

Conducting polymer soft actuators based on polypyrrole films

-Energy conversion efficiency-

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ABSTRACT

Electrochemomechanical deformation (ECMD) of conducting polymers can be utilized as soft actuators or transducers of electric power to mechanical work. Polypyrrole (PPy) films, which were electrodeposited from methyl benzoate solution of tetrabutylammonium (TBA) trifluoromethanesulfonate, TBACF₃SO₃ were employed to investigate the energy conversion efficiency. The films are known having high tensile strength, large strain and stress in ECMD. The current responses as the function of load stress under constant applied potentials vs. a reference electrode were studied in various electrolytes. Reduction currents increased with increasing the load stress for contraction of the film (lifting weights) as well as the oxidation current (expansion), indicating that the electrical input was sensing the load hung on the actuators. During the contraction, the conversion efficiency was estimated from the mechanical work energy. The maximum work energy-per-cycle was 140 kJ/m³ at maximum. It has been found that the most of electrical input was stored, as in a battery, hence, the energy conversion efficiencies are very small (less than 0.25 %). The large consumed electrical energy beside stored is discussed.

Keywords: soft actuators, conducting polymers, polypyrrole, electrochemomechanical deformation, energy conversion efficiency.

1. INTRODUCTION

Upon oxidation the electrical conductivity of conducting polymers increases to a level of metals, while keeping the flexibility of polymeric materials. It is also known that conducting polymers swell and shrink upon electrochemical oxidation and reduction [1-5], respectively. The swelling is induced by some combination of the insertion of bulky ions and the change of polymer conformation due to the delocalization of π -electron upon oxidation. We have named this process electrochemomechanical deformation (ECMD)[2]. If the magnitudes of strain and stress are

comparable to or larger than those of skeleton muscles, then the ECMD can be utilized as artificial muscles or soft actuators.

Among various materials for soft actuators [1,6-10], conducting polymers are the most promising materials from the view point of low operating voltage and large stress, though the strain and the response times were original poor, making practical application difficult [2-5]. Amongst conducting polymers, polypyrrole (PPy) is the most investigated since PPy is electrochemically active over a wide range of pH from acid to base and easy to prepare. In the development of conducting polymer actuators, efforts have been mostly paid to improving the strain and response time[11-18].The peak strain, stress and strain rate of PPy films so far are 39 %, 22-34 MPa and 11%/s[11-19], respectively, which can be compared with those of skeleton muscles being approximately 30%, 0.4MPa and 0.1 s, respectively. High voltage application to a PPy film [20] had improved the response time, avoiding the serious degradation of the film by shaping voltage forms.

Other important factors for the better performance of actuators are the energy conversion and durability (cycle life). Spinks and Truong [21] calculated actuation behaviours based on working against isotonic actuation and working against restoring spring. They discussed how the actuator strain and work-per-cycle depended on the elastic modulus, which was varied by electrical stimulus. Madden et al. explored the load and time dependence of strain and charge in ECMD of PPy[19]. They found that the impedance dropped as load was increased, indicating that the electrical response changes upon changing of load and history of actuation. Otero and Cortes [22] reported that a triple layered bending PPy actuator with two electrical terminals had the sensing ability of temperature, concentration of electrolyte and load. The variation of these factors was monitored by the change of applied potential under the operation of galvanostatic mode. Madden et al. [23] examined also the creep and cycle life of PPy films for both passive mechanical stress and active ECMD under load to elucidate the degradation mechanisms. However, little has been studied on the problem of energy conversion efficiency from electrical input to mechanical output, except for a brief discussion[24].

In this paper, preliminary results on the energy conversion efficiency of PPy actuators are mentioned. The electrical responses of PPy actuators operated under load stress of weights in various electrolytes were monitored. In our case, a stepwise constant voltage vs. a reference electrode was applied to the actuator, the magnitude of observed reduction (contraction) currents strictly depended on the loads. By assuming that an increased current was due to the increased load stress, then the fraction of the increased electrical energy was assumed to be consumed to lift the load weights. Mechanical out put energy was estimated from the lifted distance and mass of weights under gravity.

As pointed out by Madden et al. [19] the strain to charge ratio were almost constant over wide range of loads, though the voltage depended strongly on loads as to drop of impedance. The drop of impedance should result in the increase of current under the constant voltage mode operation of actuator. We will discuss the electrical energy consumption and gain of mechanical work from the present experimental results.

2. ECMD IN CONDUCTING POLYMERS

By the electrochemical oxidation of conducting polymers, electrons are extracted from the π -electron systems of conducting polymers. The positive charge delocalizes along the backbone of the polymer chain, resulting in extension of polymer due to the conformation change of polymer backbone. An equal number of bulky anions in electrolyte solution is inserted in the polymer matrix, resulting in the swelling, since the volume of electron is negligible compared with anions. Upon electrochemical reduction of the film, the anions are released to the electrolyte solution and the film shrinks to the original volume. The electrochemical cycles are reversibly controlled by changing the polarity of applied voltage between the conducting polymer and counter electrode. Thus expansion of film upon oxidation is named as anion driven ECMD [10, 11], where anions are involved in doping and dedoping processes. It is believed that employment of larger anions results in larger strain, however, the larger the anion gives slower ECMD response.

