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Direct Measurement of Extension and Force in Conductive Polymer Gel Actuators

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DIRECT MEASUREMENT OF EXTENSION AND FORCE IN CONDUCTIVE PLOYMER GEL ACTUATORS

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ABSTRACT

The synthesis of a polythiophene-based conductive polymer gel is described. Preliminary measurements of the electrochemically driven extension and force response of this gel are reported when driven under the action of an applied square-wave potential. Over each square wave interval (i.e., one oxidation pulse followed by one reduction pulse), the axial change in dimension was found to be approximately 2%. Some hysteresis was noted in that the cylindrical specimens did not return to their original axial dimension. The axial pressure generated by the expansion of the gel against a fixed surface was also measured and found to be on the order of 15 kPa

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DIRECT MEASUREMENT OF EXTENSION AND FORCE IN CONDUCTIVE POLYMER GEL ACTUATORS

I. Introduction

Many microdevices will use fluids to carry analytes to various stations for separation, modification, combination, detection, etc. It is generally recognized that integrated microsystems for DP applications, chemical sensing, and medical devices will not be possible without development of fast and efficient microactuators that can be used as valves and pumps. As analytical equipment is scaled down, as in chemlab-on-a-chip, mechanical structures such as pumps and valves must also decrease in size. It is often the case that macroscopically engineered mechanisms, electromechanical actuators for example, cannot be scaled down into a microdevice and still function in an acceptable manner. Thus, the development of microscopic “machines” having acceptable performance characteristics requires a new approach, employing entirely new technology and material science. In this regard, the use of conductive polymer gels lends itself well to microactuation. In essence, our approach is to employ the microscopic or molecular level actions within a material as the functional basis for a discrete “macroscopic” device such as a valve.

The basic premise is that a conductive polymer gel will change dimensions upon the application of a small potential (<1 Volt). The expansion and contraction results from a potential-induced change in the oxidation state of the polymer and the associated diffusion of charge balancing ions (and their coordinated solvent) moving into or out of the gel (Figure 1). As the polymer is oxidized, it forms positive charges that reside on the backbone of the polymer chain. Solvent coordinated anions diffuse into the polymer to balance the charge, thus increasing the dimensions of the sample. The osmotic pressure developed during the influx of solvent and ions is the driving force and the essential work producing effect. That only small applied potentials are required to induce the desired effect is an added benefit, since it reduces power consumption. As a result, system power requirements are reduced, as are oxidative side-products from electrochemical oxidation of oxygen and water.

While a large body of work exists that describes electrochemically driven swelling/deswelling of conductive polymers¹ only a few papers have reported measurements of the tensile forces² generated and shear moduli³ in pre-loaded thin films. None of the work in the literature, however, 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.

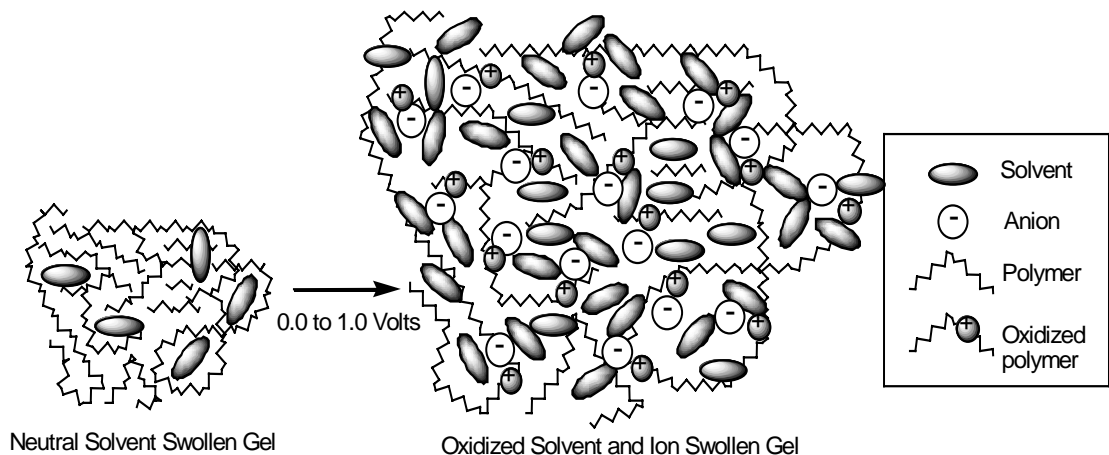


Figure 1. Neutral and oxidized conductive polymer gels.

