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Direct Measurement of Extension and Force in Conductive Polymer Gel Actuators

David J. Irvin,[*,†] Steven H. Goods, and
LeRoy L. Whinnery[*]

Materials Chemistry and Materials Mechanics
Departments, Sandia National Laboratories,
Livermore, California 94550

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A large body of work exists that describes electrochemically driven swelling/deswelling of conductive polymers.[1] Our interest in these materials stems from their potential use as small-scale actuators, valves, or pumps in microsystems applications. A few papers have reported measurements of the tensile forces[2] and shear moduli[3] generated in preloaded thin films. However, none of the work in the literature has reported the direct measurement of the mechanical response of these materials to electrochemical stimulation. In particular, the free extension or closure forces (pressures) generated by these materials, when they are confined, must be well characterized in an unambiguous manner. In this work, we describe the synthesis of polythiophene-based conductive polymer gel actuators. Preliminary measurements of extension and force in one axis under an applied square wave pulse as well as the effect of varying the square wave pulse periodicity are reported.

The synthesis of the polythiophene-based polymer gels has been published, but the supporting references give only a general synthesis of the cross-linking agent 1,6-bis(2-thienyl)hexane (BTH).[4,5] We have included the complete synthesis in the Supporting Information. We believe that purity of the gel is important to ensure its long-term chemical and mechanical stability. Cylindrical specimens for the extension/force measurements reported here were punched from a flat sheet of the gel material.

The samples synthesized by this method were found to have varying morphology, as shown in a freeze-fracture sample (Figure 1). The bottom of the as-cast material, where gel deposition initiates, has a large aggregate structure and fewer pores, and the top has a very fine structure with much smaller pores. The density of solid polythiophene is about 1 g/cm^3. The

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[*] To whom correspondence should be addressed.

[†] Current address: U.S. Navy, NAWCWD Research Department, Chemistry & Materials Division, Code 4T4200D, China Lake, CA 93555-6100.

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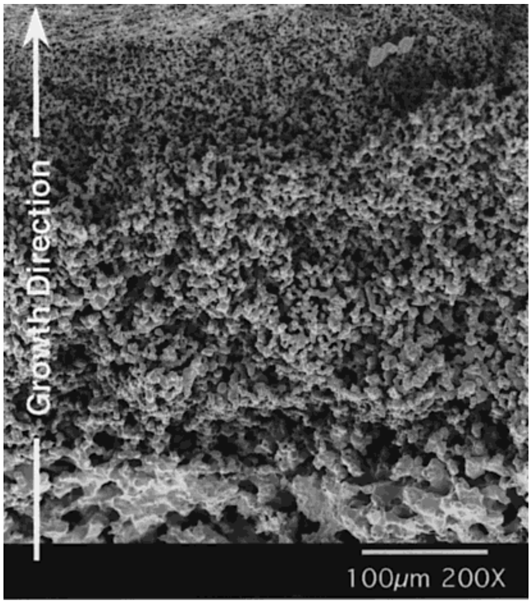

Figure 1. Morphology of a freeze-fracture surface of a polymer gel.

measured bulk density of these gels is ≈0.3 g/cm^3, indicating that they have a large free volume. This free volume is important because it will determine, in part, the rate at which solvent and ions will be able to flow into the gel.

The load and displacement characteristics of this polymer gel in acetonitrile with tetrabutylammonium perchlorate as the electrolyte have been characterized. Specimens for these measurements consisted of right cylinders (3-mm diameter × 2-mm tall) cut from a larger sheet of the gel. For each test, a cylinder was inserted into a porous polypropylene frit that had a machined bore slightly larger than the diameter of the specimen. The frit constrained the sides and bottom of the polymer sample while allowing for the influx of solvent and ion. A variety of working electrode geometries were examined. Most typically, a thin platinum wire (0.33 mm in diameter) was inserted into the bottom of the specimen along its cylindrical axis. Alternatively, a fine, wire mesh basket surrounding the specimen was used. The frit/specimen assembly was then placed in the custom electrochemical cell consisting of a glass cylinder and a PTFE spacer that was used to locate the polypropylene frit in a fixed position at the bottom of the cylinder. The spacer also had milled slots to locate the reference and counter electrodes. The testing apparatus allowed for either the measurement of the free displacement of the gel (that is, the unconstrained axial extension) or the measurement of force generation when the gel was fully constrained. The electrochemical cell assembly was then placed in an argon-purged boxed and samples were subjected to a square wave function with an oxidation pulse of 0.8 V vs Ag/Ag$^+$ for 1, 5, or 10 min, and a subsequent reduction pulse of −0.5 V vs Ag/Ag$^+$ for the same time resulting in a 2-, 10-, or 20-min period.