If anions are entangled and immobilized in the conducting polymer matrix during electrochemical reduction, cations are doped to compensate anions instead of anions being released [25]. Then the film swells. This scheme occurs when extremely large anions like dodecylbenzene sulfonic (DBS) acid are employed for the electrodeposition of PPy film [12,13,26]. Doping and dedoping of cations during reduction and oxidation, respectively, are named as cation driven ECMD[12,13,26].

Conducting polymer films are stiff in the oxidized state compared with that of neutral state [20,21,27,28], because of the strong interaction between ions and the delocalized π -electron systems in the oxidized state. When soft and flexible materials are utilized, the actuator does work to pull up weight during the contraction like natural muscles, and does not work to push up. Therefore as stated by Spinks et al.[21], it is desirable to use soft materials at expanded state and to be stiff in the contracted state to maximize work density. However, most of previous report on ECMD behaviours as the function of load stress was done for anion driven PPy films, since the film shows the larger strain and stress in ECMD and is easy to analyze. In the present work, an anion driven PPy films was

employed also. The work property in cation driven films will be reported separately in the future[29].

3. EXPERIMENTAL

Polypyrrole films were electrodeposited on a metal electrode of Ti in an electrolyte solution of 0.25 M pyrrole and 0.2 M of TBACF₃SO₃ in Methylbenzoate (MB) at a constant current of 0.2 mA/cm² for 4h vs. an platinum counter electrode [15]. The resulting film is named as PPy/CF₃SO₃ and the thickness of film was approximately 13 μm. The pyrrole and MB were obtained from Wako chemical Co. Ltd., and TBACF₃SO₃ was from Toyama Chemical Co. Ltd. They were used without further purification. The electrolyte solution were bubbled with a dried nitrogen gas to remove oxygen and followed by electrochemical polymerization. Visco-elastic and tensile properties of PPy films were measured using Perkin Elmer Dynamic Mechanical Analyzer, DMA 7e.

Figure 1 shows the schematic diagram of experimental setup for the direct measurement of expansion and contraction of films. A PPy film was hung on the working electrode (WE) of Pt wire and the bottom end of the film was connected to a thin Pt wire with the diameter of 25 μm. The Pt wire suspended a tray or reflecting plate through the pinhole of the cell. The up-down of the plate due to the contraction and expansion of the film was measured by a laser displacement meter directly with the accuracy of 10 nm. Reference electrode (RE) and counter electrode (CE) were Ag wire with diameter of 1 mm and Pt foil with 2 x 20 mm², respectively. Typical width of films was 2 mm and the length (l_0) was 7 mm and thickness of 13 μm was employed for the experiment. The density of film was approximately 1.4 g/cm³ at dried state. The ECDM of films were operated in aqueous electrolyte of 0.1 M NH₄PF₆, 0.1 M NH₄Cl and NH₄PF₆ in water/acetonitrile (4:1). The electrolyte solution of 0.1 M NH₄PF₆ showed the best ECMD response among various electrolytes tested [17,18]. The mixed electrolyte, namely denoted as PF₆/Mix gave rise to quick response, since organic solvent makes film swell and easy for diffusion [16]. The films were cycled several times without load to become equilibrium in an electrolyte solution and dopants in film before measurement.

Figure 2 shows the wave forms of applied voltage (v) vs. the reference electrode, which was a rectangular wave for PPy/CF₃SO₃ film. There might be some difference in the estimated energy conversion efficiency by wave forms, as suggested Otero [22]. However, at this stage of experiment we have not yet measured the wave form dependence of conversion efficiency. Putting various weights (m) on the tray, the ECMD strain-stress curves of the films were measured. A personal

computer was used to control the galvano/potentiostat and to collect the data. The electrical input energy was estimated from $E_{\text{Ein}} = \int vidt$, where i is current and t is time. The voltage for this calculation is tentatively given from the reference electrode (actually it should be measured against the counter electrode). The mechanical output energy was estimated from $E_{\text{Mout}} = mg\Delta l$, where g is gravity and Δl is the length lifted with the weight upon contraction of film. The maximum weights (m) were 50 g.

4. RESULTS AND DISCUSSION

Curves in Fig.3 show typical time response of ECMD under application of weights. The deformation was measured by % elongation of the PPy film. Under the load weights of less than 1g the current responses were repeatable within several cycles, however, a creep was significant under weights of larger than 10 g. Therefore the measurement of current responses under the weight larger than 10 g was done by a single shot of rectangular wave form, namely 300 s for oxidation followed by 300 s for reduction. To see the reproducibility of data and to avoid the film fatigue, weights of load were applied to the film by the sequence of 20, 1, 30, 10, and 40 g. Time for putting heavy weights was minimized in order to shorten the natural creep. The voltage was applied immediately from the rest potential after the load was applied to the film. The curves in Fig.3 were adjusted at the beginning of oxidation by $t = 0$ and 0% elongation.

It is interesting to note that creeping was obvious for reduction cycle at heavy load as shown in Fig.3, but not for oxidation. The similar result that creeping was significant at reduced state was reported by Madden et al.[19] in PPy film doped with PF_6 . The result is explained by the fact that the stiffness of film is larger than that of reduced state. In fact Young's modulus of the wet film with water was 0.29 and 0.48 GPa for the reduced and oxidized states, respectively.

