Electromechanical Properties of a Humido-Sensitive Conducting Polymer Film

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Received January 12, 2000; Revised Manuscript Received August 3, 2000

ABSTRACT: Polypyrrole films containing tetrafluoroborate were electrochemically synthesized, and stress generated in the film under application of an electric voltage was measured in air under various strains. It was found that the film generated contractile stress in response to the applied voltage that reached 6.1 MPa under 2 V, which was 4 orders of magnitude larger than its own weight. The mechanism was based on a dimensional change of the film that was expressed by two processes both caused by the Joule heating: one was the contraction due to the desorption of water vapor, and the other was the thermal expansion of polymer chains, which was different from electrochemical or chemical doping in an electrolyte solution or in a redox gas atmosphere. The generated stress under 2 V increased to 8.9 MPa upon stretching the film by 1%, which could be associated with the Young's modulus of the film rose due to the desorption of water vapor that plasticized polymer chains. The work capacity of the film increased as the applied voltage became higher and reached 48.2 kJ m^{-3} at 3 V, while the energy efficiency, defined as the ratio of work capacity to the electric energy, was on the order of 10^{-3}%.

Introduction

Conducting polymers have attracted considerable attention because dimensional changes resulting from electrochemical or chemical doping, characterized by the transportation of solvated ions between the inside of the polymer matrix and the surrounding electrolyte solution, electrostatic repulsion, and/or structural distortion through oxidation of polymers, can be applied to produce microactuators[1] or artificial muscles.[2−5] Most of them exhibit dimensional changes in an electrolyte solution or in a swollen state, while few reports have been investigated on solid-state polymers in a redox gas atmosphere[6] or that employ a polyelectrolyte solid or gel.[7−9]

In the preceding papers,[10−13] we have reported that electrochemically synthesized polypyrrole films undergo quick and intensive bending in ambient air as a result of an isotropic dimensional change due to the sorption of water vapor from one side of the film and have constructed a polymeric motor that works in air.[14] Furthermore, we have found that the polypyrrole film exhibits contraction in air under application of an electric voltage,[15] where the contraction was strongly affected by applied voltage and ambient humidity.[16]

Although the applied voltage plays a predominant role in causing a dimensional change of the film in air, little is known about changes in mechanical properties and work capacity for the polypyrrole film. In this paper, we have measured generated stress under various strains and the effects of applied voltage on Young's modulus, work capacity, and energy efficiency for the film have been investigated. This system is of interest not only in proposing a new class of electroresponsive conducting polymers but also for understanding of the electromechanical properties of humido-sensitive conducting polymers.

Experimental Section

Preparation of PPy Film. Pyrrole and propylene carbonate were purified by distillation before use. Tetraethylammonium tetrafluoroborate for use as an electrolyte was commercially available and used without further purification. Polypyrrole (PPy) films containing tetrafluoroborate (BF_4^-) were electrochemically synthesized by anodic oxidation of pyrrole in the presence of tetraethylammonium tetrafluoroborate. The pyrrole monomer and tetraethylammonium tetrafluoroborate were dissolved in propylene carbonate containing 1% v/v of water in concentrations of 0.06 and 0.05 mol L^{-1}, respectively. A constant current (0.125 mA cm^{-2}) was applied through a platinum plate (100 mm long, 50 mm wide, 0.1 mm thick) as anode and aluminum foil of 10 times in area as cathode with a potentiostat (HA-301, Hokutodenko) for 15 h at −20 °C. After polymerization, the PPy film was peeled from the platinum electrode, soaked in a large amount of propylene carbonate, and dried overnight in a vacuum. The film with a thickness of 30 μm had a composition of $PPy(BF_4)_{0.33}(H_2O)_{0.25}$, indicating that the doping ratio was 0.33 and the film contained 4.6% of moisture in air.

