

## Artificial Muscles Based on Polypyrrole Actuators with Large Strain and Stress Induced Electrically

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**ABSTRACT:** Conducting polymer actuators have been attracting researchers and engineers who need powerful and light actuators because of their electrically induced stress (3–5 MPa), 10 times larger than that (0.35 MPa) of vertebrate muscle fibres. The moderate electrically generated strain (1–3 %) has however been restricting their applications to robots, for instance, and therefore relatively huge and heavy electric motors have been inevitably used in the robotic industry. A polypyrrole (PPy) film, which was prepared electrochemically from methyl benzoate solution of tetra-*n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) on Ti electrode, exhibited 12.4 % strain and 22 MPa stress generated electrochemically in NaPF<sub>6</sub> aqueous solution. The large electrochemical strain and stress of BF<sub>4</sub><sup>-</sup>-doped PPy should meet applications of artificial muscles particularly where strong force is required. These novel conducting polymer actuators could dramatically alter any technologies concerning movements. Besides fundamental properties of the PPy actuators, some newly-devised configurations of the actuators for practical use are important. In order to fabricate actuator devices particularly where multiple layers of PPy films were required to increase force, flexible and tough CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>-doped PPy films were more suitable than BF<sub>4</sub><sup>-</sup>-doped PPy.

**KEY WORDS** Conducting Polymer Actuator / Electroactive Polymer / Artificial Muscle / Polypyrrole / Electrochemomechanical Deformation / Electrochemical Strain / Electrochemical Stress /

Electroactive polymer (EAP) actuators are roughly divided into two categories based on their activation mechanism: electronic and ionic.<sup>1,2</sup> Of electronic EAP actuators driven by electric field, electroelastomers or dielectric elastomers with up to 380 % strain developed by SRI International have attracted those who need powerful and speedy actuators.<sup>3,4</sup> Dielectric EAPs having low elastic stiffness and high dielectric constant actuate massively in an electrostatic field, and the higher electrostatic field induces larger force and strain of dielectric EAP. The disadvantage of the electronic EAP actuators is, without any doubt, their very high drive voltage of 1000–5000 V.<sup>2–5</sup> On the other hand, ionic EAP actuators such as ionic polymer gels (IPGs),<sup>6,7</sup> ionomeric polymer-metal composites (IPMCs),<sup>8,9</sup> and conducting polymers (CPs)<sup>10–13</sup> can be operational under much milder conditions: pH change, temperature control, or low drive voltage (1–2 V), and thus suitable for portable, mobile, small, and simple actuator devices as artificial muscles; for instance, robots, powered suits, artificial limbs, medical devices, and replacement of conventional electric motors. When actuator devices are designed by using EAP materials, only CP actuators are realistic choice because of their large stress generated electrically, 2–3 orders of magnitude larger than that of IPGs and IPMCs. The moderate strain (1–3 %)

of CP actuators has however been disappointing those who are in need of artificial muscles. Once the electrochemical strain of CP actuators improves massively, their applications as artificial muscles can certainly be realized.

CPs such as polypyrrole (PPy), polyaniline, and polythiophene expand and shrink with doping and dedoping, respectively, and thus they can be used as actuators. PPy actuators doped with relatively small anions such as Cl<sup>-</sup> elongate on doping of anions (oxidation of PPy) and shorten on dedoping (reduction), and are classified as anion-driven actuators. On the other hand, PPy actuators doped with relatively large anions such as dodecylbenzenesulfonate (DBS) elongate on reduction with cation insertion and shorten on oxidation with cation release because large anions do not insert or expel so that cations expel or insert, respectively, to compensate the charge, and are classified as cation-driven actuators.<sup>14,15</sup> CP actuators have some advantages over conventional electric motors such as large stress induced electrically, light in weight, small and simple mechanisms, shorable to any shape, silent movement, and low driving voltage.<sup>10–13</sup> CPs are therefore most promising candidates for artificial muscles if their electrochemical strain becomes larger. Despite the moderate strain, some applications to medical devices have been carried out,<sup>16</sup>

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and commercial products are about to launch. Conventional CPs should be used more widely by taking advantage of CP actuators mentioned above, but highly stretchable CP actuators must be much more useful for practical applications.<sup>17</sup>

There are some strategies to improve electrochemical strain of CP actuators. Bay *et al.* has improved electrochemical strain of PPy doped with DBS from 2.5 % to 5.6 % by the addition of pentanol as a co-surfactant to DBS,<sup>18</sup> and from 5.6 % to 12 % by using a compliant gold electrode.<sup>19</sup> We have fabricated fibrous PPy–metal coil composites exhibiting 11.6 % apparent strain, and 23.2 % effective strain if PPy at the gap solely works as an actuator.<sup>20</sup> These results suggest that actuators based on CPs reported so far did not bring their ability into full play. Except these approaches of new configurations to improve electrochemical strain of CP actuators, investigation of CP itself should be performed to obtain highly stretchable CP actuators. Improvement in the electrochemical strain of CP actuators without loss of the advantages mentioned above will make CP actuators fit for practical use. Our strategy is to focus mainly on improvement in interaction between pyrrole monomer and electrolyte to prepare highly stretchable PPy actuators with linear and long polymer chains.<sup>17</sup>

## EXPERIMENTAL

### Materials

Pyrrole, methyl benzoate, ethyl benzoate, *n*-butyl benzoate, 1,2-diacetoxyethane, ethyl acetate, *n*-butyl acetate, *t*-butyl acetate, dimethyl phthalate, 1,2-dimethoxyethane, 1,4-dioxane, 1-octanol, 1-hexanol, 2-phenoxyethanol, 2-(2-methoxyethoxy)ethanol, methyl 3-methoxypropionate, 4-methyl-1,3-dioxolan-2-one (PC), acetonitrile, tetra-*n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) (Sigma-Aldrich, Inc.), tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (Tokyo Kasei Kogyo Co., Ltd.), tetra-*n*-butylammonium trifluoromethanesulfonate (TBACF<sub>3</sub>SO<sub>3</sub>) (Lancaster Synthesis, Inc.), tetra-*n*-butylammonium hydrogensulfonate (TBAHSO<sub>4</sub>) (Tokyo Kasei Kogyo Co., Ltd.), potassium nonafluorobutanesulfonate (Sigma-Aldrich, Inc.), sodium benzenesulfonate, potassium 1,2-benzenedisulfonate (Sigma-Aldrich, Inc.), sodium 1,3-benzenedisulfonate (Tokyo Kasei Kogyo Co., Ltd.), tetraethylammonium *p*-toluenesulfonate (Tokyo Kasei Kogyo Co., Ltd.), sodium 1-naphthalenesulfonate, sodium 2-naphthalenesulfonate, sodium 1,5-naphthalenedisulfonate, sodium 2,6-naphthalenedisulfonate, sodium 1,3,6-naphthalenetrisulfonate, sodium 1-naphthol-3,6-disulfonate, sodium hexafluorophosphate (NaPF<sub>6</sub>) (Sigma-Aldrich, Inc.), sodium tetrafluoroborate (NaBF<sub>4</sub>), sodium chloride were purchased and

used without further purification. Tetra-*n*-butylammonium benzenesulfonate (TBAC<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>), tetra-*n*-butylammonium *p*-phenolsulfonate (TBAHOC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>), and tetra-*n*-butylammonium 1-naphthalenesulfonate (TBAC<sub>10</sub>H<sub>7</sub>SO<sub>3</sub>) were prepared by mixing tetra-*n*-butylammonium hydroxide (40 wt.% solution in water) (Sigma-Aldrich, Inc.) and the corresponding acid (Sigma-Aldrich, Inc.), followed by removal of water.