The typical current responses of oxidation and reduction are shown in Fig.4(a) and (b) respectively, indicating that the current increased with larger load stress. It is noted that the current response for reduction lasted long and was plotted by $\log t$. As seen in Fig.4 (a) the peak current of oxidation was apparently larger for heavier weights, however, the total charges for various weights were not different much. On the other hand, the reduction current apparently increased with increasing stress as shown in Fig.4 (b). There are many possible mechanisms to account for the fact taking that the reduction is the process of expelling anion from film volume and losing the conductivity of film into account. Namely, (1) a load tension to expand the film retains the charge migration (ionic conductance) easy in the film. This is clearly observed for oxidation cycle, but the transferred charges were not changed much. (2) The redox history changes the ionic conductance

with a tendency of current increase by cycle life effect. The fact of current recovery, for example, ECMD at lighter load of 3.8 MPa exhibited a smaller current after measurements of 11.4 and 15.2 MPa, may exclude this possibility. (3) The increased current or transferred charge is supposed to be consumed by lifting weights. However, this result may be inconsistent with a prediction of Madden et al. [19] that the transferred charges were basically constant for the same degree of deformation. Net charges evaluated from one cycle of charging and discharging should be zero, if a side reaction does not take place. The increased transferred charges during the reduction, despite of the oxidation charge being constant with increasing load stresses, is one of the key subject to be discussed. We discuss the conversion efficiency with the results of reduction current later, how the current increase relates to mechanical output work.

Madden [19] observed the potential variation during oxidation at galvanostat mode under load stress, which indicated the lower potential, namely, the decrease of impedance at larger loads. This result may be mainly related to the mechanism (1) as well as (2) and (3) in some extent. On the other hand, Otero [22] obtained the larger potential at larger loads, though the actuator structure of trilayer was different from the present case of linear actuator. Trilayer actuator was actually working and pushing up a weight.

Figure 5 shows E_{Ein} for the film during reduction as a function of load stress in various electrolytes. The E_{Ein} in the unloaded film was 16-22 mJ, which is attributed to charging of a battery (E_{charge}) based on oxidation of the PPy film. The E_{charge} includes also the energy to expand or contract mechanically the film itself. Most of electrical input energy stored as in a rechargeable battery may be able to be harvested again. It should be noted that the E_{Ein} for the electrolyte of NH_4Cl was nearly constant. The result contrasts to the case of PF_6 and PF_6/Mix , in which the strain of ECMD was much larger as seen in Fig.6.

Curves in Fig.6 show the strains of ECMD against the load stress of the films in various electrolytes. The strain of the films operated in aqueous NH_4PF_6 under no load was approximately 6 %, decreasing monotonically to zero at approximately 15 MPa (as a blocking force [21]). The operation of the film in NH_4Cl solution showed small strain, likely due to the transfer of Cl^- ions, whose small size produces little strain. The film operated in mixed solvent of water/acetonitrile shows large strain of 9% under no load and smaller blocking force of approximately 9 MPa. This result is consistent with the small modulus of film wetted with the mixed solvent being 0.12 and 0.17 GPa, respectively.

According to analysis by Spinks et al. [21] for an electrochemical actuator, for the first order approximation, the strain (Δl) can be expressed by,

$$\Delta l = \Delta l_0 - f l_0 / (SE'), \quad (1)$$

where Δl_0 , f , S and E' are the strain at zero applied force, force applied to the film, cross section and the modulus of the film at the reduced state, respectively. The dotted line in Fig.6 shows a fitted line to the curves of the film operated in NH_4PF_6 , giving the parameters of $\Delta l_0/l_0 = 7\%$ and $E' = 0.21$ GPa. The E' can be compared with the measured value of 0.29 GPa, indicating fairly good agreement within an experimental error.

The half cycle mechanical output energies (E_{Mout}) as a function of load stress are shown in Fig.7. For instance, when 20 g was lifted up by a film with a length of 7.0 mm it strained by approximately 4 %, and the corresponding energy was approximately 52 μJ or the normalized value of 140 kJ/m^3 . It is noted that E_{Mout} showed maximum (f_{max}) at approximately several MPa, which is obvious from the mechanical out put energy is derived from the well known relationship [21] of

$$E_{\text{Mout}} = f\Delta l = f\Delta l_0 - f^2 l_0 / (SE') \quad (2),$$

$$f_{\text{max}} = \Delta l_0 SE' / 2l_0 . \quad (3)$$

The curves in Fig.7 show good agreement with the analytical prediction being a parabolic curve for various electrolyte solutions.

The conversion energy efficiencies of the films as a function of load stress are shown in Fig.8. The conversion energy efficiency showed a maximum at several MPa, and was 0.25% operated in NH_4PF_6 electrolyte at best. The conversion efficiency was of course similar to the curves of work done shown by Fig.7, since the electrical input energy increased slightly.