Measurements. The contractile stress generated in PPy film by application of an electric voltage was measured under isometric conditions with a tensile tester, Tensilon II (Orientec), where one end of the film (35 mm long, 5 mm wide, and 30 μm thick) was attached to a strain gauge and the other to a crosshead of the tensile tester. The strain of the film under free loading conditions was measured with a laser displacementometer, LB-080 (Keyence), where the strain of the film at 50% relative humidity (RH) was adjusted to zero. The voltage was applied to the film with a potentiostat, HA-301 (Hokutodenko), through copper wires attached to both ends of the film with silver paste. The temperature at the film surface was measured with an infrared thermometer, THI-500S (Tasco), and RH in the vicinity of the film was measured with a hygrometer, MC-P (Panametrics), the probe of which was located 1 mm from the film surface. The isothermal sorption of water vapor to the PPy film was measured at 25 °C with a Belsorp18 (Bel Japan). Prior to the measurements, the film of 43.4 mg was dried in a vacuum at room temperature for more than 10 h until the weight reached a constant. The degree of sorption, defined as the weight ratio between sorbed water and dry polymer, was measured at each water vapor pressure after reaching the equilibrium (usually it took about

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10.1021/ma0000531 CCC: $19.00

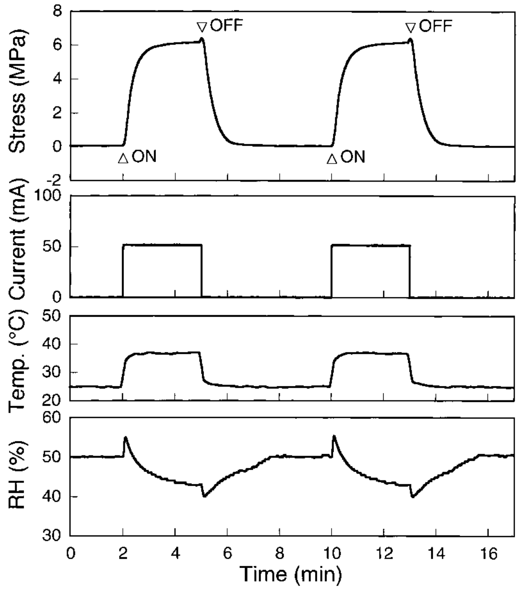

Figure 1. Time profiles of contractile stress, electric current, surface temperature of the PPy film, and RH in the vicinity of the film surface under 2 V measured at 25 °C under 50% RH.

500 s). The thermal contraction and expansion of the film were measured by a thermal mechanical analysis with a TMA8140C (Rigaku) in air of 50% RH and in a vacuum at a heating rate of 5 °C min^{-1} under a constant tension of 49 kPa that was the minimal value to tense the film.

Results and Discussion

Generation of Stress under Electric Voltage. Figure 1 shows time profiles of the contractile stress, electric current, surface temperature of the PPy film, and RH in the vicinity of the film surface. When dc 2 V is applied to the film under the thermostatic conditions (25 °C, 50% RH), the film generates contractile stress repeatedly in response to the applied voltage. The stress reaches 6.1 MPa, corresponding to an equivalent contractile force of 93 gf, which is 4 orders of magnitude larger than its own weight (7.6 mg) and is nearly 20 times that of skeletal muscle in animals (0.3 MPa).[17] The value is comparable to that generated by electrochemical doping of conducting polymers in an electrolyte solution.[18,19] Here, the PPy film generates the stress in ambient air without the use of an electrolyte solution or a redox gas, indicating that the mechanism differs from the electrochemical doping. The electric current passing through the film is 52 mA, and the temperature at the film surface increases from 25 to 36 °C. It is noted that RH in the vicinity of the film surface abruptly rises by the applied voltage, demonstrating that water vapor sorbed in the film desorbs and scatters into ambient air, while a gradual decrease of RH will be due to the temperature rise near the film because saturated water vapor pressure increases with the temperature.[16] On the other hand, a drop of the RH, when the 2 V is turned off, can be explained as the resorption of water vapor from the air surrounding the film. Because the changes in the stress coincide with that in the RH, the generation of the stress is associated with contraction of the film due to the desorption of water vapor.

