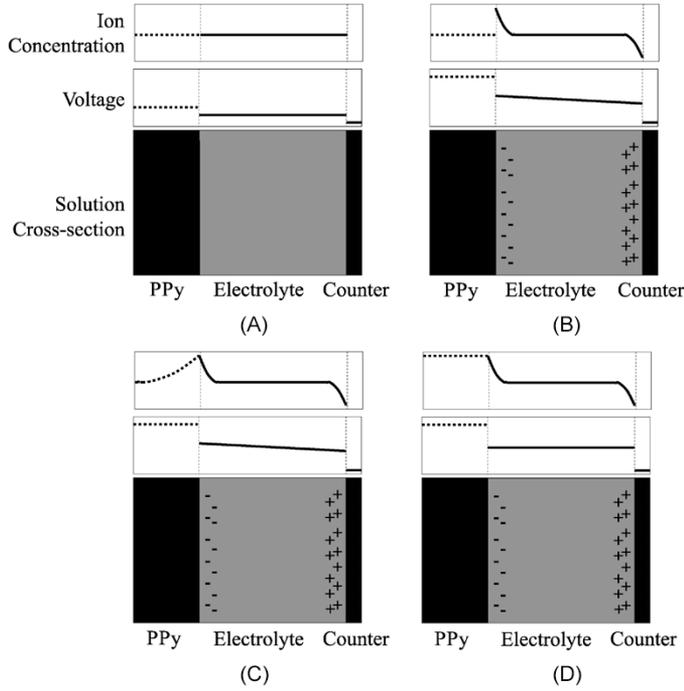


Fig. 1. Charging of the conducting polymer. Electronic charges are white while ionic charges are black. The upper two plots of each subfigure show the ion concentration and the voltage in the polymer (polypyrrole, cross-hatched), in the electrolyte (gray), and in the counter electrode (black). (A) The polymer at rest. There is a voltage difference at the interface between the polymer and the electrolyte and at the interface between the electrolyte and the counter electrode. (B) When a potential is applied, a current begins to flow through the electrolyte and ionic charge builds up in the double layers. (C) The concentration of ions at the polymer surface drives the diffusion of ions into the polymer. Inside the polymer the ions are paired with holes or electrons to form neutral species. (D) The polymer is fully charged when the concentration of ions in the polymer is equal to the concentration of ions in the double layer at the polymer electrolyte interface. The figure depicts charging for single ion (anion) movement into and out of the polymer.

The relative size of the salt ions is important: when the polymer potential is changed, very large ions are effectively blocked from entering the polymer because they are unable to diffuse between the polymer chains but the smaller ions are able to enter or leave the polymer.

To expand or contract the polymer, a voltage is applied to the polymer film between the polymer and the counter electrode. As soon as the voltage is applied, ions at the polymer surface will begin charging the electrochemical double layer capacitance at the film surface [Fig. 1(B)]. In the diffusive elastic model, the charge is directly proportional to the double layer voltage (the capacitance of the double layer is assumed to be independent of voltage).

As the double layer charges or discharges the ion concentration at the surface changes. If the polymer voltage is negative, positive ions are attracted to the polymer and negative ions are driven away. If the polymer is positive, negative ions are attracted and the positive ions are driven away. The resulting changes in concentration will in turn drive diffusion of ions into or out of the polymer film to cause expansion and contraction.

Typical values for the double layer capacitance are available in the literature and are generally around 0.1 to 0.4 F/m² [3]. The amount of charge (and the number of moles of ions) can be

estimated by using $\Delta Q = C_{dl}\Delta V$ ($N = C_{dl}\Delta V/N_A e$) where ΔQ is the change in double layer charge, C_{dl} is the double layer capacitance, and ΔV is the change in the voltage applied to the polymer film (e and N_A are the charge on the electron and Avogadro's number, respectively).

To calculate the ion concentration, the volume occupied by the ions must be known. While the concentration does vary with the distance from the electrode, an effective or average double layer thickness can be used. In the model, the double layer thickness is related to the double layer capacitance by the dielectric constant following the parallel plate or Helmholtz model: $\delta = \epsilon A/C_{dl}$ (where δ is the double layer thickness, ϵ is the solvent dielectric constant, and A is the surface area). Once the double layer thickness is known or estimated, the concentration at the surface can be calculated.¹

The concentration of ions at the surface of the polymer drives ionic diffusion into or out of the polymer [Fig. 1(C)]. Diffusion continues until a uniform concentration is reached inside the polymer and equilibrium is reached between the ion concentration in the polymer and in the double layer (Fig. 1(D)). The diffusion rates in the solid polymer are much slower than in the liquid electrolyte and so diffusion in the liquid is assumed to be instantaneous.

It should be noted that in the diffusive elastic model, movement of ions is not driven by an electric field within the polymer. Because the conductivity of the polymer is assumed to be very high, electronic charge moves quickly to shield the charges on the ions.² Even in the presence of an electric field within the material, ion migration will be negligible because the ionic charge is effectively neutralized by much more mobile electronic charge carriers in the polymer.