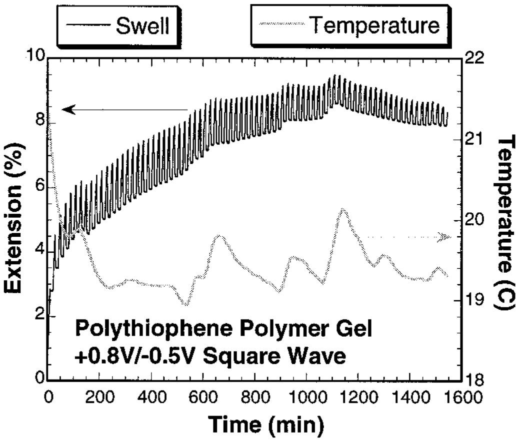

Figure 2. Swell response of polythiophene gel as a function of time for a 20-min period, +0.8/−0.5 V applied square wave potential. Hysteresis in expansion and contraction is evident from the progressive increase in the swell with increasing time. Fluctuation in the swell response correlate with small changes in the ambient cell temperature.

The extension of the gel along the cylindrical axis was measured using a precision linear displacement transducer from Microstrain Inc. (Burlington, VT). The absolute change in axial dimension is normalized to the initial height of the gel cylinder and is reported as "Extension (%)". Figure 2 shows the typical extension vs time behavior over a long period of time for a gel specimen driven under a +0.8/−0.5 V square wave function having a 20-min period. Over each interval (i.e., one oxidation pulse followed by one reduction pulse), the axial change in dimension is approximately 2%. The extension is not fully recovered at the end of each reduction pulse and therefore there is a net increase in the axial length of the specimen over >24 h of total testing. The discontinuities in the evolution of the specimen length correspond to minor variations in the ambient temperature. We believe that this effect is mostly an artifact resulting from thermal expansion and contraction of the test apparatus. The local temperature trace is also shown in Figure 2. Figure 3 shows the 300−400-min portion of this test in greater detail. Figure 3a shows both the axial extension as well as the applied voltage waveform. It is clear from this figure that, within each oxidation pulse, the axial extension is not linear with time. Rather, it falls monotonically with increasing pulse time. It can also be seen that the extension of the specimen does not commence instantaneously upon the onset of the oxidation pulse. Instead, there is an approximately 90-s lag time before the specimen begins to swell axially. Figure 3b shows the current generated in the cell over the same time period. The current waveform is quite reproducible, peaking at ≈8 mA at the onset of the reduction pulse and gradually approaching a minimum value of ca. −2 mA early in the oxidation pulse. Unlike the extension, the current switches instantaneously with the applied voltage waveform. Figure 4 shows the relationship between the change in the axial gel dimension and current flow in the cell during one arbitrary oxidation pulse. The trace represents a linear best fit through the data. Since the current is a measure of electron flow (and therefore counterion flow in the cell), it is clear that there is a direct relationship between ion flow, uptake into the specimen, and the resulting dimensional change of the gel.