A clear indication of the importance of sorption of water vapor on dimensional change of the film is demonstrated in Figure 2. Note that water content and strain of the film are measured individually at each RH, where the strain at 50% RH, corresponding to 6.1% of water content, is adjusted to zero. One can see the film undergoes linear elongation with increasing water content that is proportional to ambient RH. Assuming that the dimensional change of the film occurs isotropically, the volume change in the RH range from 10% to 90% is calculated to be 0.54 × 10^{-3} cm^3, which corresponds to 10.4% of volume of the dry film (5.25 × 10^{-3} cm^3). On the other hand, the amount of water sorbed to the film in the same RH range is 0.56 × 10^{-3} g calculated using the volume and density of the dry film (1.452 g cm^{-3}). Thus, the apparent density of water in the film is estimated as 1.02 g cm^{-3}, which is close to that of liquid water. DSC thermograms of the film, however, exhibited no apparent endothermic peak relating to the melting of freezable liquid water in the heating trace up to the water content of 14%.[20] This fact suggests that the water sorbed in the film behaves as a nonfreezing water bound to the polymer chains and/or dopant ions. The average number of bound water per PPy repeated unit is calculated as 0.32 at 50% RH (6.1% of water content) and 0.5 at 90% RH (9.5% of water content).

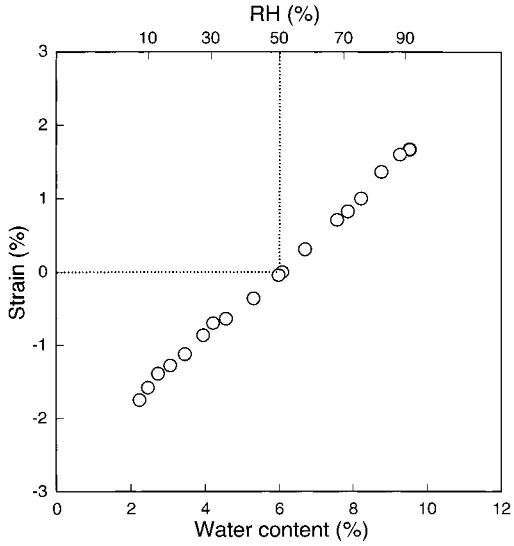

Figure 2. Sorption-induced strain of the PPy film measured at 25 °C. Note that water content and strain of the film were measured individually at each RH, and the strain of the film at 50% RH (6.1% of water content) was adjusted to zero.

To clarify the role and effect of the applied voltage on electroresponsive behavior of the film in more detail, the generated stress is measured under various voltages, and the results are shown in Figure 3. The electric current is proportional to the voltage, and the resistance of the film calculated from the slope of the current–voltage relationship is 35 Ω, which is consistent with the value expected from the conductivity measured by a normal four-probe method (67 S cm^{-1}), demonstrating that the film is ohmic in the experimental range of the voltage. The temperature of the film rises with the square of voltage, indicative of the Joule heating. On the other hand, the electrically generated stress increases with the applied voltage and reaches 9.6 MPa at 3 V, while a further increase of the voltage results in a decrease of the value.

A similar tendency is observed in the contractile behavior of the film. Figure 4 shows strain of the PPy film under free loading conditions in air of 50% RH and in a vacuum under different temperatures of the film

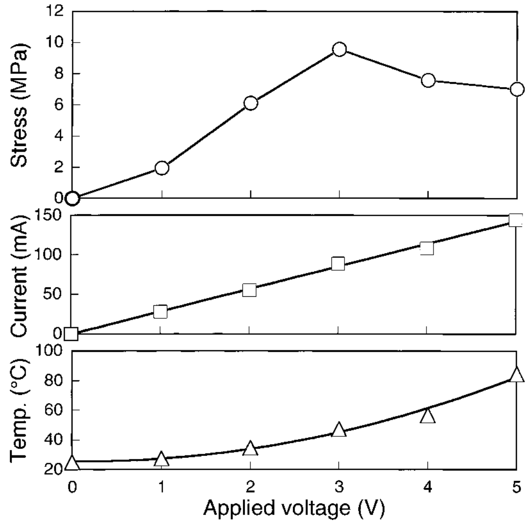

Figure 3. Voltage dependence of contractile stress, electric current, and surface temperature of the PPy film measured at 25 °C under 50% RH.