When the ions enter or leave the polymer, the polymer expands or contracts. If both positive and negative ions diffuse into and out of the polymer, expansion due to influx of one ion will be counteracted by contraction due to outflow of the ion with opposite charge [26], [27], [32], [36]. By choosing salts with one small and one very large ion, the influx and outflow are dominated by the smaller ion. In the salt TEAP, the negative ions (the hexafluorophosphate) are smaller and can squeeze between the polymer chains while the cations are generally too big to diffuse into the polymer bulk. With TEAP in propylene carbonate, the expansion and contraction of the polymer appear to be due only to the movement of the negative hexafluorophosphate ions [11], [13], [28].

A. Equations of the Diffusive Elastic Model

In the diffusive elastic model, the admittance of a polymer strip in an electrolyte solution is given by

$$Y(s) = \frac{s}{R} \cdot \frac{\frac{1}{\sqrt{\tau_{DDL}}} \cdot \tanh(\sqrt{s \cdot \tau_D}) + \sqrt{s}}{\frac{\sqrt{s}}{\tau_{RC}} + s^{3/2} + \frac{s}{\sqrt{\tau_{DDL}}} \cdot \tanh(\sqrt{s \cdot \tau_D})} \quad (1)$$

¹In the diffusive elastic model, the double layer thickness can also be calculated from the bulk capacitance of the polymer ([13, Section 10.4.1.4]).

²If the conductivity of the polymer is not high, then electronic charge may not compensate the ionic charge. The effect of migration, which will increase the charging rate, must then be taken into account to properly model the polymer behavior.

where

$$\tau_D = \frac{h^2}{4 \cdot D} \quad (2)$$

$$\tau_{RC} = R \cdot C_{dl} \quad (3)$$

$$\tau_{DDL} = \frac{\delta^2}{D} \quad (4)$$

and $Y(s)$ is the admittance as a function of the Laplace variable s , h is the thickness of the polymer strip, D is the diffusion coefficient of the ion within the polymer, R is the series resistance (which includes any wiring or contact resistance and the resistance of the electrolyte), C_{dl} is the double layer capacitance, and δ is the thickness of the double layer³. A full derivation of the admittance is given in [13] and [16]. An equivalent circuit is shown in Fig. 2.

The admittance (or its inverse the impedance) relates the current through the polymer to the voltage ($I(s) = Y(s)V(s)$). A second equation relates the charge injected into the polymer to the expansion

$$\varepsilon(s) = \alpha \frac{q(s)}{LWh} + \frac{\sigma(s)}{E(s)} \quad (5)$$

where ε is the strain, α is the strain/charge ratio, q is the charge injected into the polymer bulk, L , W , and h are the length, width, and thickness of the polymer strip, respectively, σ is the stress applied to the strip, and E is the Young's modulus of the polymer. We can substitute $q(s) = I(s)s/s$ to find

$$\begin{aligned} \varepsilon(s) &= \alpha \frac{I(s)}{s \cdot LWh} + \frac{\sigma(s)}{E(s)} \\ &= \alpha \frac{Y(s) \cdot V(s)}{s \cdot LWh} + \frac{\sigma(s)}{E(s)} \end{aligned} \quad (6)$$

to relate stress and strain to the voltage or current applied to the conducting polymer film.⁴ The strain/charge ratio α for polypyrrole doped with hexafluorophosphate in propylene carbonate solvent is $\sim 10^{-10} \text{ m}^3/\text{C}$.

Each of the time constants in the admittance equation has a specific physical interpretation. The first, τ_D , is the time constant for the diffusion of ions into the polymer. At times longer than τ_D after a change in applied potential, the concentration of ions is essentially uniform through the thickness of the film. For times less than τ_D , the concentration of ions must be found by solving Fick's law of diffusion [2], [13].

The second time constant τ_{RC} is related to the charging time of the double layer. If either the double layer capacitance or the series resistance (the electrolyte and contact resistance) increase, the time taken for the double layer to fully charge will increase. When the double layer charging time is lengthened, the concentration of ions at the surface of the polymer builds up more slowly and the rate of diffusion of ions into the polymer

³The admittance is given for a film with both sides exposed to solution.

⁴In fact, the use of $q(s) = I(s)/s$ is an approximation. The charge that causes expansion is the charge that diffuses into the polymer bulk. The current $I(s)$ includes both the current due to charge that diffuses into the polymer and the current due to charging the double layer capacitance. In practice for polypyrrole, except at very short time scales ($\sim 1 \mu\text{s}$) or extremely thin films ($< 200 \text{ nm}$) the charge stored in the double layer capacitance is negligible compared to the charge that has diffused into the polymer bulk [18].

