Encapsulated Polypyrrole Actuators

John D. Madden, Ryan A. Cush, Tanya J. Kanigan, Colin J. Brenan and Ian W. Hunter

Abstract

Conducting polymer-based actuators undergo volumetric changes as they are oxidized or reduced, from which mechanical work can be obtained^{1,2}. Polypyrrole^{3-10,19} and polyaniline-based¹¹⁻¹⁴ actuators have attracted recent interest because of the high forces per cross-sectional area (stress) and relatively large strains generated at low activation voltages. However, with the notable exception of some bilayers^{5, 11, 13, 19}, the operation of these actuators has largely been constrained to bulk liquid environments. Operation out of solution is clearly desirable for many potential applications. Linear actuators that contract in length like muscle fibers¹⁵ fully exploit the high forces produced by conducting polymers. Results presented here demonstrate the operation in air of polypyrrole linear actuators. These actuators are capable of generating stresses exceeding those of mammalian skeletal muscle¹⁵.

Keywords: actuator, artificial muscle, polypyrrole, gel electrolyte.

Introduction

Actuators exhibiting muscle-like properties¹⁵ are important to the development of lifelike robots, artificial limbs, and other bio-mimetic devices. These properties include relatively high stress, and large strain linear actuation at moderate strain rates and efficiencies. While the development of conducting polymer-based actuators is still at an early stage, they already demonstrate some muscle-like properties. Work is derived from material dimensional changes in both conducting polymers and muscle. Stresses are fifteen times³ those generated in mammalian skeletal muscles¹⁵, and could reach 200 MPa, 600 times greater¹. Strains in conducting polymers are typically between 1 % and 10 %^{1-3,9,12,14}, compared to 20 % in muscle. Nevertheless, several obstacles to the widespread application of conducting polymer-based actuators remain, including relatively low strain rates, (< 0.03 %·Hz^{2,3,12-14}), and the requirement of operation in a liquid environment. In this paper the latter issue is addressed.

The use of a liquid environment stems from the mechanisms employed to stimulate polymer contraction. Chemical activation involves immersion of polymer actuators alternately in aqueous acids and bases¹². Electrochemical stimulation involves the use of electrolytes, which have in general been liquid-based. Liquid based electrolytes, and in particular polar solvents such as water and propylene carbonate offer environments that allow high ion mobility and concentration, and therefore are generally preferred over solids.

Several exceptions to the use of liquid environments exist. These exceptions have been restricted to bilayer actuators, in which a differential expansion between two thin, adjoining layers results in bending and force generation, as in bimetallic strips. In 1993 Pei reported a polypyrrole/ polyethylene bilayer as a chemical sensor, generating deflection upon exposure to ammonia gas⁵. Other bilayers operating out of solution are electrochemically activated, employing gel or encapsulated liquid electrolytes^{11,13,19}.

Bilayers are mechanical amplifiers, generating large deflections, but low forces. An important step in proving the value of conducting polymer actuators is to demonstrate a linear actuator operating in air, thereby fully exploiting the large forces per crosssectional area of which conducting polymers are capable. However, electrochemical activation of conducting polymers requires a cell, including the polymer as working electrode, an electrolyte, and a counter electrode. The challenge is to find an electrolyte whose mechanical stiffness does not impede the polymer contraction, while offering high ionic conductivity, and which can be readily encapsulated for operation out of bulk solution. Alternatives to the use of bulk liquid electrolytes include solid electrolytes, such as polyethylene oxide (PEO), gels and encapsulated liquids.

Solid electrolytes have the advantage of relatively easy construction. The electrolyte is sandwiched between the polymer and a counter electrode. Unfortunately, solid electrolytes suffer from low ionic conductivities¹⁶, and provide high stiffnesses against which the polymer actuator must work, reducing the available force and displacement. PEO, perhaps the most widely used solid electrolyte, has the further disadvantage that it only becomes significantly conductive at temperatures above $60 \, {}^{\circ}C^{16}$. For these reasons, solid electrolytes were not employed.

Liquids offer high conductivity and low mechanical interference, but must be sealed. It is also necessary to prevent electronic conduction between the polymer and the counter electrode, which requires some form of spacer separating them. Adding sealant and spacers not only complicates the manufacturing process, but these elements also provide mechanical impedance to actuator deformation. Gels offer moderately high ionic conductivity, and low mechanical impedance. They also provide sufficient stiffness to separate the actuator electrodes. It is for these reasons that gel electrolytes are chosen.

Experiment

A representation of the cross-sectional geometry of the actuators constructed, including the active polypyrrole film, the gel electrolyte and the counter electrode, is shown in Figure 1 (inset). The polypyrrole active layer is galvanostatically polymerized on a glassy carbon substrate from mixture of 0.06 M freshly distilled pyrrole monomer and 0.05 M tetraethylammonium hexafluorophosphate in propylene carbonate. Deposition takes place at -30 °C in a nitrogen atmosphere at a current density of 1.25 A·m⁻², following methods of Yamaura¹⁸. Film dimensions are typically 35 mm long x 6 mm wide x 40 to 100 µm thick. The resulting material has a density of 1.4×10^3 kg·m⁻³, a conductivity in the range of 1 to $3x10^4$ S·m⁻¹, a glassy modulus of 0.5 GPa (wet) and 1.0 GPa (dry), and a tensile strength of > 25 MPa. Two gels were tried, a PMMA-based gel¹⁷ and agar. Agar containing tetraethylammonium hexafluorophosphate salt produces the most repeatable results, as presented here. This was prepared by adding 1 g of agar (Aldrich, Milwaukee, WI) per 150 ml saturated (0.04 M) aqueous tetraethylammonium hexafluorophosphate solution, which is then heated to form a gel. A polyethylene film is sputter coated with a 400 nm thick gold layer to form the counter electrode.