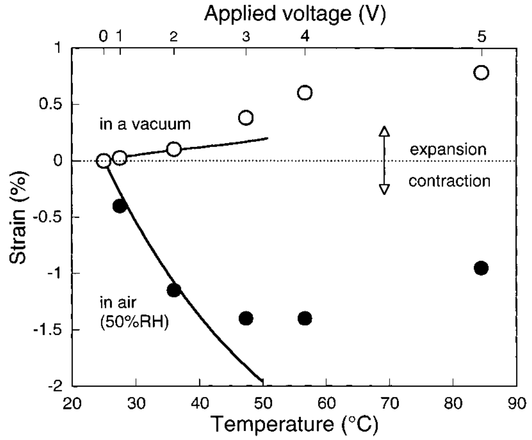

Figure 4. Strain of the PPy film under free loading conditions in air (50% RH at 25 °C) and in a vacuum under different temperatures of the film measured at various applied voltages. The strain in a vacuum was measured after the strain reached a constant on exposing to a vacuum, where the initial contraction of the film was about 2.6%. The thermal contraction and expansion of the film in air and in a vacuum without the electric field measured by thermal mechanical analysis were represented as solid lines.

measured at various applied voltages, where the results of the thermal mechanical analysis without the electric field are represented as solid lines. It can be seen that the degree of contraction in air tends to level off at 3−4 V and decreases at 5 V, which is consistent with the results of the contractile stress in Figure 3. In contrast, the film in a vacuum undergoes elongation that increases as the applied voltage becomes higher, where the film significantly contracts by exposing to a vacuum due to the desorption of water vapor by about 2.6%. It is noted that the thermal contraction and expansion of the film without the electric field obtained by the thermal mechanical analysis coincide with the experimental data at voltages lower than 2 V. This demonstrates that the apparent strain of the film can be expressed by two processes both caused by the Joule heating: one is the contraction due to the desorption of water vapor, and the other is thermal expansion of polymer chains. Therefore, the size or shape of the film should affect the electroresponsive behavior of the PPy film because the electric current and bulk resistance of the specimen characterize the Joule heating. On the other hand, at voltages higher than 3 V, the contraction of the film measured in air is smaller compared with the thermal contraction, which may arise from the fact that the expansion of the film in a vacuum remarkably increases above 3 V. Since the thermal expansion coefficient of the film is calculated as 7.25×10^{-5} °C^{-1} in the temperature range from 25 to 50 °C, the expansion at voltages higher than 3 V is still larger even taking account of the ununiformity of a temperature rise by the local Joule heating. Ouyang and Li[21] investigated that an application of voltage higher than 3 V brought about a shift of vis and NIR absorption spectra of PPy films to longer wavelength and enhancement of electrical conductivity, indicating that the apparent π-conjugation length increased. In the present system, however, the current−voltage relationship is ohmic as indicated in Figure 3; in other words, the electrical conductivity is almost constant in the experimental range of the applied voltage. In consideration of these results, the inconsistent of the strain with the thermal expansion may be ascribed to the structural distortion of polymer chains induced by the applied voltage or current, but the detailed mechanism is still under debate.