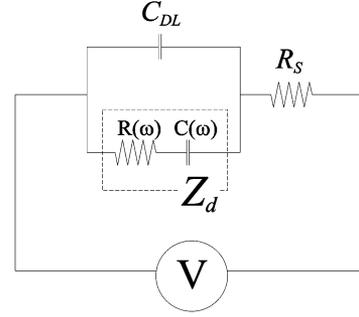


Fig. 2. Circuit model of conducting polymer in solution. The resistance R_s includes the resistance of the electrolyte solution and any contact resistance. C_{dl} is the capacitance of the double layer at the polymer electrolyte interface. Z_d is the impedance of ions diffusing into or out of the polymer and includes a bulk capacitance term. Charging of the bulk capacitance leads to expansion and contraction of the polymer while charging of the double layer does not.

is also slowed. Usually, τ_{RC} is much less than τ_D and so the double layer charging does not limit performance.

Finally, τ_{DDL} is the time constant for the diffusion of ions through the double layer thickness. After a step change in voltage, the diffusion of ions into the polymer is insignificant until at least τ_{DDL} . Before the time has reached τ_{DDL} , ions have not yet diffused across the double layer thickness and there cannot have been any expansion or contraction due to ion influx or outflow. τ_{DDL} can be thought of as a fundamental limit on the response speed of actuation for conducting polymers. Ions are in essence unable to move into or out of the polymer in a time shorter than τ_{DDL} .

While there is no time constant directly associated with the series resistance and the ionic charge that diffuses into the volume of the polymer (with an associated volumetric capacitance), these can also limit the performance. If there is a large diffusion current flowing to charge the volumetric capacitance, there can be a large voltage drop through the series resistance which reduces the voltage across the double layer and as a consequence the surface concentration of ions.

III. CONSEQUENCES OF THE DEM MODEL FOR ACTUATION PERFORMANCE

The diffusive elastic model as developed by J. Madden matches the experimental admittance of thin PF_6 doped polypyrrole films in electrolyte solution over more than eight orders of magnitude of frequency [13], [15]. The equations of conducting polymer behavior given by the theory have led to a much better understanding of what limits the performance of polymer actuators but did not directly connect the specific material properties of the conducting polymer to different performance limitations. In addition, the diffusive elastic model was derived for a conducting polymer film with negligible resistive voltage drop along the film. In a real polymer, the resistance reduces the voltage and slows the contraction rates.

In this section, using the diffusive elastic model as a starting point, conducting polymer actuator performance is related to material properties of both the polymer and the electrolyte. In Section IV, performance-related issues that are not described by the diffusive elastic model (such as the resistive drop in the film) are addressed and related to material properties. Finally,

in Section V, important material properties are enumerated and the mechanisms by which they affect actuator performance are described.

Strategies to increase the response speed of the polymer include:

- 1) increasing the charging rate in the polymer (increasing $(\partial\rho/\partial t)$, where ρ is the charge density) without sacrificing the strain/charge ratio;
- 2) increasing the strain/charge ratio without sacrificing the charging rate;
- 3) ensuring that the double layer is charged as quickly as possible using resistance compensation.

An important consequence of diffusion driven expansion and contraction is that strain rates depend on the difference between the polymer ion concentration and the double layer concentration. The change from minimum to maximum concentration will create the highest concentration gradients at the surface. Changing from an intermediate concentration to the maximum (or minimum) will generate lower concentration gradients and lower strain rates. When the concentration is close to the maximum, only slow rates can be achieved moving to higher concentration (and vice versa for concentrations close to the minimum). Thus the peak strain rate depends on the polymer charging level and the direction of strain.

It is worth calculating the amount of charge that flows into a conducting polymer. A typical value for the volumetric capacitance of polypyrrole in propylene carbonate with TEAP is 10^8 F/m³ [13]. A linear actuator could use a strip of polypyrrole 100 mm by 10 mm by $10\ \mu\text{m}$ that has a volume of 10^{-8} m³. The strip has a resulting capacitance of 1 F, which is remarkably high.

How much will the strip contract if the voltage changes by 1 V? The volumetric capacitance is charged with 1 C when the potential changes by 1 V. The strain is the product of the charge density $\rho = 1\text{C}/10^{-8}\ \text{m}^3 = 10^{-8}\ \text{C/m}^3$ and the strain/charge ratio $\alpha \approx 10^{-10}\ \text{m}^3/\text{C}$

$$\varepsilon = \alpha\rho \approx 10^{-2} = 1\% \quad (7)$$

or about 1 mm. To achieve this strain in 1 s, 1 C of charge must be delivered; the current must be 1 A. It can be seen that increasing the strain/charge ratio is very important for reducing the current magnitude.

A. Increasing the Charging Rate

The charging rate of the polymer can be increased in four ways. The first three require improved material properties while the fourth relies on changes in the geometry of the polymer.

Because the charging rate is controlled by diffusion of ions into the polymer, increasing the diffusion coefficient will improve the response speed. For a given material, changing the salt ion can change the diffusion coefficient [6], [21], [29]. Smaller ions usually move more quickly into the interstitial spaces than do larger ions. But changes in ion size likely also affect the strain/charge ratio. An expected increase in strain rate because of a higher charging rate can be offset by a decrease of the strain/charge ratio. The tradeoff between the two has not yet been well studied.