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 are reported, as well as the effect of varying the square wave pulse periodicity.

II. Experimental Procedure

Gel Synthesis

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} The BTH was synthesized using a Ni-catalyst to cross-couple 3-bromothiophene and 1,6-diiodohexane.⁶ The 1,6-diiodohexane was dissolved in ether containing 2.1 equivalents of magnesium turnings under an argon purge. 1,2-Dibromoethane (0.2 eq in ether) was added slowly to allow control of the ether reflux. When the spontaneous reflux subsided, the reaction mixture was heated at reflux for 1h. The reaction mixture was then cooled with an ice bath and slowly transferred via polytetrafluoroethylene (PTFE) cannula to a chilled flask containing 3-bromothiophene (3 eq), and [1,3-bis(diphenylphosphino)propane]dichloronickel (II) (Ni(dppp)Cl₂)(0.09 eq) in ether, such that the temperature did not rise above 5°C. After the transfer was completed, the reaction was stirred at room temperature for 24h. The mixture was poured into a ten-fold excess of ice/1M HCl. The organic layer was washed with 1M HCl and water and dried over anhydrous NaHCO₃. The mixture was filtered, and the ether was removed by reduced pressure distillation. The remaining red oil was quickly distilled under vacuum to yield three fractions. The samples were refrigerated over 48h to yield white crystals in two of the fractions. The solid was collected by suction filtration and recrystallized to yield BTH. The structure was verified by ¹H and ¹³C NMR and GC-MS.

The gels were prepared as in the literature.⁷ Ferric chloride (2.3 eq) powder was placed in a reaction vessel and cold chloroform was added slowly to minimize disruption of the FeCl_3 . The vessel was then chilled to -30°C . After 2h, a solution of 3-octylthiophene (OT), BTH and CHCl_3 was added and the vessel was placed in a refrigerator ($4-5^\circ\text{C}$) for 4d. The supernant was then decanted from the resulting polymer mass. Methanol was added to the vessel to contract the chloroform-swollen gels. The polymer mass was then removed from the mold, placed in a Soxhlet thimble and extracted with hot methanol for 24h. The resulting material contained less than 0.4% iron as determined by elemental analysis and inductively coupled plasma mass spectroscopy (ICP-MS), indicative of the effectiveness of this purification method. We believe that purity of the gel is important to ensure its long term chemical and mechanical stability. It is also important to note that only methanol, a mild reducing agent, was necessary. Cylindrical specimens for the extension/force measurements reported here were punched from a flat sheet of the gel material.

Displacement and Force Measurements

For mechanical testing, specimens of the gel were cut into cylinders nominally 3 mm in diameter and 2 mm tall. The test apparatus for the displacement and force measurements is shown in Figure 2. For each test, a gel 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 have been used. 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 formed to surround the specimen, yields equivalent response. 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 entire electrochemical cell assembly was then placed in an argon-purged box for testing. The samples were subjected to a square wave function with an oxidation pulse of 0.8 V vs. Ag/Ag^+ for one, five, or ten minutes, and a subsequent reduction pulse of -0.5 V vs. Ag/Ag^+ for the same time resulting in a two, ten, or twenty minute period.