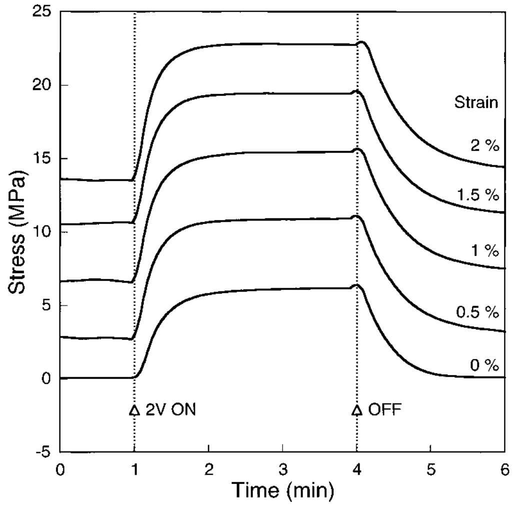

Figure 5. Changes in the stress generated by application of 2 V under various strains measured at 25 °C under 50% RH.

Strain Enhancement of Generated Stress. Upon stretching the film by bringing down the crosshead of the tensile tester at a constant speed, 2 mm min^{-1}, the stress increases with the strain due to the elastic nature of the film, while stress relaxation occurs after the crosshead is stopped. For example, when the crosshead has been stopped after stretching the film by up to 2%, the stress abruptly drops from 14.9 to 14.2 MPa and reaches a constant value of 13.6 MPa after 5 min. It is seen from Figure 5, when 2 V is applied to the film after the stress reaches a constant at each strain, the stress increases reversibly under the electric field. Interestingly, the stress generated, defined as the difference of the stress under 2 V from that without the electric field, increases by stretching the film. As shown in Figure 6, the generated stress increases from 6.1 to 9 MPa by stretching and tends to level off at strains larger than 1%. This implies that the film amplifies the contractile stress in response to the strain, suggesting a positive feedback mechanism. However, no notable changes in the electric current, surface temperature of the film, and RH in the vicinity of the film surface are observed in this strain range, suggesting that the strain enhance-

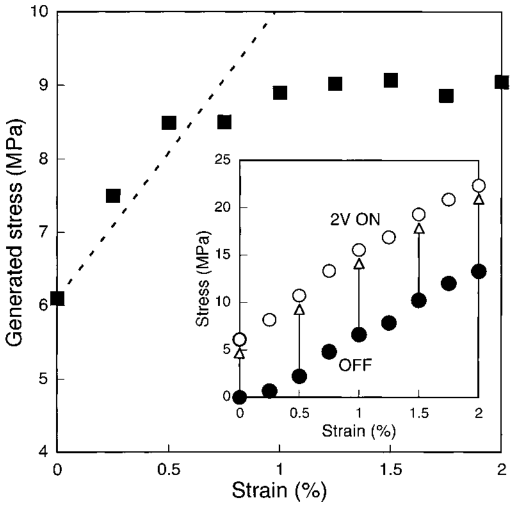

Figure 6. Strain dependence of the generated stress defined as the difference of the stress between 2 and 0 V measured at 25 °C under 50% RH.

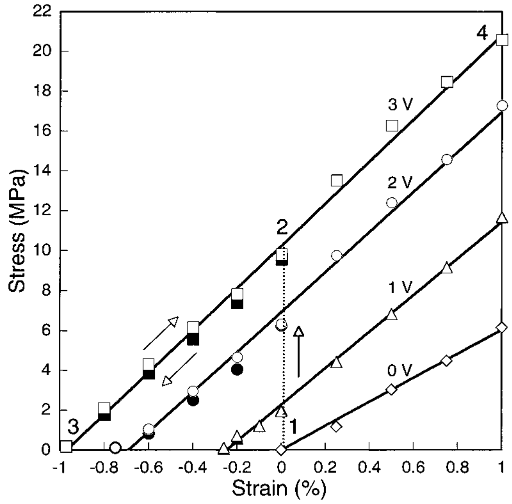

Figure 7. Stress–strain relationship for the PPy film under various applied voltages where the strain of the film at 25 °C under 50% RH without electric field was adjusted to zero. The voltage was applied to the film at zero tension (path 1–2). The film was then loosened so as to make the film contract until the stress becomes almost zero (path 2–3, filled symbols) and was stretched again by up to 1% (path 3–2–4, open symbols).