### Preparation of PPy Films

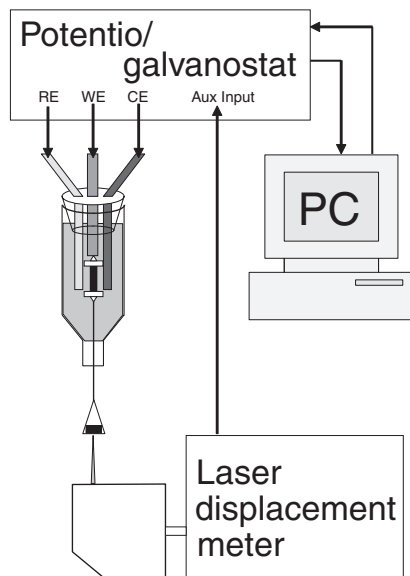
Preparation of PPy films was performed by galvanostatic electropolymerization of pyrrole (0.25 mol dm<sup>-3</sup>) (typically 0.2 mA cm<sup>-2</sup> for 4 h) by using a potentiogalvanostat (Hokuto Denko Co. HA-151) in organic solvent with TBABF<sub>4</sub> (0.5 mol dm<sup>-3</sup>) or TBACF<sub>3</sub>SO<sub>3</sub> (0.2 mol dm<sup>-3</sup>) as the electrolyte in a two-electrode cell where the working electrode was ITO, Ni, or Ti, and the counter electrode was Pt or Ni. PPy films obtained on the working electrode were peeled off and rinsed with acetone, followed by being air-dried.

### Measurements of Fundamental Properties of PPy Films

Electric conductivity of PPy films was measured by using a 4-point probe technique with Loresta-GP (Mitsubishi Chemical Co.). Film thickness was measured with a micrometer (Mitsutoyo Co.). Film morphology was observed by using a scanning electron microscope (SEM) (Hitachi High-Technologies Co. S-3000N).

### Measurements of Electrochemical Strain and Stress of PPy Actuators

Measurement of electrically induced strain and stress was carried out in a glass cell with a pinhole at the bottom through which a tungsten wire passed in order to suspend a load (Figure 1).<sup>14,21</sup> A PPy strip (typically 14-mm length × 2-mm width) was put in the cell using a Pt plate and used as the working electrode by sweeping the potential driven by a potentiogalvanostat (PAR 263A) between -0.9 V and +0.7 V vs. Ag/Ag<sup>+</sup> at 2 mV s<sup>-1</sup> unless otherwise cited. A Pt plate and an Ag wire were used as the counter electrode and the reference electrode, respectively. Change in length ( $\Delta l$ ) of the strip was monitored by using a laser displacement meter (KEYENCE LC-4000) and divided by the original length ( $l_0$ ) of the strip. The definition of electrochemical strain (%) of PPy actuators was  $(\Delta l/l_0) \times 100$ . The load (typically *ca.* 0.4 g) for the strip for measuring maximum strain was *ca.* 0.1 MPa. To evaluate the maximum stress induced electrically of the strip, the load was increased until the strip was broken or unable to pull up the load, when the potential was swept between -0.9 V and



**Figure 1.** An apparatus to measure electrochemical strain of PPy actuators.

+0.7 V vs. Ag/Ag<sup>+</sup> at 10 mV s<sup>-1</sup>.

Mechanical tensile strength of PPy films was evaluated by using a digital force gauge Model-9810N (Aiko Engineering Co.) to pull a PPy film at tensile rate of 6 mm min<sup>-1</sup>. Mechanical properties of some PPy films were also measured at DJK lab.

## RESULTS AND DISCUSSION

### Fundamental Properties of PPy Films Used as Actuators

Table I indicates electric conductivity and thickness of PPy films prepared electrochemically used as linear

actuators, together with their preparation conditions. Apart from the film thickness (*ca.* 20 μm), much thicker than ordinary PPy films because the PPy films were prepared as actuators, the electric conductivity was almost the same as that of ordinary PPy films prepared electrochemically. Electric conductivity of PPy films prepared at lower temperature such as 0 °C tended to be slightly higher than that prepared at room temperature. All the PPy films were black, and no electrochromic phenomena were observed due to the film thickness.

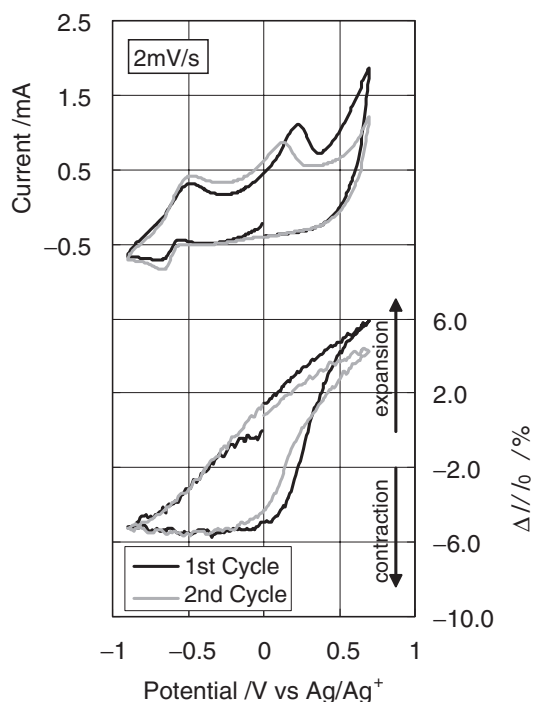
### Electrochemomechanical Deformation of PPy Actuators

Figure 2 depicts a cyclic voltammogram (CV) and an electrochemomechanical deformation (ECMD) of PPy, prepared on ITO electrode by using tetra-*n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) and methyl benzoate as the electrolyte and the solvent, respectively, when cycled between -0.9 V and +0.7 V vs. Ag/Ag<sup>+</sup> at 2 mV s<sup>-1</sup> in NaPF<sub>6</sub> aqueous solution (1.0 mol dm<sup>-3</sup>). A PPy strip (14 mm × 2 mm) gradually shortened with dedoping of BF<sub>4</sub><sup>-</sup> incorporated previously in the film during the electropolymerization of pyrrole, and the contraction ratio ( $\Delta l/l_0$ ) was 5.7% at -0.9 V vs. Ag/Ag<sup>+</sup>. On applying potential toward +0.7 V, the PPy strip became longer with doping of PF<sub>6</sub><sup>-</sup> together probably with BF<sub>4</sub><sup>-</sup>, and the total expansion-contraction ratio (electrochemical strain) for one redox cycle was 11.4%, much larger than that (1–3%) of conventional conducting polymer actuators. Rapid elongation shown in Figure 2 (bottom) corresponded to a sharp oxidation peak of the CV (Figure 2, top) even though the PPy film was very