It is interesting to note that the net consumed electrical energy of $E_{\text{Ein}} - E_{\text{charge}}$ for half cycle is tremendously large compared with the energy worked by lifting weights. This is clear by taking the electrical energy, $E_{\text{Ein}} - E_{\text{charge}}$, which is order of mJ as seen from Fig.5, and comparing it with the mechanical energy, E_{Mout} , which is on the order of several tens of μJ . The large unknown consumed electrical input energy is puzzling, in spite of the careful recalculation. By comparison of curve shapes in Fig. 5 and Fig.7 at higher stresses, however, one may aware that $E_{\text{Ein}} - E_{\text{charge}}$ does not directly related to the mechanical work. In the case of ECMD operated in NH_4Cl solution, the small $E_{\text{Ein}} - E_{\text{charge}}$ and a little strain compared with the case of PF_6 and PF_6/Mix were obtained, though the

same magnitude of mechanical work energy was observed. The results may suggest that the large consumed electrical input energy under large load stress may be used to enhance the creeping or degradation of films. Further investigations are needed to elucidate the details of conducting polymer actuators as an energy transducer.

5. Summary

The conversion energy efficiency from electrical input to mechanical output in PPy soft actuators has been studied. It was found the conversion efficiency without recovering stored electrical energy was found to be quite low with 0.25 % of the input electrical energy most being converted to work. The maximum efficiency was obtained under loads of several MPa. The mechanism of the electrical energy loss (not including charging or oxidizing PPy) is not known at the present state and a problem to be solved. A simple calculation from the mechanical work of the PPy actuator operated in aqueous NH_4PF_6 showed the volumetric work-per-cycle was 140 kJ/m^3 at the maximum.

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References

- [1] Y. Bar-Cohen, *Electroactive Polymer (EAP) actuators as artificial muscles*, SPIE, Bellingham, WA, 2001.
- [2] K. Kaneto, Y. Sonoda and W. Takashima. *Jpn. J. Appl. Phys.* 39 (2000) p. 5918.
- [3] R. H. Baughman, *Synth. Met.* 78 (1996) p. 339.
- [4] D. De Rossi, A. Della Santa and A. Mazzoldi, *Synth. Met.* 90 (1997) p. 93.
- [5] A.S. Hutchison, T.W. Lewis, S.E. Moulton, G.M. Spinks and G.G. Wallace, *Synth. Met.* 113 (2000), p. 121.
- [6] T. Osada, H. Okiizaki and H. Hori, *Nature* 355 (1992) p. 242.
- [7] K. Oguro, Y. Kawami and H. Takenaka, *J. Micromach. Soc.* 5 (1992) p. 27.

- [8] K. Onishi, S. Sewa, K. Asaka, N. Fujiwara and K. Oguro, *Electrochem. Acta* 46 (2001), p. 1233.
- [9] M. Watanabe and T. Hirai, *Appl. Phys. Lett.*, 74 (1999) p. 2717.
- [10] R.H. Baughman, C. Cui, A.A. Zakhidov, Z. Iqbal, J.N. Barisci, G.M. Spinks, G.C. Wallace, A. Mazzoldi, D.D. Rossi, A.G. Rinzler, O. Jaschinski, S. Roth and M. Kertesz, *Science*, 284 (1999) p. 1340.
- [11] S. Hara, T. Zama, S. Sewa, W. Takashima and K. Kaneto, *Chem. Lett.*, 32 (2003) p. 576.
- [12] W. Takashima, S.S. Pandey, and K. Kaneto, *Thin Solid Films* 438 (2003) p. 339.
- [13] W. Takashima, S.S. Pandey, and K. Kaneto, *Chem. Lett.* 33 (2004) p.996.
- [14] S. Hara, T. Zama, W. Takashima and K. Kaneto, *Polym. J.*, 36 (2004) p.151.
- [15] S. Hara, T. Zama, A. Ametani, W. Takashima and K. Kaneto, *J. Mater. Chem.*, 14 (2004) p.2724.
- [16] S. Hara, T. Zama, W. Takashima and K. Kaneto, *Synth. Met.* 146(2004) p.199.
- [17] S. Hara, T. Zama, W. Takashima and K. Kaneto, *Polym. J.*, 36 (2004) p. 933.
- [18] S. Hara, T. Zama, W. Takashima and K. Kaneto, *Smart Mat. Struct.*, 14 (2005) p1502.
- [19] J. D. Madden, P.G. Madden, P.A. Anquetil and I.W. Hunter, *Proceeding of MRA Fall Meeting 2001*, Vol. 698.
- [20] J. D. Madden, R.A. Cush, Y.S. Kanigan and I.W. Hunter, *Synthetic Metals* 113 (2000) p.185.
- [21] G.M. Spinks, V.- Tan Truong, *Sensors and Actuators A* 119 (2005) p.455.
- [22] T.F. Otero and M. T. Cortes, *Sensors and Actuators B* (2003) p.152.
- [23] J.D. Madden, D. Rindernecht, P.A. Anquetil and I. W. Hunter, *Sensors and Actuators*, (2006) in press.
- [24] J.D. Madden, PhD Thesis MIT (2000) Chapter 8.
- [25] Q. Pei, O. Inganas, *Solid State Ionics* 60 (1998) p.65.
- [26] K. Yamato and K. Kaneto, *Analytica Chimica Acta*, 568 (2006) 133.
- [27] S. Koehler, A. Bund and I. Efimov, *J. Electroana. Chemistry*, 589 (2006) p.82.
- [28] T.F. Otero, J.J. Lopez and G.V. Arenas, *Mat. Scie. And Eng.:C* in press (2006) (on line)
- [29] T. Sendai, H. Fujisue, W. Takashima and K. Kaneto, to be published.

