Fast Contracting Conducting Polymer-based Actuators

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Conducting polymer-based actuators are capable of producing ten times more force for a given cross-sectional area (stress) than skeletal muscle[1,2], and potentially one thousand times more[2-5]. They also generate strains in the range of one to ten percent[1-7], and are driven by potentials of between less than one volt and up to ten volts[1-14]. While these features distinguish them relative to other technologies, including electrostatic, piezo-electric and magneto-strictive atuators[4], small strain rates (< 0.03 %·Hz)[1,2] and low power-to-mass ratios (< 1 $\mathrm{W \cdot kg^{-1}}$)[1] have restricted the breadth of their application. In this article millisecond scale response to electrochemical activation is investigated, leading to the observation of strain rates two orders of magnitude larger than previously reported, and of continuous power to mass ratios equaling that of muscle. Rapid deflection is shown for polypyrrole actuators operating both in and out of a liquid environment. The form of the frequency response suggests that diffusion is the rate-limiting factor.

Polypyrrole, polyaniline and other conducting polymers undergo volumetric changes that may be exploited to perform work[1-14]. Polymer expansion appears to be the result of ionic and molecular influxes that occur as oxidation state is altered either chemically or electrochemically[3,4]. Mass fluxes resulting from capacitive charging of the polymer may also contribute to material dilatation. Electrochemical experiments show that strain is directly proportional to the magnitude of charge transfer[1,2,9] and, equivalently, that strain rate is proportional to current. Reaction kinetics, mass transport and capacitive charging are hence the candidate rate limiting factors.

Polypyrrole and polyaniline are observed to displace rapidly upon initial application of an oxidizing or reducing potential, but then to slow over time[13,14]. Such an initially rapid, but decreasing rate is consistent with the behavior of diffusion limited processes[15], and could also result from capacitive charging. Previous results have not related the observed rapid deflections to strain, strain rate, and power to mass, making it difficult to evaluate objectively actuator performance. This paper aims to quantify actuator behavior in terms of these intrinsic figures of merit, and to study frequency response as a preliminary attempt to elucidate the underlying rate limiting mechanisms. Frequency response is obtained both for devices operating in liquid, and for encapsulated actuators operating in air. Operation in air is of interest as it is a requirement of many potential applications.

To determine strain rate, the amplitude of deflection produced in bilayer conducting polymer actuators is measured as a function of the frequency. Bilayer actuators consist of laminated strips of material in which a differential expansion leads to bending. These devices act as mechanical amplifiers, generating relatively large displacements in response to miniscule deformations, thus allowing ready measurement of small material strains. Linear elasticity theory is employed to relate bilayer deflections to material strain[9,16]. The effective strain, α, for a given bilayer deflection, δ, is determined by first solving for the change in film curvature, $\Delta\rho$, in terms of deflection and bilayer length, L:

$$\delta^2 = \frac{2\delta}{\rho} + \frac{\sin(L\rho)}{\rho}^{2} \quad . \tag{1}$$

The strain is then related to the relative thickness of the two layers, h_1, and, h_2, as well as the elastic moduli divided by one minus the Poison’s ratio for each layer, as represented by E_1' and E_2':

$$\Delta\rho = \frac{6\alpha}{\dfrac{\left(E_1{}'h_1{}^2 - E_2{}'h_2{}^2\right)^2}{E_1{}'E_2{}'h_1h_2\left(h_1+h_2\right)} + 4\left(h_1+h_2\right)} \quad . \qquad (2)$$