**Table I.** Fundamental properties of PPy films used as actuators

Electrolyte	Solvent	Electrode	Conductivity (S cm <sup>-1</sup> )	Thickness (μm)
TBABF <sub>4</sub>	Methyl benzoate	Ti	87	32
TBABF <sub>4</sub>	Methyl benzoate	Ni	112	18
TBABF <sub>4</sub>	Methyl benzoate	Pt	55	26
TBABF <sub>4</sub>	Methyl benzoate	ITO	53	24
TBABF <sub>4</sub>	Ethyl benzoate	Ti	86	23
TBABF <sub>4</sub>	Butyl benzoate	Ti	41	26
TBABF <sub>4</sub>	<i>t</i> -Butyl acetate	Ti	59	26
TBABF <sub>4</sub>	1,2-Dimethoxyethane	Ti	124	31
TBABF <sub>4</sub>	1-Octanol	Ti	97	13
TBABF <sub>4</sub>	Propylene carbonate	Ti	108	8
TBAPF <sub>6</sub>	Methyl benzoate	Ti	72	28
TBAPF <sub>6</sub>	Propylene carbonate	Ti	127	13
TBACF <sub>3</sub> SO <sub>3</sub>	Methyl benzoate	Ti	113	31
TBACF <sub>3</sub> SO <sub>3</sub>	Methyl benzoate	Ni	107	19
TBACF <sub>3</sub> SO <sub>3</sub>	Methyl benzoate	ITO	145	11
TBACF <sub>3</sub> SO <sub>3</sub>	1,2-Dimethoxyethane	Ti	61	16
TBACF <sub>3</sub> SO <sub>3</sub>	Propylene carbonate	Ti	47	19

Polymerization time: 4 h, Current density: 0.2 mA cm<sup>-2</sup>.



**Figure 2.** A CV and an ECMD of a PPy film actuator prepared from methyl benzoate solution of TBABF<sub>4</sub> on ITO electrode. The actuator was driven by sweeping potential between  $-0.9$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $2$  mV s<sup>-1</sup> in  $1.0$  mol dm<sup>-3</sup> NaPF<sub>6</sub> aq.

thick ( $24\ \mu\text{m}$ ), compared with most of CP films when measured electrochemically. The sharp oxidation peak is one of the characteristics for the PPy actuators exhibiting large electrochemical strain. The relation between the elongation of PPy and the sharp oxidation peak suggests that doping of anions contributed significantly to the expansion of the PPy film. The second and the following redox cycles gave a similar CV and an expansion–contraction profile where the expansion–contraction ratio was  $10.0\%$ , slightly smaller than that ( $11.4\%$ ) of the first cycle presumably because the tight packing of PPy chains was unable to revert to the as-grown form after the redox cycle with doping–dedoping. It seems however stability of the PPy actuators was not very good when they performed their maximum strain or stress. CP actuators should be used at far below their maximum strain or stress if the repeated performance is significant. The strict durability of the actuation has not yet been tested, but we will investigate and improve the stability of PPy actuators mainly under their operational conditions rather than in the maximum performance.

#### *Effect of Electrolytic Solution for Electropolymerization on Electrochemical Strain of PPy Actuators*

Expansion–contraction ratios for one redox cycle of various BF<sub>4</sub><sup>-</sup>-doped PPy actuators prepared electro-

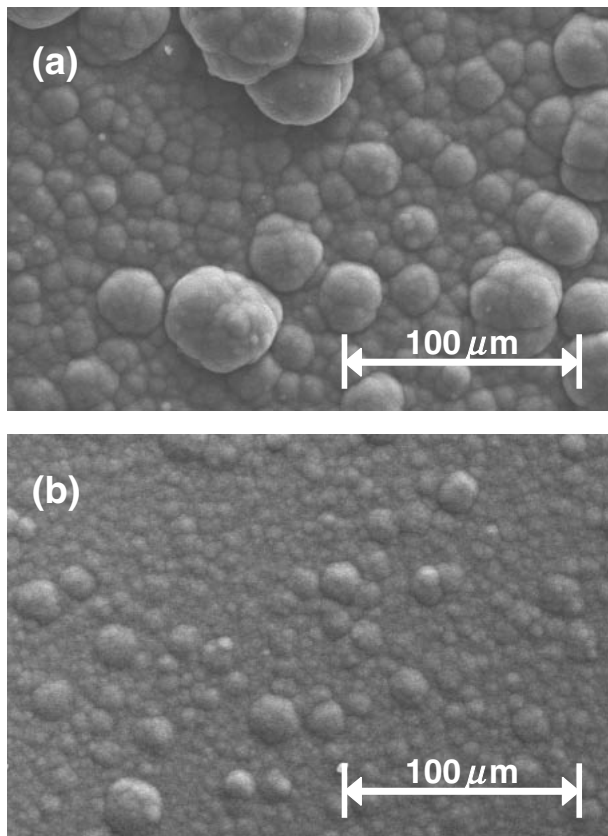
chemically in a similar manner in esters (ethyl acetate ( $10.3\%$  strain of PPy prepared on Ti), *n*-butyl acetate ( $11.2\%$ ), *t*-butyl acetate ( $12.8\%$ ), 1,2-diacetoxyethane ( $10.0\%$ ), methyl benzoate ( $12.4\%$ ), ethyl benzoate ( $11.6\%$ ), *n*-butyl benzoate ( $12.3\%$ ), and dimethyl phthalate ( $12.6\%$ )), ethers (1,2-dimethoxyethane ( $10.5\%$ ) and 1,4-dioxane ( $10.8\%$ )), and higher alcohols (1-octanol ( $11.5\%$ ) and 1-hexanol ( $11.1\%$ )) were more than  $10\%$  as long as TBABF<sub>4</sub> was used as the electrolyte. These solvents are not very common for the electropolymerization of pyrrole as water ( $7.0\%$ ) and acetonitrile ( $5.3\%$ ) that provided brittle PPy actuators showing moderate strain generated electrochemically. 2-Phenoxyethanol ( $12.6\%$ ), 2-(2-methoxyethoxy)ethanol ( $10.3\%$ ), and methyl 3-methoxypropionate ( $10.0\%$ ) having both an ether group and a hydroxyl (or an ester) group also gave highly stretchable PPy actuators. The reason why these solvents are suitable for preparing highly stretchable actuators may be attributable to functional groups of the solvents, which could make PPy films compact and smooth. Figure 3 shows SEM photographs of PPy films prepared from methyl benzoate solution of TBABF<sub>4</sub> on ITO (a) or Ti (b) electrode. Larger grains of PPy were observed on the surface of PPy film deposited on ITO electrode, which had faced to electrolytic solution during electropolymerization, so that roughness of PPy film prepared on ITO electrode appeared to be higher than that prepared on Ti electrode.

Electrochemical strain of PPy prepared similarly on Ti electrode was  $12.4\%$ ,<sup>17</sup> slightly larger than that deposited on ITO electrode as mentioned above, when cycled also similarly in NaPF<sub>6</sub> aq. Ti electrode as well as other metal electrodes showed the maximum strain cycled at  $2$  mV s<sup>-1</sup>, and did not fully actuate at  $10$  mV s<sup>-1</sup> exhibiting  $8.9\%$  strain, whereas ITO electrode showed  $11.4\%$  and  $9.3\%$  at  $2$  mV s<sup>-1</sup> and  $10$  mV s<sup>-1</sup>, respectively, so the decrease in electrochemical strain at the faster scan was small. It seems that metal electrodes gave more compact films, resulting in slow diffusion of dopant anions in the film so that the higher scan rate ( $10$  mV s<sup>-1</sup>) did not bring out the maximum strain.