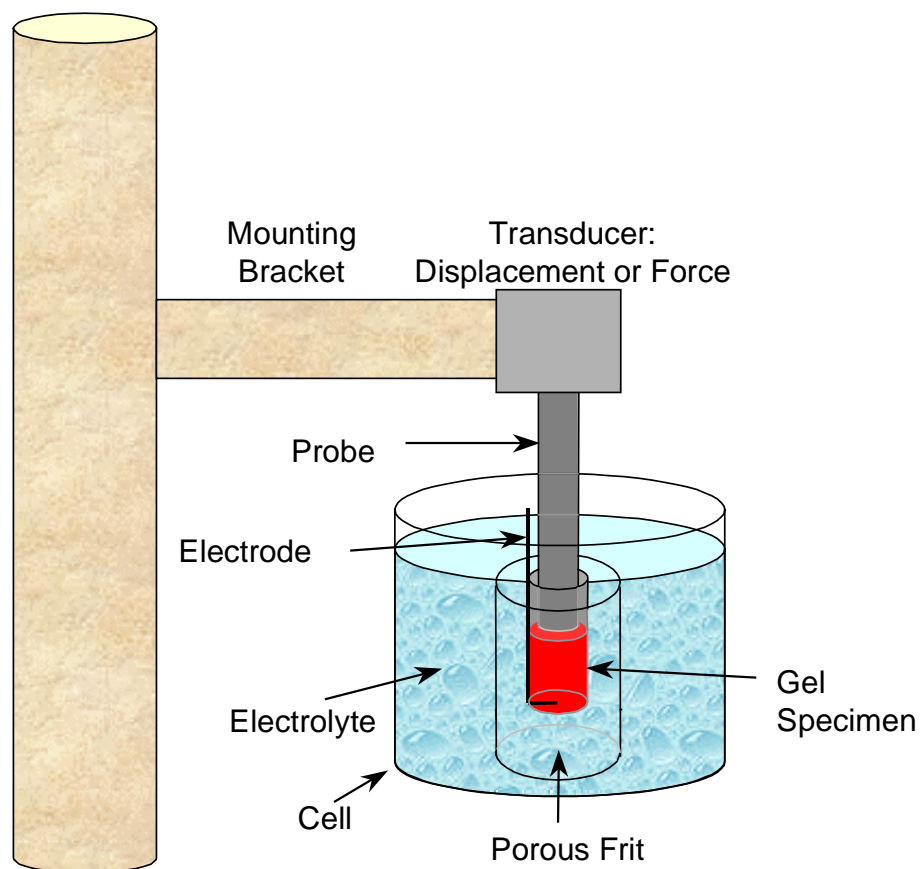


Figure 2. Schematic illustration of displacement/force measuring apparatus.

The extension of the gel along the cylindrical axis was measured using a precision linear displacement transducer obtained from Microstrain Inc. (Burlington, VT). Alternatively, the axial pressure generated by the expansion of the gel was directly measured using a precision force transducer (Sensotec, Inc., Columbus, OH).

III. Results

Gel Morphology

The samples synthesized by this method were found to have varying morphology as shown in a freeze-fracture sample (Figure 3). The bottom of the as-cast material, where gel deposition initiates, has a large aggregated structure and few pores, the top has a very fine structure with much smaller pores. The density of solid polythiophene is about 1 g/cm³. The measured bulk density of these gels is ~0.3 g/cm³ indicating that they have a large, overall, 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.

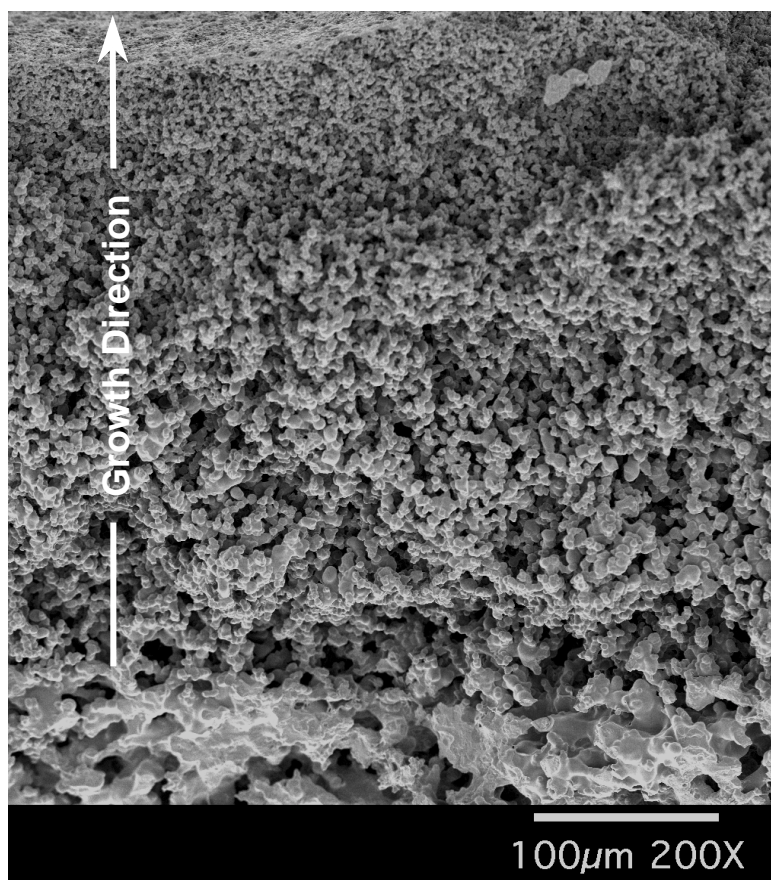


Figure 3. Morphology of freeze fracture surface of polymer gel.