The diffusion rate can also be changed using different synthesis methods. The morphology of the synthesized polymer changes considerably depending on the electrochemical potential of the deposition, the current density, and the shape of the deposition waveform [30]. Typically in the past, synthesis of polypyrrole has been optimized for conductivity [31], [38] but improvements in actuator performance might be realized by optimizing deposition for faster diffusion. The effect of deposition conditions on diffusion speed and contraction rate has also not been well studied.

The third way to increase the charging rate is to increase the concentration gradients. Gradients within the polymer are determined by the concentration in the double layer. The maximum double layer concentration is limited by the maximum potential—the degradation potential—of the polymer or of the electrolyte. Above (or below) the degradation potential, higher (or lower) concentrations can be reached but at the expense of unwanted chemical reactions that affect long term performance. If the capacitance is linear with voltage, doubling the maximum potential applied to the polymer will double the concentration and hence the charging rate.⁵

Strategies to increase the stable potential range include changing the chemical structure to block reactive sites or removing oxygen and other impurities that react with the polymer. The best performance may be achieved only in pure environments within hermetically sealed packages.

Finally, the rate of charge density change can be improved by altering the geometry of the polymer and the electrolyte. If the same voltage is applied along two polymer strips of different thickness, the charge density increases faster in the thinner strip. The faster rate is a consequence of there being less volume to charge in the thinner strip. The time constant $\tau_D = h^2/4D$ (the diffusion time constant) relates the strip thickness h to the charging time. Halving the thickness can reduce the charging time by a factor of four.

B. Increasing the Strain/Charge Ratio

Increasing the strain/charge ratio can also increase the polymer contraction rate. While it may be that the strain/charge ratio generally increases as ion size increases, this has yet to be proven. Part of the difficulty is that the strain/charge ratio is also solvent dependent with some solvent molecules (in particular water) getting entrained with the ions [5], [8], [24]. However, as mentioned in the discussion of diffusion speed, even if ion size does raise the strain/charge ratio, increased ion size can slow diffusion and so mitigate the potential improvements.

While in polypyrrole, the strain observed is due to the intercalation of ions between the polymer chains, new polymer structures are being developed that use hinging mechanisms along the polymer backbone to boost the strain/charge ratio dramatically [1], [17], [20]. The amount of contraction and expansion is expected to be far less dependent on ion size since ion influx will not be directly responsible for volume change but will only trigger the conformational change. Smaller faster ions should therefore be used to trigger volume changes.

⁵If the charge in the double layer is proportional to the voltage, doubling the maximum potential should double the concentration at the polymer surface.

C. Resistance Compensation

While diffusion of the ions into the polymer poses a fundamental limit, the charging of the double layer can be a practical limit to actuator rates. If the series resistance for charging the double layer is significant, the double layer voltage and hence the double layer concentration increase can be slow enough that ionic diffusion has time to equilibrate. The dominant material property that affects the series resistance is the electrolyte conductivity. Series resistance is also affected by any contact resistance with or resistance in the external circuitry used to drive the polymer.

For the fastest rate, the maximum double layer voltage must be reached as quickly as possible. This can be done by eliminating the effect of the series resistance using resistance compensation techniques [14].

When current is flowing in the circuit shown in Fig. 2, there is a voltage drop $V_R = iR_s$ across the series resistance R_s . At very high currents, the voltage across the double layer can be considerably less than the voltage applied to the entire circuit. Resistance compensation increases the voltage applied to the circuit by iR_s ($V_{\text{applied}} = V + iR_s$) so that the controlled voltage is the voltage across the double layer.⁶

Without resistance compensation, every effort should be made to reduce the series resistance. Lowering the series resistance by reducing contact resistance, by improving the electrolyte conductivity or by changing the electrolyte geometry, will improve the double layer charging time. Reducing the series resistance will also improve the actuator by increasing efficiency.

IV. BEYOND THE DEM MODEL

There are three properties that can have a large effect on performance but are not included in or described by the diffusive elastic model. The first, creep, comes into play at high stresses or over long times. Creep is also important at lower stresses if the polymer weakens by electrochemical degradation because of too extreme a potential. The second property is the conductivity of the polymer itself. In the derivation of the diffusive elastic model it is assumed that the entire conducting polymer is at the same potential. However, for either low conductivity polymers or for geometries with long current paths (such as long strips with voltage applied at one end) there can be considerable potential drop due to resistance. Finally, the transference number⁷

⁶In practice, the series resistance can be measured by applying a very fast voltage pulse to the circuit and measuring the current. For a short pulse, most of the voltage drop is across the resistor and $R_s = V/i$. When resistance compensation is being used, the measured current is multiplied by the resistance to give $V = V_{\text{double layer}} + iR_s$.

⁷The transference number is the ratio of the conductivity of one charge carrying species (e.g., one ion) to the total conductivity of the material. Larger ions typically have smaller transference numbers because of their lower mobility.