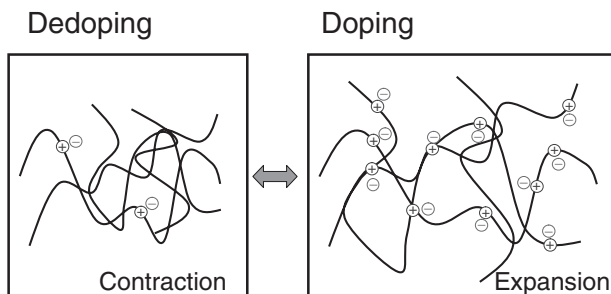
The electrochemical strain of PPy actuators depended on anions used for the electrochemical stretching as follows:



The order of electrochemical strain strongly supports the proposed mechanism of electrochemical stretching of CP actuators,<sup>12,22,23</sup> where expansion and contraction occur on doping and dedoping of anions, respectively, as shown in Figure 4. Here, change in volume of CP actuators was ascribed to insertion and release

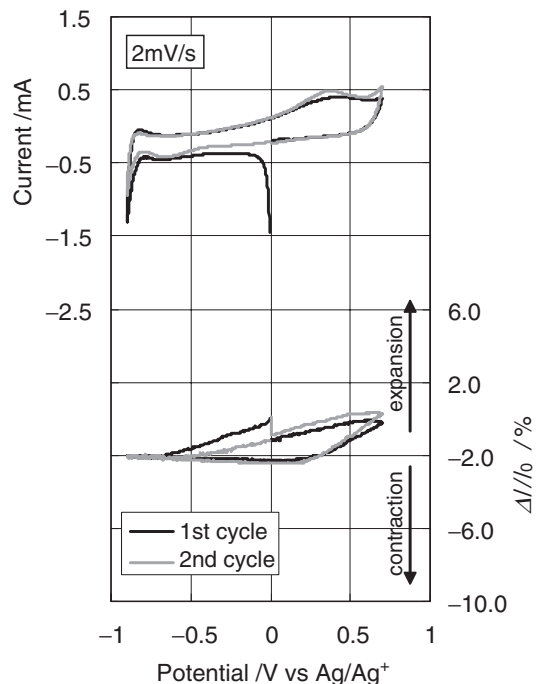


**Figure 3.** SEM photographs of PPY films prepared from methyl benzoate solution of TBABF<sub>4</sub> on ITO (a) or Ti (b) electrode.



**Figure 4.** A plausible mechanism of electrochemical stretching of CP actuators.

of anion. Figure 5 shows a CV and an ECMD of PPY prepared on Ti electrode, cycled in NaCl aq. (1.0 mol dm<sup>-3</sup>), and the electrochemical strain was 2.8%. The as-grown BF<sub>4</sub><sup>-</sup>-doped PPY shrank with dedoping of BF<sub>4</sub><sup>-</sup> by 2.3%, but the film did not elongate effectively with doping of Cl<sup>-</sup> because Cl<sup>-</sup> is too small to expand PPY previously doped with BF<sub>4</sub><sup>-</sup>. Moreover, the PPY film became brittle after the measurement because the BF<sub>4</sub><sup>-</sup>-doped PPY film eventually transformed into a Cl<sup>-</sup>-doped PPY film. Apparently, Cl<sup>-</sup> was not a suitable anion to drive the PPY actuator doped with BF<sub>4</sub><sup>-</sup>. When Cl<sup>-</sup> was employed as the electrolyte for electropolymerization of pyrrole, PPY films obtained also tended to be fragile. It seems that interaction between PPY and dopant anion affected



**Figure 5.** A CV and an ECMD of a PPY actuator prepared from methyl benzoate solution of TBABF<sub>4</sub> on Ti electrode. The actuator was cycled between -0.9 V and +0.7 V vs. Ag/Ag<sup>+</sup> at 2 mV s<sup>-1</sup> in 1.0 mol dm<sup>-3</sup> NaCl aq.

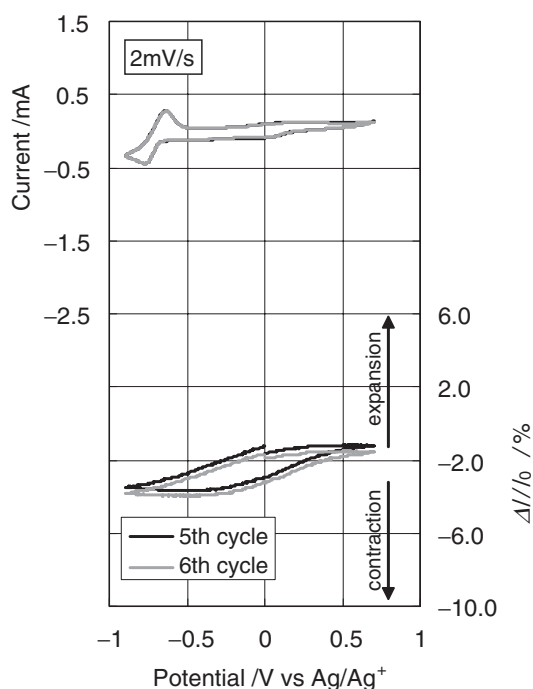
significantly mechanical properties of PPY films. The Cl<sup>-</sup>-doped PPY films, transformed from BF<sub>4</sub><sup>-</sup>-doped PPY and prepared directly from electrolytic solution containing Cl<sup>-</sup> as the electrolyte, were fragile. The mechanism of electrochemical stretching of the PPY actuators cannot however be totally elucidated by the doping–dedoping of anions because conventional CP actuators exhibited moderate strain (1–3%) even when PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> was used as the dopant anion so that some conformational change of PPY chains, triggered presumably with doping–dedoping of anions, affects considerably to the electrochemical stretching of the PPY actuators.

Another important factor for preparing highly stretchable PPY actuators is the electrolyte used for the electrochemical polymerization of pyrrole. Only electrolytes composed of BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> gave highly stretchable PPY actuators as shown in Table II, whereas hydrogensulfonate (HSO<sub>4</sub><sup>-</sup>) and benzenesulfonate (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup>) produced PPY actuators exhibiting moderate strain up to 3.4%. Some other electrolytes such as C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>4</sub>(SO<sub>3</sub><sup>-</sup>)<sub>2</sub>, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>, HOC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>, C<sub>10</sub>H<sub>7</sub>SO<sub>3</sub><sup>-</sup>, C<sub>10</sub>H<sub>6</sub>(SO<sub>3</sub><sup>-</sup>)<sub>2</sub>, C<sub>10</sub>H<sub>5</sub>(SO<sub>3</sub><sup>-</sup>)<sub>3</sub>, HOC<sub>10</sub>H<sub>6</sub>SO<sub>3</sub><sup>-</sup>, and HOC<sub>10</sub>H<sub>5</sub>(SO<sub>3</sub><sup>-</sup>)<sub>2</sub> showed small strain around 1%, not shown in Table II. It should be emphasized that large anions and multivalent anions tended to give cation-driven actuators, whereas the highly stretchable PPY films doped with BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> were