The active material employed in bilayers operating in both solution and in air is polypyrrole. Polypyrrole films are deposited under two different conditions. Films employed in air are grown from a solution of 0.06 M freshly distilled pyrrole monomer and 0.05 M tetraethylammonium hexafluorophosphate in propylene carbonate, following the procedure of Yamaura[17]. Polypyrrole is deposited galvanostatically on to polished 50 mm x 50 mm glassy carbon substrates at current densities of 1.25 $A\cdot m^{-2}$, resulting in a typical film thickness of 40 μm. Deposition takes place at -30 °C in a nitrogen saturated solution. The resulting films have conductivities on the order of 1 to 3×10^4 $S\cdot m^{-1}$, and tensile strengths of 25 MPa. The polypyrrole films employed in liquid environments are synthesized electrochemically from a 0.1 M Pyrrole, 0.1 M sodium dodecylbenzenesulfonate (DBS) aqueous solution, following the methods of Smela[10]. Deposition takes place on a 250 nm thick platinum film that has been e-beam evaporated on to mylar tape. Deposition is performed galvanostatically against a large stainless steel counter electrode, 20 times the surface area of the working electrode. 150 μA of current are delivered over 8 to 17 hours to yield 30-60 μm thick films. Films prepared by both methods have elastic moduli of between 0.5 GPa (wet) and 1 GPa (dry). Creep behavior is observed, with a time constant of roughly 200 s.

In fabricating the liquid-based bilayers, the DBS-doped polymer and the platinum backing are peeled from the Mylar layer and cut to form actuators. Two were employed to obtain the results presented, one being 0.75 mm wide, 7 mm long and 60 μm thick and the second having a length of 3 mm, a width of 1.5 mm and a thickness of 31 μm. The actuators are immersed in 0.1M sodium DBS aqueous solution. Square wave potentials are applied between the platinum backing and a stainless steel counter electrode. The square wave amplitude is ± 7 V, and applied frequencies range from 1 Hz to 30 Hz. The current through the actuator is typically several milliamperes. Bilayer deflection, resulting from the expansion and contraction of the polypyrrole layer relative to the platinum, is observed under a microscope. The microscope image is recorded using a CCD camera (Hitachi VK-C630) sampling at 30 frames per second, coupled to a video tape recorder. The magnitude of deflection is determined from these images. Normally digital sampling is limited at the high end by the Nyquist frequency, which is 15 Hz in this case. However, the CCD camera collects light continuously, so that fast moving objects appear blurred on each frame. By analyzing the data frame by frame and between frames, the extent of deflection was determined at slightly higher frequencies. Strain, strain rate and force are calculated from the measured displacements, bilayer geometry and mechanical properties using the Equations 1 and 2 and standard linear elasticity theory[9,16].

Strain amplitudes and the corresponding strain rates from two bilayers are shown as functions of frequency in Figure 1. The magnitude of deflection at 1 Hz is 2 mm for the 7 mm long actuator (triangular markers). The error bars shown account for uncertainties in the measurement of deflection, which are larger for the shorter beam due to its smaller deflections. Uncertainties in the measurement of actuator lengths and thicknesses add a further 10 % error to all points. The average strain rates, Figure 1b, reach a peak of 4 ± 1 %·Hz at 10 and 20 Hz cycling, two orders of magnitude higher than those previously reported. The magnitude of the activation potential influences strain rate. For example, as applied potential is increased from 4 V peak-to-peak up to 8 V, beam deflection triples. Beyond 10 V peak to peak, the extent of deflection saturates.

The forces generated at the tips of the beams are estimated to be 1 mN using beam bending equations, and exceed calculated drag forces by at least two orders of magnitude. The corresponding stresses generated in the polymer reach 2 MPa. The peak power-to-mass ratio is 40 $W \cdot kg^{-1}$, exceeding that of electrostatic actuators by an order of magnitude, and matching the steady state power-to-mass ratio of mammalian skeletal muscles[5]. Cycle life is frequency dependent. At frequencies below 1 Hz, delamination occurs after several cycles as hydrogen gas forms at the platinum/polymer interface. However, at higher frequencies, much longer lifetimes are possible. An actuator was left running for 120,000 cycles at 3 Hz, producing strains of > 0.25 % at a strain rate of 1.5 %·Hz. No deterioration in amplitude was observed.