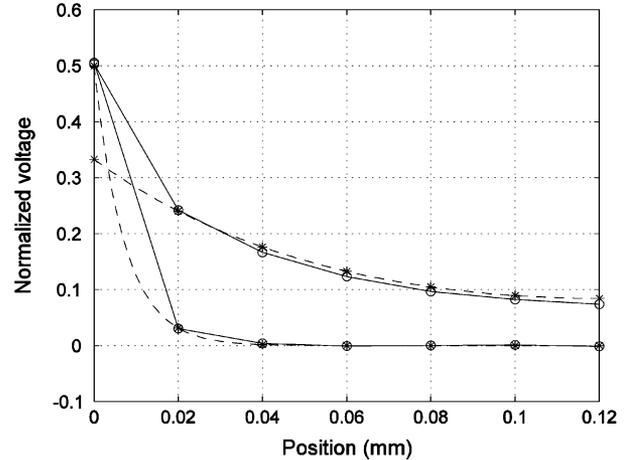


Fig. 3. Voltage along the length of two polymer strips 0.2 ms after applying a 0.5 V square wave at 0 mm. Upper curve: polymer strip resistance = 57.8 Ω. Lower curve: polymer strip resistance = 3780 Ω. The dashed lines are given by a resistance network model (with an electrolyte resistance = 13.8 Ω).

of the ions within the polymer or within the electrolyte also affects the strain and the strain rate that can be achieved.

A. Creep

Creep and the modeling of creep in polypyrrole have been discussed by Della Santa *et al.* and by Madden *et al.* [7], [13]. With the limited strain (typically ~2–4%) of conducting polymer actuators based on polypyrrole, creep of a few percent can render the actuator incapable of generating force. To compensate for the lengthening due to creep, mechanisms can be designed to adjust muscle attachment points but these are cumbersome. A ratchet muscle mechanism similar to natural muscle actin myosin cross bridges could be designed with polypyrrole but the manufacturing will be complicated. Solutions based on better design of materials are more desirable. Increased crosslinking of the polymer, higher molecular weight, construction of composite materials, or even molecular scale ratcheting mechanisms should reduce creep but no systematic studies have yet been published.

B. Conductivity

The conductivity of the polymer begins to affect the polymer potential if there are high currents or long electronic current paths through the polymer bulk. Fig. 3 plots the voltage in two 120 mm long strips of polypyrrole at 0.2 ms after a 0.5 V step has been applied at $x = 0$ mm. The strip resistance in combination

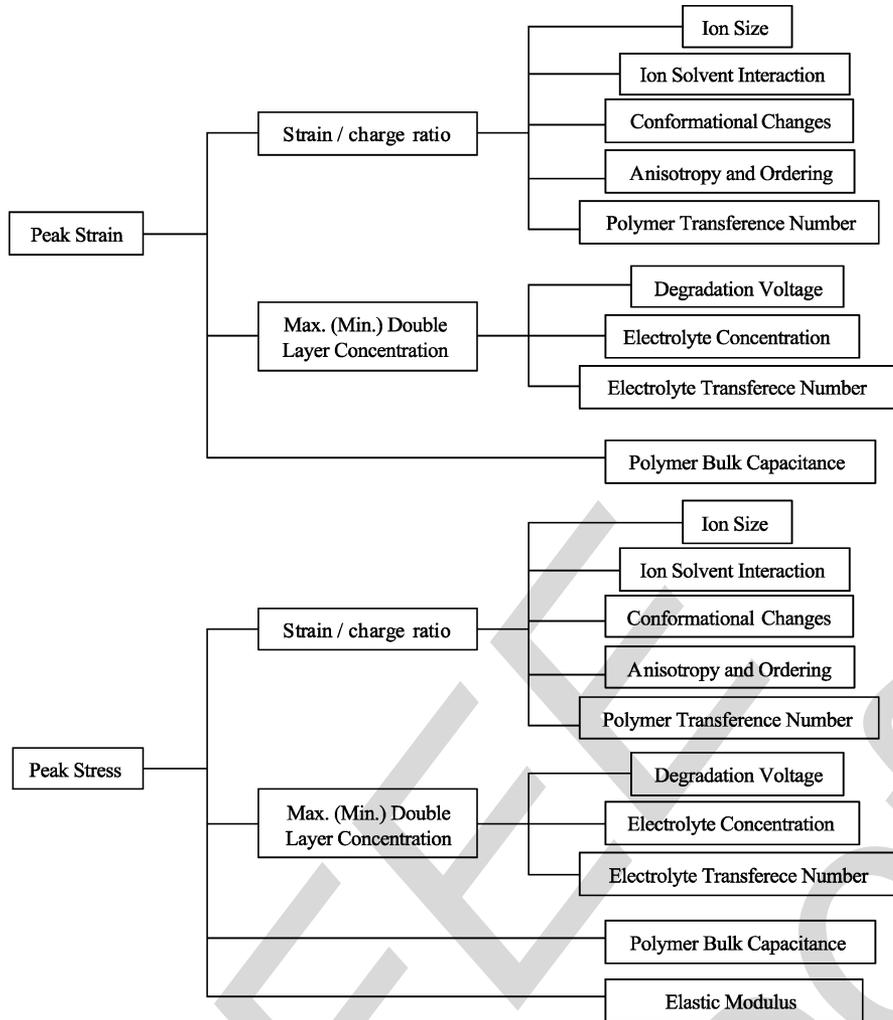


Fig. 4. Relationship of peak strain and peak stress to material properties of conducting polymer actuators.