**Table II.** Electrically induced strain (%)<sup>a</sup> of PPy actuators prepared using various electrolytes and solvents on Ni electrode

Electrolyte	Solvent <sup>b</sup>				
	MB	BB	DME	OcOH	PC
TBABF <sub>4</sub>	12.4	15.1	10.5	11.5	8.7
TBAPF <sub>6</sub>	8.8	—	9.1	—	10.1
TBACF <sub>3</sub> SO <sub>3</sub>	10.7	10.5	8.0	9.7	8.3
TBAHSO <sub>4</sub>	1.3	—	—	1.2	0.77
TBAC <sub>6</sub> H <sub>5</sub> SO <sub>3</sub>	2.6	2.6	3.4	2.6	3.1

<sup>a</sup>Cycled between  $-0.9$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $2$  mV s<sup>-1</sup> in  $1.0$  mol dm<sup>-3</sup> NaPF<sub>6</sub> aq. <sup>b</sup>MB: methyl benzoate, BB: butyl benzoate, DME: 1,2-dimethoxyethane, OcOH: 1-octanol, PC: propylene carbonate



**Figure 6.** A CV and an ECMD of a PPy actuator prepared from methyl benzoate solution of TBAC<sub>6</sub>H<sub>5</sub>SO<sub>3</sub> on Ni electrode. The actuator was cycled between  $-0.9$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $2$  mV s<sup>-1</sup> in  $1.0$  mol dm<sup>-3</sup> NaPF<sub>6</sub> aq.

anion-driven actuators. Figure 6 depicts a CV and an ECMD of PPy prepared using TBAC<sub>6</sub>H<sub>5</sub>SO<sub>3</sub> as the electrolyte. Despite the same electrolytic solution (NaPF<sub>6</sub> aq.) used for the electrochemical stretching of the PPy, the electrochemical strain was considerably smaller (2.5%) than that of BF<sub>4</sub><sup>-</sup>-doped PPy. In addition, the sharp oxidation peak, observed for BF<sub>4</sub><sup>-</sup>-doped PPy, was not seen probably because no strong interaction between pyrrole rings and benzenesulfonate anions existed in the C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup>-doped PPy film. It is therefore quite important for preparing highly stretchable PPy actuators to choose a suitable combination of electrolytes and solvents. We are currently using TBACF<sub>3</sub>SO<sub>3</sub> as the electrolyte for synthesizing large PPy films for fabricating actuator devices,<sup>24</sup>

some of which will be shown later, although the electrochemical stress of PPy prepared using TBACF<sub>3</sub>SO<sub>3</sub> as the electrolyte is slightly smaller than those prepared using TBABF<sub>4</sub> as shown in Table II; the reason will be discussed later.

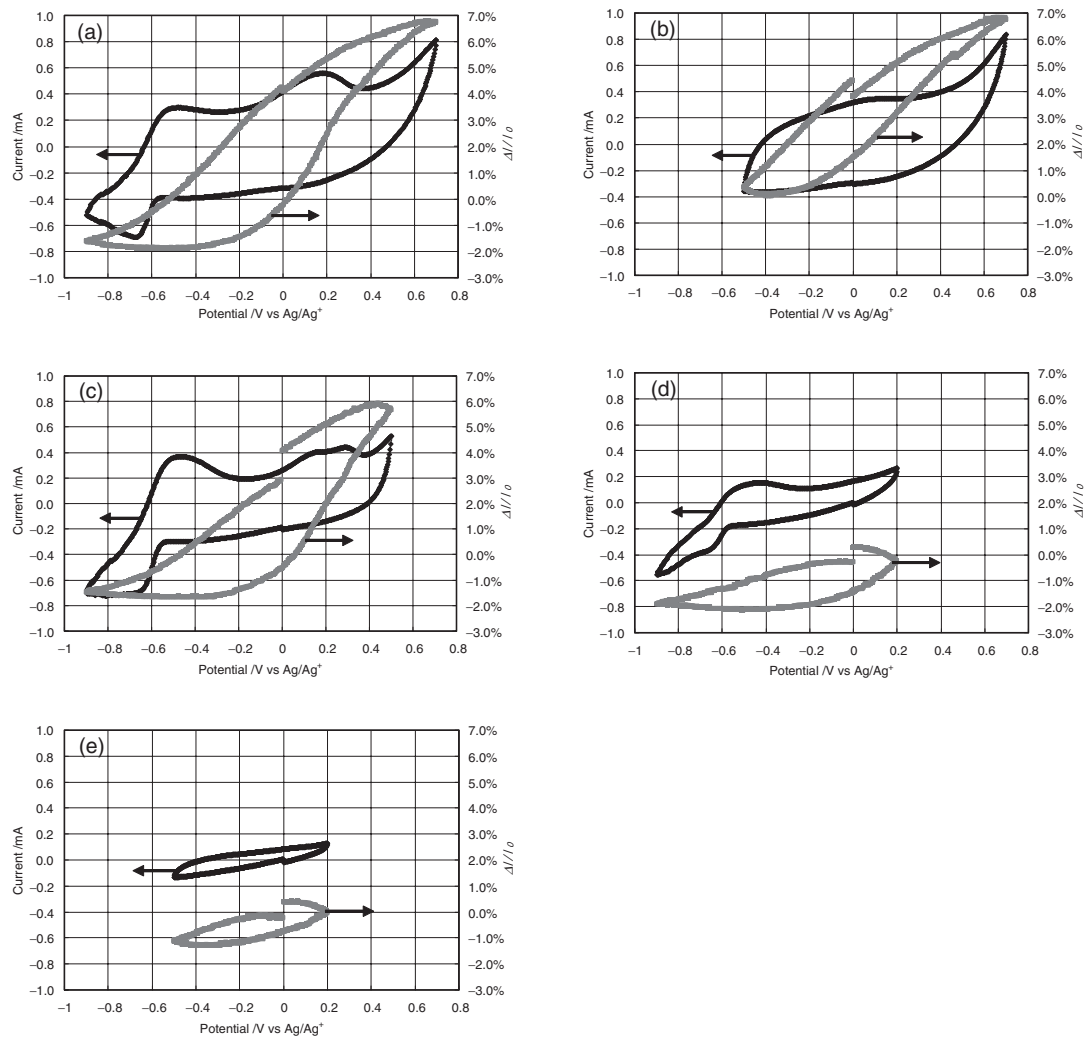
In order to obtain highly stretchable PPy actuators, interaction between pyrrole and BF<sub>4</sub><sup>-</sup> (or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) seems to be very important. The idea to choose BF<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> as the electrolyte came from highly electroactive polyparaphenylene (PPP) films prepared electrochemically from SO<sub>2</sub> solution of CF<sub>3</sub>SO<sub>3</sub>H-TBACF<sub>3</sub>SO<sub>3</sub> containing benzene, where interaction between benzene and CF<sub>3</sub>SO<sub>3</sub>H significantly reduced the oxidation potential of benzene and gave compact PPP films showing sharp and well-separated redox peaks.<sup>25</sup> The PPP possessed clear 1,4-phenylene units and large degree of polymerization. Similarly to the PPP mentioned above, it is plausible that some interaction between pyrrole and BF<sub>4</sub><sup>-</sup> (or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) improved the quality of PPy films providing highly stretchable linear actuators. To enhance the interaction, appropriate solvents such as methyl benzoate which are not common solvents for the electropolymerization should be applied because relatively weak interaction between the solvent and the electrolyte resulted in increasing the interaction between pyrrole and the electrolyte.