There are several factors that may limit the observed strain rate. These include reaction kinetics, the rate of capacitive charging, the mechanical impedance, and mass transport. The strain rates in Figure 1 appear to follow a square root relation to frequency, as is predicted in the case of semi-infinite planar linear diffusion[15]. The diffusion model is represented by the solid line in Figure 1, which fits the data to within the uncertainties represented by the error bars. This model implies a diffusion of ions to or from the polymer occurring at the liquid interface, where the thickness of the diffusion layer is proportional to the square root of the product of the diffusion coefficient and time, and is less than the film thickness. If the model is correct, then the strain in the polymer near the surface takes place on a time on the order of the width of the layer squared divided by the diffusion coefficient, suggesting that great gains in speed could be obtained by reducing actuator thickness.

For operation outside of solution, two polypyrrole strips 10 mm wide x 20 to 40 mm long x 40 μm thick are cut from the tetraethylammonium hexfluorophosphate doped films. A sandwich structure is formed, as shown in Figure 2, with the polypyrrole strips forming outer layers, and containing a gel electrolyte between them. A gold layer (< 200 nm thick) is sputtered onto the outer polymer surfaces, and the entire actuator is encapsulated in a polyethylene film, as indicated in the Figure 2. The gel layer is approximately 100 μm thick. The gel is synthesized following a procedure related by Reynolds[18]. It consists of 70 wt% acetonitrile, 20 wt% propylene carbonate, 7 wt% polymethylmethacrylate (PMMA), and 3 wt% $LiClO_4$. Actuators are soaked for 15 minutes in a solution of 0.05 M tetra ethyl ammonium hexafluorophosphate in propylene carbonate, which renders the polymer more compliant. Tests are performed as with the bilayer in liquid, except that potential is applied between the two strips of polypyrrole. The square wave peak to peak amplitudes are between 2 V and 10 V, and applied frequencies range from 0.1 Hz to 30 Hz.

Figure 2b contains a pair of images showing the deflection of the bilayer on activation with a 10 V square wave at 0.1 Hz frequency. Deflection as a function of frequency of activation and for different applied peak-to-peak voltages is shown in Figure 3. Deflection increases as applied potential is increased, with the response saturating beyond 10 V. By comparison, relative deflections at 0.1 Hz with 2 V and 3 V applied are 0.05 and 0.12, respectively. Increasing the excitation frequency in all cases decreases the deflection. This decrease is again proportional to $f^{-1/2}$ until roughly 15 Hz, above which frequency there appears to be a roll-off. The frequency dependence suggests that rate is again limited by semi-infinite planar diffusion over this range. In a second film constructed identically, but having twice the length, the roll-off frequency drops by a factor of four. Such a shift as a function of beam length is characteristic of mechanical resonance[16], suggesting that beam mechanics are at least partly responsible for the drop off at high frequency. The strain appears to flatten at lower frequencies. Another rate limiting mechanism may come into effect at such time scales, explaining the relatively slow rates observed in linear actuators at large deformations. (If the trend in strain rate observed in Figure 1 were to continue over longer time scales, 2 % contractions would occur in 16 s, as opposed to the roughly 60 s observed[1].)

Strain is not shown in Figure 3 as the mechanical impedance of the gel layer is uncertain. Also the gel layer thickness is somewhat non-uniform, and deflection does not occur uniformly throughout the beam. However, it is possible to generate a lower bound strain estimate, based on the minimum actuator thickness, the polypyrrole glassy modulus and the total deflection. The strain at 0.1 Hz is > 0.2 %, and the maximum strain rate, occurring at 15 Hz, is > 0.5 %·Hz. Lifetime of these actuators is only several hours. Evaporation of liquid solvent from the gel and the polypyrrole appears to degrade performance, which is then recovered by immersion in a liquid bath. Better encapsulation is likely the key to longer life.

Experiments performed using conducting polymer bilayer actuators demonstrate strain rates of 4 %·Hz, achieved in 30 to 60 micrometer thick polypyrrole films, with corresponding strain amplitudes of 0.2 %. Such strain rates are two orders of magnitude greater than have been previously reported. Power-to-mass ratios are estimated at 40 W·kg^{-1}, similar to that of mammalian skeletal muscle. Fast deflections are observed both in liquid and in air. In both cases, the strain rate is proportional to the square root of frequency, suggesting that diffusion is the rate-limiting factor on time scales of 0.05 s to 1 s.

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