Mechanical Property Measurements

The load and displacement characteristics of gel specimens having this morphology were characterized in the apparatus described above. For the displacement measurements, the absolute change in axial dimension was normalized to the initial height of the gel cylinder and is reported as “Extension (%)”. Figure 4 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 was approximately 2%. The extension was not fully recovered at the end of each reduction pulse and therefore there was a net increase in the axial length of the specimen over the > 24 hours of total testing. Indeed, the accumulated displacement resulted in a net axial swelling of approx. 8%. The discontinuities in the evolution of the specimen length correspond to minor variations in the ambient temperature. We believe that this effect was mostly an artifact resulting from thermal expansion and contraction of the test apparatus. The local temperature trace is also shown in Figure 4.

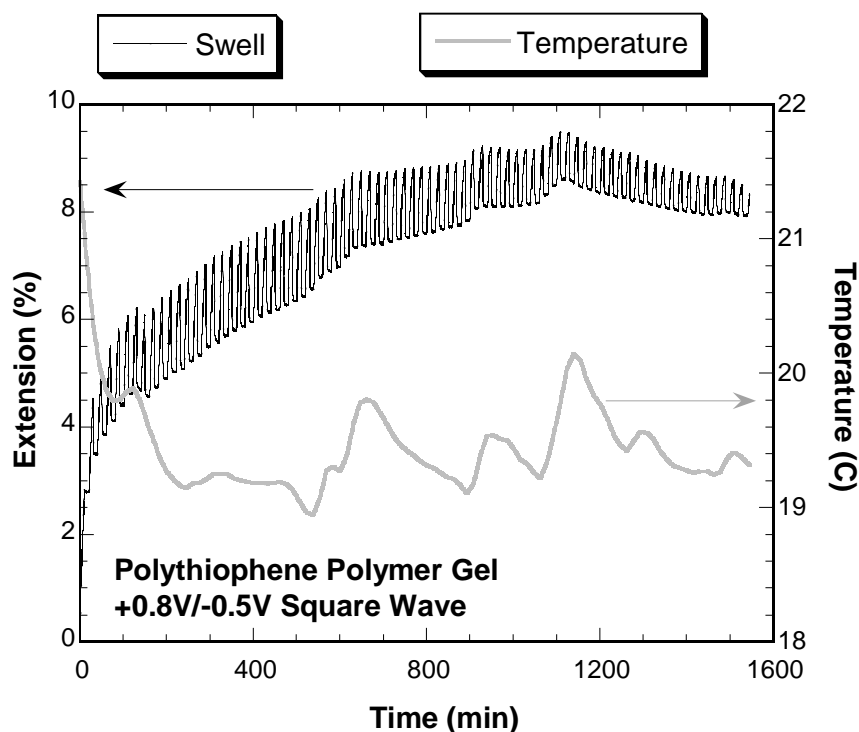


Figure 4. Swell response of polythiophene gel as a function of time for a 20 minute period, +0.8/-0.5V applied square wave potential. Hysteresis in expansion and contraction is evident from the progressive increase in the swell with increasing time. Perturbations in the swell response correlate with small changes in the ambient cell temperature.

Figure 5 shows the 300-400 minute portion of this test in greater detail. Figure 5a 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 was not linear with time. Rather, it fell monotonically with increasing pulse time. It can also be seen that the extension of the specimen did not commence instantaneously upon the onset of the oxidation pulse. Instead, there was an approximately 90 sec lag time before the specimen begins to swell axially. Figure 5b shows the current generated in the cell over the same time period. The current waveform was quite reproducible, peaking at ≈ 8 mA at the onset of the reduction pulse and gradually approaching a minimum value of ≈ -2 mA early in the oxidation pulse. We note that unlike the extension, the current switched instantaneously with the applied voltage waveform.