Figure captions

Fig.1 Experimental setup.

Fig.2 Rectangular wave forms of applied voltage to PPy/CF₃SO₃ film at -0.7 to 0.3 V vs. Ag/AgCl with the period of 600s.

Fig.3. Load dependence of ECMD in PPy/CF₃SO₃ film operated in aqueous 0.1M NH₄PF₆. Numerical in circle is sequential of measurement.

Fig.4. Current responses in ECMD of the film at various load stresses, (a) Oxidation (elongation) and (b) Reduction (contraction).

Fig.5 Load stress dependence of electrical input energies E_{Ein} .

Fig.6 Electrochemomechanical strain – stress curves in PPy/CF₃SO₃ film. Dotted line is obtained by equation (1), with the parameter of $e_0 = 7.0 \%$ and $E' = 0.21\text{GPa}$.

Fig.7 Stress dependence of mechanical output energy, E_{Mout} of PPy film operated in various electrolytes.

Fig.8 Energy conversion efficiency against load stress in various electrolytes.

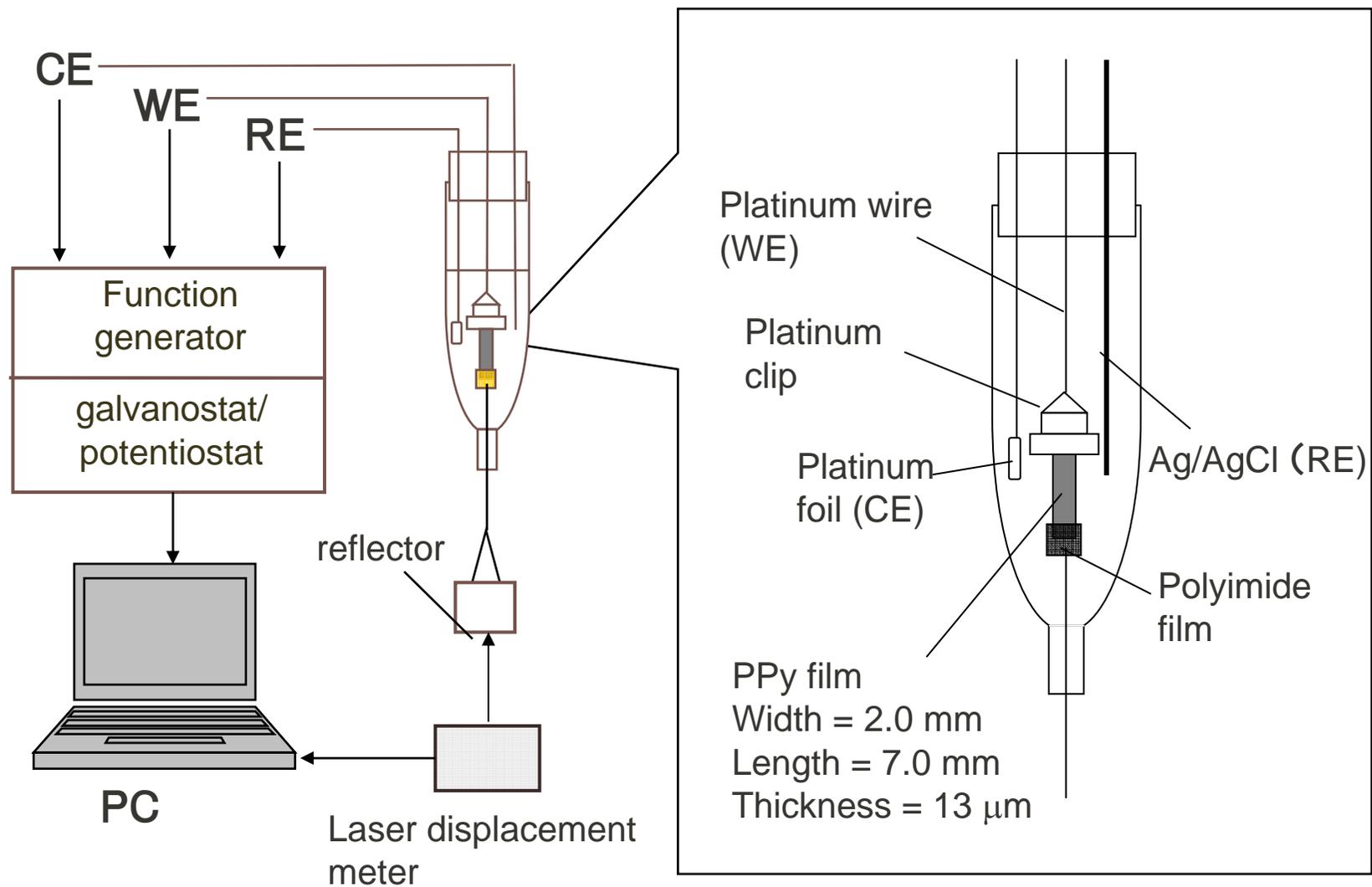


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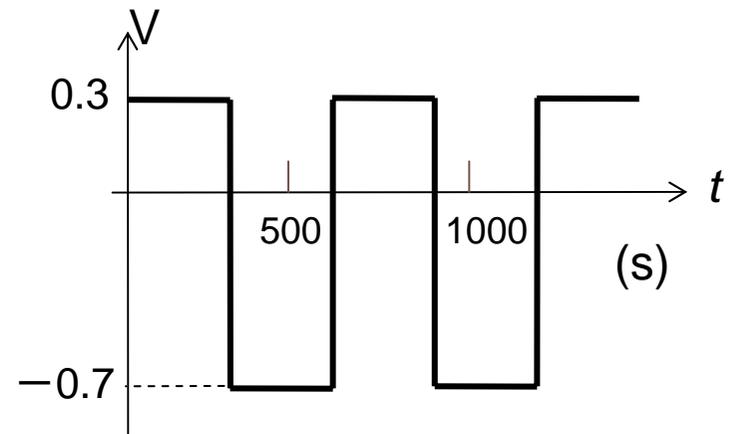


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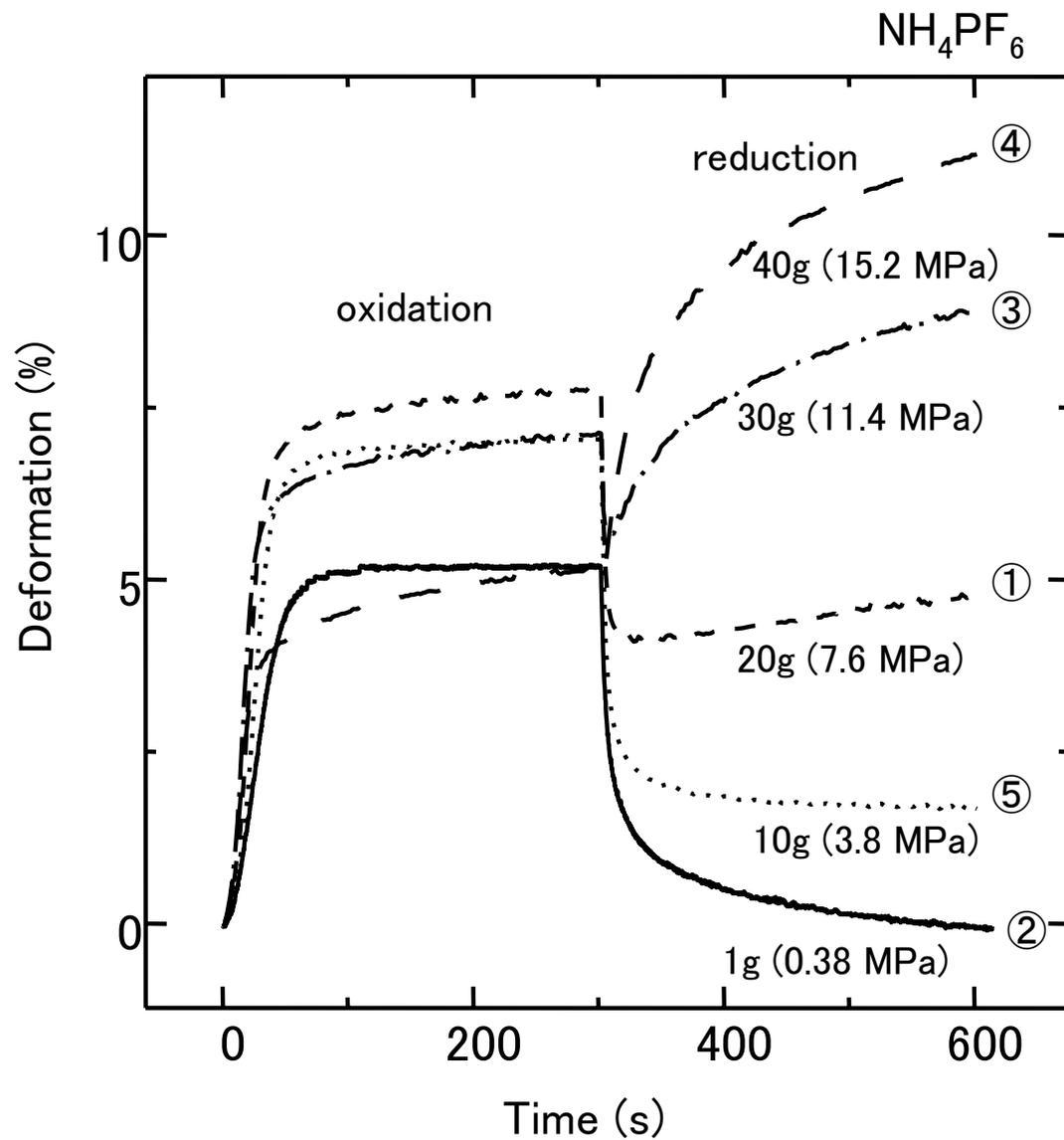


Fig.3 Load dependence of ECMD in PPy/ CF_3SO_3 film operated in aqueous 0.1M NH_4PF_6 . Numerical in circle is sequential of measurement.