#### Dependence of Potential Sweep Range on Electrochemical Strain of PPy Actuators

Figures 7a–7e indicate the dependence of potential sweep range on electrochemical strain of PPy actuators prepared with TBABF<sub>4</sub> as the electrolyte. When the potential was swept cathodically to  $-0.5$  V vs. Ag/Ag<sup>+</sup> (b), the PPy strip contracted by 4.4% and the redox peak at  $-0.65$  V/ $-0.5$  V shown in Figure 7a, which was not related to the PPy redox but to a redox of NaPF<sub>6</sub> on Pt, disappeared. On applying potential anodically to  $+0.7$  V, the PPy strip elongated normally. On the other hand, when anodic potential was limited at  $+0.5$  V (c), elongation of PPy appeared not to complete, resulting in slight decrease in electrochemical strain. When the potential sweep stopped at  $+0.2$  V (d) before the characteristic sharp oxidation peak appeared, elongation of the PPy film was very small. Both electrochemical activity and electrochemical stretching were hardly observed when the potential swept between  $-0.5$  V and  $+0.2$  V (e). Potential sweep range to drive the highly stretchable PPy actuators is therefore very important. Note that sweep time was kept constant (1600 s/cycle) in this experiment and thus scan rates were different.

#### Response Rate of PPy Actuators

Similarly to natural muscles, any highly stretchable



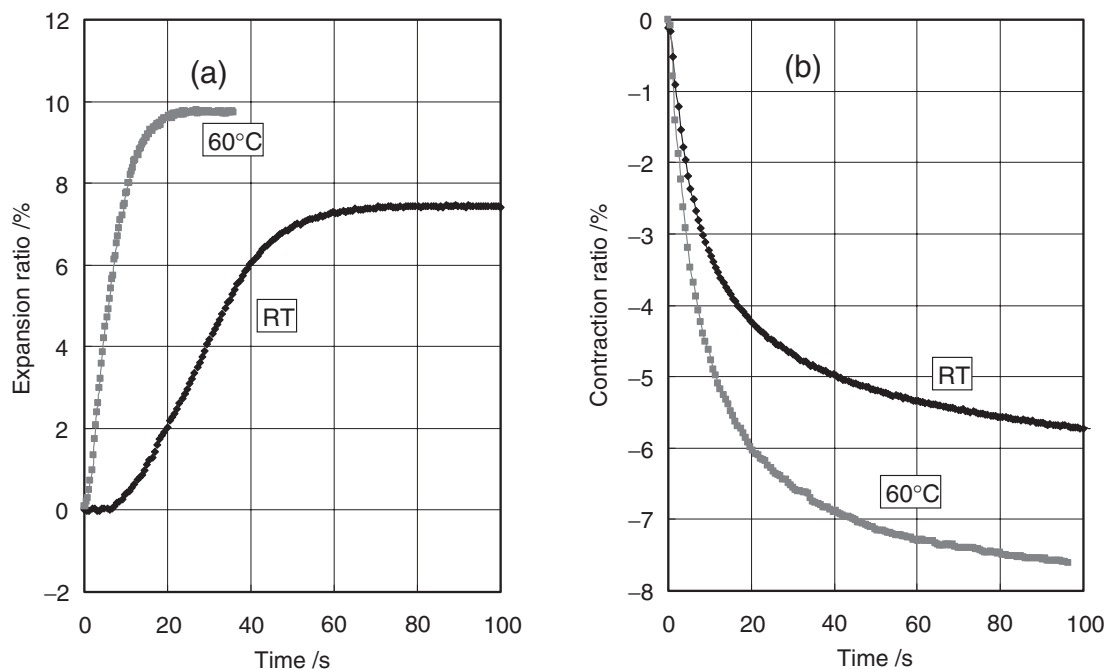
**Figure 7.** CVs and ECMDs of PPy actuators prepared from methyl benzoate solution of TBABF<sub>4</sub> on Ti electrode. The actuators were cycled between  $-0.9$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $2$  mV s<sup>-1</sup> (a),  $-0.5$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $1.5$  mV s<sup>-1</sup> (b),  $-0.9$  V and  $+0.5$  V vs. Ag/Ag<sup>+</sup> at  $1.75$  mV s<sup>-1</sup> (c),  $-0.9$  V and  $+0.2$  V vs. Ag/Ag<sup>+</sup> at  $1.375$  mV s<sup>-1</sup> (d), and  $-0.5$  V and  $+0.2$  V vs. Ag/Ag<sup>+</sup> at  $0.875$  mV s<sup>-1</sup> (e), in  $1.0$  mol dm<sup>-3</sup> NaPF<sub>6</sub> aq. A scan time was kept constant at  $1600$  s/cycle.

PPy actuators stretched faster at higher temperatures. Expansion and contraction rate of PPy film doped with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> at  $+0.7$  V and  $-0.7$  V vs. Ag/Ag<sup>+</sup> shown in Figures 8a and 8b, respectively, clearly depended on temperature. The rate-determine step of the actuation would likely to be diffusion of anions in PPy films. At higher temperatures, PF<sub>6</sub><sup>-</sup> can diffuse faster penetrating into PPy chains which are probably swollen further with water.

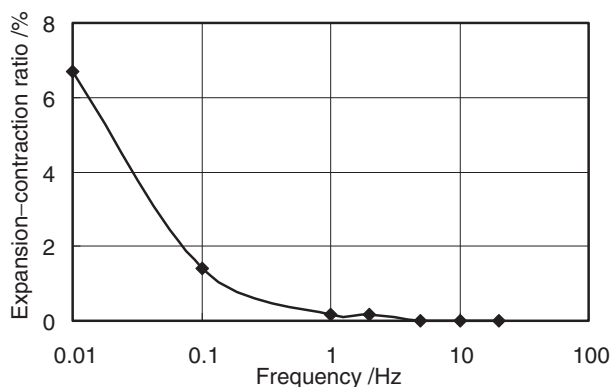
Figure 9 depicts frequency dependence on electrochemical strain of BF<sub>4</sub><sup>-</sup>-doped PPy actuator, indicating that a response up to  $5$  Hz was observed at room temperature. It is thought that the actuation should occur at higher frequencies at higher temperatures. Taking the mechanism of CP actuation depicted in Figure 4 and the rate-determine step mentioned above into account, an extremely fast response of CP actuators at over  $200$  Hz is unlikely to be achieved.