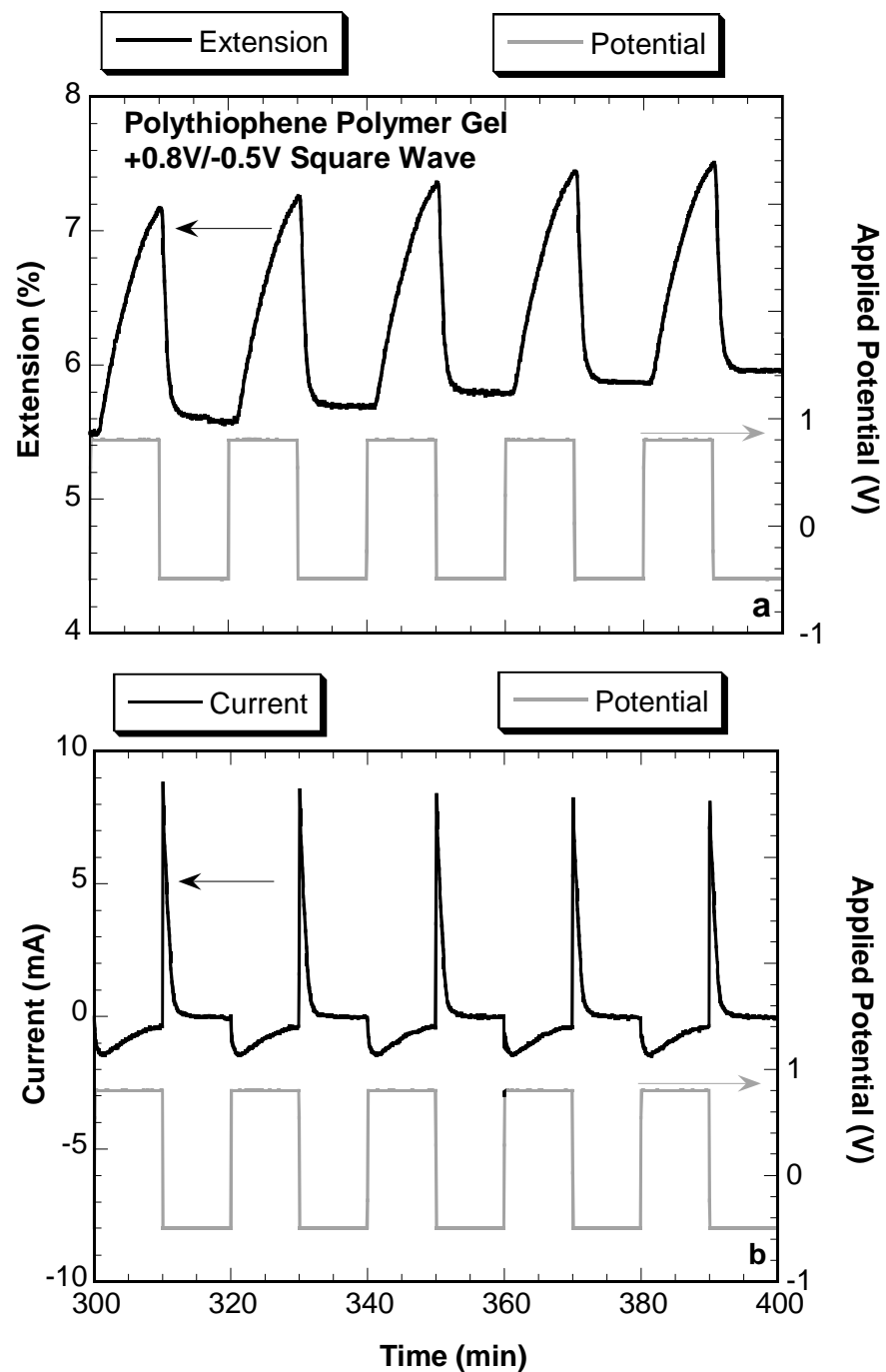


Figure 5. a) Detail view of swell and cell current vs time for a portion of the test shown in Figure 4. b) Current response of the cell for the applied square wave potential.

Figure 6 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 counter ion 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.