Table 1. Contractile Stress at $\gamma = 0$ ($\sigma_{e,0}$), Degree of Contraction at $\sigma = 0$ (γ_e), and Young's Modulus (E) for PPy Film under Various Voltages Measured at 25 °C under 50 % RH

voltage (V)	$\sigma_{e,0}$ (MPa)	γ_e (%)	E (GPa)
0			0.60
1	2.0	0.25	0.92
2	6.1	0.70	1.00
3	9.8	0.96	1.06

ment of the generated stress is not due to a structural change such as orientation of polymer chains in the stretching direction but to a change in the elasticity of the film under the voltage applied.

Assuming that the deformation of the film is elastic, the contractile stress at 0 V (σ) and under electric voltage (σ_e) at the strain of γ are respectively given by

$$\sigma = E_0 \gamma \tag{1}$$

$$\sigma_e = E_e \frac{\gamma + \gamma_e}{1 - \gamma_e} \tag{2}$$

where E_0 and E_e are Young's moduli of the film at 0 V and under electric voltage, respectively, and γ_e is the free loading contraction of the film under the voltage. Thus, the generated stress ($\Delta\sigma_e$), defined as the difference between σ_e and σ, is given by

$$\Delta\sigma_e = \frac{E_e \gamma_e}{1 - \gamma_e} + \frac{\{E_e - E_0(1 - \gamma_e)\}\gamma}{1 - \gamma_e} \tag{3}$$

If $\gamma_e \ll 1$, the equation can be approximated to

$$\Delta\sigma_e = E_e \gamma_e + (E_e - E_0)\gamma \tag{4}$$

which reveals that the $\Delta\sigma_e$ increases with the γ if $E_e > E_0$.

For evaluation of this equation, the equilibrated stress at each strain is measured under various applied voltages, and the results are shown in Figure 7, where the strain is calculated using the initial length of the film (35 mm) at 25 °C under 50% RH at 0 V. First, a voltage is applied to the film at zero tension under isometric conditions, leading to generate the contractile stress as indicated in Figure 1 (path 1–2). The film is then loosened stepwise by a strain of 0.2 so as to make the film contract until the stress becomes almost zero (path 2–3, filled symbols) and is again stretched by up to 1% (path 3–2–4, open symbols). It is found that the values of the stress in the processes of 2–3 and 3–2 at each strain are substantially the same under various applied voltages, demonstrating that the deformation of the film is reversible. The stress at $\gamma = 0$ and the strain at $\sigma = 0$ represent the generated stress without stretching ($\sigma_{e,0}$) and free loading contraction of the film under the electric voltage (γ_e), respectively. Furthermore, the stress is proportional to the strain at each applied voltage, indicating that the deformation of the film occurs elastically, where the increase in the applied voltage not only shifts the strain at which the stress begins to rise toward the negative strain side but also increases the slope of the plot. The Young's modulus of the film (E) can be calculated from the slope of the stress–strain relationship by assuming the cross-sectional area of the film is nearly constant because the γ_e values are very small, about 1%. The parameters obtained are summarized in Table 1. The values of $\sigma_{e,0}$ and γ_e increase as the applied voltage becomes higher, which are consistent with the data shown in Figures 3 and 4, demonstrating that the stress generation–contraction process is reversible. On the other hand, the Young's modulus of the film at 0 V is 0.6 GPa, which is 4 orders of magnitude higher than for swollen gels[22] and is comparable to that of undrawn commercial polymers.[23] It should be noted that the E rises with the applied voltage and achieves 1 GPa under 2 V, indicative of an increase of the value by 67%. This can be interpreted in terms of the plasticizing effect of water molecules[18] that may facilitate the motion of polymer chains to lower the elasticity of the film. In fact, tensile properties of the film are strongly affected by the water content: The Young's modulus at 50% RH (6.1% of water content) decreases to nearly half at 90% RH (9.5% of water content) though the sorption-induced dimensional change of the film is only 1.7% (Figure 2), whereas the elongation at break increases with the water content.