with the electrolyte resistance determine the voltage (the dashed lines are determined by a resistance network model.⁸

There are three ways of minimizing the ohmic potential drop. The first is to improve the conductivity of the material itself. Conductivity can be increased by better material processing [9], [37] or by coating or blending with another material of higher conductivity. For example gold ($\sigma = 4.5 \times 10^7$ S/m) on polypyrrole ($\sigma = 10^4$ S/m) will increase the conductivity of polypyrrole or a layered blending of polypyrrole ($\sigma = 10^4$ S/m) and polyquarterthiophene ($\sigma = 10$ S/m) will boost the conductivity of polyquarterthiophene (Spinks *et al.*, for example, grow conducting polymer tubes that incorporate a coiled gold wire [35]). Coating or blending also affect other averaged properties such as the Young's modulus and the overall strain/charge ratio so care must be exercised to balance the different effects.

The second method to reduce potential drop is to reduce the amount of current. To achieve the same strain rate with less current requires an increase in the strain/charge ratio (lower current gives a lower rate of charging and hence a lower strain rate un-

less the strain/charge ratio is increased). Given the very high currents required to activate the polymer (as discussed in Section III), a high priority must be placed on raising the strain to charge ratio to avoid resistive losses.

Finally, the third way to lower the potential drop is to reduce the length of the current paths. Making electrical contact at both ends or at multiple points along a strip will result in faster actuation [18].

If the polymer electronic conductivity becomes very low, conductivity also affects the rate of diffusion (and the DEM model no longer applies). At low conductivity, the assumption of the DEM model that the electronic conductivity is much higher than the ionic conductivity in the polymer breaks down. With reduced shielding of ions in the bulk, ionic charge in the polymer will generate an electric field that opposes diffusion of ions into the material and slows the strain rate.

C. Transference Numbers

For the largest strain and strain rate, only one ion species should move into and out of the polymer. If two ions are moving in the polymer bulk, the expansion due to one ion is countered by the contraction of the other [28], [32], [36].

⁸A transmission line model of distributed resistances gives an expression for the voltage $V(x) = V_o(\cosh(\kappa(L-x))/\cosh(\kappa \cdot L))$, where L is the length of the strip, V_o is the voltage applied at $x = 0$, and $\kappa = (1/L)\sqrt{(R_{\text{polymer}}/R_{\text{electrolyte}})}$ (a derivation is given in [18]).