In assembling an actuator, the polypyrrole film is held at each end by gold-coated clamps, as depicted in Figure 1. An approximately 100 μ m thick layer of gel electrolyte is applied to each side of the film. Strips of the counter electrode are wrapped around the gel-coated polypyrrole, with the gold contacting the gel. A strand of 75 μ m diameter gold wire forms the electrical contact between the counter electrode strips and the test circuit. Electrical contact to the film is made through the clamps.

Actuator displacements are applied via a stepper motor driven linear translation stage, film displacement being determined by the number of motor steps. A load cell measures force on the film. A current source is employed to drive an electrochemical reaction across the actuator cell. The apparatus is under software control from a workstation, interfacing with the actuator circuit via a data acquisition board. Actuator testing begins with the application of 2 MPa of tensile stress to the film. Following a short period (10 to 20 s), equi-amplitude cycles of positive and negative current are applied, with a brief period of no current between each change in polarity. The initial strain is then removed, returning the film to its original length. In the experiments presented force feedback is employed to maintain isotonic conditions (constant force), and the resulting displacements are recorded.

Results

Figure 2 shows the result of an isotonic test in which a 20 mA current is applied for 80 s, followed by a 10 s relaxation, followed in turn by the application of -20 mA. The applied stress is 2 MPa, as measured relative to the cross-sectional area of the polypyrrole film. When the full actuator cross-section is taken into account, the force per unit area is 0.5 MPa, 50 % larger than that of mammalian skeletal muscle. The total strain is just over 2 %. As has been demonstrated previously in polypyrrole-based actuators, strain is proportional to charge transferred into the polymer. The strain to charge ratio is 4.5×10^{-10} m³·C⁻¹, as calculated using the slope of the curve in Figure 2. Note that this corresponds to a volume change per charge (assuming isotropic expansion) of 2.2×10^{-28} m³ and 2×10^{-28} m³ respectively. Della Santa³ obtains a strain to charge ratio of 3×10^{-10} m³·C⁻¹ from polypyrrole films in aqueous solutions of sodium benzenesulfonate salt. Work using identically synthesized polypyrrole films¹⁹ activated in propylene carbonate solution results in a strain to charge ratio of 2.3×10^{-10} m³·C⁻¹. The similarity between the

strain to charge ratios observed in liquid and gel environments suggests that the gel's stiffness offers negligible mechanical impedance.

The strain rate of 0.03 %·Hz matches the highest reported^{3,9,12,14}. Strain rates and hence power to mass ratios are relatively low in conducting polymer actuators. The rates reported here, at 0.03 %·Hz, match the highest rates in the literature³, but are still three orders of magnitude lower than that of typical mammalian skeletal muscle. Further improvement may be obtained by studying the rate limiting mechanisms.

Force per cross-sectional area of the actuator is a function of both the force generated by the polymer, and the quantity of electrolyte required, as dictated by the geometry of the laminate structure. Since the electrolyte does not directly generate any force or displacement, keeping electrolyte volume to a minimum maximizes force per unit area. However, ions leaving the polymer must be solvated by the electrolyte, and vice-versa. Given the strain to charge ratio of $4.5 \times 10^{-10} \text{ m}^3 \cdot \text{C}^{-1}$, a 1 % strain generates an ionic concentration change of roughly 300 moles per m³ of polymer. In the gel/salt combination employed, concentration at saturation is 100 moles per m³ of gel. Therefore the gel layer should be several times the volume of the polymer layer in order to store and transfer the required number of ions to the actuator, and the force per cross-sectional area is correspondingly reduced. Further improvement may be obtained by employing gel/salt combinations that are capable of sustaining higher ionic concentrations.

Actuator lifetime is limited to several hours due to the drying of the agar gel, indicating that better encapsulation is required. The drying leads to stiffening of the gel and a reduction in ionic conductivity, which in turn lessen the displacement and force output by the actuator. Soaking in aqueous tetraethylammonium hexafluorophosphate solution leads to a restoration of response. In the current method of encapsulation, the gel is partially exposed to air. Sealing the cell to prevent water loss should increase lifetime.

A second factor affecting lifetime is the formation of bubbles at the counter-electrode. The bubble formation leads to peeling of the gold palladium counter electrode from the polyethylene films and to loss of contact between the counter electrode and the gel. Figure 3 demonstrates the consequences. In response to the application of $a \pm 20$ mA current a degradation of response is observed over five cycles. Prevention of such degradation may involve the use of alternate gel/salt combinations, which provide non-gas generating redox couples.

Conclusion

It is demonstrated that conducting polymer linear actuators may be operated out of solution. The strains, strain rates and strain to charge ratios are very similar to those observed in polypyrrole actuators operating in aqueous environments. Forces per cross-sectional area exceed those of mammalian skeletal muscle. Further work is required to improve actuator lifetime, which appears to be limited by gel drying and gas generation at the counter electrode. The operation of conducting polymer actuators outside of bulk liquid environments should help pave the way to broader application of this relatively new application of conjugated polymers.