Table 2. Volumetric Work Capacity (*W*), Electric Current (*I*), and Energy Efficiency (η_{eff}) for PPy Film under Various Voltages Measured at 25 °C under 50 % RH

voltage (V)	*W* (kJ m^{-3})	*I* (mA)	η_{eff}[a] (%)
1	2.4	27.8	1.5×10^{-3}
2	21.4	51.5	3.6×10^{-3}
3	48.2	77.8	3.6×10^{-3}

[a] Calculated using the typical response time of 30 s.

Using the parameters of the E_0, E_e, and γ_e in Table 1, the $\Delta\sigma_e$ is calculated from the eq 4, and the result is represented in Figure 6 as a broken line. A good coincidence with the experimental data is obtained at strains lower than 1%. On the other hand, a further stretching of the film results in a saturation of the value, which will be associated with the plastic flow of PPy chains. If the film is stretched by 2%, it does not recover to the initial length even after removing the strain where the residual strain is 0.44%. These experimental results allow us to consider that the strain enhancement of the generated stress is attributed to the increase of the Young's modulus value under application of the voltage that reveals in the strain range at which the deformation of film occurs elastically.

Work Capacity and Energy Efficiency for PPy Film. These characteristics of the PPy film are capable of producing mechanical work in air by subjecting the film to the ideal stress generation−contraction cyclic process in Figure 7. At path 1−2, the film charges contractile force as elastic energy. The tensed film then releases the elastic energy as work by contracting reversibly along the stress−strain line under the applied voltage from maximum tension to near zero (path 2−3). After removing the applied voltage, the cycle is then closed by equilibrating the contracted film on exposure to air, where the film expands to the initial length owing to the resorption of water vapor (path 3−1). Thus, the area below the stress−strain line represents the volumetric work capacity (*W*) during the process 1−2−3−1 as follows:

$$W = \frac{1}{2}\sigma_{e,0}\gamma_e \qquad (5)$$

The results are shown in Table 2. A marked rise in the *W* is observed as the applied voltage becomes higher and the value reaches 48.2 kJ m^{-3} under 3 V, which is much higher than in muscles (0.8 kJ m^{-3}) and comparable to that generated during the electrochemical doping−dedoping cycle for various conducting polymers.[19,24] It is obvious that the *W* increases by stretching the film, for example, the value under 3 V at strain of 1% attains 381 kJ m^{-3}.

If we define the energy efficiency (η_{eff}) as the ratio of work capacity to the electric energy, we obtain the η_{eff} using the volume of the film ($V = 5.25 \times 10^{-9}$ m^3) as follows:

$$\eta_{\mathrm{eff}} = \frac{WV}{EIt} \times 100 \qquad (6)$$

where *E*, *I*, and *t* are applied voltage, electric current, and typical response time, about 30 s, respectively. It is seen from Table 2 that the values of η_{eff} are on the order of 10^{-3}% regardless of the applied voltage, which is much smaller compared with electrical motors or mechanical engines. This will arise from the fact that almost of the electric energy is dissipated as the heat through the Joule heating and/or the long response time because that in muscles is 0.2−0.3 s.

We should emphasize here that the PPy film exhibits a similar performance and work capacity as that driven by the electrochemical or chemical doping. Unlike in the conducting polymers based on the electrochemical doping, this system can serve as a new type of electrically driven muscle that works in air without using an electrolyte solution or counter and reference electrodes, where the applied voltage is capable of controlling the sorption equilibrium to desorb water vapor from the film. Furthermore, this system can work at voltages 1 or 2 orders of magnitude lower than piezoelectric or electrostatic actuators because the dimensional change is owing to the electric current but the electric field. Moreover, various conducting polymers or their derivatives that undergo dimensional changes due to the sorption of water vapor can be employed on the same principle.

Acknowledgment. This research was supported in part by Grant-in-Aid for the Scientific Research from the Ministry of Education, Science and Culture of Japan.

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