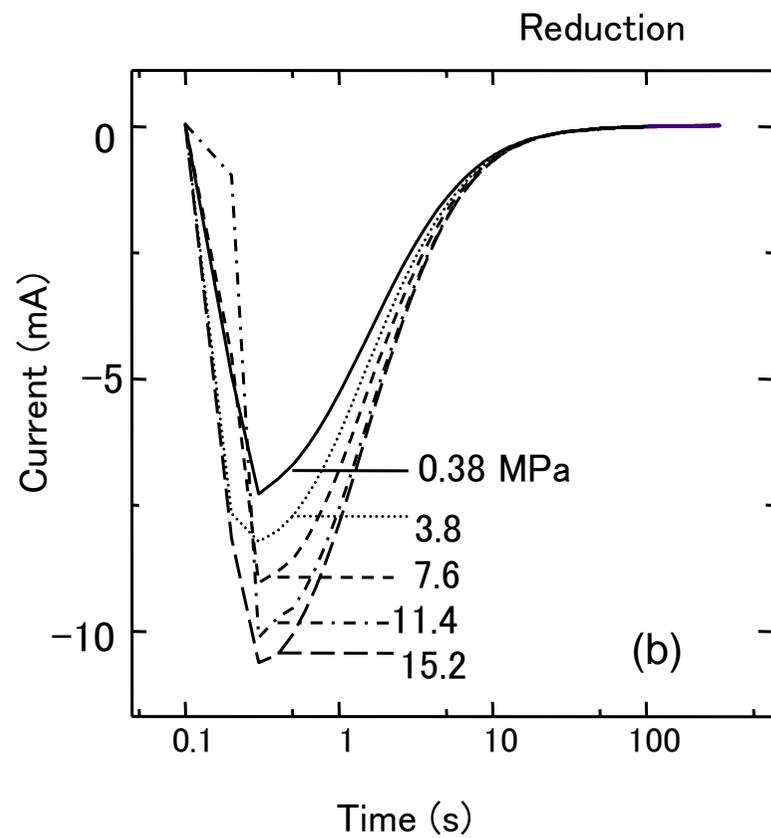
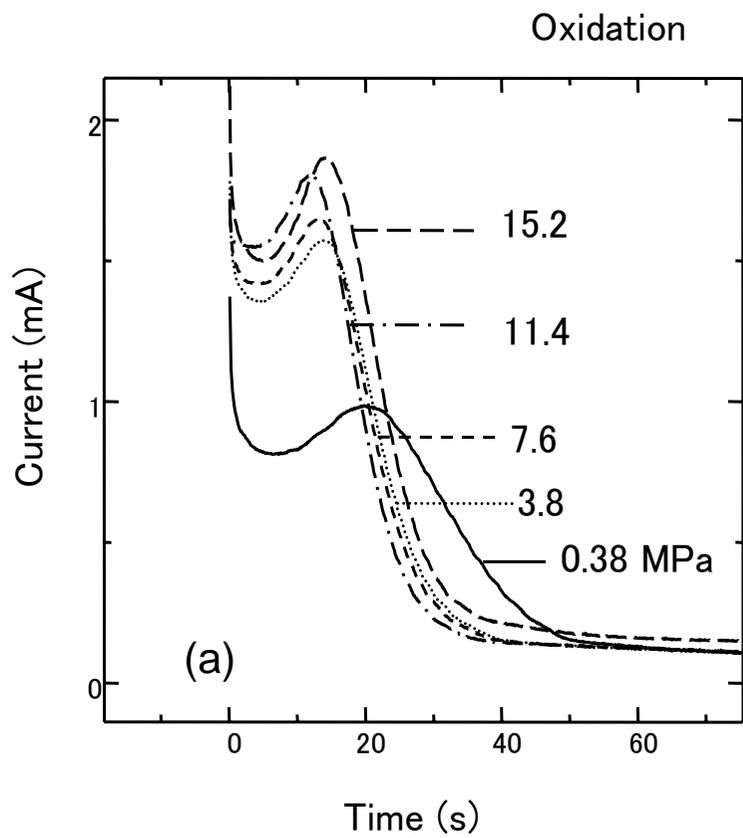


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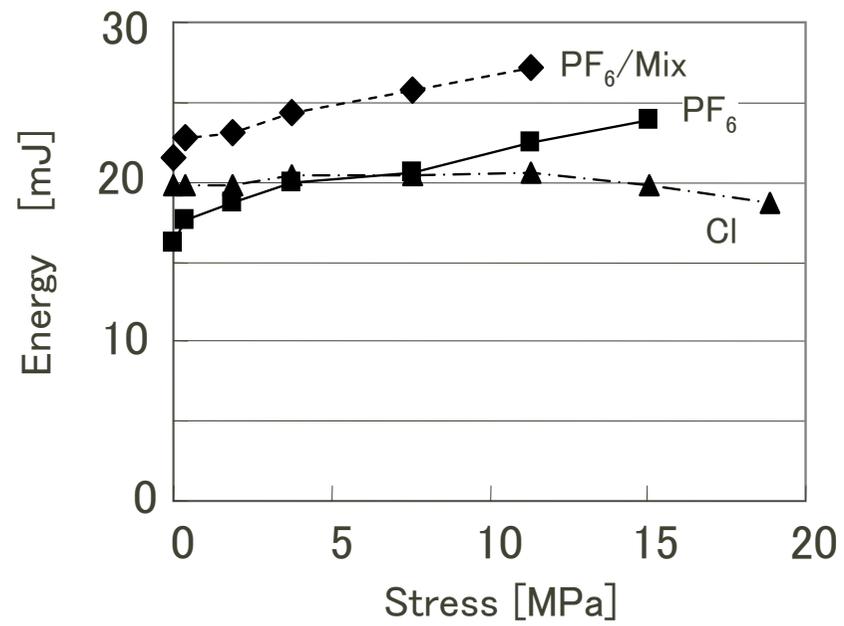