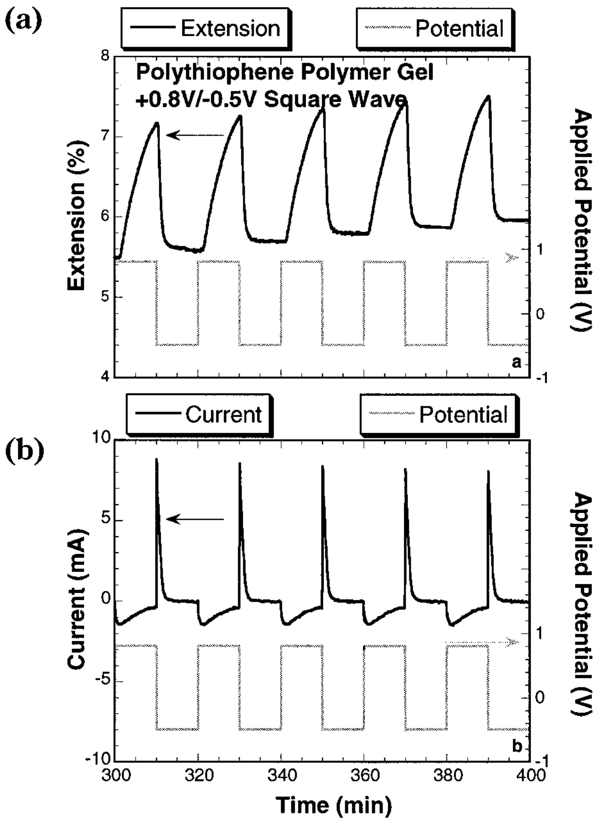

Figure 3. (a) Detail view of swell and cell current vs time for a portion of the test shown in Figure 2. (b) Applied potential waveform for the results shown in Figures 2 and 3a.

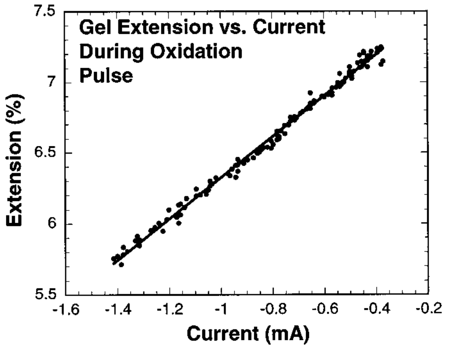

Figure 4. Relationship between gel extension and cell current for one oxidation pulse at approximately 300 min into the test shown in Figure 2. Trace through the data points is a linear curve fit ($R = 0.9965$).

The axial pressure generated by the expansion of the gel against a fixed surface was directly measured using a precision force transducer (Sensotec, Inc., Columbus, OH); results are shown in Figure 5. This measurement is equivalent to the closure pressures that would be generated if the gel were used as a valve. Given the large free volume of the gel, the pressure generation is surprisingly high, especially so for a specimen with a mass of only ≈6 mg. Pressure generation in the first few cycles is minimal as the gel expands to completely contact the transducer probe. After about three cycles, the generation of a mean pressure with increasing number of oxidation pulses reflects the hysteresis in the expansion/contraction behavior illustrated in Figures 2 and 3.

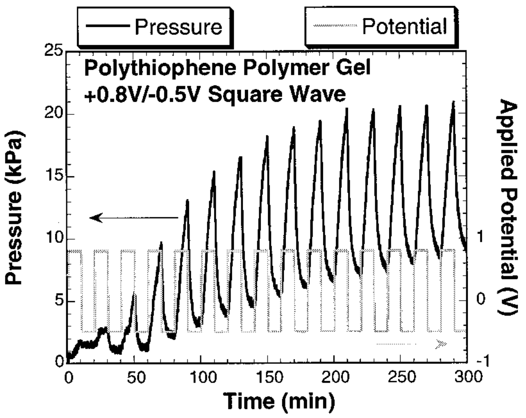

Figure 5. Axial pressure generation of polythiophene gel as a funcion of time for a 20-min period, +0.8/−0.5 V square wave potential. Hysteresis in expansion and contraction is reflected in the evolution of the mean pressure with increasing time.

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Supporting Information Available: The complete synthesis of the cross-linking agent 1,6-bis(1-thienyl)hexane (BTH) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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