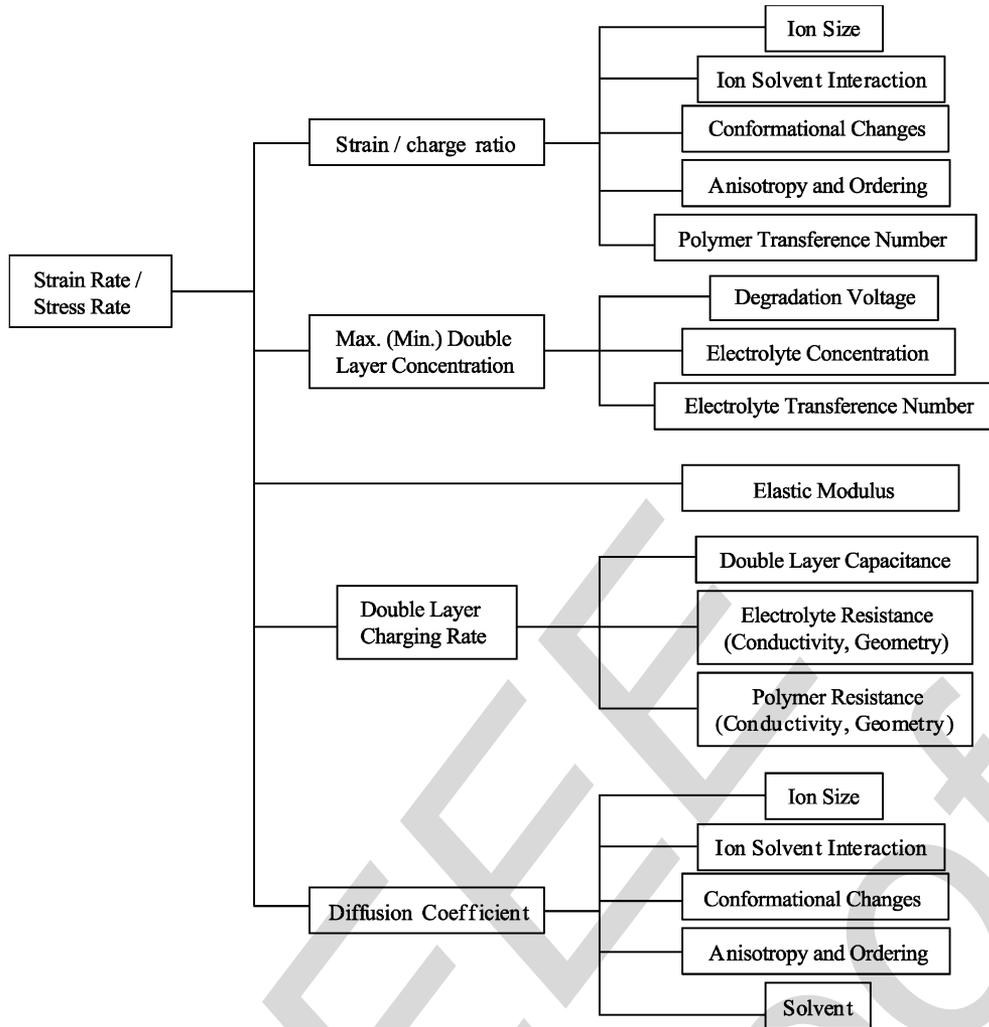


Fig. 5. Relationship of strain rate and stress rate to material properties of conducting polymer actuators.

In a polymer actuator system, ions can be mobile in the conducting polymer and in the electrolyte. In the electrolyte, the transference number of an ion is the fraction of electric field driven current carried by that ion [3]. If the electrolyte has a single current carrying ion (transference number of one) with a second stationary ion (transference number of zero), the double layer is charged (or discharged) only by the mobile ion. Concentration gradients created by the double layer will only drive diffusion of the electrolyte's mobile ion into and out of the polymer. Thus, a transference number close to zero for one ion can ensure that there is only a single ion moving into or out of the polymer.

In the polymer bulk, ions are very quickly paired with electronic charge and their motion is not driven by electric fields. The concept of a transference number as it is used for an electrolyte is not directly applicable. However, there is a net current in the polymer that is due to influx and outflow of ions. In the polymer bulk then, the transference number of one ion species should be defined as one ion's proportion of the total ion flow. Note that if the electrolyte transference number is one, the polymer transference number has to be one as there is only one ion species in the double layer.

The polymer transference number of a species is expected to be related to the ratio of ion sizes. For tetraethylammonium hexafluorophosphate, the tetraethylammonium ion is very large and is unable to diffuse or diffuses very slowly into or out of the polymer. The smaller hexafluorophosphate ion does diffuse into the bulk to change the volume.

V. OVERVIEW OF MATERIAL PROPERTIES AND THEIR RELATION TO ACTUATOR PERFORMANCE

Many of the specific material properties affect all of the bulk actuator properties. In this section, the material properties are enumerated and the mechanisms through which they influence actuator performance are described to summarize the previous two sections. The relationships introduced are charted in Fig. 4 (peak strain and peak stress) and Fig. 5 (strain and stress rate).

A. Ion Size

The ion sizes in the electrolyte affect the peak strain, the peak stress, and the strain and stress rates. In polymer actuators that operate by ion intercalation, large ions are expected to have a larger strain/charge ratio and hence larger peak strains

and stresses. Ions that are too bulky are not able to diffuse into and out of the polymer at all.

It is better to have only one ion that can diffuse in and out of the polymer. Otherwise expansion due to one ion is counteracted by contraction due to the other [28], [32]. Ideally, one ion cannot diffuse (with a transference number in either the polymer or the electrolyte of zero) while the other ion is mobile. Larger ions generally diffuse more slowly.

B. Ion Solvent Interaction

In some cases, ions may entrain solvent molecules as they diffuse into and out of the polymer. The extra volume of the solvent molecules likely increases the strain/charge ratio [5], [8], [24].

C. Conformational Changes

During the process of oxidation and reduction of conducting polymers, there is a conformational change along the backbone of the polymer. In traditional actuator materials (polypyrrole, polyaniline), calculations suggest that the change in chain length due to conformational change is small (<1%). Newer materials such as the calixarene based molecules being developed by the Swager and Hunter groups at the Massachusetts Institute of Technology could contract up to 88% [1].

D. Anisotropy and Ordering

In conducting polymer actuators, there are direction-dependent effects during the expansion and contraction. Herod and Schlenoff found that stretched films of polyaniline showed greater contraction and expansion perpendicular to the direction of stretching than in the direction of stretching (11.1% perpendicular versus 1.6% parallel to the stretch with chemical doping) [10]. Smela and Gadegaard found expansions perpendicular to the plane of thin polypyrrole films of as much as 30% of the film thickness [34]. The authors suggested that the very large expansions observed are likely due to the structuring of the polymer film in the plane of the substrate. It may be possible to reproduce such ordering effects on a larger scale if techniques can be found to better orient the polymer chains.

E. Polymer Transference Number

When both the positive and negative ion species in the electrolyte are able to diffuse into and out of the polymer, expansion due to one ion is counteracted by contraction due to the other ion. Preventing one of the ion species from diffusing into the polymer will result in greater expansion and contraction (larger strain/charge ratio and higher strain/stress rates). Ideally, the transference number of one ion species will be very close to one while the transference number of the oppositely charged species will be effectively zero. The transference number is closely tied to ion size.