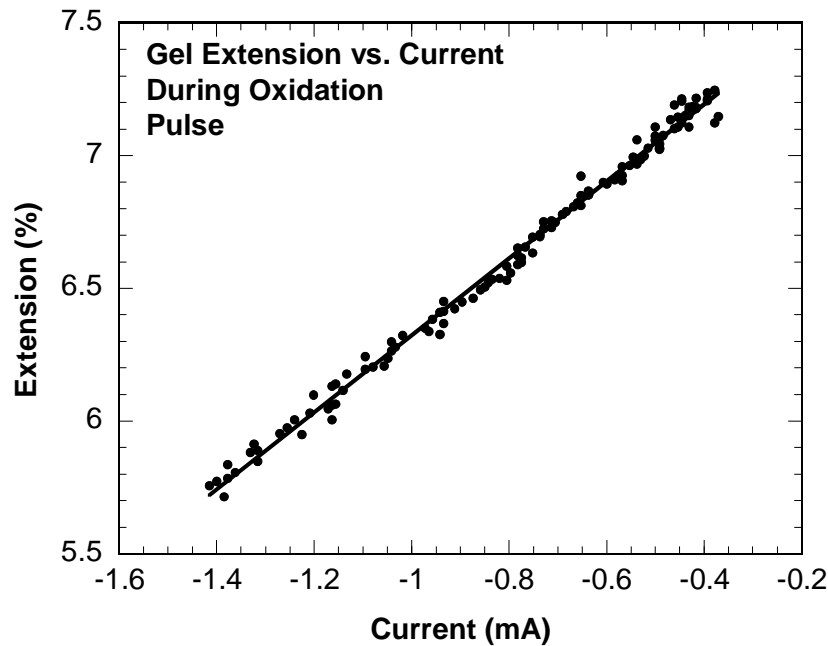


Figure 6. Relationship between gel extension and cell current for one oxidation pulse at approximately 300 minutes into the test shown in Figure 4. Trace through the data points is a linear curve fit ($R=0.9965$).

Lastly, the axial pressure generated by the expansion of the gel against a fixed surface was directly measured and the results are shown in Figure 7. Such a measurement is equivalent to the closure pressures that would be generated if the gel were used as a valve to seal an orifice. Pressure generation in the first few cycles was minimal as the gel expands to completely contact the transducer probe. After this initial conditioning, a cyclic pressure generation of about 15 kPa developed. Given the large free volume of the gel, the pressure generation was surprisingly high, especially so for a specimen with a mass of only ca. 6mg. The generation of a mean pressure with increasing number of oxidation pulses reflects the hysteresis in the expansion/contraction behavior illustrated in Figures 4 and 5.

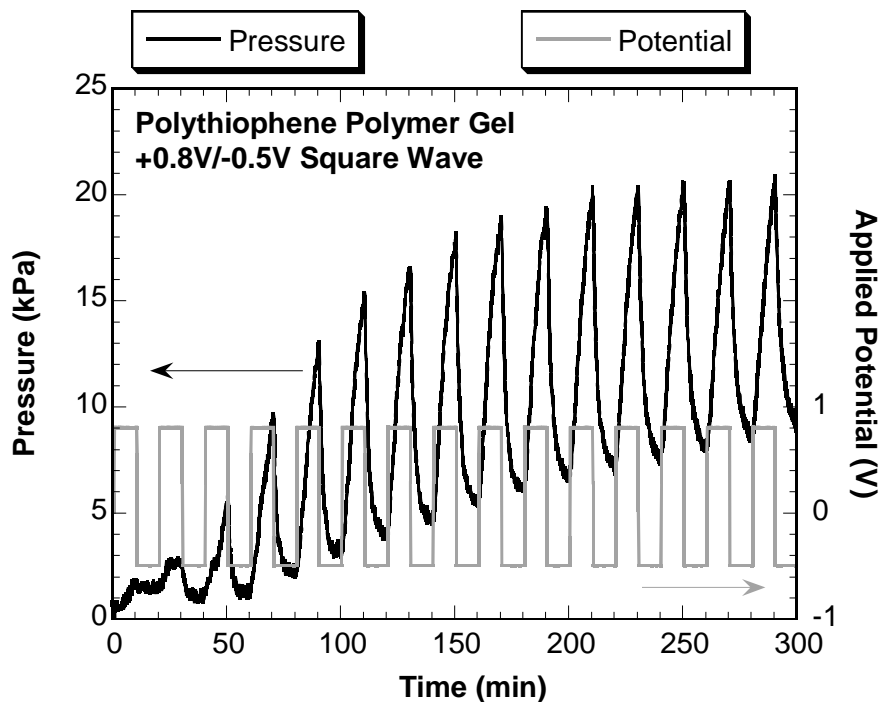


Figure 7. Axial pressure generation of polythiophene gel as a function of time for a 20 minute period, +0.8/-0.5V square wave potential. Hysteresis in expansion and contraction is reflected in the evolution of the mean pressure with increasing time.

IV. Conclusions

While much work needs to be done, the preliminary results presented here suggest that these kinds of conductive polymer gels may be useful in microsystem applications. For the particular gel chemistry examined, each oxidation/reduction cycle resulted in an axial change in dimension of approximately 2%. After a few conditioning cycles, the axial pressure generated by the expansion of the gel against a fixed surface was about 15 kPa. The hysteresis in both the extension and force generation poses some potential problems with regard to the continuous operation of gel-based devices although the solution to this may be found in refinements to the gel microstructure. Additional work will focus on this issue and on optimizing the gel microstructure to improve its response characteristics.

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