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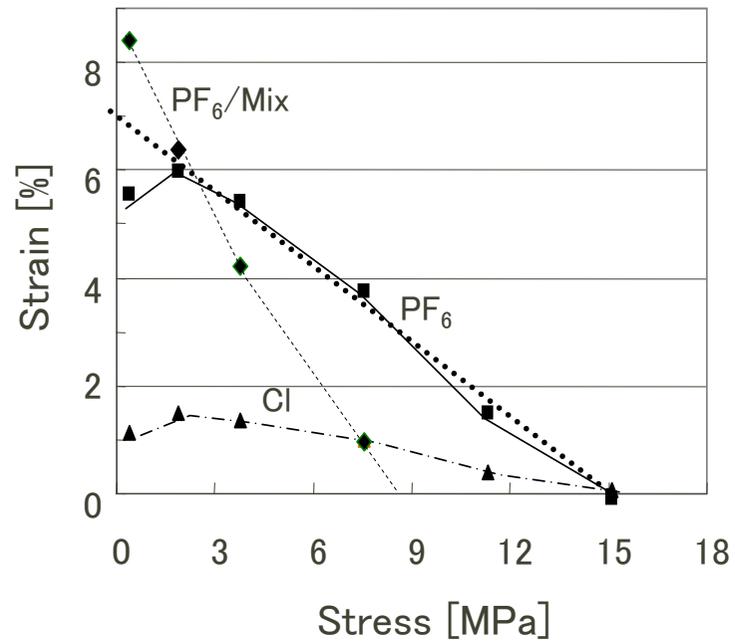


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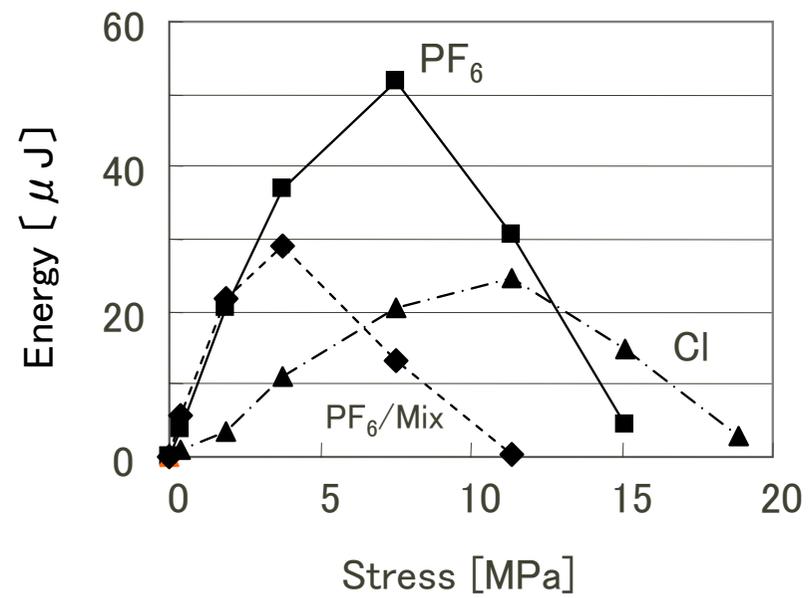


Fig.7 Stress dependence of mechanical output energy, E_{Mout} of PPy film operated in various electrolytes.

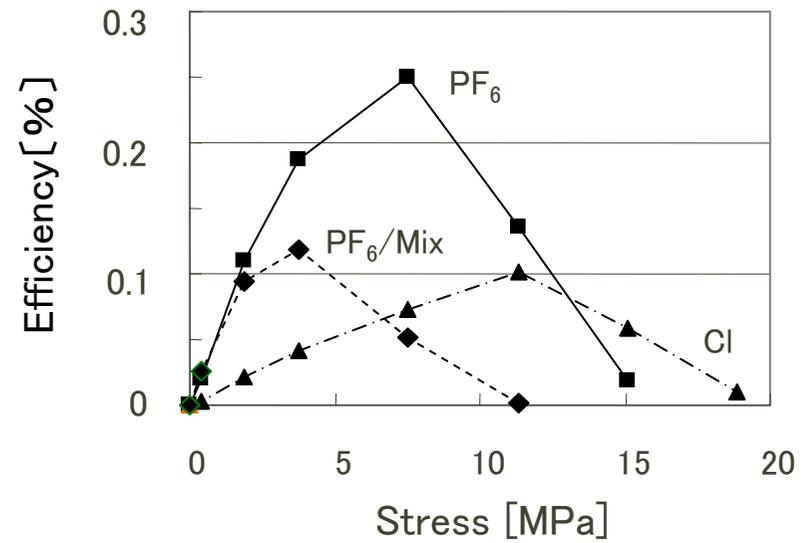


Fig.8 Energy conversion efficiency against load stress in various electrolytes.