#### Electrically Generated Stress of PPy Actuators

Electrically generated strain (expansion–contraction ratio) decreased gradually with increasing the load,<sup>26</sup> as depicted in Figure 10. Here, the potential was swept between  $-0.9$  V and  $+0.7$  V vs. Ag/Ag<sup>+</sup> at  $10$  mV s<sup>-1</sup>. The maximum electrically generated stress of PPy prepared from methyl benzoate solution of TBABF<sub>4</sub> on Ti electrode was  $22$  MPa, much larger than those of other conducting polymer actuators. The maximum stress was observed just before the actuator was broken where the expansion–contraction ratio was  $1.0$  %. The BF<sub>4</sub><sup>-</sup>-doped PPy actuator exhibited  $7$  % strain at a fairly heavy load of  $5$  MPa (Figure 10). To our knowledge, this is the only CP actuator able to show large strain and stress induced electrically at the same time. A CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>-doped PPy actuator also exhibited large maximum stress ( $20.4$  MPa), but a PPy film doped with *p*-phenolsulfonate did not, and the maximum stress generated elec-



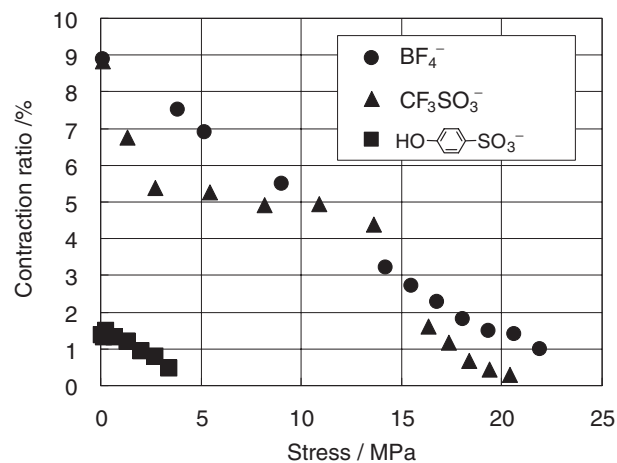
**Figure 8.** Elongation (a) and contraction (b) of PPy actuators prepared from methyl benzoate solution of TBACF<sub>3</sub>SO<sub>3</sub> on Ti electrode. The potential was set constant at +0.7 V and -0.7 V vs. Ag/Ag<sup>+</sup> for elongation and contraction, respectively, in 1.0 mol dm<sup>-3</sup> NaPF<sub>6</sub> aq. at room temperature (*ca.* 20 °C) and 60 °C.



**Figure 9.** Correlation between electrochemical strain and frequency to actuate a PPy film prepared from methyl benzoate solution of TBACF<sub>3</sub>SO<sub>3</sub> on Ti electrode. The potential was set constant at -0.7 V and +0.7 V vs. Ag/Ag<sup>+</sup> in 1.0 mol dm<sup>-3</sup> NaPF<sub>6</sub> aq.

trically was only 3.4 MPa, much smaller than those doped with BF<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. Similar small maximum stress was observed for PPy actuators doped with benzenesulfonate (0.6 MPa). Those PPy films exhibiting small stress, even though their film quality was good, did not have any strong interaction between pyrrole rings and dopants, or between PPy chains as the PPy actuators doped with BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> did.

The maximum electrically generated stress of PPy actuators depended very much on electrodes and solvents used for the electropolymerization of pyrrole. Table III indicates electrically generated stress and



**Figure 10.** Correlation between electrically generated stress and contraction of PPy actuators prepared from methyl benzoate solution of TBABF<sub>4</sub> (●), TBACF<sub>3</sub>SO<sub>3</sub> (▲), or TBAHOC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub> (■) on Ti electrode, cycled between -0.9 V and +0.7 V vs. Ag/Ag<sup>+</sup> at 10 mV s<sup>-1</sup> in 1.0 mol dm<sup>-3</sup> NaPF<sub>6</sub> aq.

strain of PPy actuators prepared on various electrodes in methyl benzoate or 1,2-dimethoxyethane. Methyl benzoate gave powerful actuators showing more than 10 MPa whatever the electrode was used, whereas PPy prepared in 1,2-dimethoxyethane tended to break at a smaller load presumably because PPy prepared in methyl benzoate is more compact and mechanically stronger than that prepared in 1,2-dimethoxyethane. Actually, mechanical tensile strength of PPy film prepared from methyl benzoate on Ti electrode was 93.0 MPa, larger than that (84.9 MPa) prepared from



**Table III.** Effect of electrode and solvent used for the preparation of PPy actuators on electrochemical stress and strain.

Solvent		Electrode		
		ITO	Ni	Ti
MB	Maximum stress / MPa	13.3	17.7	22.0
	Strain at 5 MPa / %	4.9	6.9	7.0
DME	Maximum stress / MPa	1.4	4.7	14.2
	Strain at 5 MPa / %	—	—	5.8

Electrolyte: TBABF<sub>4</sub>; Scan rate: 10 mV s<sup>-1</sup>

1,2-dimethoxyethane. The difference in mechanical tensile strength between PPy prepared in methyl benzoate (39.4 MPa) and that prepared in 1,2-dimethoxyethane (16.7 MPa) was more prominent when they were deposited on ITO electrode. The reason why metal electrodes gave PPy films with larger stress generated electrically than ITO electrode did might be attributable to more active sites existing on metal electrodes for the electropolymerization, so as to give more compact and dense, possibly well-entangled PPy. It is not clear why Ti electrode gave PPy actuators showing the largest stress, but possibly resulted from well-packed PPy chains because PPy films deposited on Ti were compact and smooth.

Electrochemical stress of PPy actuators measured by using the method described above appeared to be underestimated because the method kept fairly elongated state of the PPy strip, possibly the weakest state of the film during the potential sweep, at a heavy load for long time, so the film tended to break easily. Breakage of the PPy strip determined the maximum stress induced electrically, even if the PPy strip was potentially able to pull up a heavier load. Another procedure, which was to contract a PPy strip at a specified load at  $-0.7\text{ V vs. Ag/Ag}^+$  after elongation of the PPy strip at a light load, gave larger maximum stress generated electrically because the light load used for the latter procedure did not break the PPy strip easily. The PPy actuators should therefore exhibit much larger electrochemical stress than those described earlier.

#### *Newly-devised Structures of PPy Actuators for Practical Use*

It is of great importance to improve fundamental capability of actuators based on CPs such as electrically generated strain and stress, response rate, electric conductivity, mechanical strength, etc. Practical use of the PPy actuators cannot however be achieved without newly-devised structures of the PPy actuators.