F. Degradation Voltage

The degradation voltage of the polymer or of the electrolyte is a practical limit on the peak concentrations of ions in the double layer [11], [12], [35]. Because the peak double layer concentrations determine the peak ion concentrations in the

polymer, degradation limits the maximum strain or stress inside the polymer.

The maximum concentration in the double layer also determines the maximum ionic gradient and hence the maximum ion diffusion rate into or out of the polymer. The maximum diffusion rate in turn determines the maximum stress and strain rates.

G. Electrolyte Concentration

The concentration of ions in the electrolyte determines the conductivity of the electrolyte. Higher electrolyte conductivity will shorten the double layer charging time and will also increase efficiency by reducing resistive loss. The electrolyte concentration may also affect the charge storage capacity of the polymer [24] and thus maximum strain.

H. Electrolyte Transference Number

If the transference numbers of the ions in the electrolyte are one and zero, then only one ion will charge and discharge the double layer. If only one ion charges and discharges the double layer, that ion in turn will be the only one that diffuses into and out of the polymer causing expansion and contraction. Single ion flow is desirable so that expansion from one ion entering is not counteracted by contraction from the other ion leaving the polymer volume.

I. Polymer Bulk Capacitance

The maximum expansion and contraction of the polymer actuator depends on the maximum number of ions that can be inserted and removed. At the maximum voltages that can be applied, the polymer bulk capacitance is a measure of the total charge that can be exchanged. The maximum strain is

$$\varepsilon_{\max} = \int_{V_{\min}}^{V_{\max}} \alpha \cdot C_{\text{vol}} \cdot dV \quad (8)$$

where V_{\max} and V_{\min} are the maximum and minimum voltages that can be applied, α is the strain/charge ratio, and C_{vol} is the capacitance per unit volume of the polymer. If the polymer is being driven by a voltage source rather than a current source, the polymer bulk capacitance also determines the ratio of strain to voltage

$$\frac{d\varepsilon}{dV} = \alpha \cdot \frac{d\rho}{dV} = \alpha \cdot C_{\text{vol}} \quad (9)$$

where α is the strain/charge ratio, C_{vol} is the bulk capacitance per unit volume, and V is the applied voltage. The bulk capacitance is closely related to the double layer capacitance since it is the double layer concentration that determines the bulk ion concentration.

J. Double Layer Capacitance

The double layer capacitance determines the voltage needed to create a given concentration at the polymer surface. If the double layer capacitance increases without changing the double layer thickness, there will be more charge per volt in the double layer and the concentration of ions per volt will also be greater. The greater ionic concentration will in turn drive diffusion faster so that the actuator will contract or expand faster. If there is

more charge in the double layer at the maximum voltages (just within the degradation voltages) the maximum expansion of the polymer should also be greater.

K. Elastic Modulus

In the diffusive elastic model the displacement per charge inserted does not depend on the elastic modulus.

The stress generated does depend on the Young's modulus

$$\sigma = E\varepsilon + \alpha E\rho \quad (10)$$

where E is the Young's modulus, ε is the strain, α is the strain/charge ratio, and ρ is the charge density. Increasing the Young's modulus increases the stress that can be generated per unit charge.

If the elastic modulus is low, large displacements will result from changes in the actuator load. A high elastic modulus on the other hand will reject such disturbances more easily.

L. Electrolyte Conductivity

Increasing the electrolyte conductivity will result in faster charging of the double layer at the surface and will also reduce ohmic energy losses to increase actuator efficiency.

M. Polymer Conductivity

The conductivity of the polymer actuator affects performance in two ways.

First, as current flows through the polymer, energy is lost through resistive heating. Second, voltage drops due to current flow reduce the voltage across the double layer (as shown in Fig. 3). A lower voltage across the double layer reduces the concentration of ions in the polymer and the contraction or expansion of the polymer is slower. Polymer closest to the point where current is delivered will contract the fastest while polymer further from the current delivery point which is at a lower voltage will contract more slowly.

VI. CONCLUSION

In this paper, important material properties have been enumerated and their relationships to actuator performance have been outlined. Electrolyte properties such as conductivity and transference number are considered along with the polymer properties because conducting polymer actuators rely on the flow of ions from an electrolyte into the polymer.

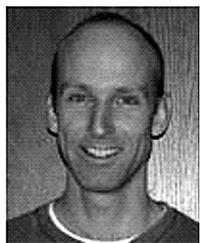
Using the DEM model, a few of the properties (e.g., diffusion coefficient, electrolyte series resistance, double layer capacitance) can be quantitatively related to behavior while for other properties a quantitative relationship has yet to be found (e.g., ion size or choice of solvent).

Continued research is required to determine the magnitude of improvements that can be achieved and the tradeoffs that might occur by optimizing different material properties. By listing and examining the material properties that affect the performance of conducting polymer actuators, directions for research into new materials can be better chosen.

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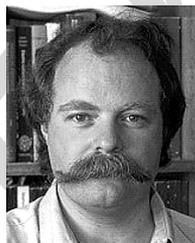
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