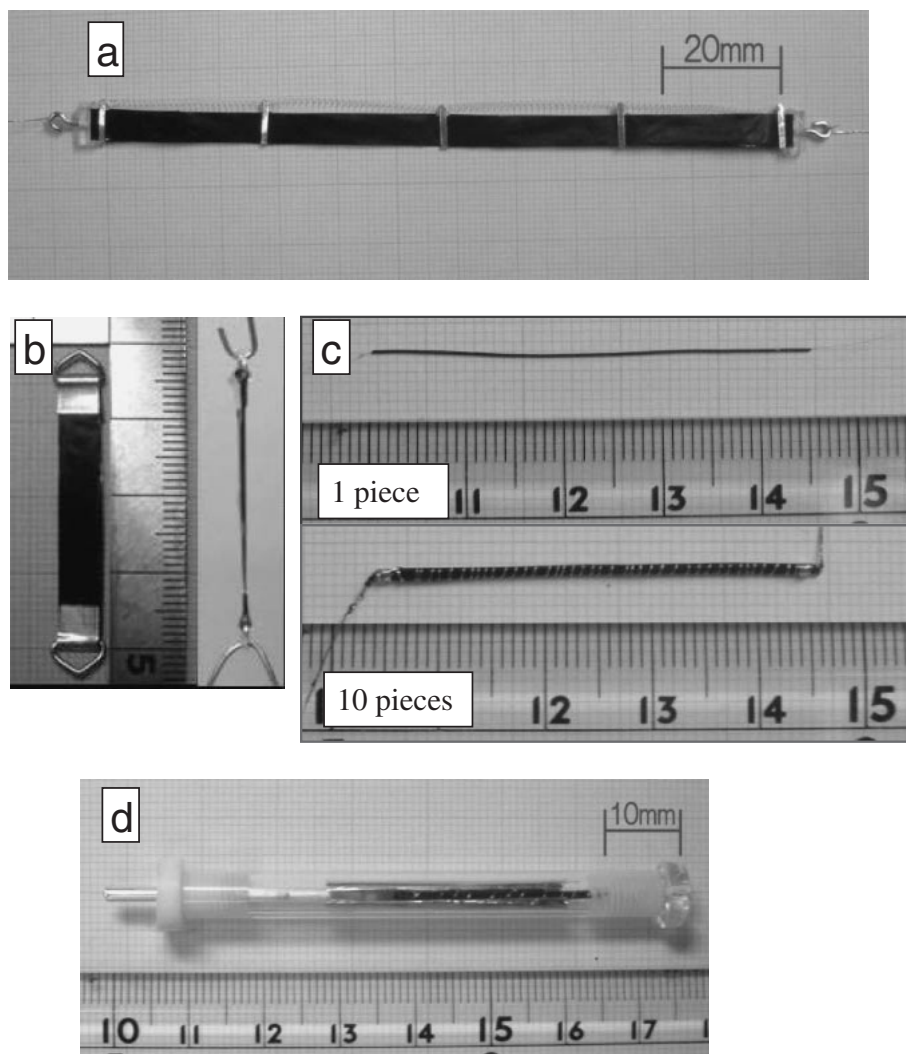
Figure 11a shows a long PPy actuator having additional electrodes to decrease an *iR* drop (voltage drop) along the PPy strip. Despite the electric conductivity (*ca.* 80–100 S cm<sup>-1</sup>) of PPy, the *iR* drop is considerably large to lower the performance of actuation partic-

ularly when the PPy is in dedoped state where the conductivity is much lower than 100 S cm<sup>-1</sup>. Note that PPy was not totally neutral, as shown in Figure 4, even in dedoped state, exhibiting electric conductivity of 5.4 S cm<sup>-1</sup>. It is thus necessary to add some flexible coil-like electrodes at every 3–5 cm to maintain large strain as shown in Figure 12. More additional electrodes attached to the 10-cm-long PPy strip, more effective contraction of the PPy occurred. Fairly fast electrochemical stretching of a 10-cm-long PPy strip was visually recognized by using a dry cell (1.5 V) even though the expansion–contraction ratio of the strip was not more than 10% under the operation condition.<sup>24</sup> The flexible coil-like electrodes did not interfere very much the actuation.

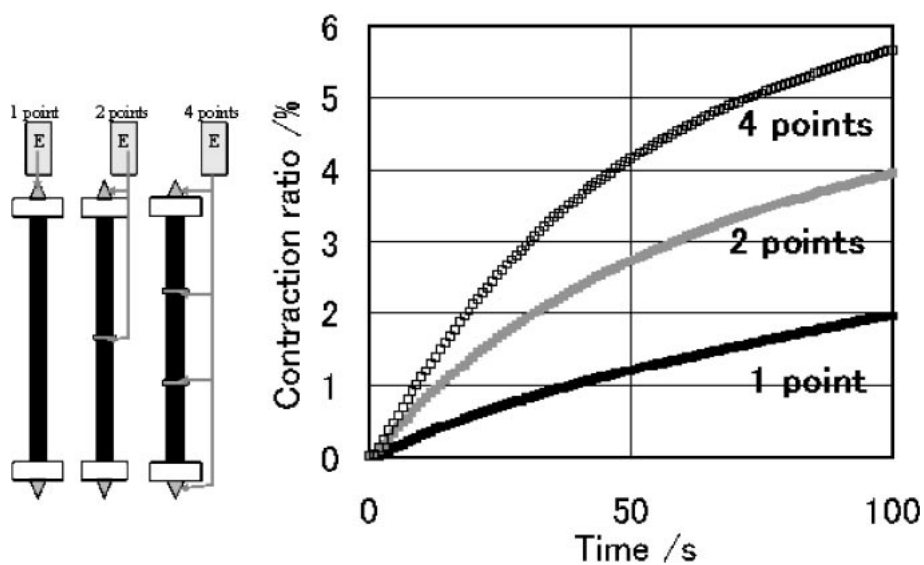
Figure 11b shows a tightly wound (5 times) PPy actuator, whose electrically generated force should be 10 times as large as a piece of PPy actuator at the same size, exhibiting actually 13.7 N force (the efficiency of winding: 78%). The winding technique requires a flexible and tough PPy tape; otherwise the PPy tape is cut especially at the edges. Of electrolytes giving highly stretchable PPy actuators, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> is solely appropriate for the requirement because, unlike most CP films prepared by electropolymerization, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>-doped PPy was elongated mechanically by 40–80%.

Figure 11c depicts a fibrous PPy–metal coil composite (artificial muscle fibre) of which the metal coil reduced the *iR* drop to improve performance of the actuator. More importantly, the PPy–metal coil composite can easily push at fairly large force although natural muscle cannot push but pull. These configurations of PPy actuators shown in Figures 11a–11c are practically important to fabricate actuator devices because electrically induced displacement and force can easily be tailored by adjusting the length and the number of pieces, respectively.

A capsule containing a bundle of 10-piece artificial muscle fibres (Figure 11d) can realize actuation in air even though CP actuators cannot essentially stretch without electrolytic solution. We believe that the quasi-solid systems<sup>27,28</sup> together with the excellent fundamental capability of the PPy actuators and the tailor-made configurations mentioned above can make a massive progress in the technology of CP actuators. The breakthrough in both strain and stress induced electrically together with the excellent mechanical properties of the PPy actuators will make artificial muscles practical, and possibly alter any technology concerning movements. We hope many products using the PPy actuators with large strain and stress will appear soon.



**Figure 11.** Photographs of PPy actuators: (a) a long PPy actuator with additional electrodes connected by a limp Au coil; (b) a multi-wound PPy actuator; (c) a bundle of fibrous PPy-metal composites; (d) a capsule of (c).



**Figure 12.** Time-course of electrochemical contraction of a 10 cm-long PPy actuator, prepared from methyl benzoate solution of TBACF<sub>3</sub>SO<sub>3</sub> on Ti electrode, attached with additional electrodes. The potential was set at  $-0.7\text{ V vs. Ag/Ag}^+$  in NaPF<sub>6</sub> aq.

## CONCLUSION

PPy films, prepared electrochemically from methyl benzoate solution of TBABF<sub>4</sub> on Ti electrode, exhibited 12.4% maximum strain and 22 MPa maximum stress generated electrically, much larger than those of conventional CP actuators. Appropriate combinations of electrolyte and solvent for electropolymerization of pyrrole as well as electrolyte to drive actuators were extremely important for PPy actuators with large strain and stress. PPy films doped with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, more flexible than BF<sub>4</sub><sup>-</sup>-doped PPy, were more suitable for fabricating actuator devices. The breakthrough both in electrochemical strain and stress together with mechanical properties of the PPy actuators makes them practical as artificial muscles.

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